URBAN STORMWATER RUNOFF CONTAMINATION ASSOCIATED WITH GUTTER AND PIPE MATERIAL DEGRADATION

by

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A DISSERTATION

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ABSTRACT

In addition to typical stormwater pollutant sources (erosion materials, automotive activity, landscaping chemicals, pet wastes, etc.), urban stormwater runoff can also be contaminated with substances that leach from materials with which the water contacts as the rain water travels through an urban area to the discharge point. Prior studies have shown that the composition of roofing materials and the drainage system pipes can significantly affect the amounts of pollutants, particularly heavy metals, released into the runoff, especially for roof runoff. This dissertation research indicated that water chemistry (pH, salinity, major ions, etc.) and time of contact may also affect the release of contaminants from materials.

The primary objective of this research was to examine how different drainage system and tank materials, water chemical characteristics, and exposure times affect contaminant losses during controlled tests examining the expected range of these characteristics. Static leaching tests for eight pipe and gutter materials were conducted over two separate three month periods during which pipe and gutter test materials were exposed to roof runoff and stormwater buffered to pH 5 and 8 and for exposure to different salinity conditions. A suite of heavy metal and nutrient constituents were periodically analyzed during the exposure periods. Also, pH, Eh, toxicity, alkalinity, total and calcium hardness, chloride and sulfate analysis were evaluated.

This research found that the metallic gutter and pipe materials released significant heavy metals. Some of these materials were found to release large amounts of zinc, copper, and lead during the tests, with galvanized steel materials being the most significant sources of lead and zinc, while copper materials were the most important source of copper (as expected). Zinc, copper, and lead releases were detected during both short and long exposure times under low and high pH conditions and low and high salinity conditions.

Statistical analyses were conducted to determine the effects of time, pH, salinity and each type of material on the release of the metals. Model fitting was performed on the time series plots to predict the release rate of metals as a function of exposure time and surface area. Chemical speciation modeling was also conducted to predict the forms of the measured metals, to compare the maximum concentrations observed with the expected solubility conditions, and to predict the relative toxicities and treatabilites of the different metallic compounds and ionic species likely present. A simple model was developed that quantified the expected pollutant releases for various materials for different uses (drainage systems vs. storage tanks) and water types (low and high pH conditions, saline and non-saline waters).

DEDICATION

To Dr. Robert Pitt

To My Family and Friends

LIST OF ABBREVIATIONS AND SYMBOLS

μg/L	Microgram per Liter
mg/L	Milligram per Liter
mol/L	Mole per Liter
g/L	Gram per Liter
mg/m^2	Milligram per Square Meter
%	Percentage
<	Less Than
>	Greater Than
Σ	Sum
Al	Aluminum
AL	Alabama
ANOVA	Analysis of Variance
BDL	Below Detection Limit
Ca	Calcium
Cd	Cadmium
cm	Centimeter
COD	Chemical Oxygen Demand
COV	Coefficient of Variation
Cr	Chromium
Cu	Copper
DI water	Distilled Water
DL	Detection Limit

DO	Dissolved Oxygen
Eh	The Half-cell Potential Relative to the Standard Hydrogen Electrode
E_{SHE}	The Half-cell Potential Relative to the Standard Hydrogen Electrode
EP-SCoR	Experimental Program to Stimulate Competitive Research
EWRI	Environmental and Water resources Institute
Fe	Iron
ft.	Feet
G.	Gutter
GAC	Granular Activated Carbon
H^+	Hydrogen Ion
HDPE	High Density Polyethylene
HNO_3	Nitric Acid
hr.	Hour
IC50	Approximate Concentration Required for 50% Inhibition of Bacterial Fluorescence
K	Potassium
KCl	Potassium Chloride
kg	Kilogram
K_{SP}	Solubility Product Constant
L	Liter
m	Meter
M	Molar
MDL	Method Detection Limit

Mg	Magnesium
mL	Milli Liter
mm	Milli Meter
mo	Month
N	Nitrogen
na	Not Available
Na	Sodium
NaOH	Sodium Hydroxide
ND	Not Detected
Ni	Nickel
NO_3	Nitrate
NSF	National Science Foundation
ORP	Oxidation Reduction Potential
QAQC	Quality Control Quality Assurance
P	Phosphorus
P.	Pipe
Pb	Lead
PO_4^{3-}	Phosphate Ion
PVC	Polyvinyl Chloride
SD	Standard Deviation
TDS	Total Dissolved Solids
US EPA	United States Environmental Protection Agency
WEFTEC	Annual Water Environment Federation Technical Exhibition and Conference

Zn	Zinc
ZVI	Zero-valent Iron

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1. INTRODUCTION

Heavy metals can occur in the environment from natural or from anthropogenic sources. Currently, heavy metals amounts coming from anthropogenic sources exceed those existing in the environment (NCSU Water Quality Group). Anthropogenic sources can include urban stormwater runoff (from roads and roofing materials), and corrosion of stormwater drainage systems in addition to surface runoff from mines and heavy metal particles coming from combustion of fossil fuels and settling down from the atmosphere to the ground etc. (NCSU Water Quality Group).

Some heavy metals are nutritionally essential elements for all life forms and are needed in small concentrations. However exposures to elevated metal concentrations can have significant health effects on wildlife and humans. Heavy metals do not degrade in the environment, and therefore have the potential to accumulate within living organisms and increase in concentration within each successive link in the food chain. Adverse effects of high concentrations or accumulations of these metals can lead to many diseases and even mortality (US EPA 2007a). The US Environmental Protection Agency (US EPA) has established aquatic life criteria and human health criteria for many heavy metals.

Population increases lead to concurrent increases in land development, with corresponding increases in rooftop areas and stormwater drainage system expansions, the metal sources being examined during this research. Often, roof runoff systems are directly connected to the storm drainage system and then to the receiving waters. Contaminated roof runoff, due to heavy metal roofing or drainage system materials, can have detrimental effects on stormwater runoff and receiving water quality (Burton and Pitt 2002).

The US EPA has established stormwater discharge regulations under the Clean Water Act (CWA). Under these regulations, stormwater is considered a point source that must be regulated through permits issued under the National Pollutant Discharge Elimination System (NPDES) (Welty et al. 2009). The permits require plans to identify best management practices (BMPs) for source control of stormwater pollution (Good 1993).

Heavy metals are commonly found in stormwater runoff, mostly from automobile related sources, but also from material degradation. Roofing and drainage system materials and their coatings can be made of metals or have metals as a component. Metal corrosion and paint have been identified as copper, lead, zinc, and chromium sources of stormwater contamination (U.S. EPA 2011; Wallinder et al. 2002a, 2001; Davis and Burns 1999; Simmons et al. 2001; Burton and Pitt 2002; Kingette Mitchell Ltd. And Diffuse Sources Ltd. 2003). Elevated metal concentrations in the runoff can contaminate water bodies, soils during infiltration, and subsequently contaminate groundwater (Veleva et al. 2010; Gromaire-Mertz et al. 1999).

In previous research, scientists found that water quality was greatly affected by the materials used in the manufacture of roofing materials and drinking water pipes and chemical water parameters such as pH, chloride content, etc. (Clark et al. 2008a, b; Clark et al. 2007; Dietz et al. 2007;Sandberg et al. 2006; Lasheen et al. 2008; Al-Malack, et al., 2001; Lagos, et al., 2001; Edwards, et al., 1996; Edwards, et al., 2001; Merkel, et al., 2002; Pehkonen, 2002; Mansouri, et al., 2003; Schock, et al., 1995; US EPA, 1995; Boulay and Edwards, 2001). Burton and Pitt (2002) noted that zinc contributions from rooftops can make up about one fourth of the total zinc discharges in the stormwater runoff. Notable roof runoff zinc sources are associated with galvanized roofing and drainage system materials (rain gutters and downspouts).

The main goal of this dissertation research was to determine the metal and nutrient releases from different gutter and pipe materials, and their associated toxicity, under a wide range of environmental conditions. This research has quantified the concentrations of these contaminants from different pipe and gutter materials for different conditions and predicted the forms of the leached metals. Statistical analyses were also conducted to identify the significant factors affecting the releases of these contaminants from the test samples as a function of time for the different materials.

1.1 Dissertation Organization

This dissertation has seven chapters and contains: a literature review (Chapter 2), hypotheses and experimental design (Chapter 3), observed heavy metal releases (Chapter 4), toxicity effects (Chapter 5), nutrient releases (Chapter 6), and summary of the findings and conclusions of this research (Chapter 7). The appendices include heavy metal, toxicity, nutrients, and major constituent data, and the results of the statistical analyses and water chemistry modeling.

The preliminary findings from this dissertation research were published as a book chapter and presented at the following conferences:

Peer-Reviewed Book Chapter:

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2. LITERATURE REVIEW

Urban runoff is a major contributor to the impairment of water quality in urban rivers and streams and to habitat degradation (Burton and Pitt 2002; NRC 2008). Roofing drainage systems are often made of metallic materials or may have metals as components, including aluminum, zinc, and copper. Researchers have determined these heavy metals are common contaminants in roof runoff at potentially high concentrations (Clark et al. 2008 a, b; Wallinder 2001; Pitt et al. 1995; Förster 1996; Morquecho 2005; Tobiason 2004). When released into the environment, metals can bioaccumulate and pose a threat because of their toxicity (US EPA 2007a). Some heavy metals are essential for all living organisms. However, at high concentrations, they might be toxic and pose significant health risks. In the environment, metals are found in many forms including ionic, chemical complexes, colloidal, and particulate forms (Morquecho 2005), which all affect their toxicity levels and fates in the environment (Pitt et al. 1995). The metal's chemical forms (speciation) are determined by such factors as pH, temperature, and inorganic and organic anionic complexation. The presence of other cations in the water also influences metal bioaccumulation and toxicity (US EPA 2007a; Morquecho 2005).

2.1 Contaminants Associated with Rooftop and Pipe Materials and Parameters that Influence Metal Releases into the Environment

2.1.1 Introduction

Over the past two decades, researchers have expressed concerns about the quantity of metal being released from roofing materials during precipitation events and the potentially harmful effects the metals may have on the environment (He et al. 2001a). A number of studies have been undertaken to address these concerns by providing quantitative data on the metal runoff rates from new and naturally aged copper and zinc roofing materials which have been exposed to different atmospheric environments (He et al. 2001a,b; Wallinder et al. 2009, 2002 a,b; 2001, 2000, 1998, 1997; Cramer et al. 2002; Faller and Reis 2005; Clark et al. 2008a).

Metal corrosion and paint were identified as copper, lead, zinc, chromium, iron, and aluminum sources (Burton and Pitt 2002; Gromaire et al. 2002; Förster 1996; USEPA 2011; Davis and Burns 1999; Simmons et al. 2001; Gumbs and Dierberg 1985, Lasheen et al. 2008, Mendez et al. 2011).

Zinc, copper, and other metals are frequently used in outdoor structures. For example, in southeastern Mexico, 63% of roofs and walls are made from galvanized steel sheets which undergo corrosion. As dew and rain dissolve zinc corrosion products, zinc ions leach from the corroded surfaces (Veleva et al. 2010). Annually, runoff from Parisian zinc roofs generated approximately 34 to 64 metric tons of zinc which is about half the load produced by runoff from the total Paris area (Gromaire et al. 2002).

The following discussions summarize key findings of metal releases from different exposure experiments, including summary tables containing observed concentrations from the different monitoring studies.

2.1.2 Zinc

When exposed to the atmosphere, metal material surfaces are in contact with many forms of moisture (condensed water from high humidity, rain, mist, dew, or melting snow) and the materials undergo corrosion (oxidation) processes (Veleva et al. 2007). When zinc material is exposed to the atmosphere, a protective layer (zinc oxides/hydroxides/carbonates) called patina is formed, which serves as a physical barrier between the metal surface and the atmosphere, slowing down further oxidation (Legault and Pearson 1978; Zhang 1996). Patina can be removed physically by winds and sand erosion or by partial dissolution of some soluble patina components when exposed to rain or water condensation on the metal surface, re-exposing the material to continued oxidation. Zinc runoff can lead to zinc accumulations in the soils, and in surface and ground waters (Veleva et al. 2007). In urban areas, the highest zinc runoff concentrations are found in roof runoff from roofs having galvanized steel components (such as roofing sheets, flashing, or gutters and downspouts) (Burton and Pitt 2002; Förster 1999; Bannerman et al. 1983; Pitt et al. 1995). Zinc contributions from rooftops can make up about one fourth of the total zinc discharges from an area's total stormwater runoff (Burton and Pitt 2002).

Clark et al. (2008a) studied runoff water quality from uncoated galvanized steel roofing materials during four months of exposure to rain on the campus of Penn State Harrisburg and found that this material can be a significant source of zinc. Figure 1.1 compares runoff zinc concentrations (after background correction) from different roofing materials (Clark et al. 2008a). The greatest zinc concentrations were from runoff from galvanized materials. The authors didn't observe any consistent decreases in runoff concentrations during the four months of roof exposure. The median zinc concentrations in the runoff from uncoated galvanized metals were about 5.5 mg/L (about 1,400 times higher than the criterion established by the EPA for aquatic toxicity) with maximum concentrations about 10 mg/L. All other roofing materials tested had zinc runoff concentrations much less than 1 mg/L, as shown on Figure 1.1.

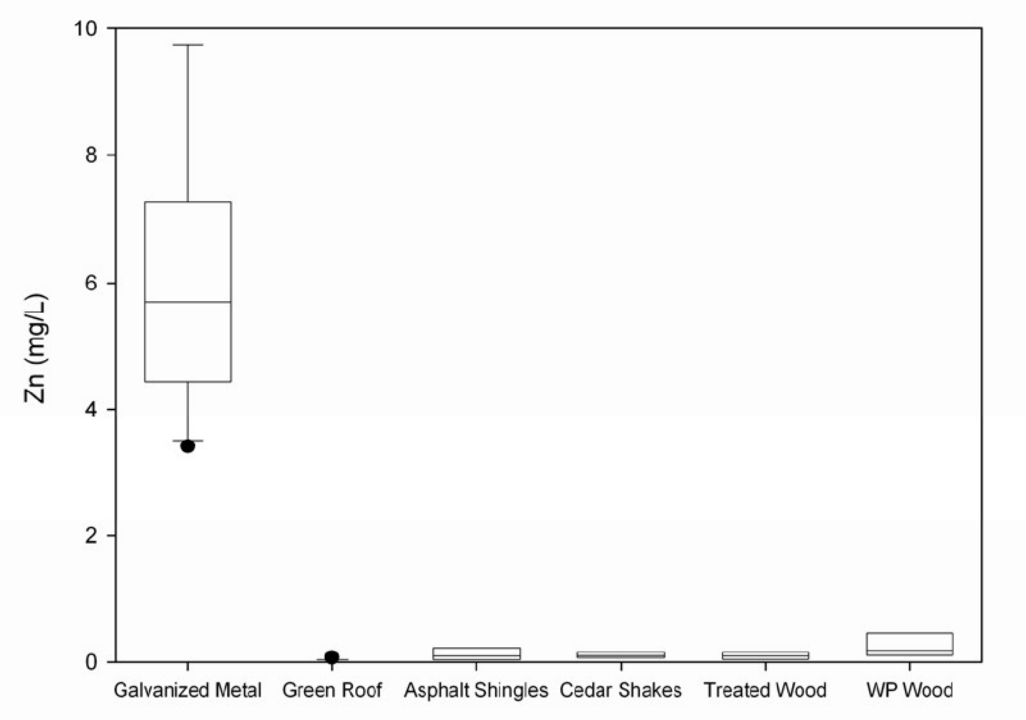


Figure 1.1. Runoff zinc concentrations from roofing materials. Background corrected.
Source: Clark et al. (2008a).

Clark et al. (2007), based on their laboratory testing on aged galvanized roofing panels, concluded that there can be elevated concentrations of pollutants in roof runoff over a long period of time. Clark et al. (2008b) further studied leaching of heavy metals from several materials including two 60 year old painted galvanized metal roofing panels (one galvanized metal panel had been exposed to the weather for 60 years, while the other was stored in the barn for roof repairs) in the laboratory and in the field. They also studied galvanized corrugated aluminum, prepainted 55% aluminum-zinc alloy coated steel (Galvalume), and corrugated polyvinyl chloride panels. After monitoring runoff from a naturally-exposed pilot-scale test of these materials for 2 years, the authors noted substantial zinc release from uncoated galvanized metals during the early part of the materials' lifespan. Within two weeks of the installation, the authors noticed visible degradation on the galvanized metal (Clark et. al. 2007). The authors also found that aged roofing panels have the potential for pollutant releases, even after 60 years of exposure.

Good (1993) studied heavy metal concentrations and aquatic toxicity of roof runoff from different roofing materials at a sawmill on the coast of Washington. The roofing materials included a rusty galvanized metal roof, a weathered metal roof that may have been coated with aluminum paint many years age, a tar roof sealed with aluminum paint, and a relatively new aluminum roof. Zinc concentrations in roof runoff samples surpassed the water quality criteria. Zinc was leaching out of each type of roofing material, however zinc concentrations were extremely high (up to 12.2 mg/L of total zinc and 11.9 mg/L of dissolved zinc) in the runoff samples from galvanized roofing materials.

Tobiason and Logan (2000) and Tobiason (2004) measured zinc concentrations in the runoff from an unpainted Galvalume metal roof at Seattle Tacoma International Airport. Zinc concentrations varied over an order of magnitude during the rain events ranging from 0.03" to 0.38" total rainfall, and decreased with rainfall volumes and possibly seasonal factors. The authors observed that such commonly used galvanized products such as fencing, guardrails, light poles and unpainted Galvalume metal roofing leach substantial concentrations of dissolved zinc in stormwater runoff. Galvanized material was contributing zinc concentrations ranging from 100's of µg/L to the 10's of mg/L (Tobiason 2004; Tobiason and Logan 2000; Good 1993).

Veleva et al. (2007) studied zinc runoff due to atmospheric corrosion of products during exposure of pure Zn and hot dip galvanized steel materials in the Gulf of Mexico (urban and rural) during 18 months. High annual rates of zinc runoff were observed. The authors found that zinc runoff rates ranged between 6.5 to 8.5 ± 0.30 g Zn/(m^2yr).

Gromaire-Mertz et al. (1999) studied runoff from zinc roofs and gutters in an old densely populated district of central Paris, France, between July 1996 and May 1997. Roofing materials included clay tiles (70%) and zinc sheets. Zinc concentrations in roof runoff frequently exceeded level 2 of the French water quality standards of 0.05mg/L (observed zinc concentrations in the runoff were between 1 and 5 mg/L).

Schriewer et al. (2008) studied runoff from 14 year-old zinc roofs in Germany for a period of 1 year. Roof runoff quality was affected by the titanium–zinc gutters and down spouts. Samples were collected directly in the gutter. The authors observed high zinc concentrations in the roof runoff. The flow-weighted average zinc concentration was 4.9 mg/L. Zinc runoff rates of 3.73 g/m^2were determined for the zinc roof during868 mm of precipitation during the 12 months of the study.

Zobrist et al. (2000) measured the concentrations of heavy metals in runoff from tile, polyester, and gravel roofs located at a suburb of Zurich, Switzerland. The drainage system for the tile (clay) roof was made of 15-year old copper; new copper for the polyester roof, and PVC material for the gravel roof. Runoff from the polyester and gravel roofs was sources of zinc. Observed zinc concentrations were between 0.005 and 0.85 mg/L.

Wallinder et al. (2001 and 2000) investigated zinc yields in the runoff from 15 different zinc panels or zinc coatings, which included new and naturally aged sheets, commercial zinc-based construction materials (different zinc panels or zinc coatings, which included new and naturally aged sheets) located in Stockholm, Sweden and Olen, Belgium during 1 year exposures. Zinc runoff yields ranged from 0.07 g/m^2/year (prepainted galvanized steel) to 3.5

g/m^2/year (40 year old zinc panels). Zinc runoff yields from hot dip galvanized steel panels were 2.7 g/m^2/year.

Faller and Reiss (2005) studied the exposure of different metallic materials to the open atmosphere in Dubendorf, Switzerland. The materials included: copper and zinc with different surface treatments, including tinned copper, galvanized steel, aluminum, stainless steel, tinned stainless steel, titanium, and lead. Zinc materials released measurable amounts of metallic ions. The largest source of zinc was prepatinated zinc sheets, while black phosphatated titanium-zinc sheets released the least zinc concentrations. The corrosion rates of the untreated zinc sheets decreased with time during the early exposure periods. However the runoff rate was relatively constant in time after one year of exposure. They concluded that the corrosion and runoff rates will equalize with time. The zinc runoff yield from untreated zinc sheets was approximately 80% of its mass corrosion rate. Metal runoff yield is the metal concentration in the runoff times the actual runoff water volume; corrosion rate is the rate of degradation of the metal based on the measured mass loss (He 2002).The runoff rate for the titanium-zinc sheet after 5 years exposure was 2.6 g/m^2/year, compared to 3.2 g/m^2/year for prepatinated zinc. At the Stockholm site, the runoff rate for zinc was 3.1 g/m^2/year and at the Hannover, Germany site, the runoff rate for zinc was 4.51 g/m^2/year measured after 3 years of exposure. Also, studies conducted by Wallinder et al. (2000 and 2001) on zinc runoff yields from zinc coatings show that in general, at least during the first year of exposure, zinc runoff yields were substantially lower than the corresponding corrosion rates and constituted 50-90% during exposure times up to five years.

In contrast to the findings by Faller and Reiss (2005), Veleva et al. (2010) (who studied zinc concentrations leaching from hot dip galvanized (HDG) steel that were exposed to the Gulf of Mexico environments for two years) observed that the annual zinc runoff yields in both test sites decreased by 50% during the second year and ranged between 2.70 and 3.28 g m^{-2}/year compared to the first year's yields that were between 6.52– 7.98 g m^{-2}/year. Zinc concentrations in the runoff appeared to diminish its rate of release with time, possibly due to the doubled rain amounts during the second year of the experiment. More frequent and intense rains wash off aggressive contaminants and shorten the dry period of time during which the corrosion products form (Veleva et al. 2010).

Förster (1996 and 1999) studied heavy metals in roof runoff in Bayreuth, Germany. Förster found that metal flashings used on the roofs released very high concentrations of Zn and concluded that the best management practice would be to stop using exposed metal surfaces on roofs and walls of buildings. The differences in the pollution yields between different roofs were sometimes as high as three orders of magnitude. The variability was also high within a single roof and for different storm events. Roofing materials studied included concrete tiles, clay pantiles, fibrous cement, tar felt, and zinc sheet. Zinc and PVC gutters were used. Förster (1999) found that zinc concentrations in the zinc sheet roof runoff was two to three orders of magnitude above the concentrations measured in runoff from roofing materials that didn't have any metal components (fibrous cement roof). Zinc concentrations were elevated in the runoff from roofs that had metal gutters and downspouts. The total zinc concentrations in the zinc sheet runoff were approximately 18 mg/L. Total zinc concentrations from zinc gutters at Keuperstr and Konigsallee, Germany, were approximately 2 and 4 mg/L, respectively.

Gumbs and Dierberg (1985) studied three components of 46 single-family rainwater storage cisterns with a domestic water delivery system (roof, cistern, and distribution system) on St. Maarten Island. The elements of the monitored cistern water supply system included the house roof, cistern, pressure tank, and water distribution system. The potential heavy metal sources were airborne soils and auto emissions, corrosion of galvanized iron roof and roof paint, dissolution of sediments in the cistern and corrosion within the distribution system. The metal concentrations in the harvested rainwater increased as it passed over the galvanized roofing surfaces and through gutter and downspouts connected to the cisterns. They observed that zinc concentrations (0.006 to 2.29 mg/L with an average of 0.192 mg/L) in the tap samples (water supplied by the distribution system from the cistern) were significantly higher than in the surface water (0.001 to 1.16mg/L with an average of 0.084mg/L) of the cisterns. The elevated levels of zinc concentrations at the tap were attributed to the corrosion of the galvanized metal components within the distribution systems that connected the cistern with the tap due to the longer residence time.

Mendez et al. (2011) also studied the effects of roofing materials on water quality for rainwater harvesting systems. The authors examined the quality of harvested rainwater using several pilot-scale roofs (asphalt fiberglass shingle, Galvalume® metal, concrete tile, and a green roof that contained a substrate, drainage layer, and membrane roof barrier and native perennial plants) and three full-scale roofs (two asphalt fiberglass shingle and one Galvalume® metal). The full-scale site was located at the University of Texas at Austin Child Development Center and had a 7-year-old Kynar®-coated Galvalume® roof. Also, new and artificially aged coupons of asphalt fiberglass shingle, Galvalume® metal, and concrete tiles were examined in lab-scale studies to determine the potential for changes in harvested rainwater quality influenced by aged roofing materials. The authors found high zinc concentrations leaching out of pilot-scale Galvalume and full-scale Kynar®-coated Galvalume® roof. Zn concentrations in the harvested rainwater from the pilot-scale Galvalume® roofs ranged between 0.21 and 0.85 mg/L for the first flush sample, and between 0.08 and 0.36 mg/L for later samples. Ambient rain zinc concentrations were between 0.001 and 0.1 mg/L. Zn concentrations in the harvested rain water from full-scale Kynar$^{®}$-coated Galvalume$^{®}$ roof ranged between 0.1 and 0.2mg/L for the first flush sample and between 0.06 and 0.18 mg/L for later samples.

Shahmansouri et al. (2003) conducted a study on pilot scale drinking water distribution systems in Zarrinshahr and Mobarakeh, Iran. The piping system materials in houses and buildings were galvanized, the distribution piping systems were made of asbestos, polyethylene, and occasionally iron pipes. Copper brass taps and valves were possibly used in some homes. A minimum of 6 hours of retention time for tap water samples was used. The authors found that the samples analyzed along the domestic water distribution system showed significant increases in zinc concentrations. Zinc concentrations sometimes exceeded the recommended maximum contaminant levels (MCL). Zinc concentrations released in the drinking water distribution systems ranged between 0.001 and 0.006 mg/L in Zarrinshahr and between 0.0002 and 0.006 mg/L in Mobarakeh.

Heijerick et al. (2002) studied the bioavailability of zinc in runoff from 15 different zinc-based roofing materials in Stockholm, Sweden. High zinc concentrations were released from roofing materials made using zinc, galvanized steel and galvalume materials. The highest zinc concentrations were found in runoff from 40 year old uncoated zinc roofing materials (up to 8.4 mg/L), while the lowest runoff concentrations were from prepainted galvanized steel materials (up to 0.63 mg/L).

Table 1.1 summarizes zinc concentrations or runoff yields from different materials found by various researchers.

Table 1.1. Zinc releases from various sources.

Materials	Test conditions	Zn concentrations or runoff yields	Reference
Uncoated Galvanized Steel Roofing Materials			
New uncoated galvanized steel roof	4 mo field test. Pilot Scale. Harrisburg, PA.	3.5 and 9.8 mg/L	Clark et al. (2008a)
Galvanized metal roof	Field Seattle	0.09 and 0.48 mg/L	Tobiason and Logan (2000)
Hot dip galvanized steel	2 year field test. The Gulf of Mexico	6.52– 7.98 g m^{-2} during the 1st year 2.70 and 3.28 g m^{-2} during the 2nd year	Veleva et al. (2010)
Hot dip galvanized steel panel	Stockholm, Sweden. 1 year test	2.7 g/m^2 per year	Wallinder et al. (2001)
Hot-dip galvanized steel	5 years pilot scale test. Dubendorf, Switzerland	2.4 g/m^2 per year	Faller and Reiss (2005)
Galvanized steel roof	Stockholm, Sweden. 1 year test.	1.2-5.5 mg/L	Heijerick et al. (2002)
Galvanized material	Hannover, Germany, 3 year test	4.51 g/m^2 per year	Lehmann (1995)
Pure Zn and hot dip galvanized steel	Urban and rural areas. The Gulf of Mexico, 18 mo test	6.5 – 8.5 ± 0.30 g/m^2 per yr.	Veleva et al. (2007)
14 year old zinc roof	Germany, 1 year test	0.3 - 30 mg/L 3.73 g/m^2 per year	Schriewer et al. (2008)
40 year old zinc panel	Stockholm, Sweden. 1 year test	3.5 g/m^2 per year	Wallinder et al. (2001)
Zinc roof	Filed test. Bayreuth, Germany.	17.6 mg/L	Forster (1999)
Zinc roof	Stockholm, Sweden. 1 year test.	3.8-4.4 mg/L	Heijerick et al. (2002)
40 years old zinc roof	Stockholm, Sweden. 1 year test.	8.4 mg/L	Heijerick et al. (2002)
Zinc materials	Stockholm, Sweden. 1 year test.	3.0 - 3.3 g/m/^{2} per year	He et al. (2001a)
Zinc sheet (0.07% Ti, 0.17% Cu) panel	1 year field test. Olen, Belgium. Industrial area	4.5 and 5.7 g/m^2 per year	Wallinder et al. (2000)
Clay tiles (70%) + zinc sheets, zinc sheets; roofs and gutters	Field test. Central Paris. July 1996 and May 1997	0.8 - 38 mg/L	Gromaire-Mertz et al. (1999)
Zinc gutters	Filed test. Bayreuth, Germany.	2-4 mg/L	Forster (1999)
zinc roofing	Paris, France. 10 mo. test	34 - 64 metric tons per year for	Gromaire et al. (2002)

		whole City	
Coated Galvanized Steel Roofing Materials			
New coated galvanized metal roof	4 mo field test. Pilot Scale. Harrisburg, PA	< 0.5 mg/L	Clark et al. (2008a)
60 years old painted galvanized metal roof in the field	Leaching test in the lab	5 - 30 mg/L	Clark et al. (2008b)
60 years old painted galvanized metal roof stored in the barn	Leaching test in the lab	5 - 30 mg/L	Clark et al. (2008b)
Prepainted galvanized steel panel	Stockholm, Sweden. 1 year test	0.07 g/m^2 per year	Wallinder et al. (2001)
Zinc with different surface treatment	5 years pilot scale test. Dubendorf, Switzerland	1.9 to 3.2 g/m^2 per year	Faller and Reiss (2005)
Prepatinated zinc	5 years pilot scale test. Dubendorf, Switzerland	3.2 g/m^2 per year	Faller and Reiss (2005)
Prepainted galvanized steel roof	Stockholm, Sweden. 1 year test.	0.16-0.63 mg/L	Heijerick et al. (2002)
Uncoated Galvanized Aluminum Roofing Materials			
Galvalume roofs	Pilot-scale scale in Austin, Texas. Several rain events in 2010	0.208 – 0.852 mg/L during the first flush; 0.077 – 0.362 mg/L for later samples	Mendez et al. (2011)
Galvalume roof	Stockholm, Sweden. 1 year test.	0.6-1.6 mg/L	Heijerick et al. (2002)
Unpainted Galvalume roof	Field	0.42 - 14.7 mg/L	Tobiason (2004)
Coated Galvanized Aluminum Roofing Materials			
Kynar®-coated Galvalume®	Full scale in Austin, Texas. Several rain events in 2010	0.098 – 0.179 mg/L during first flush, 0.058 – 0.177 mg/L for later samples	Mendez et al. (2011)
New prepainted 55% aluminum-zinc alloy coated steel (Galvalume) roof	2 years field test. Pilot Scale. Harrisburg, PA	<0.25 mg/L	Clark et al. (2008b)
Other Roofing Materials			
Black phosphatated titanium-zinc	5 years pilot scale test. Dubendorf, Switzerland	1.9 g/m^2 per year	Faller and Reiss (2005)
Titanium-zinc sheet after 5 years exposure	5 years pilot scale test. Dubendorf, Switzerland	2.6 g/m^2/year	Faller and Reiss (2005)
Aluminum, stainless steel and titanium	5 years pilot scale test. Dubendorf, Switzerland	< detection limit (0.01 mg/L)	Faller and Reiss (2005)

Polyester roof	Zurich, Switzerland. 2 year test	<0.160 mg/L	Zobrist et al. (2000)
Gravel roof	Zurich, Switzerland. 2 year test	<0.035 mg/L	Zobrist et al. (2000)
Drinking Water Distribution Systems (DWDS)			
At the tap after galvanized metal parts in distribution systems	St. Maarten Island, Netherlands	0.006 to 2.29 mg/L (average of 0.19 mg/L)	Gumbs and Dierberg (1985)
DWDS made of asbestos, polyethylene, and iron pipes; piping system materials in houses and buildings were galvanized	DWDS in Zarrinshahr, Iran	$0.73*10^{-3}$ - $5.80*10^{-3}$mg/L	Shahmansouri et al. (2003)
DWDS made of asbestos, polyethylene, and iron pipes; piping system materials in houses and buildings were galvanized	DWDS in Mobarakeh, Iran	$0.20*10^{-3}$ - $5.80*10^{-3}$ mg/L	Shahmansouri et al. (2003)

Summary. The largest sources of zinc in stormwater runoff are zinc-based roofing materials (Clark et al. 2008a, b; Good 1993; Tobiason and Logan 2000; Tobiason 2004; Faller and Reiss 2005; Schriewer et al. 2008; Förster 1996, 1999; Gromaire-Mertz et al. 1999; Gumbs and Dierberg 1985; Heijerick et al. 2002), galvanized roof drainage systems (Burton and Pitt 2002; Bannerman et al. 1983; Pitt et al. 1995; Förster 1996 and 1999), and galvanized pipes (Gumbs and Dierberg 1985; Shahmansouri et al. 2003). Galvanized materials have a large potential for contributing zinc to runoff during their useful life (Clark et al. 2008a, b; Wallinder et al. 2001, 2000; Heijerick et al. 2002). Zinc runoff yields were generally observed to increase with the age of the material (Clark et al. 2008b; Schriewer et al. 2008; Wallinder et al. 2001; Heijerick, et al. 2002). Zinc concentrations in runoff from galvanized materials ranged from 100's of µg/L to 10's of mg/L (Tobiason 2004; Tobiason and Logan 2000; Clark et al. 2008a, b; Heijerick et al. 2002; Good 1993). Zinc concentrations in roof runoff samples frequently exceeded the water quality criteria established by the U.S. EPA and regulatory agencies from other countries (Good 1993; Clark et al. 2008a; Gromaire-Mertz et al. 1999).

2.1.3 Copper

Clark et al. (2008 a and b) monitored runoff from a pilot-scale set upon the campus of Penn State Harrisburg examining various roofing and building materials for 2 years under natural rain conditions and noted substantial copper releases from pressure treated and waterproofed woods. The copper concentrations from non-copper metal and vinyl materials did not exceed 25 µg/L (a typical toxicant value for certain aquatic plants). The results from laboratory leaching tests showed that copper concentrations may continue to leach out in an acid rain environment during the material's useful life (Clark et al. 2008b).

Wallinder et al. (2000) studied the effect of exposure direction and inclination on the runoff rates of zinc and copper from roofs located in Olen, Belgium (Zn measurements) and Stockholm, Sweden (Cu measurements). For copper, the yearly runoff rate on the average ranged between 1.3 and 1.5 g/m^2. The copper runoff yield constituted 20-50% of the observed corrosion rate during exposure times up to two years. The mass loss due to corrosion was estimated by the difference between the weights before exposure and after chemical removal of the corrosion patina.

Sandberg et al. (2006), Wallinder and Leygraf (1997), and Leuenberger-Minger et al. (2002) also noted that the copper runoff rate is significantly lower than the corrosion rate. The runoff rate is lower than the corrosion rate because the runoff does not wash away all the corrosion products that are formed, such as the patina. For example, the annual total copper runoff rate was 1.5 g/m^2/year from fresh copper sheet and was substantially lower than the annual copper corrosion rate (19 g/m^2/year) (which was decreasing with time).

Sandberg et al. (2006) examined corrosion-induced copper concentrations in the runoff from copper sheet, naturally patinated copper, and pre-patinated copper in a chloride-rich marine environment near Brest, France during one year. For some roof panels a comparison was made with results from an urban site in Stockholm, Sweden. At similar rain quantities, copper runoff rates were significantly lower at the marine site compared to data acquired in an urban environment, despite substantially higher chloride deposition rates at the marine location. For naturally patinated copper, there were no large variations noted in runoff rates with time. However, for the fresh copper sheet, the runoff rate increased from a fairly constant rate of 1.1 g/m^2/year, during the first 4 months of exposure, to a relatively constant rate of 1.5 g/m^2/year during the remaining exposure period as a result of the formation of paratacamite ($Cu_2(OH)_3Cl$).

For fresh copper sheet, cuprite (Cu_2O) was the main crystalline patina constituent during the first 12 weeks of exposure, followed by the formation of paratacamite ($Cu_2(OH)_3Cl$) after that exposure period. Formation of paratacamite was a result of significantly higher deposition rates of chlorides between 12 and 26 weeks. After months of atmospheric exposure, basic copper compounds like ($Cu_2(OH)_3Cl$), brochantite ($Cu_4SO_4(OH)_6$) and cuprite (Cu_2O) and Posnjakite ($Cu_4SO_4(OH)_6 \cdot H_2O$) can be formed depending on the contamination in the environment (Sandberg et. al. 2006; Faller and Reiss 2005; Kratschmer et al. 2002). Brochantite ($Cu_4SO_4(OH)_6$) and posnjakite ($Cu_4SO_4(OH)_6 \cdot H_2O$) are common compounds in sulfate containing environments; ($Cu_2(OH)_3Cl$) are often found in chloride rich environments (Kratschmer et al. 2002). The brochantite phase was still detected after one year of exposure (Sandberg et al. 2006). The bioavailable portion (available for uptake by an organism) of the released copper was a small fraction (14–54%) of the total copper concentration due to Cu complexation with organic matter in impinging seawater aerosols (Sandberg et al. 2006).

Faller and Reiss (2005) studied the exposure of different metallic materials to the open atmosphere in Dubendorf, Switzerland. Figure 1.2 shows copper, lead, and zinc runoff rates from different materials (listed on the left side of the figure) after 5 years of exposure. Copper runoff rates were high for copper materials. After 5 years of exposure, the Cu runoff yield from the untreated rolled copper sheet was 1.3 g/m^2/year, which was about 30% of the corrosion rate. The Cu corrosion rate decreased with time; however the runoff rate was relatively constant with time. The authors noted that the corrosion and runoff rates would likely equalize with time. At the Stockholm site, the copper runoff rate observed after 2 years of exposure was similar to that at the Dubendorf site. Stockholm and Dubendorf test sites have similar atmospheric SO_2 concentrations.

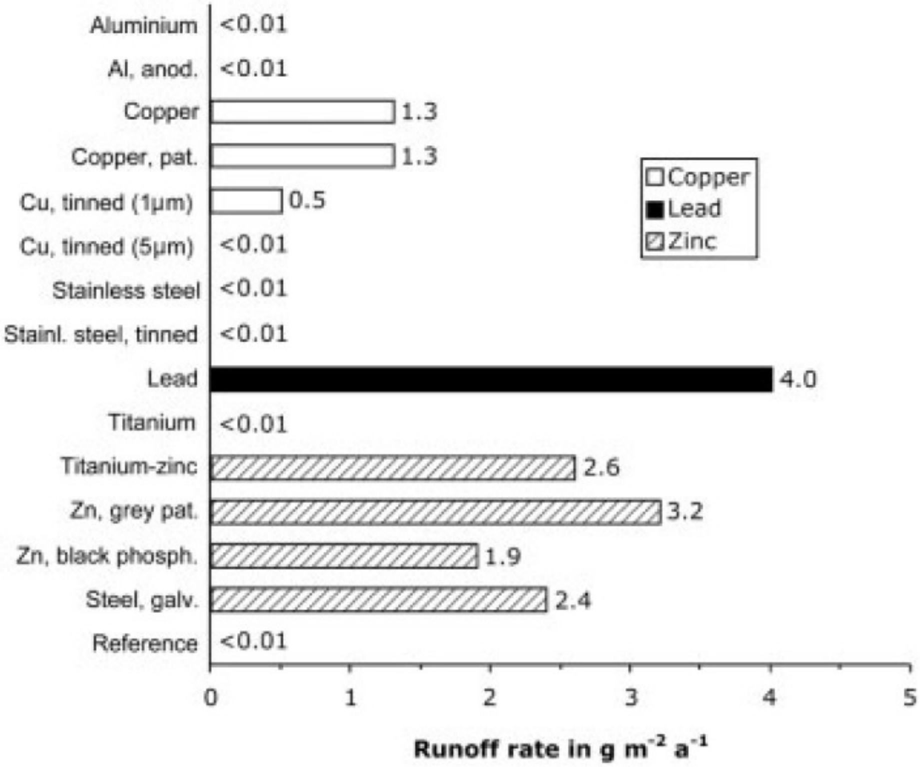


Figure 1.2. Runoff rates of copper, lead, and zinc from different materials after 5 years of exposure.
(Faller and Reiss 2005).

Wallinder et al. (2009) studied the copper releases from a naturally aged copper roof on a shopping center building in a suburban site near Stockholm, Sweden, along with the interactions of copper with the internal drainage system and storm drains made of cast iron and concrete. Annual runoff rates of copper from the naturally oxidized copper roof ranged from 0.74 to 1.6 g/m^2/year (with the median being 1.0 g/m^2/year). The authors also studied runoff from a copper roof at a shopping center in Farsta, another suburban area near Stockholm. Roof runoff was sampled after transport through the internal drainage system consisting of downspouts made of cast iron and concrete (site A) and after approximately 50 m in a storm drain pipe made of concrete (site B). Generally, total copper concentrations at sites A and B were very similar. The total copper concentrations ranged between 5 to 101 µg/L (with a median of 15 µg/L) and between 2 to 175 µg/L (with a median of 18 µg/L), for sites A and B respectively. The majority of the copper released from the roof was retained in the runoff during transport through the internal drainage system of the building. However, the internal drainage system changed the chemical speciation of the released copper and its bioavailable fraction. Most of the copper in the runoff flowing through the cast iron and concrete pipes was complexed with organic matter, significantly reducing the bioavailable fraction. Bertling et al. (2006), Boulanger and Nikolaidis (2003), and Wallinder et al. (2009) also found that the interaction of copper released from outdoor structures with different solid surfaces resulted in changes in the chemical speciation of the released copper and subsequently greatly reduced the bioavailable copper fraction. In another study, Michels et al. (2003) studied the impact of stormwater runoff from a copper roof on the environment. The authors found that the toxicity of the stormwater roof runoff decreased as it passed through the drainage system.

Other laboratory and field studies have shown that concrete pipes and concrete-based pavement materials have a high capacity to retain copper released from roofs by forming corrosion product malachite, $Cu_3(CO_3)_2(OH)_6$ (Bahar et al. 2008a,b; Sundberg 1998; Boulanger and Nikolaidis 2003; Wallinder et al. 2009). For a given rainfall quantity, the amount of copper retained on concrete surfaces increases with decreasing rain intensity as a result of prolonged contact time (longer duration rains). At a given rainfall quantity, low rain intensities also result in a higher released amount of copper from a copper roof (He et al. 2001; He 2002; Wallinder et al. 2009).

Good (1993) investigated chemical concentrations and aquatic toxicity of roof runoff from different roofing materials at a sawmill on the coast of Washington. Copper leached from tar-covered roofs at concentrations averaging 166 µg/L. The authors concluded that copper may be a component in the roof coating.

Dietz et al. (2007) investigated copper releases from distribution systems made of various materials. Water was passed through copper pipes with embedded lead coupons to simulate residential systems. The use of phosphate-based inhibitors reduced the copper concentrations by more than 50% (the concentrations of copper were between 200 and 800 µg/L when using the inhibitors). Gumbs and Dierberg (1985) reported in a literature review that heavy metal concentrations in drinking water can increase due to the corrosion of the distribution system and household plumbing. They reported that other researchers found significantly higher copper concentrations in tap water compared to cistern water.

Gromaire-Mertz et al. (1999) studied runoff from roofs and gutters in an old, densely populated district of central Paris, France, between July 1996 and May 1997. Roofing materials included clay tiles, zinc sheets, and slate. Copper concentrations observed in the roof runoff ranged between 3 and 247 µg/L, with a median of 37 µg/L.

Zobrist et al. (2000) measured the concentrations of heavy metals in runoff from tile, polyester, and gravel roofs located in the suburb of Zürich, Switzerland. The roof drainage system for the tile (clay) roof was made of 15-year old copper, the polyester roof had new copper drainage, and the gravel roof had PVC material drainage. The average runoff copper concentrations from the tile roof were 304 µg/L and from polyester roof 842 µg/L. Higher copper concentrations were associated with smaller rain depths.

Mendez et al. (2011) studied the effects of roofing material on water quality for rainwater harvesting systems using five pilot-scale (asphalt fiberglass shingle, Galvalume® metal, concrete tile, cool, and green) roofs and three full-scale roofs (two asphalt fiberglass shingle and one 7-yar-old Kynar®-coated Galvalume® metal). The flat cool roof consisted of a white, acrylic-surfaced 2-ply atactic polypropylene (APP) modified bituminous membrane.

The test site was located at University of Texas in Austin. Cu concentrations in the harvested rainwater from the full-scale Kynar®-coated Galvalume® roof were lower than from pilot-scale uncoated Galvalume roofs. Cu concentration in the harvested rainwater from pilot-scale Galvalume roofs ranged between <0.6 and 9.9µg/L for the first flush sample, and between <0.6 and 4.8 µg/L for later samples. The rain water quality was between <0.6 and 12 µg/L. Cu concentrations in harvested rainwater from full-scale Kynar®-coated Galvalume® roof were <0.02µg/L for the first flush sample, for later samples, and for the ambient rain (Mendez et al. 2011).Mendez et al. (2011) also examined the contaminants in harvested rainwater from coupons of new and artificially aged roofing materials in lab-scale studies. The aging process did not significantly affect Cu concentrations from the Galvalume® metal roofing coupons.

Förster (1996) studied heavy metals and major ions in roof runoff in Bayreuth, Germany. He found that copper flashings used on the roofs released very high concentrations of Cu (up to 640 µg/L) and concluded that the best management practice would be not to use exposed metal surfaces on roofs and walls of buildings. Also, copper-based algaecide paints can be significant sources of copper as was shown during investigations conducted in several boat marinas (US EPA 2011).

Karlen et al. (2002) studied runoff rates from naturally patinated copper roofs of varying age (0 and 30 years) during a three-year field exposure study in Stockholm, Sweden. Annual runoff rates for naturally patinated copper of varying ages ranged between 1.0 and 1.5 g/m^2 year and have been found to increase slightly with patina age which was attributed to the enhanced first flush noted on thicker patina layers. The major portion of the released copper (60 – 100%) was present as the free hydrated cupric ion, $Cu(H_2O)_6^{2+}$, which is the most bioavailable copper species. Other copper species in the roof runoff water ($Cu(OH)^+$ and $Cu_2(OH)_2^{2+}$), were also bioavailable.

Wallinder et al. (2002a) examined the atmospheric corrosion of naturally and pre-patinated copper roofs in Singapore and Stockholm. Similar copper runoff rates between fresh and brown-patinated copper roof sheet and between green naturally patinated and green pre-patinated copper roof sheet at each site were linked to similar morphology and composition of the patina.

Boller and Steiner (2002) studied the release and control of copper from roofs and roads in urban stormwater in Basle and Zürich, Switzerland. A large copper building facade was examined for copper concentrations in the runoff. The concentrations ranged from 1 to 10 mg/L during the first year of investigation.

Corvo et al. (2005) investigated changes in Cu corrosion rates caused by chloride ions in rain. Test materials included copper and steel that were exposed in two atmospheric test stations located in Havana, Cuba and Medellin, Colombia. The samples were subjected to accelerated outdoor tests by intermittent spraying of a salt solution. The addition of salt spray at Havana increased the corrosion rate of the copper material (33 g/m^2 of Cu) compared to the samples at the same location but under natural conditions (9.4g/m^2 of Cu) .Metal mass losses were proportional to the chloride deposition rate. The authors found that the acceleration of copper corrosion caused by chloride ions was notably higher at Havana(33 g/m^2 of Cu) compared to Medellin(17 g/m^2 of Cu) and was explained by lower frequencies and amounts of rain at Havana during the 1 year of exposure. A higher washing and cleaning effect took place at Medellin. Additionally, rain diminishes chloride surface concentrations; the acceleration rate caused by chloride ions is likely to lessen with the increase of rain amount at constant exposure time.

Atmospheric-induced corrosion causes an alternately growing and decreasing layer of electrolyte, which is often very thin. In the presence of corrosion products at the metal–atmosphere interface, the sorption properties of these products and salts (usually hygroscopic) deposited or formed by corrosion, determine the possibilities of superficial wetness. The amount of water on the corroding surface plays an important role in the corrosion rate. The formation of green rust in the presence of chloride ions involves an incorporation of the chloride ions from solution into the inter-layers of green rust and an oxidation of Fe (II) to Fe (III) without any structural changes (Corvo et al. 2005).

Table 1.2 summarizes copper concentrations or runoff yields from different materials found by various researchers.

Table 1.2. Copper releases from various sources.

Material	Test descriptions	Cu concentrations or runoff yields	Reference
Uncoated Copper Roofing Materials			
Copper roof	2 year field test. Stockholm, Sweden	Average 1.3 - 1.5 $g/m^2/year$	Wallinder et al. (2000)
Copper roof	Stockholm, Sweden. 2 year test	1.3 $g/m^2/year$	Faller and Reiss (2005)
Fresh copper sheet	Brest, France. 1 year test	1.5 $g/m^2/year$	Sandberg et al. (2006)
Untreated rolled copper sheet	Dubendorf, Switzerland. 5 year test	1.3 $g/m^2/year$	Faller and Reiss (2005)
After copper roof and cast iron and concrete downspouts	Field. Suburban Farsta, Stockholm. Several rains during 2006-2008	5-101 µg/L (median 15 µg/L)	Wallinder et al. (2009)
After copper roof and cast iron and concrete downspouts and concrete drain system pipe	Field. Suburban Farsta, Stockholm .Several rains during 2006-2008	2 -175 µg/L (median 18 µg/L)	Wallinder et al. (2009)
Copper material	(salt spray) Medellin, Colombia. 1 year test	16.0 $g/m^2/year$ mass loss	Corvo et al. (2005)
Copper material	(salt spray) Havana, Cuba. 1 year test	32.8 $g/m^2/year$ mass loss	Corvo et al. (2005)
Copper material	(natural conditions) Havana, Cuba. 1 year test	9.4 $g/m^2/year$ mass loss	Corvo et al. (2005)
Copper materials	Stockholm, Sweden	1.0 - 2.0 $g/m^2/year$	He et al. (2001a)
Other Roofing Materials			
Pilot-scale Galvalume roofs	Austin, Texas. Several rain events in 2010	<0.63 - 9.88 µg/L during first flush; <0.63 - 4.84 µg/L for later samples	Mendez et al. (2011)
Full-scale Kynar®-coated Galvalume® roof	Austin, Texas. Several rain events in 2010	<0.02 µg/L	Mendez et al. (2011)
New uncoated galvanized steel roof	4 mo. Field test. Pilot Scale. Harrisburg, PA	< 3µg/L	Clark et al. (2008a)
Clay tiles, clay tiles (70%) + zinc sheets, zinc sheets, and slate	Central Paris. July 1996 and May 1997	3 - 247 µg/L (median 37 µg/L)	Gromaire-Mertz et al. (1999)
Metal and vinyl materials panels	4 mo. Field test. Pilot Scale. Harrisburg, PA	< 25 µg/L	Clark et al. (2008a)
New vinyl roof	14 mo. Field test. Pilot Scale. Harrisburg, PA	< 20 µg/L	Clark et al. (2007)
Tile roof	Zurich, Switzerland. 14 rain events	400 and 50 µg/L; average 1623	Zobrist et al. (2000)

		µg/m^2	
New asphalt shingles roof	4 mo. Field test. Pilot Scale. Harrisburg, PA	25 µg/L (median) 112 µg/L (75th percentile	Clark et al. (2008a)
Tar-covered roofs	Washington	166 µg/L	Good (1993)
New cedar shakes roof	4 mo. Field test. Pilot Scale. Harrisburg, PA	from 1,500 to 27,000 µg/L	Clark et al. (2008a)
Aged/Patinated Copper Materials			
Naturally patinated copper sheet	Brest, France. 1 year test	1.3 g/m^2/year	Sandberg et al. (2006)
Naturally aged copper roof	Field. Suburban Stockholm, Sweden. Several rains during 2006-2008	0.74 - 1.6 g/m^2/year (median 1.0 g/m^2/year)	Wallinder et al. (2009)
Naturally patinated copper of varying age	Field. Stockholm, Sweden	1.0 - 1.5 g/m^2/year	Karlen et al. (2002)
Naturally patinated copper of varying age	Field. Stockholm, Sweden	900 - 9700 µg/L	Karlen et al. (2002)
Fresh and brown prepatinated copper roofs	Stockholm, Sweden	1.1-1.6 g/m^2/year	Wallinder et al. (2002a)
Fresh and brown prepatinated copper roofs	Singapore	5.5-5.7 g/m^2/year	Wallinder et al. (2002a)
130 years old copper roof sheet and green prepatinated copper sheet	Singapore, Stockholm	1.6-2.3 g/m^2/year	Wallinder et al. (2002a)
Green pre-patinated copper roof sheet	Singapore	8.4-8.8 g/m^2/year	Wallinder et al. (2002a)
Copper Pipes			
Copper pipes		200 - 800 µg/L	Dietz et al. (2007)
New copper drains	Zurich, Switzerland. 14 rain events	7.8 g/(m^2 y^1)	Zobrist et al. (2000)
15 - year old drains	Zurich, Switzerland. 14 rain events	3.5 g/(m^2 y ^{1})	Zobrist et al. (2000)
Copper facade	1 year test	10^3 – 10^4 µg/L	Boller and Steiner (2002)

Summary. The highest copper runoff rates were noted from exposed copper materials (Wallinder et al. 2000; Sandberg et al. 2006; Wallinder and Leygraf 1997; Leuenberger-Minger et al. 2002; Sandberg et al. 2006; Faller and Reiss 2005; Zobrist et al. 2000, Boller and Steiner 2002, and Förster 1996). Copper-based paints can also be a significant source of copper in runoff

(US EPA 2011). Some studies indicated relatively constant copper runoff yields with time during 5 years of exposure (Faller and Reiss 2005). However, other studies found that new copper materials had higher copper runoff yields compared to older copper materials (Zobrist et al. 2000). Galvanized steel, vinyl, and galvalume materials had copper runoff concentrations that were less than 25 µg/L (Clark et al. 2008a; Mendez et al. 2011).

The major portion of the copper in the runoff at the source was in the most bioavailable form (hydrated cupric ion), but when the stormwater runoff passes through cast iron and concrete drainage systems, copper may be retained or form complexes with organic matter and change chemical speciation to less toxic or less bioavailable forms (Karlen et al. 2002; Wallinder et al. 2009; Bertling et al. 2006; Boulanger and Nikolaidis 2003; and Sandberg et al. 2006). Copper runoff yields were proportional to the chloride deposition rate on the surfaces and were also influenced by rain frequencies and amounts (Corvo et al. 2005).

2.1.4 Lead

Clark et al. (2007) studied three samples of galvanized metal: a rusted sample with no paint, bare metal with no paint and no visible degradation, and painted metal. Lead was released from all three types of galvanized steel roofing materials during the natural rain test period and was just above the method detection limit of 1µg/L. Tobiason and Logan (2000) found that zinc-galvanized metal roof was not a source of lead.

Good (1993) studied chemical concentrations and aquatic toxicity of roof runoff from different roofing materials at a sawmill on the coast of Washington. The authors found that lead was leaching from the rusty galvanized metal roof and reached 300 µg/L.

Lasheen et al. (2008) studied the effect of pH, stagnation time, pipe age, and pipe material on the concentrations of lead released from polyvinyl chloride (PVC), polypropylene (PP) and galvanized iron (GI). PVC pipes were found to be the greatest source of lead. Figures 1.3 and 1.4 show the mean lead concentrations released from PVC and galvanized iron pipes after 72 hr of exposure. The authors found that the concentrations of lead were higher after 72 hours of exposure time than after 48 hours at pH 7.5. The authors also found that as pipe age increased the lead concentrations also increased. For example, the mean lead concentrations were 95 and 120 µg/L in 2 and 20 weeks aged PVC pipes, respectively after stagnation of 72 h. For galvanized iron pipes, after 72 h of stagnation, mean lead concentrations were 53 and 64 µg/L in 2 and 20 weeks aged pipes. As pH increased (to pH=8), the concentration of lead decreased. The authors observed that increasing the ratio of Cl/SO_4 from 0.83 to 2 resulted in an increase of lead concentrations from GI pipes. The levels of lead increased in PVC pipes as the Cl/SO_4 ratio increased, however the lead concentrations were less than that in control pipes (Lasheen et al. 2008).

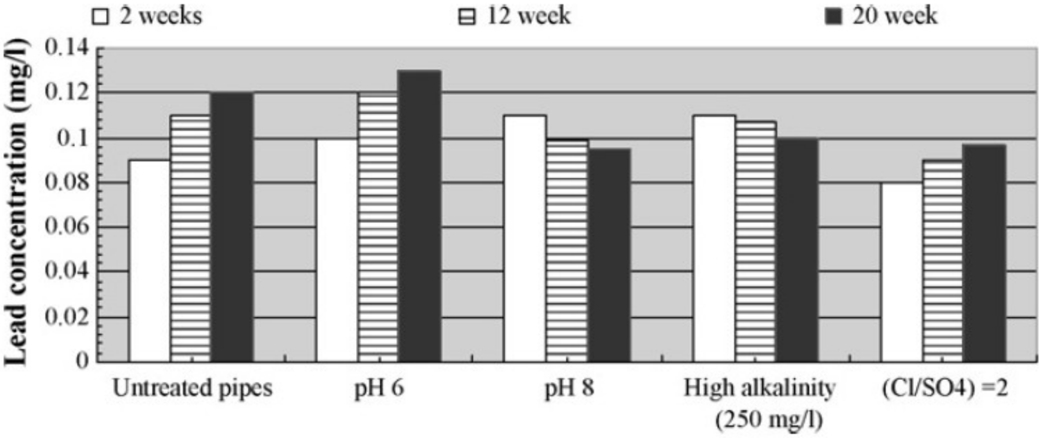


Figure 1.3. Mean lead concentrations released from PVC pipes after 72 hr. of exposure. Source: Lasheen et al. 2008

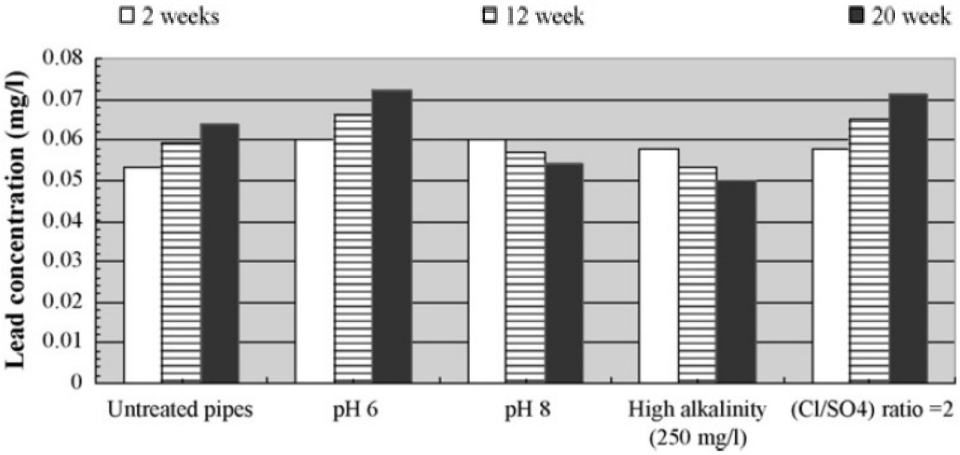


Figure 1.4. Mean lead concentrations released from galvanized iron pipes after 72 hr. of exposure.
Source: Lasheen et al. (2008).

Al-Malack (2001) studied the migration of lead, and other metal stabilizers from unplasticized polyvinyl chloride (uPVC) pipes. The author observed an increase in lead concentrations leaching from uPVC pipes with time. After 10 h of exposure, lead concentrations migrating from the uPVC pipes into the circulated water reached a value of 430µg/L and by the end of the experiment (48 h), lead concentrations had increased to 780µg/L which was more than 50 times greater than the maximum permissible level (MCL) of 15 µg/L established by US EPA for drinking water (Al-Malack 2001). The author found that the migration of lead took place in two distinct phases. During the first phase, there was a sharp increase in diffusion rate of lead with time, in the second phase after 10 h exposure time, the diffusion rate of lead slowed with time. As pH decreased, the amount of lead leaching from the uPVC pipes increased. At pH 5, about 1000 µg/L of lead migrated from the UPVC pipe into the water after 48 h of exposure. Between pH 7 and 9, the increase in lead concentrations were insignificant, which suggests that alkaline environments do not have significant effects on lead migration from uPVC pipes.

The effect of UV-radiation (a disinfection method for the control of bacteria) on the migration of lead and other metal stabilizers from uPVC pipes was investigated at different times of exposure during static tests. Exposure to UV-radiation was found to promote the migration of lead and other metal stabilizers. After 12 h of exposure, lead concentrations reached 115 µg/L. This lead concentration is approximately eight times the MCL of lead in drinking water established by EPA. Lead concentrations of 310 and 800µg/l were detected after 5 and 14 days of exposure to UV-radiation, respectively. The latter concentration is 50 times higher than the MCL in drinking water established by EPA.

Dietz et al. (2007) investigated lead releases from PVC, lined cast iron, unlined cast iron, and galvanized steel aged pipes (40+ years) with and without inhibitors. Water was also passed through copper pipes with embedded lead coupons to simulate residential systems. An increase in the phosphorus or SiO_2 inhibitor doses or pH elevation significantly decreased the lead concentrations. For the distribution systems with an inhibitor, the lead concentrations didn't exceed 5 µg/L, and were below the current action level of 15 µg/L for lead. For the distribution systems with the pH control, some lead concentrations reached 65 µg/L. Operation without inhibitors often resulted in lead concentrations which exceeded the action level, whereas the use of an inhibitor consistently provided compliance with the action level (Dietz et al. 2007).

Gromaire-Mertz et al. (1999) studied lead in roof runoff from clay tiles, zinc sheets, and slate roofing materials in Paris, France. Lead concentrations detected in the roof runoff ranged between 16 and 2,800 µg/L, with a median of about 500 µg/L. Lead concentrations in roof runoff exceeded level 2 of French water quality standards of 50 µg/L for practically all samples. Lead was bounded to particulates in nearly all samples.

Schriewer et al. (2008) studied lead in roof runoff from 14 year-old zinc roofs in Germany. Roof runoff was also affected by titanium–zinc gutters and downspouts. Five chimneys were soldered on the roof with tin-solder, which contains small amounts of lead. Samples were collected directly in the gutter. Lead was detected in only a few samples, with the maximum lead concentration observed being 31 µg/L.

Zobrist et al. (2000) measured the concentrations of heavy metals, including Pb, in runoff from a tile roof located in suburb of Zürich, Switzerland. The average runoff lead load in tile roof runoff was 250 $\mu g/m^2$per event.

Davis and Burns (1999) examined lead release in stormwater runoff from painted structures located at the University of Maryland, College Park Campus and in surrounding commercial and residential neighborhoods in Prince George's and Montgomery Counties, Maryland and the District of Columbia. Lead concentrations were the highest from painted wood structures (geometric mean, median, Q10-Q90): 40, 49, 2.6-380 µg/L, respectively), followed by painted bricks (22, 16, 3.3-240 µg/L) and painted concrete blocks (9.7, 8.0, <2-110 µg/L). Lead concentrations were considerably affected by paint age and condition: paint age [>10 y] (77, 88, 6.9 - 590 µg/L), [5-10 y] (22, 16, <2-240 µg/L), [0-5 y] (8.4, 8.1, <2-64 µg/L). Lead releases from washes of older paints were significantly higher than from fresh paints. It was found that old surface paints have the potential to release large amounts of lead into a watershed. Simmons et al. (2001) investigated rainwater quality harvested from residential roofs in New Zealand for beneficial uses. He also found that lead was released from the roofs that were coated with lead-based paint. The concentration ranged between 11 and 140 µg/L.

Förster (1999) examined the variability of roof runoff quality from different roofing materials, including zinc sheet in Bayreuth, Germany. Zinc and PVC rain gutters were used. The author attributed lead contamination in the roof runoff to particulate dry deposition and/or dissolution of lead components on the roofs. Total lead concentrations in roof runoff from the zinc roofs were about 10μg/L, with dissolved lead being only about 15% of the lead particulate-bound concentrations.

Heavy metal concentrations in drinking water can increase due to corrosion of distribution system and household plumbing materials; this was also noted for cistern water systems (Gumbs and Dierberg 1985; Shahmansouri et al. 2003). Gumbs and Dierberg (1985) studied three components of 46 single-family cistern water systems having piped water delivery systems (corrugated galvanized iron roof, cistern, and distribution system) on St. Maarten Island. Lead concentrations in bulk precipitation ranged between 5.8 and 15.9 μg/L, with an average of 9.9 μg/L. They found that lead was bound with particulate matter and settled to the bottom of the cistern. The metal concentrations in the rainwater increased as it passed over the galvanized roof surface and through the gutter and downspouts connected to the cisterns. The elevated levels of lead at the final water tap compared to the cistern's lead water concentrations were attributed to corrosion of the galvanized metal parts within the distribution systems (galvanized iron pressure tanks) due to the longer residence time. The surface water concentrations for lead ranged between 0.1 and 75 μg/L with the average of 0.9 μg/L; the lead concentrations in the tap samples ranged between 0.2 amd70 μg/L with the average of 2.1 μg/L. The pipes before and after the pumps were mostly made of galvanized iron and PVC.

Mendez et al. (2011) investigated the effects of roofing material on water quality for rainwater harvesting systems. The authors examined the quality of harvested rainwater using several pilot-scale roofs (asphalt fiberglass shingle, Galvalume® metal, concrete tile, and planted green roofs) located at the Lady Bird Johnson Wildflower Center, Austin, Texas and three full-scale roofs (two asphalt fiberglass shingle and one 7-year-old Kynar®-coated Galvalume® metal roofs). The full-scale site was located at the University of Texas at Austin Child Development Center, Comal location, Austin, Texas. Also, new and artificially aged coupons of asphalt fiberglass shingle, Galvalume® metal, and concrete tile were examined in lab-scale studies to determine the potential for changes in harvested rainwater quality influenced by aged roofing materials. Pb concentrations in the harvested rainwater from the Galvalume roofs were greater than for the Kynar®-coated Galvalume® roof. Lead concentrations in harvested rainwater from pilot-scale Galvalume roofs ranged between <0.1 and 6.4 µg/L for the first flush sample, and between <0.1 and 5.7 µg/L for later samples. The rain lead concentrations ranged between <0.1 and 0.9 µg/L. Lead concentrations in harvested rainwater from full-scale Kynar®-coated Galvalume® roof ranged between <0.01 and 0.2µg/L for the first flush sample and were <0.12µg/L for later samples. The rain lead concentrations during this test series ranged between <0.01 and 1.54 µg/L. The aging process conducted during the lab-scale studies did not significantly affect Pb concentrations from the Galvalume® metal roofing coupons (Mendez et al. 2011).

Shahmansouri et al. (2003) conducted a study on pilot-scale drinking water distribution systems in Zarrinshahr and Mobarakeh, Iran. The piping system materials in houses and buildings were galvanized iron, the distribution piping systems were made of asbestos, polyethylene, and occasionally iron pipes. The authors found that the samples analyzed along the distribution system show significant increases in concentrations of lead. The lead concentrations increased up to an average of 5.7 and 7.8 µg/L in Zarrinshahr and Mobarakeh respectively; the lead concentrations sometimes exceeded the MCL. Table 1.3 summarizes lead concentrations or release rates from different materials found by various researchers.

Table 1.3. Lead releases from various sources.

Material tested	Test conditions	Observed lead concentrations, or runoff yields	Reference
Uncoated Galvanized Steel Roofing Materials			
Galvanized roof	Pilot scale	Just above 1 µg/L	Clark et al. (2007)
Galvanized roof	Leaching test in the lab	0.002-0.02 g/kg/48hr	Clark et al. (2007)
Zinc sheet, zinc and PVC gutters	Bayreuth, Germany	10µg/L	Forster (1999)
Clay tiles, flat clay tiles (70%) + zinc sheets, zinc sheets, and slate roofing materials	Field. Paris, France.	16 - 2764 µg/L (the median 493 µg/L)	Gromaire-Mertz et al. (1999)
Cistern surface water (after galvanized iron roof)	St. Maarten Island, Netherlands	0.1 - 75.1 µg/L (avg. 0.9 µg/L).	Gumbs and Dierberg (1985)
The bottom of the cisterns (after galvanized iron roof)	St. Maarten Island, Netherlands	Avg. 19.4 µg/L	Gumbs and Dierberg (1985)
Uncoated Galvanized Aluminum Roofing Materials			
Galvalume roofs	Pilot-scale. Austin, Texas	<0.12 - 6.40 µg/L during first flush, <0.12 - 5.65 µg/L for later samples	Mendez et al. (2011)
Coated Galvanized Aluminum Roofing Materials			
Kynar®-coated Galvalume® roof	Full-scale Austin, Texas	<0.01 - 0.21µg/L during first flush; <0.12µg/L for later samples	Mendez et al. (2011)
Aged Galvanized Steel Roofing Materials			
Rusty galvanized metal roof	Field test during first flush. The coast of Washington	302 µg/L	Good (1993)
60 years old painted galvanized metal roof exposed in the filed	Leaching test in the lab	0.01 - 1 g/kg/48hr	Clark et al. (2008b, 2007)
60 years old painted galvanized metal roof stored in the barn	Leaching test in the lab	0.01 - 1 g/kg/48hr	Clark et al. (2008b, 2007)
14 year-old zinc roof, titanium–zinc gutters and the down spout	Germany	31 µg/L	Schriewer et al. (2008)
Other Roofing Materials			
Tile roof	Zurich, Switzerland, 14 rain events	249 µg/m^2	Zobrist et al. (2000)
Painted Materials			
Metal roof coated with aluminum paint, tar roof painted with fibrous reflective aluminum paint, anodized aluminum roof	Field test during first flush. The coast of Washington	10 - 15 µg/L	Good (1993)

Painted wood	Field test	2.6-380 µg/L (Q10[1]-Q90[2])	Davis and Burns (1999)
Painted brick	Field test	3.3-240 µg/L (Q10-Q90)	Davis and Burns (1999)
Painted block	Field test	<2-110 µg/L (Q10-Q90)	Davis and Burns (1999)
>10 year paint	Field test	6.9 - 590 µg/L (Q10-Q90)	Davis and Burns (1999)
5-10 year paint	Field test	<2-240 µg/L (Q10-Q90)	Davis and Burns (1999)
0-5 year paint	Field test	<2-64 µg/L (Q10-Q90)	Davis and Burns (1999)
Drinking Water Distribution Systems			
Galvanized iron pipe after 2 weeks of use, 72 hr of stagnation	increasing the ratio of Cl/SO_4 from 0.83 to 2	58 µg/L	Lasheen et al. (2008)
Galvanized iron pipe after 20 weeks of use, 72 hr of stagnation	increasing the ratio of Cl/SO_4 from 0.83 to 2	70 µg/L	Lasheen et al. (2008)
PVC pipes after 2 weeks of use, 72 hr of stagnation	pH 7.5	95 µg/L	Lasheen et al. (2008)
PVC pipes after 20 weeks of use, 72 hr of stagnation	pH 7.5	120µg/L	Lasheen et al. (2008)
PVC pipes after 2 weeks of use, 72 hr of stagnation	pH 6	100µg/L	Lasheen et al. (2008)
PVC pipes after 20 weeks of use, 72 hr of stagnation	pH 6	130µg/L	Lasheen et al. (2008)
PVC pipes after 2 weeks of use, 72 hr of stagnation	pH 8	110µg/L	Lasheen et al. (2008)
PVC pipes after 20 weeks of use, 72 hr of stagnation	pH 8	20µg/L	Lasheen et al. (2008)
PVC pipe after 2 weeks of use, 72 hr of stagnation	increasing the ratio of Cl/SO_4 from 0.83 to 2	80µg/L	Lasheen et al. (2008)
PVC pipe after 20 weeks of use, 72 hr of stagnation	increasing the ratio of Cl/SO_4 from 0.83 to 2	100µg/L	Lasheen et al. (2008)
Unplasticized PVC pipe after 10 h of exposure	-	430µg/L	Al-Malack (2001)
Unplasticized PVC pipe after 48 h of exposure	-	780µg/L	Al-Malack (2001)
Unplasticized PVC pipe after 48 h of exposure	pH 5	1000µg/L	Al-Malack (2001)
Unplasticized PVC pipe after 12 h of exposure	UV exposure	115µg/L	Al-Malack (2001)
Unplasticized PVC pipe after 5 days of exposure	UV exposure	312 µg/L	Al-Malack (2001)
Unplasticized PVC pipe after 14 days of exposure	UV exposure	799µg/L	Al-Malack (2001)
PVC, lined cast iron, unlined cast iron, and galvanized steel aged pipes (40+ years)	Phosphorus or SiO_2 inhibitor	< 5 µg/L	Dietz et al. (2007)

PVC, lined cast iron, unlined cast iron, and galvanized steel aged pipes (40+ years)	pH control	max.65 µg/L	Dietz et al. (2007)
Galvanized piping systems, asbestos, polyethylene, iron pipes	Pilot scale. Zarrinshahr, Iran	1.60 - 16.00 µg/L (avg. 5.7 µg/L)	Shahmansouri et al. (2003)
Galvanized piping systems, asbestos, polyethylene, iron pipes	Pilot scale. Mobarakeh, Iran	0.60 - 18.70 µg/L (avg. 7.8 µg/L)	Shahmansouri et al. (2003)
At the tap (after galvanized iron roof, gutter and down spout, distribution system)	St. Maarten Island, Netherlands	0.2-70.0 µg/L (average of 2.1 µg/L)	Gumbs and Dierberg (1985)

[1] and [2] 10th and 90th percentiles of data values, respectively

Summary. Galvanized steel, PVC and unplasticized PVC, (Gromaire-Mertz et al. 1999; Schriewer et al. 2008; Förster 1999) Galvalume (Mendez et al. 2011), and zinc materials can be sources of lead concentration increases in water (Clark et al. 2007; Lasheen et al. 2008; Al-Malack 2001; Gumbs and Dierberg 1985; Shahmansouri et al. 2003). Lead concentrations released from galvanized steel and PVC materials increase with increased exposure time, increased pipe age, and pH decreases (Lasheen et al. 2008; Al-Malack 2001; Dietz et al. 2007). Also, exposure to UV-radiation was determined to promote the migration of lead from unplasticized PVC pipes (Al-Malack 2001). Additionally, painted materials can be a source of lead in stormwater, with lead releases being higher from older types of paints (Davis and Burns 1999; Simmons et al 2001). The rise in the ratio of Cl/SO_4 from 0.83 to 2 resulted in an increase in lead concentrations from galvanized iron and PVC pipe exposure (Lasheen et al. 2008).

2.1.5 Cadmium

Al-Malack (2001) investigated the effect of water quality parameters and direct exposure to UV-radiation on the migration of metal stabilizers, including cadmium, from unplasticized polyvinyl chloride (uPVC) pipes. As exposure time increased, cadmium concentrations in the runoff also increased. Cadmium concentrations increased from below detection limit level (<50 μg/L) to 88 μg/L after 48 hrs of exposure. It was observed that exposure to UV-radiation promoted the migration of metal stabilizers and that this increased the Cd concentrations with time. As water pH decreased, the cadmium concentrations released from the uPVC pipes increased. A pH change from pH 9 to pH 6 caused cadmium concentrations increase from 53 to 89 μg/L. The water temperature reached 35°C after 24 h of exposure to the UV radiation, and remained at that level till the end of the study.

Gromaire-Mertz et al. (1999) examined runoff from different roofing materials and gutters in Paris, France, between July 1996 and May 1997. Roofing materials included clay tiles, zinc sheets, and slate. Cadmium concentrations in roof runoff (1 to 5 μg/L) were below the level 2 water quality criteria (1,000 μg/L) with the exception of runoff from the zinc sheet roof runoff samples. Cadmium concentrations were extremely high in roof runoff from the zinc roofs. Leaching of cadmium is explained by the erosion of the zinc roofing material, in which cadmium is a minor constituent. Förster (1996) found that for cadmium, the association with dissolved and particulate fractions varied, however, it was noted that generally, the dissolved fraction of cadmium was greater than the particulate fraction for the roof runoff.

Schriewer et al. (2008) studied runoff from 14 year-old zinc roofs in Germany during a period of 1 year. Roof runoff flowed into titanium–zinc gutters and downspouts. Five chimneys were also soldered on the roof with tin-solder, which contains fractions of other metals. Samples were collected directly in the gutter. Cadmium concentrations (0.5 - 0.8 μg/L) were detected only in a few samples.

Zobrist et al. (2000) measured the concentrations of heavy metals including Cd in runoff from tile, polyester, and gravel roofs located in a suburb of Zürich, Switzerland. The roof drainage system for the clay tile roof was made of 15-year old copper; for polyester roof out of new copper; and for gravel roof out of PVC material. Average runoff total cadmium losses from tile roof were2.5 µg/m^2 per event. Cd was chiefly associated with the dissolved fraction.

Tar felt roofing was found to be a source of cadmium in roof runoff monitored by Förster (1999) in Bayreuth, Germany. Roofing materials examined included concrete tiles, clay pantiles, fibrous cement, tar felt, and zinc sheet. Zinc and PVC gutters were used. The dissolved cadmium concentrations were about ten times the particulate-bound cadmium concentrations in the runoff.

Gumbs and Dierberg (1985) investigated 46 single-family water cistern systems having piped delivery systems (roof, cistern, and distribution system) on St. Maarten Island. The roof catchment surface for the cisterns was made of corrugated galvanized iron sheets. Most of the cistern systems had galvanized iron pressure tanks. The pipes before and after the pumps were mainly made out of galvanized iron and PVC pipes. The authors found that cadmium concentrations in bulk precipitation were between 0.5 and 1.1 µg/L with the average of 0.8 µg/L. The elevated levels of cadmium at the tap (<0.02 to 30 µg/L with the average of 0.1 µg/L) compared to the cistern surface water concentrations (< 0.02-0.4 µg/L with the average of 0.03 µg/L) were attributed to the corrosion of the galvanized metal parts within the distribution systems (mostly the galvanized pressure tanks) due to the extended residence times in the tanks. Average concentrations of cadmium at the bottom of the cisterns (mixture of water and sediment) were significantly higher than in the surface and tap water samples (Gumbs and Dierberg 1985).

Shahmansouri et al. (2003) conducted a study on drinking water distribution systems in Zarrinshahr and Mobarakeh, Iran. The piping system materials in houses and buildings were galvanized, the distribution piping systems were made of asbestos, polyethylene, and iron pipes. The researchers found that the samples analyzed before and after the distribution system indicated significant increases in cadmium concentrations of up to 0.1 and 0.8 μg/L in Zarrinshahr and Mobarakeh respectively. Gromaire et al. (2002) examined cadmium concentrations in stormwater runoff from zinc roofing in Paris. Annually, runoff from Parisian zinc roofs generated approximately 15 to 25 kg of cadmium. Table 1.4 summarizes cadmium concentrations and release rates from different materials found by various researchers.

Table 1.4. Cadmium releases from various sources.

Materials tested	Test conditions	Observed cadmium concentrations or runoff yields	Reference
Uncoated Galvanized Roofing Materials			
Parisian zinc roofs	Paris, France	15 - 25 kg/year for the city	Gromaire et al. (2002)
Cistern surface water (after galvanized iron roof)	St. Maarten Island, Netherlands	< 0.02-0.40 μg/L (avg. 0.03 μg/L)	Gumbs and Dierberg (1985)
The bottom of the cisterns (after galvanized iron roof)	St. Maarten Island, Netherlands	Avg. 0.99 μg/L	Gumbs and Dierberg (1985)
clay tiles, flat clay tiles (70%) + zinc sheets, zinc sheets, and slate	Paris, France. July 1996 and May 1997	0.1-32 μg/L (median of 1.3 μg/L)	Gromaire-Mertz et al. (1999)
Aged Galvanized Steel Roofing Materials			
14 year-old zinc roof runoff	Germany, 1 year test	0.5 μg/L (DL) – 0.8μg/L	Schriewer et al. (2008)
Other Roofing Materials			
Clay tile roof with 15-year old copper gutter	Filed test. Tuffenwies, Switzerland	2.5 μg/m^2 per event	Zobrist et al. (2000)
Tar felt roof	Bayreuth, Germany	0.5μg/L	Forster (1999)
Drinking Water Distribution Systems (DWDS)			
Unplasticized PVC pipe after 48 hrs of exposure	-	88 μg/L	Al-Malack (2001)
Unplasticized PVC pipe after 14 days of exposure	Change from pH 9 to pH 6	increase from 53 to 89 μg/L	Al-Malack (2001)
Unplasticized PVC pipe after 48 hrs of exposure	Exposure to UV-radiation	800 μg/L	Al-Malack (2001)
At the tap (after galvanized iron roof, gutter and down spout, distribution system)	St. Maarten Island, Netherlands	<0.02-30.2 μg/L (average 0.12 μg/L)	Gumbs and Dierberg (1985)
Drinking Water Distribution System (asbestos, polyethylene, and iron pipes), after min of 6 hrs.	Zarrinshahr, Iran	Before DWDS 0.08 μg/L, after DWDS 0.11 μg/L	Shahmansouri et al. (2003)
Drinking Water Distribution System (asbestos, polyethylene, and iron pipes), after min of 6 hr.	Mobarakeh, Iran	Before DWDS 0.06 μg/L, after DWDS 0.8 μg/L	Shahmansouri et al. (2003)

Summary. PVC, zinc, tile, tar felt, and galvanized iron materials can all be sources of cadmium in runoff (Al-Malack 2001; Gromaire-Mertz et al. 1999; Zobrist et al. 2000; Förster 1999; Schriewer et al. 2008; Gumbs and Dierberg 1985; Shahmansouri et al. 2003; Gromaire et al. 2002). Exposure to UV-radiation promoted the migration of cadmium stabilizers from unplasticized PVC pipes. A decrease in the pH of the water was also found to increase the cadmium concentrations released from the uPVC pipes (Al-Malack 2001).

2.1.6 Chromium

Zobrist et al. (2000) examined the concentrations of heavy metals, including Cr, in runoff from various roofing materials that were installed in a suburb of Zürich, Switzerland. The drainage system for the monitored clay tile roof was made of 15-year old copper. Tile roof was a source of chromium. Average runoff total chromium losses from tile roof were10 µg/m^2 per event. Cr was chiefly associated with the dissolved fraction.

Faller and Reiss (2005) investigated the exposure of different metallic materials to the open atmosphere in Dubendorf, Switzerland. The roof runoff concentrations of chromium were less than the detection limit (10µg/L) from aluminum, stainless steel and titanium test roofs. However, a study on the release rates of chromium from stainless steel roofs determined runoff rates in the range of 200 to 700 µg/m^2/year (Wallinder et al. 2002b).

Gumbs and Dierberg (1985) examined three components of 46 single-family cisterns with a piped water delivery system (roof, cistern, and distribution system) on St. Maarten Island. The roof catchment surface was made of corrugated galvanized iron sheets. The majority of the cisterns systems had galvanized iron pressure tanks. The pipes before and after the pumps were mostly made out of galvanized iron and PVC pipes. Chromium was not a significant constituent of the galvanized materials and there was no increase of chromium noted in the delivered tap water (Gumbs and Dierberg 1985). Table 1.5 summarizes chromium concentrations and release rates from different materials found by various researchers.

Table 1.5. Chromium releases from various sources.

Material tested	Test method	Observed chromium concentrations or runoff yields	Reference
Tile roof with 15-year old copper drainage system	Zurich, Switzerland. 14 rain events	Avg. runoff load 10 µg/m^2 per event	Zobrist et al. (2000)
Aluminum, stainless steel and titanium roofs	Stockholm, Sweden. 2 year test	< DL (10µg/L)	Faller and Reiss (2005)
Stainless steel	-	200 - 700µg/m^2/year	Wallinder et al. 2002b)
Cistern surface water (after galvanized iron roof)	St. Maarten Island, Netherlands	< 0.04 - 13.4 µg/L (avg. 0.4 µg/L)	Gumbs and Dierberg (1985)

Summary. Tile and stainless steel materials can be sources of chromium in runoff (Wallinder et al. 2002b; Zobrist et al. 2000).

2.1.7 Iron

Lasheen et al. (2008) investigated the effect of water quality parameters, holding time, pipe age, and pipe material on heavy metal concentrations of iron (and other metals) released from different types of water pipe materials, including polyvinyl chloride (PVC), polypropylene (PP) and galvanized iron (GI) pipes. The authors found that the concentrations of iron were higher after 72 hours holding time than for 48 hours at pH 7.5. The authors also analyzed iron concentrations as a function of pipe material and pipe age at pH 7.5. The galvanized pipes released the highest concentrations of iron when compared to PVC or polypropylene pipes, as expected. The lowest concentrations of iron were released from the PP pipes. The concentrations of iron were not different for the PVC and PP pipes, but for galvanized iron pipes, the concentrations were different from both plastic pipes. The experiments conducted by Lasheen et al. (2008) showed that as pipes age, the iron concentrations also increase. For example, for PVC pipes, after 72 h of contact time, the mean iron concentrations were 58 and 70 µg/L in 2 and 20 weeks aged pipes, respectively. For PP pipes, the mean iron concentrations were 60 and 70 µg/L in2 and 20 weeks aged pipes for 72 h stagnation time. The galvanized pipes released the highest concentrations of iron, with the mean concentrations of 700 and 1440 µg/L in 2 and 20 weeks aged pipes after 72 hours of contact. The authors also found that at low pH conditions (pH = 6), the concentrations of iron increased. The greatest increase in iron concentrations at pH 6 was observed in GI and PP pipes, while the lowest increase was noted in PVC pipes. For PVC pipes, the mean iron concentrations were found to be 68 and 80 µg/L for 2 and 20 weeks after 72 hr of stagnation. In PP pipes, the mean iron release was 73 and 83 µg/L and in GI pipes 990 and 1,650 µg/L for 2 and 20 weeks after 72 hr stagnation. As the pH increased (pH = 8), the concentrations of iron decreased. The mean iron concentrations dropped from approximately 70 to 60 µg/L for PVC pipes and from about 69 to 60 µg/L for PP pipes for 20 weeks aged pipes. The reduction of iron release was 14 and 13% for PVC and PP pipes, respectively when compared to the control pipes. For GI pipes, the concentration of iron decreased by 9.7 % compared to control pipes and the mean iron concentration dropped from 1,440 to 1,300 µg/L for 20 weeks aged pipes. Also, the authors found that high Cl^-/SO_4^{2-} ratios increased iron concentrations in all pipes.

Dietz et al. (2007) examined iron releases from PVC, lined cast iron, unlined cast iron, and galvanized steel aged pipes (40+ years) with and without inhibitors. Water was also passed through copper pipes with embedded lead coupons to simulate residential systems, as the use of lead solder with copper pipes is common (US EPA, 1993). Four inhibitors were examined at three doses each: blended ortho/poly phosphate (BOP), ortho-phosphate (OP), zinc ortho-phosphate (ZOP), and silicate (SI). Dietz et al. (2007) observed a modest decrease of iron releases associated with addition of inhibitor, or elevation of the pH. For example, increasing the dose of silicate inhibitor also increased alkalinity due to the high pH of that inhibitor. The elevated alkalinity decreased iron concentrations (Dietz et al. 2007).

Zobrist et al. (2000) examined the concentrations of heavy metals including Fe in runoff from tile and polyester roofs located in a suburb of Zürich, Switzerland. The drainage systems for the clay tile roof was 15-year old copper and for the polyester roof, new copper. Average iron runoff loads from the tile roof were 2,050 µg/m^2 per event. Fe in tile and polyester roof runoff samples were mainly associated with the particulate fraction. During another study, runoff rates of iron from stainless steel roofs were found to be between 10 and 200 mg m^2/year Fe (Wallinder et al. 2002b).

Mendez et al. (2011) investigated the quality of harvested rainwater from five pilot-scale roofs (which included Galvalume® metal) and three full-scale roofs (which included one 7-year-old Kynar®-coated Galvalume® metal located in Austin, Texas). The Kynar®-coated Galvalume® roof released lower iron concentrations compared to the uncoated Galvalume roof. Iron concentrations in harvested rainwater from pilot-scale Galvalume roofs ranged between 18 and 1,700 µg/L for the first flush sample, and between 8.9 and 560 µg/L for later samples. The rain had iron concentrations between 12 and 1,100 µg/L. Fe concentrations in harvested rainwater from full-scale Kynar®-coated Galvalume® roof ranged between 6.2 and 24µg/L for the first flush sample and between 4.1 and 7.9µg/L for later samples. During these tests, the rain had iron concentrations ranging between 12 and 42 µg/L.

Shahmansouri et al. (2003) conducted a pilot-scale drinking study of water distribution systems in Zarrinshahr and Mobarakeh, Iran. The piping system materials in the houses and buildings were galvanized iron, while the distribution piping systems were made of asbestos, polyethylene, and occasionally iron pipes. The authors found that samples collected along the distribution system showed significant increases in iron concentrations, which sometimes exceeded the recommended levels. For Zarrinshahr, the iron concentrations before the distribution systems were 0.08 µg/L and after distribution systems 0.71 µg/L. For Mobarakeh, the iron concentrations before the distribution systems were 0.05 µg/L and after distribution systems 0.85 µg/L.

Sarin et al. (2004) investigated the effects of dissolved oxygen (DO) on iron releases from old corroded iron pipes. They found that corrosion scales from 70-year-old galvanized iron pipe were characterized as porous deposits and were made of Fe (III) phases (goethite (a-FeOOH), magnetite (Fe_3O_4), and maghemite (a-Fe_2O_3)) with a shell-like, dense layer near the top of the scales and high concentrations of readily soluble Fe (II) content which was present inside the scales. Small amounts of siderite ($FeCO_3$) were also found as a component phase. It was determined that corrosion scales can alter the behavior of metal pipes such that they behave differently compared to non-corroded metal. The authors examined iron releases from the corroded pipes under flow and stagnant water conditions. Iron released from corroded iron pipes were mainly in the ferrous form (Fe^{2+}).

Sarin et al. (2004) observed that when oxidants were present in water, greater iron releases was found during water storage in comparison to flowing water conditions. After 24 hours of the experiment, the amount of iron released from iron pipes under stagnation conditions (initial DO = 1.0 and 6.2 mg/L) reached 150µg/m of pipe length and under flow conditions (initial DO = 2.74 mg/L) iron release was75 µg/m of pipe length. Also, it was determined that increasing DO concentrations in water from 6.2 mg/L to 16 mg/L under stagnant conditions decreased the amount of iron released from approximately 360 µg/m of pipe length to 225 µg/m of pipe length. They concluded that increasing the concentrations of oxidants in the water and maintaining flowing conditions can lower the amount of iron released from corroded iron pipes. The authors suggested that iron is released from corroded iron pipes by dissolution of corrosion scales, and that the microstructure and composition of the corrosion scales are important factors that can affect the amount of iron leaching from the system. The rate of depletion of oxidants (e.g. DO) in water was faster during flowing conditions than during stagnation conditions. The oxidants present in water were chiefly consumed in oxidizing the Fe (II) inside the scales or the Fe (II) present in the water. Also, oxidants are likely to be consumed in later pipe metal corrosion.

Corrosion scales can have a negative effect on water quality during water distribution, which includes ''red water'' or ''colored water'' when iron is released from corrosion scales, high demand for chlorine and dissolved oxygen (DO), biofilm growth, and adsorption and accumulation of substances such as arsenic, and radium, which can be released during changes in the water quality. Colored water is formed when iron is released into the bulk water as ferric particles, or as Fe (II) that then oxidizes and then forms ferric particles (Sarin et al. 2004).

In the absence of any corrosion scales, corrosion of iron is the primary cause of iron release. When metal surfaces are covered with corrosion scales, iron may be released by the corrosion of iron metal, the dissolution of ferrous components of the scales, and hydraulic scouring of particles from the scales (Sarin et al. 2004). The corrosion rate of clean iron surfaces typically increases with the increase of the oxidant (such as oxygen) concentrations. When scale layers are formed during the corrosion process, they can influence the rate of diffusion of oxygen to the metal, and slow down corrosion. The environment inside the corrosion scales present in water distribution pipes is characterized with highly reducing conditions and high concentrations of Fe (II). They found that for metal pipes with oxide scales less than one year old, the rate of dissolved oxygen decrease could not be used as a measure of the corrosion rate. It was suggested that oxygen was primarily consumed in oxidizing Fe (II) within the iron oxide layers, and not in the corrosion reaction at the metal/electrolyte interface (Sarin et al. 2004). Sarin et al. (2004) also noted that iron releases increased with stagnation time, while the DO concentration diminished. For initial DO concentration of 6.2 mg/L and pH of 8.9, iron releases from the iron pipe wereapproximatelly100 µg/m of pipe length after 20 hours of stagnation, and reached 375 µg/m of pipe length after 120 hours of stagnation.

Corvo et al. (2005) examined changes in the atmospheric corrosion rate caused by chloride ions based on rain conditions. Test materials included plain carbon steel that were exposed in two atmospheric test stations in Havana, Cuba and Medellin, Colombia. The samples were subjected to accelerated outdoor tests by intermittent spraying of a salt solution. The acceleration of corrosion caused by chloride ions was notably higher at Havana for steel during the 1 year of exposure. Iron mass losses were lower at Medellin (1280 g/m^2 mass loss after 1 year) in comparison with Havana (samples were completely destroyed by corrosion after six months of exposure) due to higher frequencies and amounts of rainfall at Medellin. The authors found that metal mass loss was proportional to the chloride deposition rate and that rain amount and frequency have a great influence on the acceleration rate caused by chloride ions on atmospheric corrosion of steel due to rain’s washing effect. The authors found that large amounts and durations of rain correspond to a lower corrosion rate for a given chloride deposition rate. Additionally, rain diminishes chloride surface concentrations; the corrosion acceleration rate caused by chloride ions is likely to lessen with an increase in rain amounts at constant exposure time. The addition of salt spray at Havana increased the corrosion rate of iron materials when compared to the samples at the same location but under natural conditions. The formation of green rust in the presence of chloride ions involves an incorporation of the chloride ions from solution into the inter-layers of green rust and an oxidation of Fe (II) to Fe (III) without any structural changes. Table 1.6 summarizes iron concentrations and runoff yields from different materials found by various researchers.

Table 1.6. Iron releases from various sources.

Materials tested	Test conditions	Observed iron concentrations or runoff yields	Reference
Uncoated Galvanized Aluminum Roofing Materials			
Galvalume roofs	Pilot-scale. Austin, Texas	18 - 1690 µg/L during first flush, and 8.94 - 563.00 µg/L for later samples	Mendez et al. (2011)
Coated Galvanized Aluminum Roofing Materials			
7-year-old Kynar®-coated Galvalume® roof	Full-scale. Austin, Texas	6.23 - 23.8 µg/L during first flush; 4.10 - 7.88 µg/L for later samples	Mendez et al. (2011)
Other Roofing Materials			
Stainless steel	1 year field exposure. Stockholm, Sweden	10 - 200 mg/ m^2/year	Wallinder et al. (2002b)
Carbon steel	(salt spray) Medellin, Colombia. 1 year test	1280 g/m^2/year mass loss	Corvo et al. (2005)
Carbon steel	(salt spray) Havana, Cuba. 1 year test	Samples (2mm x100 mm x150 mm) completely destroyed by corrosion after 6 months of exposure	Corvo et al. (2005)
Carbon steel	(natural conditions) Havana, Cuba. 1 year test	280 g/m^2/year mass loss	Corvo et al. (2005)
Clay tile roof with 15-year old copper	Field test. Tuffenwies, Switzerland	Average 2.05 mg/m^2 per event	Zobrist et al. (2000)
Drinking Water Distribution Systems (DWDS)			
2 weeks aged galvanized iron pipes after 72 h of contact time	Lab test	Avg. 0.7 mg/L	Lasheen et al. (2008)
20 weeks aged galvanized iron pipes after 72 h of contact time	Lab test	Avg. 1.44 mg/L	Lasheen et al. (2008)
2 weeks aged galvanized iron pipes after 72 h of contact time	pH = 6	Avg. 0.99 mg/L	Lasheen et al. (2008)
20 weeks aged galvanized iron pipes after 72 h of	pH = 6	Avg. 1.65 mg/L	Lasheen et al. (2008)

contact time			
2 weeks aged galvanized iron pipes after 72 h of contact time	pH = 8	Avg. 1.44 mg/L	Lasheen et al. (2008)
20 weeks aged galvanized iron pipes after 72 h of contact time	pH = 8	Avg. 1.3 mg/L	Lasheen et al. (2008)
Drinking Water Distribution System (asbestos, polyethylene, and iron pipes), after min of 6 hrs.	Zarrinshahr, Iran	Before DWDS 0.08 µg/L, after DWDS 0.71 µg/L	Shahmansouri et al. (2003)
Drinking Water Distribution System (asbestos, polyethylene, and iron pipes), after min of 6 hrs.	Mobarakeh, Iran	Before DWDS 0.05 µg/L, after DWDS 0.85 µg/L	Shahmansouri et al. (2003)
2 weeks aged PVC pipes after 72 h of contact time	Lab test	Avg. 0.058 mg/L	Lasheen et al. (2008)
20 weeks aged PVC pipes after 72 h of contact time	Lab test	Avg. 0.07 mg/L	Lasheen et al. (2008)
2 weeks aged PVC pipes after 72 h of contact time	pH = 6	Avg. 0.068 mg/L	Lasheen et al. (2008)
20 weeks aged PVC pipes after 72 h of contact time	pH = 6	Avg. 0.08 mg/L	Lasheen et al. (2008)
2 weeks aged PVC pipes after 72 h of contact time	pH = 8	Avg. 0.07 mg/L	Lasheen et al. (2008)
20 weeks aged PVC pipes after 72 h of contact time	pH = 8	Avg. 0.06 mg/L	Lasheen et al. (2008)
2 weeks aged polypropylene pipes after 72 h of contact time	Lab test	Avg. 0.06 mg/L	Lasheen et al. (2008)
20 weeks aged polypropylene pipes after 72 h of contact time	Lab test	Avg. 0.07 mg/L	Lasheen et al. (2008)
2 weeks aged polypropylene pipes after 72 h of contact time	pH = 6	Avg. 0.073 mg/L	Lasheen et al. (2008)
20 weeks aged polypropylene pipes after 72 h of contact time	pH = 6	Avg. 0.083 mg/L	Lasheen et al. (2008)
2 weeks aged polypropylene pipes after 72 h of contact time	pH = 8	Avg. 0.069 mg/L	Lasheen et al. (2008)
20 weeks aged polypropylene pipes after 72 h of contact time	pH = 8	Avg. 0.06 mg/L	Lasheen et al. (2008)

Summary. PVC, polypropylene, galvanized iron, clay tile, polyester, stainless steel, galvanized iron, and Galvalume® metal materials were found to release iron to the runoff water (Lasheen et al. 2008; Shahmansouri et al. 2003; Zobrist et al. 2000; Wallinder et al. 2002b; Mendez et al. 2011). Exposure time had an effect on iron released from PVC, polypropylene, and galvanized iron materials (Lasheen et al. 2008). Greater iron runoff concentrations were observed for aged PVC, polypropylene, and galvanized iron pipes compared to new materials (Lasheen et al. 2008). As pH decreased, iron concentrations leaching from PVC, polypropylene, and galvanized iron, cast iron, and galvanized steel materials increased (Lasheen et al. 2008; Dietz et al. 2007). High Cl^-/SO_4^{2-} ratios increased iron concentrations from PVC, polypropylene, and galvanized iron pipes. In iron pipes, in the presence of oxidants, greater releases of iron were observed under stagnant conditions compared to flowing conditions (Sarin et al. 2004). The amount of iron released in water under stagnant conditions was decreased when the DO concentrations increased. The level of iron from corroded iron pipes was lowered when the water was flowing and the concentration of oxidants were raised. Compared to stagnant conditions, the depletion rate of oxidants in water was more rapid than during flowing conditions. When the oxidant concentrations increase, there is usually an increase in the corrosion rate of clean iron surfaces. Corrosion can be retarded and the rate of diffusion of oxygen to the metal can be influenced when scale layers are formed. The mass loss of carbon steel is influenced by the frequency and the amount of rain and is proportional to the chloride deposition rate (Corvo et al. 2005). For a given chloride deposition rate, a lower corrosion rate occurs during heavy, long duration rains.

2.1.8 Aluminum

Mendez et al. (2011) studied the effects of roofing material on water quality for rainwater harvesting systems. The authors examined the quality of harvested rainwater using five pilot-scale roofs (asphalt fiberglass shingle, Galvalume® metal, concrete tile, cool, and green) and three full-scale roofs (two asphalt fiberglass shingle and one 7-year-old Kynar®-coated Galvalume® metal) in Austin, Texas. The authors found that aluminum concentrations released by full-scale 7 year old Kynar®-coated Galvalume® roof were substantially lower than from the pilot-scale Galvalume® roof. Aluminum concentrations in harvested rainwater from pilot-scale Galvalume roofs ranged between 20 and 2,000 µg/L for the first flush sample, and between 14 and 550 µg/L for later samples. The aluminum concentrations in the rain ranged between 4.1 and 560 µg/L. Aluminum concentrations in harvested rainwater from full-scale Kynar®-coated Galvalume® roof ranged between 0.06 and 12 µg/L for the first flush sample, and between 0.06 and 6.7µg/L for later samples. The aluminum concentrations in the rain water during these tests ranged between 12 and 55 µg/L. Table 1.7 summarizes aluminum concentrations from different materials.

Table 1.7. Aluminum releases from various sources.

Materials tested	Test conditions	Observed aluminum concentrations	Reference
Pilot-scale Galvalume roofs	Austin, Texas. Several rain events in 2010	20 to2050 µg/L during first flush; 14 to555 µg/L for later samples	Mendez et al. (2011)
Full-scale Kynar®-coated Galvalume® roof	Austin, Texas. Several rain events in 2010	0.06 to 12µg/L during first flush sample; 0.06 to6.7µg/L for later samples	Mendez et al. (2011)

Summary. Galvalume materials have been found to be a source of aluminum with concentrations in the 10's of µg/L (Mendez et al. 2011).

2.1.9 pH

Pitt et al. (2004) evaluated runoff characteristics during wet weather conditions for different source areas and found that pH varied widely. pH values of roof runoff were more acidic than other runoff sources and ranged between 4.4 and 8.4, with a mean value of 6.9. The highest pH was observed for storage areas at a concrete batch plant with the range between 6.5 and 12, and a mean of 8.5. Different pH conditions can have a great effect on the speciation of the metals (Pitt et al. 2004).

Rainwater pH influences the degradation of roofing and gutter materials. An acidic environment dissolves the $CaCO_3$ content of concrete and metal ions from metal roofing materials. This results in corrosion and damage of the roofing and piping materials and the change of the roof runoff pH. In the case of concrete and metal materials, the pH of the roof runoff is usually higher than that of rainwater, attributed to the $CaCO_3$ and metal ions (Horvath 2011).

Clark et al. (2007 and 2008b) investigated pollutant release from commonly used roofing materials including galvanized metals: the rusted portion with no paint, the bare metal with no paint and no visible degradation, and the painted metal. The test site was located on the campus of Penn State Harrisburg. The authors found that pH values of the runoff were below neutral, ranging between 5 and 6.5. Clark et al. (2008a) further investigated runoff water quality from different roofing materials during the first four months of their exposures to rain. Figure 1.5, from Clark et al. (2008a), shows the pH of the roof runoff from different roofing materials. The roof runoff from all the materials was slightly acidic (25th and 75th percentile values for galvanized steel were between pH 6 and 7, except for green roofs which were close to neutral, and cedar shakes that further decreased roof runoff pH).

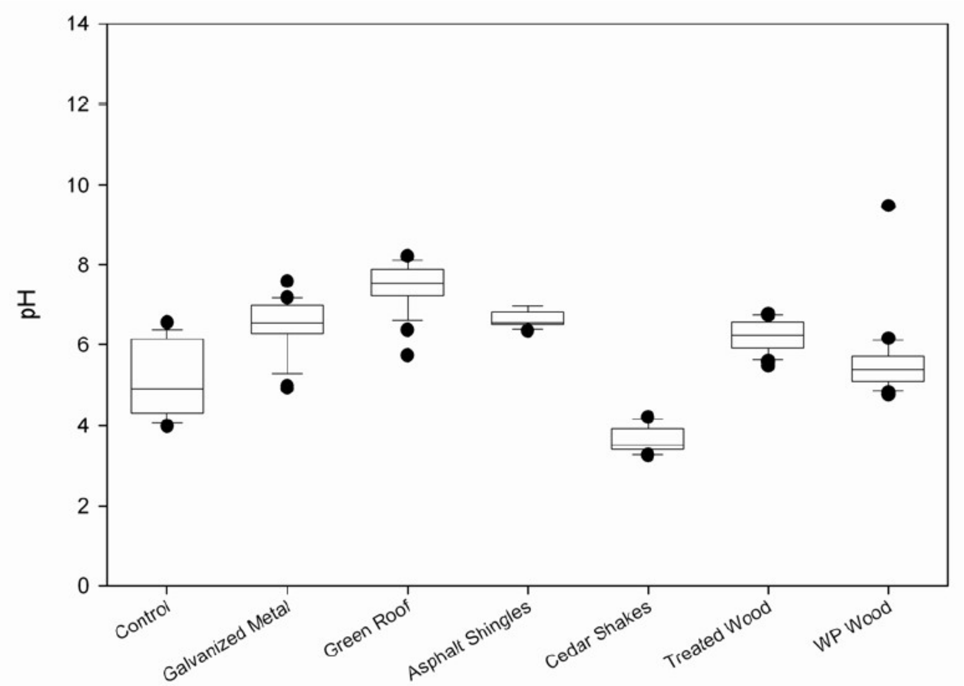


Figure 1.5. Runoff pH from roofing materials and control (Rainfall pH ranged between 3.9 and 6).
Source: Clark et al. (2008a)

Tobiason (2004) investigated unpainted Galvalume metal roof runoff quality at Seattle Tacoma International Airport (STIA) and found the runoff pH to be slightly acidic. Tobiason and Logan (2000) studied pollutant concentrations in roof runoff from four areas at the Seattle-Tacoma International Airport. The pH of the uncoated galvanized steel roof runoff ranged from 6.1 to 8, with the average value of 6.9.

Veleva et al. (2010) studied zinc concentrations leaching from hot dip galvanized (HDG) steel. Samples of galvanized steel were exposed to the Gulf of Mexico environment for two years. pH values of the runoff collected after the first flushes of rain were in the range 5.5–7.0, while pH values of the rainwater were between 4.7 and 6.10.

Schriewer et al. (2008) studied roof runoff from 14 year-old zinc roofs in Germany for a period of 1 year. Roof runoff was directed to titanium–zinc gutters and the downspouts. The pH of the roof runoff ranged between 5.8 and 8.4, with a median value of 6.7. Förster (1999) studied roof runoff from different roofing materials (concrete tiles, clay pantiles, fibrous cement, tar felt and zinc sheet) in Bayreuth, Germany, followed by zinc and PVC gutters. The runoff pH from the zinc roofs was between 6.2 and 6.5, and between 7.1 and 7.5 from fibrous cement.

Zobrist et al. (2000) measured the concentrations of heavy metals in runoff from tile, polyester, and gravel roofs located in the suburb of Zürich, Switzerland. The drainage system for the clay tile roof was 15-year old copper, new copper for the polyester roof, and PVC material for the gravel roof. pH values of the roof runoff were between 6.5 and 7.5 and those in rain events ranged mainly from 5.3 to 6.2.

Table 1.8 summarizes pH values from different materials found by various researchers.

Table 1.8. pH values from various sources.

Material tested	Test conditions	Observed pH values	Reference
Uncoated Galvanized Steel Roofing Materials			
14-year old zinc roof	Field study. Germany	5.8-8.4 (avg. 6.7)	Schriewer et al. (2008)
Zinc roof with zinc and PVC gutters	Field study. Bayreuth, Germany	6.2-6.5	Forster (1999)
New uncoated galvanized steel roof	4 mo field test. Pilot Scale	4.5-7	Clark et al. (2008a)
Uncoated galvanized steel roof	Field study. Seattle	6.1-8 (avg. 6.9)	Tobiason and Logan (2000)
Galvanized steel	Filed study. Mexico	5.5-7.0	Veleva et al. (2010)
Uncoated Galvanized Aluminum Roofing Materials			
New galvanized corrugated aluminum roof	2 year field test. Pilot Scale	5 - 6.5	Clark et al. (2008b)
Other Roofing Materials			
Cement roof with zinc and PVC gutters	Field study. Bayreuth, Germany	7.1-7.5	Forster (1999)
New corrugated polyvinyl chloride roof	2 year field test. Pilot Scale	5 - 6.5	Clark et al. (2008b)
Tile, polyester, and gravel roofs	Filed study	6.5 – 7.5	Zobrist et al. (2000)
Other Materials			
Storage areas at a concrete batch plant	Field study.	6.5-12 (avg. 8.5)	Pitt et al. (2004)

Summary. The pH of rainwater can range between approximately 3.9 and 6.10 depending on the region (Horvath 2011; Clark et al. 2007; Veleva et al. 2010; Zobrist et al. 2000). When rainwater comes in contact with concrete, plastic, metals, and other materials, its pH usually increases to close to neutral conditions. The pH of stormwater runoff varied widely for different source areas (Pitt et al. 2004). The pH values of roof and gutter runoff usually ranges between 4.4 and 8.4, with a mean value of 6.9 (Pitt et al. 2004; Clark et al. 2007 and 2008b; Veleva et al. 2010; Tobiason 2004; Tobiason and Logan 2000; Veleva et al. 2010; Schriewer et al. 2008; Zobrist et al. 2000). The runoff pH from cement materials is usually higher than from metallic materials (Förster 1999; Pitt et al. 2004). The speciation of metals can be greatly affected by changing pH conditions (Pitt et al. 2004).

2.1.10 Nutrients

Clark et al. (2007, 2008 a, b) studied runoff water quality from different roofing materials during exposure to rain. Figures 1.6 and 1.7 represent nitrate and phosphorus concentrations released from several types of roofing materials. They observed that the nutrient concentrations (ammonia, nitrates, total nitrogen, and phosphate) from uncoated galvanized steel and vinyl roofing materials were closer to the background levels, but with intermittent elevated concentrations. Plastic/vinyl materials didn’t release any noticeable concentrations of COD. Cedar shakes and asphalt shingles were a significant source of nitrates; asphalt shingles were also the most significant source of total phosphorous. They also concluded that certain growth media and substrate components of green roofs can be a significant source of nutrients.

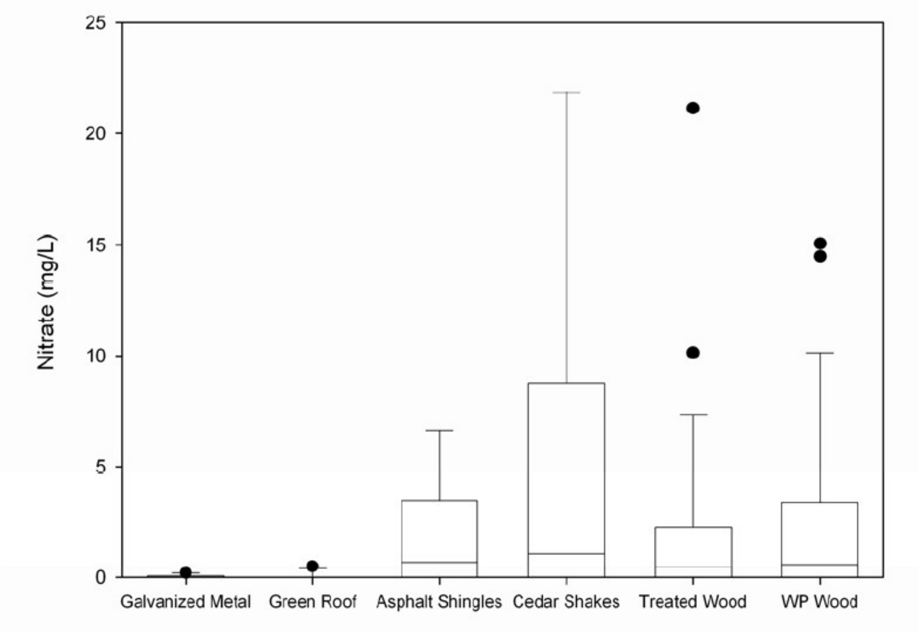


Figure 1.6. Runoff nitrate concentration from roofing materials, background corrected.
Source: Clark et al. (2008a).

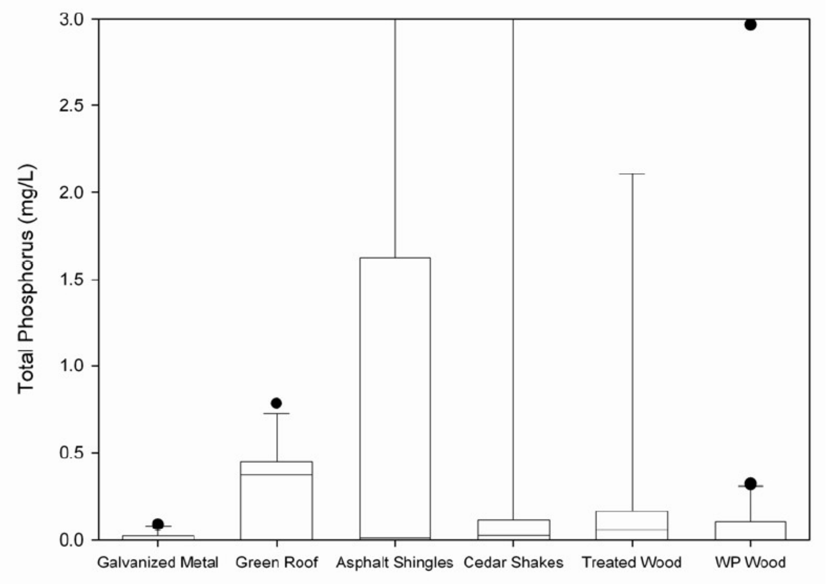


Figure 1.7. Runoff phosphorus concentration from roofing materials, Background corrected.
Source: Clark et al. (2008a).

Clark et al. (2008b) studied the leaching of metals and nutrients from two sixty year old painted galvanized metal roofing panels during laboratory studies. They also studied leaching of nutrients from several materials including galvanized corrugated aluminum, prepainted 55% aluminum-zinc alloy coated steel (Galvalume), and corrugated polyvinyl chloride panel during pilot-scale testing for 2 years. The nutrient concentrations for metal and vinyl roofs were closer to the background levels with periodic spikes in the runoff, compared to the other materials. For example, for galvanized aluminum, there was a nitrate spike of 35 mg/L at Day 50. Similar trends were noted for total nitrogen, ammonia, and total phosphorus. It was noted that the potential for nutrient release exists in the galvanized metal probably as a result of phosphate washes and binders used in the material's preparation and in wood products due to natural degradation (Clark et al. 2008b).

Table 1.9 and 1.10 summarize nutrient concentrations from different materials found by various researchers.

Table 1.9. Nitrate releases from various sources.

Material tested	Test conditions	Time Frame	Observed nitrate concentrations or runoff yields	References
New uncoated galvanized steel roof	Field. Pilot Scale	4 mo.	< 1 mg/L	Clark et al. (2008a)
New coated galvanized metal roof	Field. Pilot Scale	4 mo.	< 1 mg/L	Clark et al. (2008a)
60 years old painted galvanized metal roof exposed	Leaching test in the lab	-	60 mg/kg/48hr	Clark et al. (2008b)
60 years old painted galvanized metal roof, stored in the barn	Leaching test in the lab	-	60 mg/kg/48hr	Clark et al. (2008b)
New galvanized aluminum roof	Field. Pilot Scale	14 mo.	35 mg/L at day 50	Clark et al. (2007)
New planted green roofs	Field. Pilot Scale	4 mo.	< 1 mg/L	Clark et al. (2008a)
New asphalt shingles roof	Field. Pilot Scale	4 mo.	0.9 mg/L (median) 3.5 mg/L (75th percentile)	Clark et al. (2008a)
New cedar shakes roof	Field. Pilot Scale	4 mo.	1.3 mg/L (median) 8.5 mg/L (75th percentile)	Clark et al. (2008a)

Table 1.10. Phosphorus releases from various sources.

Material tested	Test conditions	Time Frame	Observed phosphorus concentrations or release rates	References
New uncoated galvanized steel roof	Field. Pilot Scale	4 mo.	< 1 mg/L	Clark et al. (2008a)
New coated galvanized metal roof	Field. Pilot Scale	4 mo.	< 1 mg/L	Clark et al. (2008a)
60 years old painted galvanized metal roof. exposed	Leaching test in the lab	-	31 - 55 mg/kg/48hr	Clark et al. (2008b)
60 years old painted galvanized metal roof stored in the barn	Leaching test in the lab	-	31 - 55 mg/kg/48hr	Clark et al. (2008b)
New asphalt shingles roof	Field. Pilot Scale	4 mo.	0.02 mg/L (median) 1.6 mg/L (75th percentile)	Clark et al. (2008a)
New planted green roofs roof	Field. Pilot Scale	4 mo.	< 1 mg/L	Clark et al. (2008a)

Summary. Galvanized steel, galvalume, and vinyl roofing materials had nutrient concentrations (ammonia, nitrates, total nitrogen, and phosphate) close to background levels, but with periodic elevated concentrations (Clark et al. 2007, 2008a and b). The most significant sources of total phosphorus were asphalt shingles. It has also been noted that certain green roofs can be a substantial source of nutrients (Clark et al. 2007, 2008a and b).

2.1.11 Toxicity

Good (1993) studied metal concentrations and aquatic toxicity of roof runoff from different roofing materials at a sawmill on the coast of Washington. The roofing materials included a rusty galvanized metal roof, weathered metal roof that may have been coated with aluminum paint many years ago, roof coated with tar, tar roof sealed with aluminum paint, and a relatively new aluminum roof. Zinc leached out of each type of roofing materials, with especially high zinc releases observed from galvanized roofing materials. Copper leached out of tar-covered roofs. Lead leached out of plastic rain gutters. Lead, zinc, and copper concentrations in roof runoff samples surpassed the water quality criteria for the corresponding constituents. Though the concentrations of copper and zinc were lower three hours after the beginning of the storm event but still during the rain, high dissolved metal concentrations remained higher than water quality criteria and the roof runoff was still highly toxic to rainbow trout.

Tobiason and Logan (2000) studied the whole effluent toxicity (WET) of stormwater samples from four outfalls at Seattle-Tacoma International Airport. For the WET tests, water fleas and fathead minnows were used. It was found that the source of the toxicity was the 10-year old unpainted galvanized metal roofs. They determined that zinc-galvanized metal roofs were a source of the zinc that ranged from 66 to 92% dissolved. Samples with low pH adjusted to pH values within acceptable ranges produced little to no toxicity reductions (Tobiason and Logan 2000). Mason et al. (1999) also found that the leaching of metals from galvanized metal roofing materials can cause aquatic toxicity. Tobiason (2004) also observed that such commonly used galvanized products as fencing, guardrails, light poles and unpainted Galvalume metal roofing leach substantial concentrations of dissolved zinc in stormwater runoff causing toxicity.

Bailey et al. (1999) studied toxicity of stormwater runoff samples from three sawmills on Vancouver Island, British Columbia. Zinc in runoff from the galvanized roofs from the sawmills was found to be the major source of toxicity, based on rainbow trout toxicity tests. All except 1 of 27 samples were found to be toxic. In 24 of the samples, the toxicity was linked to divalent cations, especially zinc.

Zinc toxicity is commonly linked to water hardness (Leland and Kuwabara 1985; Bradley and Sprague 1985). The toxicity is high with low hardness in the majority of the samples. For values of hardness ranging from 9 to 100 mg/L, the LC_{50} (as dissolved zinc) was between 72 and 272 µg/L tested with juvenile rainbow trout (Bailey et al. 1999).

The zinc contaminants in the roof runoff originate from dissolution of the roofing and gutter materials rather than from atmospheric deposition. Zinc in the roof runoff was predominantly in ionic form (Zn^{2+}), which is the most bio-available form (Heijerick et al. 2002; Schriewer et al. 2008).

Heijerick et al. (2002) studied the bioavailability of zinc in runoff from 15 different zinc-based roofing materials in Stockholm, Sweden. The authors found that most zinc (94.3-99.9%) was present as the free Zn ion, which is the most bioavailable speciation form. Biosensor tests (Biomet™) that use genetically modified bacterium (the bacterial biosensor emits light in the presence of bioavailable zinc) also confirmed the findings that all zinc was bioavailable. Analysis of the ecotoxicity (conducted using the internationally recommended 72 h algal toxicity test with *R. subcapitata*) data also suggested that the toxic effects were due to the presence of Zn^{2+} ions.

Shokes and Moller (1999) and Cantrell et al. (1995) have indicated that a significant decrease of copper levels have been noted over a short period of time when the water is in contact with iron surfaces, likely due to co-precipitation. Sundberg (1998) also noted that concrete can reduce copper from roof runoff. Michels et al. (2003) found that the toxicity of stormwater runoff decreased as it passed through cast iron and concrete drainage systems. Michels et al. (2002) suggested passing roof runoff through filters that contain iron filings to reduce copper release into the environment.

Veleva et al. (2010) studied zinc leaching from hot dip galvanized (HDG) steel in humid tropical climates. Samples of galvanized steel were exposed in the state of Tabasco, along the Gulf of Mexico, for two years. High zinc concentrations released from zinc sheet roofing were observed and compared with different criteria (aquatic toxicity, sewage sludge, soil). The results showed that the zinc concentrations exceeded the threshold values by up to three orders of magnitude.

Wallinder et al. (2001) investigated zinc in runoff from 15 different zinc panels or zinc coatings, which included new and naturally aged sheets, all being commercial zinc-based construction materials. Almost all of the zinc (greater than 95%) found in the runoff was in the form of hydrated Zn^{2+} ions, which is the most bioavailable form (Wallinder et al. 2000; He et al. 2001). The toxicity effect was studied using the alga R. Subcapitata. The toxicity effects were highly correlated with zinc concentrations. The authors concluded that most zinc found in the runoff was in the form of Zn^{2+} and bioavailable for algae.

Sandberg et al. (2006) examined corrosion-induced copper runoff from copper sheeting, naturally patinated copper, and pre-patinated copper in a chloride-rich marine environment during one year of tests. The bioavailable concentrations (the portion that is available for uptake by an organism) of released copper comprised a low fraction (14–54%) of the total copper concentration due to complexation towards organic matter in impinging seawater aerosols (Sandberg et al. 2006). The authors concluded that released copper is complexed with other ligands which reduce the copper bioavailability. Factors that influence the bioavailability of copper include alkalinity, hardness, pH and dissolved organic matter.

Wallinder et al (2009) studied the copper released from a naturally aged copper roof (installed 48 years) on a shopping center building in Farsta, Stockholm and the interaction of copper with the internal drainage system and storm drains made of cast iron and concrete. Wallinder et al. 2009 observed that the major part of the copper released from the roof was already retained during transport through the internal cast iron and concrete drainage system of the building. The laboratory and field studies showed that the concrete pipes and concrete-based pavement materials have a high capacity to retain copper released from roofs by forming corrosion product malachite, $Cu_3(CO_3)_2(OH)_6$ (Bahar et al. 2008a,b; Sundberg 1998; Boulanger and Nikolaidis 2003; Wallinder et al. 2009). The interaction of roof runoff water and the drainage system also changes the chemical speciation of non-retained copper. Most copper that was not retained by cast iron and concrete surfaces was strongly complexed with organic matter, which significantly reduced the bioavailable fraction. Bertling et al. (2006) and Boulanger and Nikolaidis (2003) studied the copper runoff process and its environmental fate and also found that released copper as a result of atmospheric corrosion is retained by different solid surfaces located in the close proximity of its source.

Förster (1999) investigated the variability roof runoff from different roofing materials (concrete tiles, clay pantiles, fibrous cement, tar felt, and zinc sheet) in Bayreuth, Germany. Drainage systems were made of zinc and PVC gutters. Zinc concentrations (from zinc roofs and ordinary roofs with zinc gutters) were compared to aquatic toxicity, sewage sludge, soil, etc. criteria and were found to exceed those standards up to three orders of magnitude and advised to connect roofs having metal surfaces to infiltration facilities. Förster (1999) also found very high copper concentrations in the runoff from copper sheets as fittings around roof windows and chimney bases. The dissolved to particulate copper concentration ratio was on the order of 1.4.

Copper concentrations were compared to aquatic toxicity criteria and were also found to exceed those standards by up to three orders of magnitude.

Karlen et al. (2002) sampled roof runoff directly after the release from the naturally patinated roofs of varying age (0 and 30 years) in Sweden and found that the roof runoff containing 60-100% free hydrated cupric ion, $Cu(H_2O)_6^{2+}$, $Cu(OH)^+$ and $Cu_2(OH)_2^{2+}$ ions which caused significant reduction in growth rate of green algae during the 72-hr growth inhibition test.

2.1.11.1 Effect of pH on toxicity

Jennings et al. 2001 studied the inhibition of light emitted by the bioluminescent bacterium, Vibrio fischeri by various chemicals at eight concentrations using reagents from three commercial assay systems (ToxAlert 101, Microtox1 and LUMIStox1). They noted an apparent relation of the toxicity of many chemicals to their pH in solution and at high chemical concentrations, and to osmotic imbalances. In highly acidic or alkaline solutions, pH can be the primary cause of toxicity (Jennings et al. 2001; Chou and Hee 1993; Carlson- Ekvall and Morrison 1995; Ho et al. 1999; Sinclair et al. 1999).

Chou and Hee (1993) and Ho et al. (1999) found that the toxicity of chemicals in bioluminescent assays depend on the pH of the solution. This effect was also observed by Jennings et al. (2001) for potassium dichromate the toxicity was high when the pH of the stock solution was outside of acceptable range for the assay (pH 6.0-8.5), however, when the pH was adjusted to 7.0, the toxicity was substantially decreased For some relatively non-toxic chemicals, very high concentrations were used to give a full dose/ response and in these cases, an increase in osmolarity may be been the main cause of toxicity. In addition to these differences, it has also been suggested that different batches of luminescent bacterial media and reagents from the same manufacturer can contribute to some of the observed variation. The author noted that antagonistic and synergistic interactions with other compounds are complicating factors that can significantly influence toxic responses of test organisms.

Ho et al. (1999) found that metals have pH dependent toxicity. The scientists determined that alteration of pH can change the toxicity of Cu, Cd, Ni, Pb, and Zn to Mysidopsis Bahia (mysid), Ampelisca abdita (amphipod) and Vibrio fischeri (Microtox solid phase test (MSP)). For the MSP assay, the authors observed, as the pH decreased, the toxicity for Pb, Ni, Cd, and Zn also decreased and the toxicity of for Cu increased. Studies were conducted at three pH values of 6, 7, and 8 for the MSP. Metal toxicity is often dependent upon pH in freshwater and soils.

Ho et al. (1999) noted that changes in toxicity with changing pH are metal and marine test organism specific. For the MSP assay, Cu was the most toxic metal, followed by Pb and Zn, Ni the least toxic. For the MSP assay, as pH decreased, toxicity for Pb, Ni, Cd, and Zn also decreased, however the toxicity for Cu increased. Based upon these tests on the three marine species, Cu toxicity was the most dependent on pH. The authors found that IC50 values vary with changing pH and noted that their IC50 values for metals with M. bahia were higher than the literature values, however Ho's metals IC50 values for A. abdita generally agreed with the values for Cd and Cu previously obtained by another authors, but were two orders of magnitude higher for Pb. This discrepancy was explained by different exposure conditions (p. 237).

Ho et al. (1999) reviewed studies conducted by different researchers and noted that change in toxicity is frequently metal and test species dependent, indicating that at lower pH values, the toxicity of Cd, Cu, and Zn generally decreased, however at lower pHs the toxicity of Pb generally increased. It was shown that the toxicity of Cu and Zn for Ceriodaphnia dubia increased as pH decreased. Another study examined *C*. dubia, Pimphales promelas, and Hyalella azteca and concluded that the toxicity of Zn, Cd, and Ni decreased at lower pH conditions, while the toxicity of Pb and Cu increased at lower pH conditions. In his study, Ho et al. (1999) noted that for three marine organisms, pH generally caused a change in metal toxicity, and this change was different for different organisms and metals. The authors concluded that it is reasonable to expect that different metals have different modes of action and that different species would evolve different approaches to compensate for metal toxicity. It was found that the toxicity of metals depend on the pH.

Walker et al. (1996) noted that the increase of metal toxicity with decreasing pH can be explained by a number of factors including changes in speciation of metals in solution and increased desorption of metals from surfaces at lower pH values.

Summary. High metal concentrations of zinc, copper, and lead can leach from various roofing and pipe materials and are usually in the most bioavailable form (ions) and can cause aquatic toxicity (Good 1993; Tobiason and Logan 2000; Tobiason 2004; Mason et al. 1999; Bailey et al. 1999; Heijerick et al. 2002; Schriewer et al. 2008; Veleva et al. 2010; Wallinder et al. 2000; He et al. 2001; Förster 1999; Karlen et al. 2002). The toxicity of zinc, copper, lead, cadmium, etc. is dependent upon water hardness and is higher with lower hardness (Leland and Kuwabara 1985; Bradley and Sprague 1985; Bailey et al. 1999). Metals can be retained by the drainage system or form complexes with organic matter, changing the chemical speciation of metals and reducing toxicity (Shokes and Moller 1999; Cantrell et al. 1995; Sundberg 1998; Michels et al. 2003; Sandberg et al. 2006; Wallinder et al 2009; Bahar et al. 2008a,b; Sundberg 1998; Boulanger and Nikolaidis 2003; Bertling et al. 2006; and Boulanger and Nikolaidis 2003). pH can be the major cause of toxicity under extremely low and high pH conditions (Jennings et al. 2001; Chou and Hee 1993; Carlson-Ekvall and Morrison 1995; Ho et al. 1999; Sinclair et al. 1999).

2.1.12 Conductivity

Schriewer et al. (2008) studied runoff from a 14 year-old zinc roof in Germany. Roof runoff was collected into titanium–zinc gutters and the downspout. The authors found that increasing zinc concentrations in the roof runoff contribute to increases in electrical conductivity.

Horvath (2011) observed the first flush effect in conductivity values measured in the runoff from a 9 year old bituminous roof located in Budapest, Hungary. The author found that the conductivity of the roof runoff was higher than that of the rainwater by one order of magnitude. This can be explained by the dissolution of dry deposition materials from the atmosphere and weathering products of the roofing materials. Reductions in conductivity during rain events were attributed to the wash off of deposited contaminants. Consequently, the roof runoff quality is dependent upon the duration of dry antecedent period (Horvath 2011); in this study, as the duration of the antecedent period increased, the conductivity of the roof runoff samples also increased (Horvath 2011).

Förster (1996) found the conductivity in the runoff from a cement roof was the highest, followed by runoff from concrete tile and zinc roofing materials. Research conducted in the US showed that the conductivity of runoff from wood shingle roofs were the highest in comparison with other roofing materials and was attributed to the accumulation of contaminants in the cracks, and subsequent dissolution during rainfall events (Chang et al. 2004).

Summary. As the concentrations of metals in roof runoff increase, electrical conductivity also increases (Schriewer et al. 2008; Chang et al. 2004).

2.1.13 Other Constituents

Al-Malack (2001) studied the effect of water quality parameters on the migration of metal stabilizers from unplasticized polyvinyl chloride (uPVC) pipes. The author found that the metal stabilizer's concentrations (tin, Ba, Ca) leaching out of uPVC pipes increased with the duration of the study. As water pH decreased, Ca and Ba concentrations increased. Tin, barium, and calcium concentrations increased with a temperature increase from 35 to 45^{o}C by 42, 85 and 29%, respectively. The concentrations of tin increased with the increase in the concentration of TDS. Also, it was observed that exposure to UV-radiation promoted the migration of tin, and other metal stabilizers.

Veleva et al. (2010) studied roof runoff from hot dip galvanized (HDG) steel roofs in the Gulf of Mexico environments. The carbonate ion CO_3^{2-} concentrations measured in the runoff were 1.6–1.7 times higher than those measured in rainwater, because of the dissolved zinc carbonate. Also, the authors detected several chloride containing corrosion products which were not released by the rain events.

2.1.14 Protective Coatings and Additives

Zinc coating are frequently applied to steel in order to prevent steel from corrosion (Degremont 1979; Veleva et al. 2010). Zinc or aluminum is intentionally sacrificed when these metals are used for the cathodic protection of steel structures (Shreir 1976). Zinc has a negative standard redox potential of -0.76 V and therefore zinc is a very active metal and tends to corrode when it is in contact with oxygen and moisture (Veleva et al. 2010). Zinc coatings are most commonly used to protect such materials as aluminum and iron from corrosion.

Hot-dip galvanization is a process in which steel material is immersed in a bath of zinc at 450 ^{o}C (Degremont 1979). The zinc layer is strongly bonded to the steel and its external surface is oxidized with the formation of zinc hydroxide ($Zn(OH)_2$), oxide (ZnO), or hydroxycartonate ($(Zn)_x(OH)CO_3$) depending on the temperature and alkalinity of the water. Corrugated galvanized iron sheets have lead and cadmium as typical additives in the zinc coatings (Gumbs and Dierberg 1985; Uhlig 1953). Additions of lead in small concentrations (0.04-0.2 %) improve the zinc coating uniformity and its adhesion to the steel substrate (Sere 1999).

If calcium carbonate is present in the water, it may protect galvanized steel pipe by forming a protective layer. When calcium carbonate in water exceeds the saturation concentration, and in the presence of zinc, the excess is deposited as a very thin insoluble protective hydrous-oxide coating on the surface of the galvanized steel pipe and isolates the metal from water. If damaged, this protective coat repairs itself rapidly; precipitates of calcium carbonate are formed which are insoluble scale deposit that protects the metal from corrosion (Gabriel and Moran 1998).

To protect corrugated steel and spiral rib steel pipes from aggressive drainage waters and soils, pipes are coated with zinc, aluminum, asphalt, asphalt with aramid fiber (derived from nylon), thermosetting epoxy, PVC, ethylene acrylic acid, and polyethylene layer. Concrete lining can also be used (Gabriel and Moran 1998).

When aluminum is exposed to the atmosphere, a very thin natural coating of aluminum oxide forms and securely adherers to the metal surface, thus enhancing its resistance to corrosion. If a fresh surface is exposed by abrasion or cutting, a new film is quickly formed in the presence of air or water. With some exceptions, the protective oxide film that is created is soluble in alkaline solutions and in strong acids, however it is stable in the middle range of pH values between 4 and 9. Under soft water conditions, the resistance to pitting is high. Pitting corrosion is more likely to take place in waters containing ions of copper, chloride, sulfate, and oxygen. Such heavy metal ions as copper and iron increase the possibility of electrochemical corrosion by forming stray electrical currents and galvanic couples. Combinations of low resistivity with low pH values tend to increase the average metal loss (Gabriel and Moran 1998).

A Florida study of aluminum pipe observed failure of coatings and advance pitting corrosion in a coastal area where the soil became saturated with chlorides as a result of tidal effects when the pH was between 6.5 and 7.0 (Gabriel and Moran 1998).

In order to prevent the polymer from decomposing and disintegrating, heat stabilizers are used. Stabilizers improve the resistance of the polymer or composite to various degradation-promoting factors during processing, storage, and service (Al-Malack 2001). For unplasticized PVC pipe, mixtures of lead, cadmium, barium, and organotin compounds are used as heat stabilizers (Al-Malack et al. 2000). In Australia, Asia and Europe, lead-based stabilizers have traditionally been used during the unplasticized PVC pipe manufacturing process. In the United States tin-based stabilizers are commonly used (Al-Malack 2001).

In construction and other extended-life applications, lead and other heavy metal stabilizers such as cadmium and zinc are added to PVC materials. Stabilizers, plasticizers, colorants, and other additives are mixed with pure PVC to produce a usable plastic with desired properties. In its pure form, PVC is rigid and brittle, and it gradually catalyzes its own decomposition when exposed to ultraviolet light. Additives are mixed with the PVC polymer to make it flexible, moldable, and long lasting. Studies have shown that lead can leach into water carried in PVC pipes that contain lead stabilizers (Thornton 2002)**.**

Roof paints used to prolong the lifespan of a roofing material or for aesthetic reasons can include metallic compounds which supply another source of metal (Gumbs and Dierberg 1985). Davis and Burns (1999) examined lead release in stormwater runoff from painted structures in an urban area. The author observed lead concentrations which ranged from 10’s to 100’s of µg/L. It was found that old surface paints have the potential to release large amounts of lead.

2.1.15 First flush of runoff from exposed roofing materials

The first flush effect is the initial period of runoff from a roof having elevated concentrations of contaminants compared to concentrations during the later stages of the rain event (Gupta and Saul 1996). Zinder et al. (1988) pointed out that the first flush effect is caused by one or a combination of three processes: (1) matter deposited on the roofing material during antecedent dry period which is washed off by the initial period of rain; (2) the initial rain washes off weathering and corrosion products of the roofing material and drainage system; and (3) the increasing in total rainfall depth causes concentrations in the falling rain itself to diminish due to scavenging of gases, particles, and aerosols by rain drops (Zinder et al. 1988). For each contaminant, the comparative importance of the potential sources and the physical – chemical properties of respective contaminant affect the contributions of processes mentioned above to concentrations found in roof runoff. Zobrist et al. (2000) found that heavy metal concentrations were influenced by the first and ultimately second process. It was observed that, for heavy metals, the washout effect in the atmosphere was significantly less important than the other processes.

He et al. (2001a) noted that the magnitude of the first flush is determined by a combination of several parameters including dry deposition, length of dry and wet periods, and characteristics of the corrosion layer prior to a precipitation event. A sufficient rain volume is needed in order to transport soluble corrosion products from the surface. The rain intensity governs the contact time during which the stormwater is in contact with the surface and therefore determines the rate at which the easily soluble corrosion products are washed off and consequently determines the magnitude of the first flush (He et al. 2001a; Schriever 2008).

Dry atmospheric deposition and the degradation of the roofing material affect the suspended solid concentration of roof runoff. As the duration of the dry period between rainfall events increases, the concentration of suspended solids also increases (Quek and Förster 1993; Horvath 2011). Van Metre and Mahler (2003) noted that most of the particulates which can be easily mobilized are washed off during the first 2.6 mm (0.1 in) of rain. Transport and dissolution processes during washoff are correlated with runoff volume (Förster 1999). Faller and Reiss (2005) also found that the total copper and zinc concentrations in the rain runoff for copper and titanium-zinc materials were a function of the total rain depth of the event. The concentrations in smaller rains were found to be higher than those in larger rains. In the beginning of a rain event, water-soluble compounds like sulfates, nitrates and chlorides are washed from exposed surfaces (Faller and Reiss 2005).

Veleva et al. (2007) observed that zinc runoff concentrations are higher after dry periods of when the rain events are scarce and more time is available for the formation of new corrosion products on the surface of zinc during the time of wetness, without the loss of corrosion products during runoff.

Gromaire-Mertz et al. (1999) studied runoff from zinc roofs and gutters in Paris between July 1996 and May 1997. Mean metal concentrations in the roof runoff varied greatly and were mainly correlated with the antecedent dry period. Zobrist et al. (2000) also observed the first flush effect with very high concentrations that declined rapidly to lower constant levels for the inclined tile and polyester roofs.

Roof runoff first flushes were observed during 93% of runoff events in the research conducted by Schriewer et al. (2008). Zinc concentrations were higher at the beginning of the runoff events and averaged 13.4 mg/L in the first sample bottles and decreased to comparatively constant concentrations of approximately 5 mg/L. pH of the roof runoff ranged between 5.8 and 8.4 with median values of 6.7. High variations of zinc concentrations during runoff events were observed.

Horvath (2011) studied roof runoff from bituminous roofs in Budapest, Hungary. They observed the first flush effect in the following roof runoff water constituents: conductivity, turbidity, suspended solids, and dry and organic matter concentration. This effect is explained by the dissolution of deposited aerosols and weathering products on roofing materials. Consequently, the roof runoff quality was found to be dependent upon the duration of the dry antecedent period. Horvath (2011) also observed that the suspended solids concentrations of the first roof runoff samples ranged between 86 and 155 mg/L and were several times higher than that of in rainwater (ranging between 14 and 54 mg/L). The variability in the conductivity of roof runoff during three rainfall events was explained by the different durations of antecedent dry periods. In this study, as the duration of the antecedent period increased, the conductivity of the roof runoff samples also increased.

Good (1993) studied metal concentrations and aquatic toxicity of roof runoff from different roofing materials at a sawmill on the coast of Washington. They observed first flushes in samples that were collected after more than a week of dry weather. They sampled roof runoff from aluminum painted metal roofs at the beginning of the storm and approximately three hours later. He found that the concentrations of many parameters (including copper and zinc) were lower in the samples collected after three hours (especially zinc).

Other researchers have also noted roof runoff first flushes (He 2002; Gumbs and Dierberg 1985; Yaziz et al. 1989; He et al. 2001a). Faller and Reiss (2005) observed some rain events, which did not show a first flush effect, which could have been explained by the different length of dry periods and different degrees of dry deposition before the rain event.

Veleva et al. (2010) studied zinc concentrations leaching from hot dip galvanized steel exposed in the Gulf of Mexico. The first flush (rain event which occurs after a long dry period) was one of the most important factors explaining zinc releases during runoff events. During first flushes, weakly acidic rain dissolves the zinc carbonate corrosion product, hydroxycarbonate $[Zn_5(OH)_6(CO_3)_2]$–hydrozincite, and releases carbonate ions $CO^{2-}{}_3$ from zinc galvanized steel surfaces. The amount of dissolved carbonate ions is a function of the rain pH, its periodicity and intensity. The authors note that during the dry period, neutral zinc salts such as $ZnSO_4$ or $Zn(NO_3)_2$ are often formed, they have high solubility and are readily dissolved during the first flush, and less soluble zinc salts are formed, including zinc hydrosulphates and hydroxychlorosulphates. During steady state runoff, further dissolution is controlled by the solubility properties of the latter salts (Veleva et al. 2010).

Förster (1999) investigated the variability roof runoff from different roofing materials in Bayreuth, Germany. They observed that first flushes from roofs were frequently heavily contaminated and therefore should be treated.

2.1.16 Summary: factors affecting roof runoff contaminant concentrations

Roof and gutter materials are susceptible to changes over time due to photo degradation via UV light from the sun, wind (which can physically remove patina, bring aerosols and particles of different composition), elevated temperature and temperature variations, moisture, the chemical composition of the atmosphere (concentration of SO_2, Cl^-, etc.), the contaminants physic-chemical properties, and microbial growth (Berdahl et al. 2008; Mendez et al. 2011;

Faller and Reiss 2005; He et al. 2001a; Sarin et al. 2004; He 2002; Gumbs and Dierberg 1985; Horvath 2011; Cramer et al. 2002; Schriewer et al. 2008; Förster 1999; Lasheen et al. 2008). Atmospheric corrosion of metals is an electrochemical process governed by parameters like the climate and relative humidity (Faller and Reiss 2005; Horvath 2011; Schriewer et al. 2008; He et al. 2001a).

Roof runoff yields also depend on such environmental parameters as dry atmospheric deposition, the length of the precipitation events and the dry periods between them (or frequency), the meteorology (wind speed and wind direction), the rainwater quality including rainwater pH, amount of rain impinging the surface and its intensity, the material of the roof and of the gutter, as well as surface characteristics of the exposed metal such as corrosion layer, age, thickness, porosity, specimen orientation and inclination, height, degree of sheltering, and sun hours (He 2002; He et al. 2001a, b; Schriewer et al. 2008; Horvath 2011; Gumbs and Dierberg 1985; Förster 1999; Faller and Reiss 2005; Veleva et al. 2010, 2007; Cramer et al. 2002; Lasheen et al. 2008; Sarin et al. 2004; Berdahl et al. 2008; Mendez et al. 2011; Sandberg et al. 2006; Wallinder et al. 2000). Runoff yields and corrosion rates also depend on exposure time (Faller and Reiss 2005; Gumbs and Dierberg 1985; Schriewer et al. 2008).

The parameters mentioned above cause very high variabilities within individual rain events, between different rain events, between different roofing and gutter materials, and various roof and gutter locations; therefore, contaminant concentrations in the storm runoff vary significantly (Förster 1999).

Horvath (2011) and Schriewer et al. (2008) found that zinc concentration increases with the increase in contact time of roofing and gutter materials and rainwater. Al-Malack (2001) also observed the increase of metal stabilizer (lead, cadmium, tin, calcium, barium) concentrations released from for unplastizied PVC pipes with time. Lasheen et al. 2008 found that for PVC, polypropylene, and galvanized iron pipes, the concentration of lead and iron increased with exposure time.

Roofing materials change with age and therefore the release of certain elements and compounds from a roofing material can change as the roof ages (Mendez et al. 2011). The experiments conducted by Lasheen et al. (2008) showed that as pipe (PVC, polypropylene, and galvanized iron pipes) ages, the lead and iron concentrations in the water in contact with these pipes also increase. Davis and Burns (1999) examined lead releases in stormwater from painted structures. Lead concentrations were considerably affected by paint age and condition. Lead releases from washes of older paints were significantly higher than from fresh paints. It was found that old surface paints have the potential to release large masses of lead.

Wallinder et al. (2000) studied the effect of exposure direction and inclination on the runoff rates of zinc. The study showed that metal runoff rates increase for low inclinations from horizontal and for exposures directed towards the prevailing wind direction. It is likely that orientation also affects sunlight degradation of the roofing material. Also, it was observed that exposure to UV-radiation promoted the migration of lead, tin, cadmium, calcium, and barium) from unplastizied PVC pipes (Al-Malack 2001).

The effect of water temperature was not significant for the losses of lead and cadmium from unplastizied PVC pipes. However, tin, barium, and calcium concentrations increased with temperature increases from 35 to 45^{o}C by 42, 85 and 29%, respectively (Al-Malack 2001). Also, it was found that each increase in temperature by 10^{o} C resulted in acceleration of the corrosion process by one order of magnitude (Veleva et al. 2010). High rooftop temperatures also affect the roof runoff water quality by speeding up the chemical degradation of the roofing surfaces and deposited materials (Chang and Crowley 1993). High rooftops temperatures are associated with a lower albedo of the surface, and higher inclination angles towards the solar radiation (Horvath 2011).

Horvath (2011) noted that the sources of roof surface contamination include dry and wet atmospheric deposition, and weathering of the roofing material. The dry and wet deposition materials are affected by particle size and concentrations in the atmosphere, weather conditions, and rooftop surface quality (Gadd and Kennedy 2001). Veleva et al. (2007) observed that zinc runoff is higher after dry periods or when the rain events are scarce and more time is available for the formation of new corrosion products on the surface of zinc during the time of wetness, without the loss of corrosion products during runoff (Veleva et al. 2007). More frequent and intense rains wash off aggressive contaminants and shorten the dry period of time during which the corrosion products form (Veleva et al. 2010). For a given rainfall quantity, the amount of washed-off copper increases with decreasing rain intensity as a result of a prolonged contact time with the concrete surface (He et al. 2001; He 2002; Wallinder et al. 2009). Negative correlations were found between rainfall intensity and zinc concentrations (He et al. 2001a, b; Schriewer et al. 2008). The lower the storm intensity, the higher the zinc concentrations in the roof runoff due to the longer time of contact. Wallinder et al. (2000) found that at a given pollution concentration, the metal runoff is highly dependent on the precipitation volume hitting the surface. Förster (1999) also concluded that transport and dissolution processes during washoff are also correlated with runoff volume.

Water quality parameters that affect iron release from corroded iron/steel pipes in distribution systems include DO and water flow characteristics (Sarin et al. 2004). It was determined that increasing DO concentration in water under stagnant conditions decreased the amount of iron released.

Lasheen et al. (2008) observed that increasing the ratio of Cl/SO_4 from 0.83 to 2 resulted in an increase in lead concentrations in galvanized iron, polypropylene, and PVC pipes.

Veleva et al. (2007 and 2010) determined that zinc corrosion mass losses (C) are controlled by several independent factors through a linear equation ($C = C_0 + x_1 [TOW] + x_2 [SO_2] + x_3 [Cl^-]$), where TOW is time of wetness, h, of the metal surface as an effective time for the corrosion progress for each period of evaluation, C_0 is the zinc mass loss in absence of contaminants (only wetness on the metal surface); SO_2 and Cl^- are the amount of sulfur dioxide and chloride contaminants deposited on the metal surface for each period of evaluation (g/m^2); x_1, x_2 and x_3 are the coefficients.

Veleva et al. (2007 and 2010) noted that sulfur dioxide, SO_2, has the greatest influence on the zinc mass loss due to the acidification of rains on metal surface. The activation of corrosion usually occurs when SO_2 is adsorbed onto the metal surface. Faller and Reiss (2005) and Wallinder et al. (1998) also found that higher atmospheric SO_2 pollution levels can increase zinc runoff rates.

The TOW of the metal surface (TOW is the calculated Time of Wetness of the metal surface and is the effective time for the corrosion progress) was found to be the second most important independent factor which controls the corrosion development (Veleva et al. 2007, 2010). The increase in TOW contributes to the acceleration of zinc corrosion, as compared to the one in moderate climates. During wetting and drying periods, the pH of the condensed water layers changes substantially, therefore changing the intensity of the corrosion attack.

The chloride ion Cl^- was a minor factor affecting galvanized steel corrosion (Veleva et al. 2010). The salt deposited onto the roofing materials leads to accelerated corrosion of the metal materials near a marine environment (Gadd and Kennedy 2001; Gumbs and Dierberg (1985). Sandberg et al. (2006) arrived at the opposite conclusion. Sandberg et al. (2006) examined corrosion-induced copper runoff from copper sheet, naturally patinated copper and pre-patinated copper in a chloride-rich marine environment. At similar rain quantities, copper runoff rates were significantly lower at the marine site compared to data acquired in an urban environment, despite substantially higher chloride deposition rates at the marine site. Barry et al. (1999) studied the effects of salinity on the distribution of heavy metals in the stormwater canals entering Port Jackson, Australia. The authors found that as the salinity in the lower sections of the canals increased, the dissolved fractions of copper, zinc, and lead increased also.

Corvo et al. (2005) found that metal mass losses were proportional to chloride deposition rates and that rain amounts and frequencies have great influence on the acceleration rate caused by chloride ions on atmospheric corrosion of steel and copper due to rain’s washing and cleaning effects. Additionally, rain diminishes chloride surface concentrations; the acceleration rate caused by chloride ions is likely to lessen with the increase of rain amount at constant exposure time. Rain regime could alter the acceleration caused by chloride ion on metal corrosion. During rainy and dry periods, the electrochemical mechanism of corrosion by chloride ions does not change, but the time during which chloride ions acts on the metal surface and chloride concentration may change significantly (Corvo et al. 2005).

Horvath (2011), Schriewer et al. (2008), He et al. (2001a), Lasheen et al. (2008), and Dietz et al. (2007) found that zinc and copper concentrations increase with decreases of rainwater pH. pH elevation was noted to achieve a significant mitigation of copper releases (Dietz et al. 2007).

Al-Malack (2001) observed that as pH decreased, the amount of lead leaching from the uPVC pipes increased. The authors noted that as water pH decreased, Ca, Cd, and Ba concentrations increased. Lasheen et al. (2008) also found that for PVC, polypropylene, and galvanized iron pipes, as pH decreases, the concentrations of lead and iron increase.

2.2 Corrosion Processes Affecting Contaminant Releases from Materials used in Stormwater Management

2.2.1. Introduction

Contact with water can damage materials in several ways. The corrosion of metals is one of the most common types of material damage. Other causes include the dissolving of calcareous materials and the degradation of concrete (Degremont 1979).

The products of reaction are formed under ambient conditions by a gaseous oxidizing atmosphere which results in the physical adsorption of oxygen, leading to the formation of one or more monolayers of oxide. Electron tunneling through the stable oxide film to the adsorbed oxygen also occurs, which sets up a potential. This is followed by a film rearrangement which results in the formation of oxide grains boundaries. At first, the oxide films that are formed at ambient temperatures are continuous and amorphous but may undergo local crystallization with the incorporation of the oxide “islands”, which is facilitated by water, heat, high electric fields, and mechanical stress. In dry air, films consisting essentially of an anhydrous oxide are formed and may reach a thickness of 3 nm. However, in the presence of water, which can range from condensed films deposited from humid atmospheres to bulk aqueous phases, increases in electron tunneling conductivity will result in further thickening as partial hydration increases. Other constituents, such as H_2S, SO_2, CO_2, Cl^-, present in contaminated atmospheres, may become incorporated (Shreir1976).

When metal is submerged in an electrolyte solution, the metal itself retains a negative charge but positively charged metal ions have a tendency to dissolve. An electrode with a potential which is expressed by Nernst's equation is formed (Garrels and Christ 1990; Degremont 1979). The potential for this half-cell reaction is:

$$E = E^o + RT/(nF)*\ln[\text{oxidized state}]/[\text{reduced state}] \qquad \text{Equation 1.1}$$

Where,

E^o = standard potential measured against a standard hydrogen electrode.

n = the valence of the metal ions in question

T = absolute temperature

R = the molar constant of perfect gases = 8.31 J/(mol K)

F = the Faraday number

Corrosion by oxygen is the result of an electrochemical process and can be demonstrated by submerging an iron sample into an electrolyte solution. The dissociation of water will be observed (Degremont 1979):

$$H_2O \leftrightarrow OH^- + H^+$$

Slow diffusion of O_2 occurs into the water.

This oxygenic corrosion is an electrochemical process. It creates positive and negative electric poles, called the cathode and the anode, respectively, with an electric current flowing between them. Oxidation occurs at the anode (metal dissolves), while the cathode is protected against corrosion.

Reaction of oxidation of iron:

$Fe \rightarrow Fe^{2+} + 2e^-$

Anode reactions:

$Fe^{2+} + 2OH^- \rightarrow Fe(OH)_2$

$Fe(OH)_2 + 2H_2O + O_2 \rightarrow Fe(OH)_3$

Cathode reactions:

$O_2 + 2H_2O + 4e^- \rightarrow 4OH^-$

$2H^+ + \frac{1}{2} O_2 + 2e^- \rightarrow H_2O$

The oxygen in aerated water facilitates the complementary electrode process needed to balance the electron transfers ($O_2 + 2H_2O + 4e^- \rightarrow 4OH^-$).

Because of its ability to absorb electrons, this electrode is acting as a cathode.

In this case, the equilibrium potential is governed by the concentration of OH^- ions (and therefore pH value), and by partial oxygen pressure.

$$E' = E^o - RT/F*\ln(OH^-) + RT/(4F) \ln pO_2 \qquad \text{Equation 1.2}$$

Where,

E^o = the standard potential

p = partial oxygen pressure

The electrode potential is directly proportional to the level of dissolved oxygen.

This leads to the evident paradox that if part of the metal does not come in contact with the oxygen, it becomes anodic and hence is more likely to corrode compared to the rest of the surface which is protected by the oxygen. This accounts for the damage caused by various deposits which prevent oxygen from reaching the underlying surfaces and creates an anodic area. The release of the OH^- ions at the cathode increase the pH of the water, at least in the immediate vicinity of the metal surface. Also, in the presence of oxygen, Fe^{2+} ions oxidize to Fe^{3+} ions. Ferric oxide ($Fe(OH)_3$) is only marginally soluble. Rather than being carried away by the water and leaving a clean surface, the corrosion products collect around the anode and form “pustules” which create an additional barrier to the diffusion of the oxygen and strengthen the anodic character of the covered surface. This is the reason that corrosion by oxygen perforates the metal.

Areas in the metal containing no dissolved oxygen, such as screw threads, cavities, and cracks, form anodic regions. Areas containing dissolved oxygen form cathodic regions. A difference in potential may also appear between zones where there is variation in the concentration of dissolved oxygen in the liquid film.

Therefore the concept of a large number of elementary microcells formed by the difference in oxygen concentration can be extended to all irregularities in metal parts resulting from their nature, construction, degree of fouling, or from temperature differences.

The development of corrosion by differential oxygen concentration in the interfacial layer is dictated primarily by the solubility of oxygen and, specifically, by its rate of diffusion, because slower rates boost corrosion. The solubility of oxygen is a function of temperature and partial pressure, decreasing as temperatures rise, but never dropping to zero (Degremont 1979).

In nature, water is not pure. It contains numerous dissolved chemical elements, with calcium bicarbonate being the most abundant. Chemical reactions such as the dissolution of calcium carbonate (aggressive water) or scale formation can result with any shift in equilibrium between $CaCO_3$ salt and carbon dioxide. Calcium bicarbonate is unstable in aqueous solutions and has a tendency to lose carbonic acid and precipitate $CaCO_3$:

$Ca(HCO_3)_2 \leftrightarrow CaCO_3 + H_2O + CO_2$.

A quantity of free CO_2, known as the equilibrium CO_2, is necessary to reverse the precipitation and maintain the calcium bicarbonate in solution. In natural water containing more free CO_2 than is required to keep the calcium bicarbonate in solution, the excess of CO_2 is aggressive to limestone. The water will form scale when the free CO_2 is less than the equilibrium CO_2 (Degremont 1979).

Dissociation of carbonic acid occurs according to the following equations:

$H_2CO_3\ (H_2O + CO) \leftrightarrow H^+ + HCO_3^-$

$HCO_3^- \leftrightarrow H^+ + CO_3^{2-}$

Dissociation constants for the equations above:

$K_1 = [H^+]\ [HCO_3^-]/[CO_2]$

$K_2 = [H^+]\ [CO_3^{2-}]/[HCO_3^-]$

From dissociation equations of carbonic acid, it can be seen that the proportions of free carbon dioxide, bicarbonate and carbonate in the water depend on the pH of water solving the equations; at pH values of 3.7 to 4, all carbonic acid is represented by carbon dioxide. As the pH increases, the proportion of CO_2 decreases and at the same time the proportion of HCO_3^- increases. At pH values = 8.3to 8.4, practically all carbonic acid is represented by bicarbonate ions (> 98%), and proportions of ($CO_2 + CO_3^{2-}$) account for less than 2 %. At pH values above 8.3 to 8.4, free carbon dioxide in the water is absent, the proportion of carbonate ions increases, however the proportion of bicarbonate ions decreases. At pH values of approximately 12, all carbonic acid is represented only by carbonate ions (Klyachko 1971).

Langelier (Snoeyink and Jenkins 1980) suggested the use of the Saturation Index (or the Langelier Index) to determine whether or not a water is in equilibrium with $CaCO_{3(s)}$. The

Langelier Index is the difference between the actual pH of water and the pH the water would have if it were in equilibrium with $CaCO_{3(s)}$.

$$L.I. = pH_a - pH_s \qquad \text{Equation 1.3}$$

Where,

pH_a = actual pH of water

pH_s = pH of water if it were in equilibrium with $CaCO_{3(s)}$at the existing solution concentrations of HCO^{3-} and Ca^{2+}.

If the L.I. is a positive value, the water is oversaturated with $CaCO_{3(s)}$ and will tend to precipitate $CaCO_{3(s)}$, and the water is scale-forming. If the L.I. is a negative value, the water is undersaturated with $CaCO_{3(s)}$ and will tend to dissolve $CaCO_{3(s)}$, and the water is corrosive. If L.I of the water is zero, it is in equilibrium with $CaCO_{3(s)}$.

$pH_s = pK_{a,2} - pK_{so} + p[Ca^{2+}] + p[HCO_3^-] - \log \gamma_{Ca2+} - \log \gamma_{HCO3-}$

Where,

$pK_{a,2}$ =- log (equilibrium constant of the reaction $HCO_3^- = CO_3^{2-} + H^+$)

pK_{so} =- log (equilibrium constant of the reaction $CaCO_{3(s)} = Ca^{2+} + CO_3^{2-}$)

γ_{Ca2+} = the activity coefficient of ion Ca^{2+}

γ_{HCO3}^- = the activity coefficient of ion HCO_3^-

$pK_{a,2}$ = 10.43 at 15 °C; 10.38 at 20 °C; 10.33 at 25 °C

pK_{so} = 8.22 at 15 °C; 8.28 at 20 °C; 8.34 at 25 °C

The LSI is indicative of the solubility of calcium carbonate in the water. If the LSI is positive, calcium carbonate may be deposited, if the LSI is negative, the calcium carbonate may be dissolved. Negative LSI is commonly interpreted as an indicator of corrosive water (Snoeyink and Jenkins 1980).

Calcium bicarbonate water containing enough oxygen and which is in carbonic equilibrium generates a natural protective film on the cathodic regions when cold. This layer, known as the Tillmans' film, is composed of a mixed precipitate of $CaCO_3$ and iron oxides. The process occurs in a pH range from about 7 to 8.5 (Degremont 1979). The formation of natural or manufactured protective films can reduce corrosion. Artificial protective films can be produced by the application of inhibitors or an electric voltage. The natural inhibiting process is linked to the presence of OH^- ions and consequently it can occur at neutral or alkaline pH values (Degremont 1979).

In the cathodic regions, the H^- ions are absorbed and alkalinity increases. The excess OH^- ions combine with the Fe^{2+} ions which are released to form ferrous hydroxide $Fe(OH)_2$ which precipitates as a reasonably uniform film on the cathodic or anodic zones. This hydroxide is unstable and depending on the temperature and chemical composition of the water, undergoes transformations which determine the protective nature of the film formed (Degremont 1979).

If substantial amounts of oxygen are diffused on the cathodic areas, there is direct and swift oxidation of the non-protective ferrous hydroxide (II) into ferric hydroxide (III). In the presence of enough calcium bicarbonate there is simultaneous local precipitation of $CaCO_3$ which syncrystallises with the various iron oxides and a natural protective film is formed. Oxygen can aid passivation by the formation of oxides. Chemical inhibitors, such as polyphosphates, are used when there is oxygen corrosion. Polyphosphates, which have a liner structure, decompose progressively by hydrolysis, and create orthophosphate ions (PO_4^{3-}) that precipitate in the form of tricalcium phosphate ($Ca_3(PO_4)_2$), which is only slightly soluble and results in the formation of calcium phosphocarbonate (Degremont 1979).

Oxygen and CO_2 content are two of the primary parameters influencing corrosion. Other factors affecting corrosion include the presence of dissolved salts chiefly chlorides, temperature variations, suspended solids, and the presence of microorganisms. The influence of chlorides is significant. During the initial stage of corrosion, the concentration of Cl^- ions carried by the current increases and simultaneously, H^+ ions appear because of remote precipitation of OH^- ions in the form of ferrous hydroxide. A heavy local concentration of H^+ and Cl^- ions is produced preventing local precipitation of the hydroxides. A rise in the chloride ion content of water increases the probability of the creation of huge numbers of micro-anodes and leads to an increase in general corrosion and pitting. This is the reason for the appearance of pitting corrosion due to the HCl formation. Sulfates impact corrosion by aiding the cycle of sulfate-reducing bacteria and in the spread of biological corrosion. OH^- ions, chromates, and silicates, on the other hand, have a tendency to form a protective film and to minimize corrosion (Degremont 1979). Corrosion rates were found to correlate with the content of the sulfates and chlorides in the water (Gabriel and Moran 1998). This relationship was determined to be unreliable when the sum of sulfate (SO_4) and chloride (Cl) ions was less than 100 ppm (mg/L). Chlorides and other dissolved salts increase the electrical conductivity and therefore promote the flow of corrosion currents.

Often, biological corrosion is a secondary form of corrosion. It usually manifests itself by the formation of concretions in the shape of tightly packed nodules. These nodules commonly create significant obstructions and underlying pitting which often develops into perforations. These concretions which frequently contain calcium carbonate consist of large quantities of fibrous ferro-bacteria, enclosed in partially dehydrated ferric oxide (Degremont 1979).

Existing deposits already in an old fouled system or deposits originating from the distribution of badly-filtered water can cause corrosion due either to non-aerated areas that can create anodic areas under the deposit or to the formation of regions where various strains of bacteria develop and reducing depassivating reactions occur (Degremont 1979).

Corrosion resulting from flow velocity is an important parameter involving physical, mechanical, and electrochemical phenomena (Gabriel and Moran 1998; Degremont 1979). Three types of damage can be produced as follows: 1) by cavitation caused by the existence of variation in local levels of hydrostatic pressure, above and below the vapor tension of the water, which can result in vapor bubbles being released and then annihilated by implosion at very high pressures, resulting in an uneven hollowing out of the solid metal, 2) by erosion-abrasion produced by the kinetic energy of particulate matter in the water, which results in continuous damage to the protective layer by regular, uniform abrasion of the solid metal, 3) by erosion-corrosion caused by interference with the development of the continuous film as oxygen is diffused at a rate determined by the water flow rate (Degremont 1979).

2.2.2. Concrete Corrosion

Concrete is made from various types of fine and coarse aggregate that are bonded together with a lime-based cement matrix and often contains steel reinforcement (Gabriel and Moran 1998). In theory, because of the positive electrical charge of the iron in the concrete, the reinforcement cannot corrode until degradation of the encasing concrete occurs. The iron in the concrete which has a pH of about 11.6 has a potential of approximately + 100 mV in reference to the hydrogen electrode. Any action to prevent or retard degradation must therefore be focused first on the concrete (Degremont 1979).

The causes of concrete degradation can be mechanical or chemical. The mechanical causes include excessive permeability or the existence of cavities and cracks which can occur during manufacture of the concrete. This can be minimized by increasing its plasticity by maintaining an optimal water/cement ratio, or adding a plasticizer. Another mechanical cause of concrete degradation is erosion resulting from excessive water velocities (especially if carrying sediment) through concrete pipes. The chemical causes of concrete corrosion are determined by the composition of the cement and the corrosiveness of the water. Silica (SiO_2), lime ($Ca(OH)_2$), and alumina (Al_2O_3) are the main ingredients of cement, with iron, magnesia (MgO) and alkalis being secondary constituents. Cement usually forms a very basic (high pH) medium that includes substantial quantities of soluble salts (Degremont 1979). Chemical degradation can result from the aggressiveness of CO_2, attack by strong acids (mainly produced by sulfate containing wastewaters), the action of ammonia, a content of high sulfates and chlorides, attack by strong alkalis, or bacterial corrosion with the formation of H_2S and low pH (Gabriel and Moran 1998, Degremont 1979).

Concrete is attacked by carbon dioxide (CO_2) when CO_2 concentrations exceed equilibrium CO_2 concentration $CaCO_3 + H_2O + CO_2 \leftrightarrow Ca(HCO_3)_2$. However, a high residue of lime (CaO) alkalinity in the pores of the concrete allows the precipitation of deposits of $CaCO_3$ and other salts, which delays the degradation of the concrete in the short term. When the calcium bicarbonate alkalinity of the water exceeds 61 to 73 mg/L and its pH is greater than 6.5, corresponding to conditions near $CaCO_3/CO_2$ equilibrium, the destruction can be tolerated (Degremont 1979).

Concrete is susceptible to acid attack because of its alkaline nature. Increasing corrosivity occurs in the presence of acids such as phosphoric, sulfuric, nitric, hydrochloric, etc. Organic acids are also destructive. Acids dissolve cement compounds and calcareous aggregate and form water-soluble calcium compounds that will be leached away (Gabriel and Moran 1998). Concrete is often prone to cracking and the correct coating must be used to protect it completely (Degremont 1979).

Concrete can also be attacked by strong alkalis. Water with a strong alkali content (pH >12) is harmful to all kinds of cements because certain alumina-based components are likely to be solubidized (Degremont 1979).

Ammonia in wastewater increases the degradation of concrete by facilitating nitrifying reactions which occur only in an aerobic medium and lead to the acid formation (Degremont 1979). The action of sulfates is complex and is based on the transformation of calcium sulfate ($CaSO_4$) into expanding Candlot salt (Gabriel and Moran 1998; Degremont 1979), also known as ettringite:

$$Ca(OH)_2 + Na_2SO_4 + 2H_2O \rightarrow CaSO_4{*}\ 2H_2O + NaOH$$

$$2CaOAl_2O_3,\ 12H_2O + 3CaSO_4,\ 2H_2O + 13H_2O \rightarrow 3\ CaO,\ Al_2O_3,\ 3\ CaSO_4,\ 31\ H_2O$$

Ettringite is often formed during the sulfate attack and can result in cracking and scaling of concrete. Also, sulfate attack is often manifested, not by expansion or cracking, but by loss of cohesion and strength (Quyang et al. 1988). Deteriorated invert surface becomes fragile and an abrasive bed load will more easily erode invert concrete surface at lower velocities of effluent flow (Gabriel and Moran 1998). If calcium and magnesium chlorides are present, they can react with calcium aluminate hydrates to form chloroaluminates which may result in low to medium expansion of concrete (Gabriel and Moran 1998). Seawater has a high chloride and sulfate content.

Cyclic freezing and thawing of moisture that remains in or has been absorbed by concrete will cause spalling of the surface (due to the water expansion when it freezes causing expansion and degradation of concrete). The deterioration of concrete will leave the surface open to further acid and/or sulfate attack. Too high a water/cement ratio in the concrete will cause a greater porosity of hardened concrete, faster diffusion of chloride ions to the steel/concrete interface, easier ingress of oxygen, and lower electrical resistivity, all of which will result in the reduction in the initiation time for corrosion. The larger volume required by the steel corrosion end products will lead to debonding of the steel and spalling of the concrete (Gabriel and Moran 1998).

2.2.3 Aluminum Corrosion

Aluminum is corrosive in strong acid solutions that have a pH of less than 4 and in strong caustic solutions. A protective scale forms in aerated areas (Gabriel and Moran 1998). Aluminum is passivated by oxidation in moist air and by the formation of a protective film alumina $2Al + 3H_2O - 3e^- = Al_2O_3 + 6H^+$ (Degremont 1979).

Under soft water conditions, the resistance to pitting corrosion is high. Pitting corrosion is more likely to take place in waters containing ions of copper, bicarbonate, chloride, sulfate, and oxygen. Such heavy metal ions as copper and iron increase the possibility of electrochemical corrosion by forming stray electrical currents and galvanic couples. It was noted that a combination of low resistivity with low pH values tend to increase the average metal loss. When low resistivity was paired with high pH, substantial corrosion was observed (Gabriel and Moran 1998).

2.2.4 Copper Corrosion

In copper plumbing systems, corrosion can lead to a number of problems including colored (blue) water, and pinhole leaks in the pipe or fittings. Copper can form ions in water by losing one or two electrons (e^-) (oxidation), and oxygen often accepts the electrons (reduction). Copper reacts with oxygen in water (Oliphant 2010):

$Cu(s) \leftarrow\rightarrow Cu^+ + e^-$

$Cu(s) \leftarrow\rightarrow Cu^{2+} + 2e^-$

$2Cu(s) + ½\ O_2(aq) \leftarrow\rightarrow Cu_2O(s)$

$Cu(s) + ½\ O_2(aq) \leftarrow\rightarrow CuO(s)$

Cu^{2+} ions predominate when air is present (aerobic conditions). Cu^{2+} ions can exist in the solution or form soluble or solid complexes with various anions (negatively charged ions) such as hydroxide (OH^-), chloride (Cl^-), carbonate (CO_3^{2-}), and sulfate (SO_3^{2-}). These anions along with oxygen are a part of the major corrosion products which are found on copper roofs and in copper pipes. If organic compounds are present, copper ions can combine with them and form complexes. Soluble complexes can significantly increase the copper concentration in water and thereby the corrosion rate.

Copper forms an adherent layer of green patina comprised roughly of bronchantite, $CuSO_4*3Cu(OH)_2$. Patina is protective and isolates the metal from the atmosphere (Shreir 1976). Surface patina is formed when copper is spontaneously oxidized at atmospheric conditions. Patinas have different aesthetic appearances, thicknesses, and corrosion products and evolve in different ways depending on factors such as age, environmental and pollution conditions, and building geometries (Wallinder et. al 2009). In Stockholm, the patinas are primary brownish (with the main patina constituent Cu_2O) and/or greenish (an inner layer consists of Cu_2O and an outer layer of $Cu_4SO_4(OH)_6$) (Wallinder et. al 2009; Wallinder and Leygraf 2001). Patina formation is generally governed by electrochemical processes. The rate of oxidation gradually decreases with time as an adherent and protective patina typically evolves. In the environment of repeated dry and wet cycles, patina interacts with pollutants, and can partly dissolve and either re-precipitate on the surface as corrosion products, or be released and transported from the surface during of atmospheric precipitation. This released amount of copper from the patina is referred to as metal release, or metal runoff.

Under some water conditions, the Cu^{2+} ions stay dissolved in solution rather than being precipitated. These kinds of waters are said to be cuprosolvent (copper dissolving). An example of cuprosolvent waters is the water that contains high concentration of carbon dioxide (CO_2), which lowers the water pH often to the values below 6.5 which increases the solubility of copper (Oliphant 2010) . The same effect results in very soft, low pH upland waters. The same waters cause plumbosolvency, the condition when elevated lead concentrations are present in drinking water). High copper ion Cu^{2+} concentrations are often associated with long stagnation of drinking water in the water systems. Copper (II) hydroxide, $Cu(OH)_2$ is the initial corrosion product that forms in all waters. Typically, the soluble copper (II) species precipitate in a relatively short period of time and form much less soluble copper oxides and copper carbonates depending on water composition (Oliphant 2010).

When copper comes in contact with most drinking water, it develops a protective layer of copper oxides and copper carbonates on the inside of the pipe. This protective layer limits the amount of copper that can be dissolved into the water to values well below the 2 mg/L limit stipulated in the Drinking Water Directive (European Council, Council Directive 98/83/EC) that specifies the drinking water quality to be supplied at the consumer’s tap; Oliphant 2010). Small amounts of corrosion at the pipe's surface forms a protective layer that stifles further corrosion. The amount of the corrosion that will occur and its type depends on the environment to which it is subjected. For cold waters: (1) In waters that have low oxygen content (anaerobic conditions; stagnant water) the copper itself is stable and will not corrode readily. (2) If the waters have $pH<6$ and with oxygen present (aerobic conditions; in a moving water), the copper will dissolve to form Cu^{2+} ions (the most stable form under these condition). (3) In waters with pH ranging between 6 and 8 with reasonably high oxygen level (> 2 mg O_2/L), initially insoluble layer of copper (I) oxide Cu_2O (cuprite) will be formed which has the magenta red to brown color and is the most stable species under described conditions. The cuprite will form a semi-protective scale against further corrosion. (4) In the waters with $pH>8$ with a high oxygen content, copper (II) oxide CuO (tenorite) layer will be formed. The corrosion product will have jet black to brown color and will form a protective scale against further corrosion. In hot waters the protective black tenorite is almost always formed. Of the corrosion product species mentioned above, only the Cu^{2+} ion is significantly soluble. The layers that form on the copper's surface are only semi-protective and corrosion will continue, though at much lower rates compared with that of the initial bare metal. The semi-protective scales that at first form in cases (3) and (4) frequently develop further into insoluble layers of basic copper carbonate $Cu_2(OH)_2CO_3$ (the mineral malachite) which has turquoise/green color. The water must contain carbonate and have pH high enough to produce this deposit. This copper mineral will limit the amount of copper dissolved in the water and will be beneficial in the long run. Long periods of static water conditions must be avoided for the layer to be protective (Oliphant 2010).

If the protective film that is formed on copper is broken, the pipe becomes vulnerable to various forms of pitting corrosion. The layer may be non-protective if during its formation there was a long period of stagnation or if certain water types are present. New copper pipes release considerably more copper than old ones. The copper release typically decreases with time as the protective corrosion layer develops (Oliphant 2010).

2.2.5 Steel Corrosion

When exposed to the atmosphere, steel reacts and forms the reaction product rust, of approximate composition $Fe_2O_3*H_2O$, which is loosely adherent to the surface and does not form a protective barrier that isolates the metal from the environment. Hence the reaction proceeds at a roughly linear rate until the metal is completely consumed.

2.2.6 Lead Corrosion

Lead oxide PbO and hydroxide $Pb(OH)_2$ are comparatively soluble and all waters containing oxygen are highly corrosive for lead (Degremont 1979).

2.2.7 Galvanized Steel Corrosion

Hot-dip galvanized steel when exposed to atmospheric conditions forms a passive surface layer (zinc patina) that protects galvanized steel from further corrosion. When zinc surface is exposed to the atmosphere, zinc reacts with oxygen in the air forming zinc oxide ZnO. Zinc oxide ZnO then reacts with the moisture in the air (humidity, rain events) and forms zinc hydroxide ($Zn(OH)_2$). Zinc hydroxide ($Zn(OH)_2$) reacts with carbon dioxide (CO_2) in the air and forms dense, insoluble, zinc carbonate ($2\ ZnCO_3 \cdot Zn(OH)_2$) that retards corrosion of the underlying zinc (American Galvanizers Association; http://www.galvanizeit.org/aga/animation/4741?keepThis=true&TB_iframe=true&height=480&width=640).

Coatings produced by electrodepositing of zinc or by hot dip galvanizing have variable thicknesses and are strongly bonded to the steel. The external surface of the zinc is oxidized and zinc hydroxide, oxide, or hydroxycarbonate are formed. This film impedes the corrosion of the zinc by inhibiting the diffusion of oxygen. When the water is corrosive, the film is destroyed and the zinc will undergo accelerated corrosion and rust will form. The corrosion rate increases quickly with temperature and reaches a peak at 60°C. At this temperature, all the zinc hydroxide is transformed into a more porous oxide which is not as adhesive, causing an accelerated corrosion of the bare iron surface. The zinc oxide film is conductive when Cu^{2+} ions are present in the water and may cause the iron to corrode rapidly (Degremont 1979).

Veleva et al. (2010) noted that zinc has the ability to galvanically protect steel because zinc has more negative potential than that of steel. Under neutral pH conditions, zinc is relatively resistant to corrosion, however, when chloride ions are present (marine coastal environment), zinc is prone to increased localized corrosion. Also zinc is very sensitive to atmospheric acidity, e.g. the presence of SO_2. Zinc corrosion is affected by acidic rainfall with atmospheric aerosols. Sulfuric and nitric acids are the most abundant atmospheric acids and in the environment of high humidity, or even when condensed water is available, their formation proceeds more swiftly, due to the atmospheric oxidation of the aggressive sulfur and nitrogen oxides. The corrosion layer that has formed on the zinc surface can be either removed physically by winds and sand erosion or by dissolution of soluble corrosion products during precipitation or water condensation on the metal surface. Dissolved by rain and dew, zinc corrosion products are released from the corroded surface into the environment. Factors that influence release of zinc corrosion products include the intensity, amount, flow rate, frequency, and pH of precipitation, as well as concentration and solubility of atmospheric aggressive gases during the precipitation, the relative humidity and air temperature. During the dry period, zinc salts $ZnSO_4$ or $Zn(NO_3)_2$ are often formed, which have high solubility constants, and they are easily dissolved during the first flush, whereby less soluble zinc salts are formed, including zinc hydrosulfates and zinc hydrocarbonates, which solubility properties influence the subsequent dissolution rate during the steady state runoff (Veleva et al. 2010).

2.2.8 Plastic Corrosion

Plastic pipes are very resistant to pH and to chemically and electrochemically induced types of corrosion. Pipes made of these materials are therefore highly resistant to corrosive agents, including sulfates, chlorides and other aggressive salts (Gabriel and Moran 1998). Plastic materials are nonconductors and consequently are also not subject to galvanic corrosion.

2.2.9 Eh-pH (Pourbaix) Diagrams

pH and redox potential (Eh) influence the form of the metal (US EPA 2007a). The Pourbaix diagrams show the different zones of corrosion, passivation, and immunity according to the redox potential and pH of the system (Degremont 1979). A given field is marked with the ion that is predominant within it, and a boundary is placed where the ion becomes equal to an adjacent prevailing ion (Garrels and Christ 1990). The solubility of most metal-containing minerals is greatest under acid conditions, decreasing with increasing pH. The location of measured values of oxidation potential (Eh) and pH in aquatic systems can be seen on Figure 1.8 (US EPA 2007a). The dashed lines depict the limits of measurements in natural environments. The main factors that control Eh are atmospheric oxygen and organic matter. High Eh (oxidizing or aerobic) conditions are found in the atmosphere, in most surface waters, and shallow soils in contact with atmospheric oxygen. The lowest Eh (reducing or anaerobic) conditions are observed in water-logged soils and sediments that contain organic matter and in ground waters that contain a few mg/L or more of dissolved organic carbon (DOC). Intermediate Eh conditions are maintained in waters and sediments that are only partially oxidized due to their relative isolation from the atmosphere. Measured Eh values may not coincide with Eh values computed from the concentrations of redox-sensitive species.

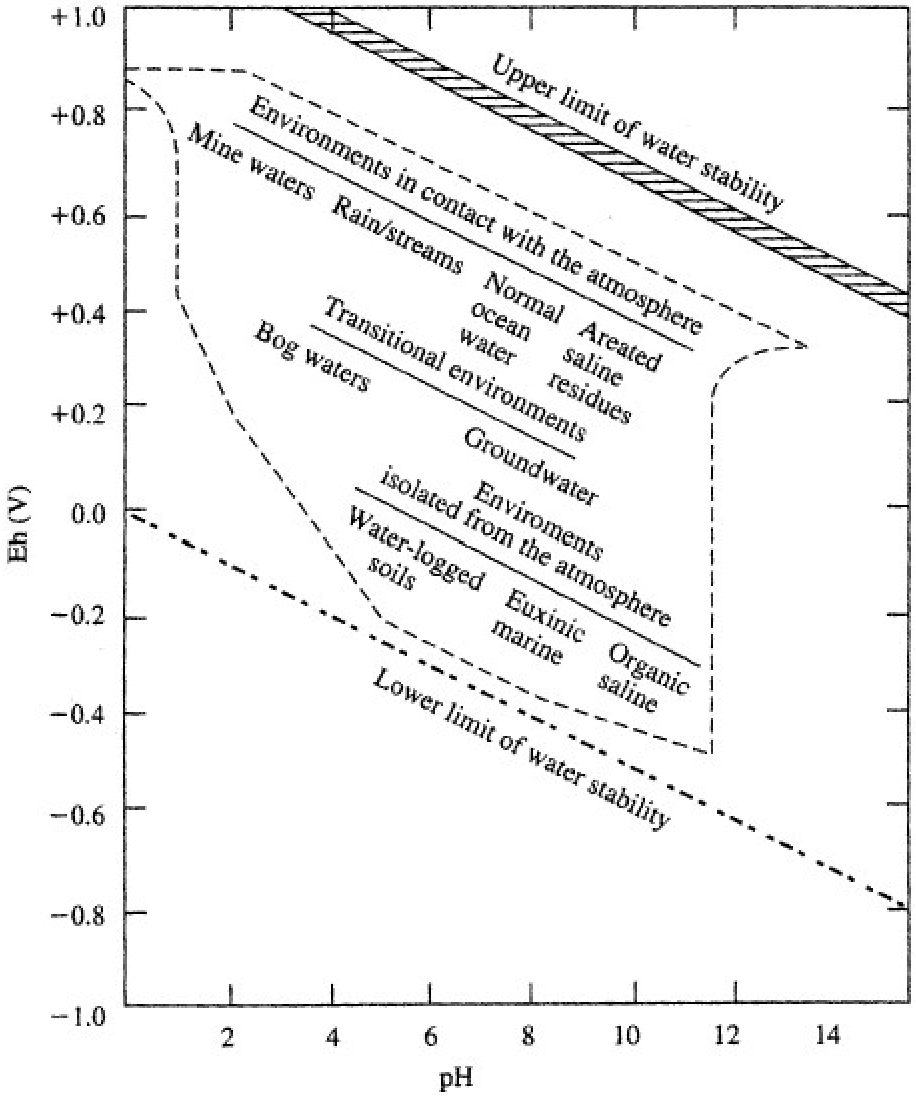


Figure 1.8. Estimated locations of some natural environments of Eh-pH diagram.
Source: US EPA (2007a).

Eh-pH diagrams of metals in aqueous solutions are a valuable means of predicting the corrosion problems and regions of stable conditions. Eh-pH diagrams delineate the predominant area of each chemical or ionic species in aqueous solutions (Garrels and Christ 1990, Degremont 1979; Chen and Aral 1982). When a metal is submerged into an aqueous solution that contains various chemicals (such as oxygen, boric acid, sulfur compounds, chlorides, fluorides, etc.) corrosion problems frequently occur. Eh-pH diagrams of metals in aqueous solutions illustrate the equilibrium phases of metal, its oxides, its ions, or metal compounds associated with the solution's components are a valuable means of predicting corrosion problems. The use of such diagrams helps to avoid separate investigations of every combination of metal, solution, pH, and temperature in order to ensure that certain corrosion problems would not take place (Chen and Aral 1982).

Silverman (1982) noted that Pourbaix diagrams can help to predict corrosion because pH is a measure of acidity and potential is a measure of oxidizing power and both are important determinants of corrosion in electrolytes. These diagrams depict the thermodynamically stable states at varied pH and potential and provide insight whether or not corrosion is possible and can predict the pH and potential conditions at which corrosion will not occur. The diagrams also allow the prediction of the effect that the changes in pH and potential are likely to have (Siverman 1982).

The construction of the Pourbaix diagrams requires that all possible species in the system that are important to corrosion are considered. If possible, actual activities in the solution should be used. For example, a Pourbaix diagram for iron (Figure 1.9) shows that during favorable oxidizing and alkaline conditions, natural passivation (formation of natural protective film) is detected. Also, passivation occurs at pH values above10.5. At Eh values below – 0.58 volt, the immunity field is noted. Immunizing the steel is the method of cathodic protection employed to protect buried pipes or equipment used in sea water. It is generally recognized that cathodic protection is effective for applied potential values between – 0.85 and -1 volt (Degremont 1979).

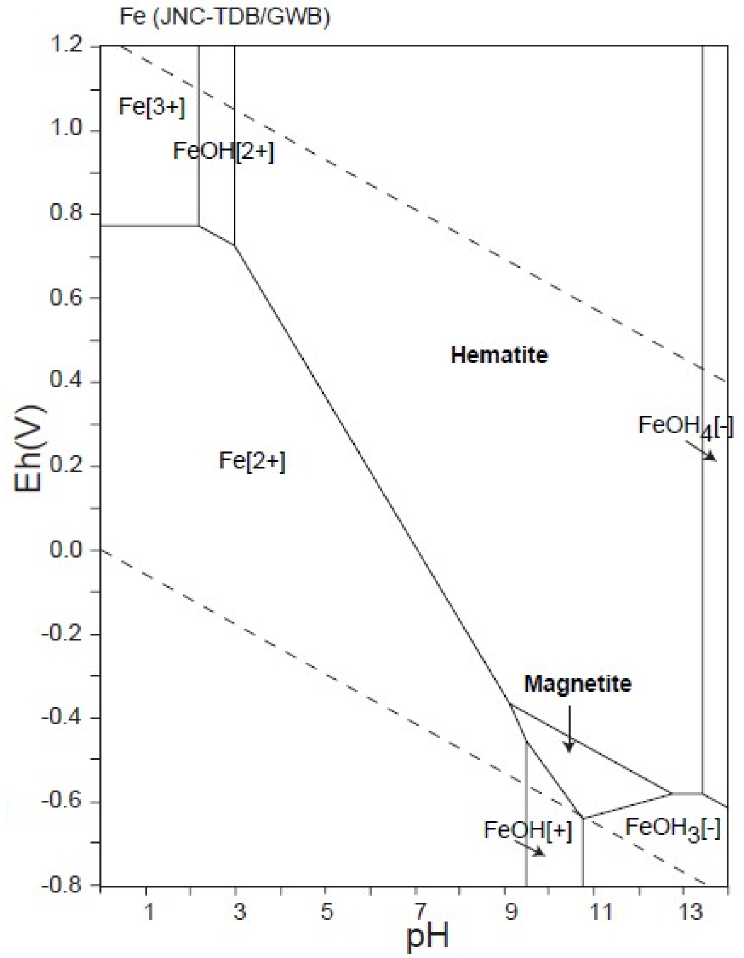


Figure 1.9. Eh-pH diagram of the system Fe-O-H.

Σ Fe = 10^{-10} mole/kg, 298.15 K, 10^5 Pa. Source: National Institute of Advanced Industrial Science and Technology (2005).

The solubility of Fe^{2+} drops significantly when pH increases, resulting in the formation of an insulating film of ferrous hydroxide and other oxides. This leads to an appreciable increase in the cathodic regions and the reduction of the anodic areas to very small surfaces. As the areas of the anodic regions decrease, the density of the corrosion current increases. As the pH approaches 10, the chance of perforating or pitting corrosion in the presence of oxygen decreases and, in most natural water, corrosion stops at pH 10.5 (Degremont 1979). Figures 1.10 a, b and 1.11 a, b show Eh-pH diagrams for zinc, copper, lead, and aluminum respectively.

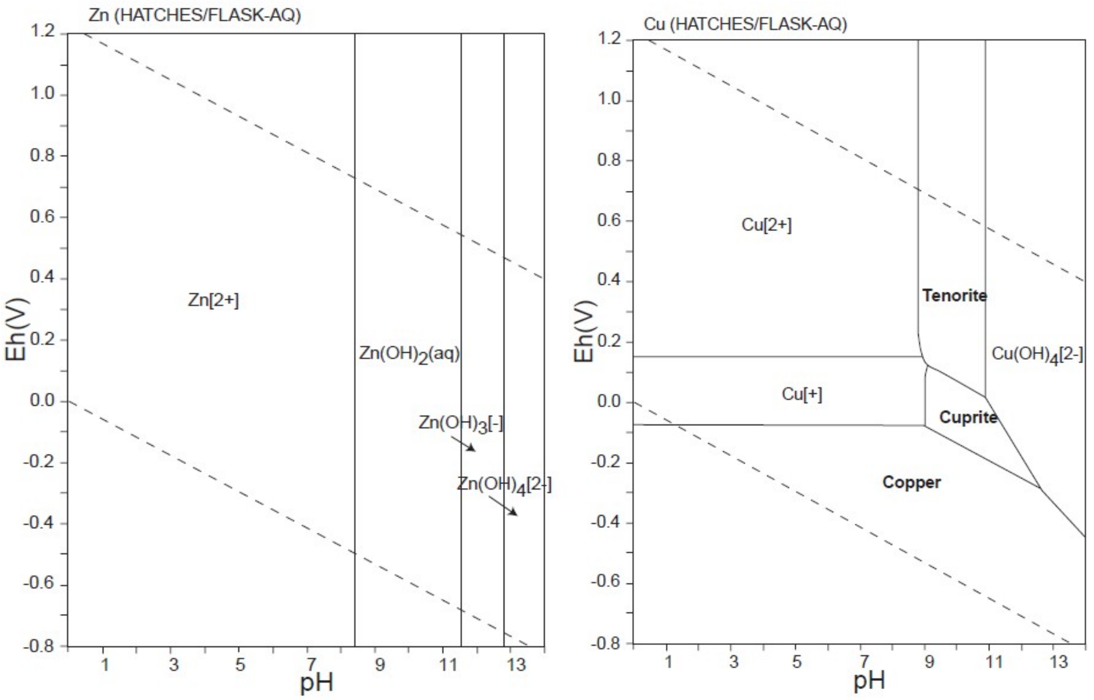


Figure 1.10, a, b. Eh-pH diagrams of the systems Zn-O-H (left) and Cu-O-H (right). Footnote: Σ Zn = 10^{-10} mole/kg, Σ Cu = 10^{-10}mole/kg, 298.15 K, 10^5 Pa. Source: National Institute of Advanced Industrial Science and Technology (2005).

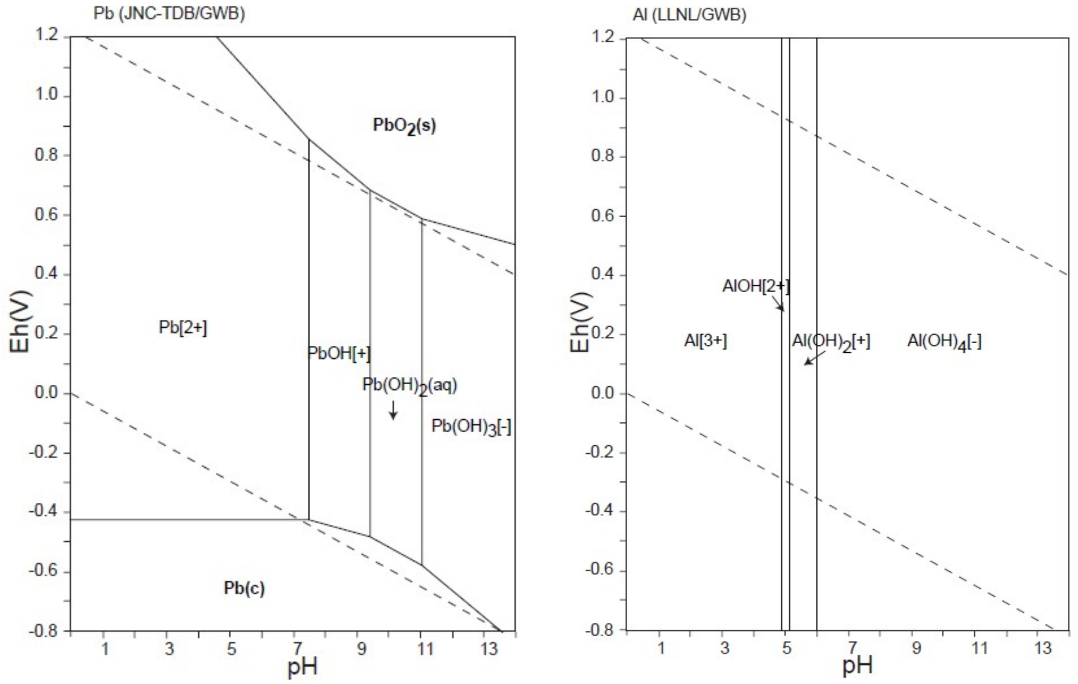


Figure 1.11, a, b. Eh-pH diagrams of the systems Pb-O-H (left) and Al-O-H (right). Footnote: Σ Pb = 10^{-10} mole/kg, Σ Al = 10^{-10}mole/kg, 298.15 K, 10^5 Pa. Source: National Institute of Advanced Industrial Science and Technology (2005).

2.2.10 pC-pH Diagrams

Phase (pC – pH) diagrams are useful in determining equilibrium concentrations of various species present in the solution and their total concentrations. The diagrams can be utilized to identify regions in which certain metal-containing species are predominant (Snoeyink and Jenkins 1980). These diagrams can also be used to show the predominant species and their concentrations in a given pH range (Snoeyink and Jenkins 1980). For example, Figure 1.12 shows a phase diagram of hydrolysis products of Fe (II). Fe^{2+} is the predominant species at pH values between 1 and 8.7. At pH values greater than 8.7, $Fe(OH)_2(c)$ precipitates. A $Fe(OH)_3^-$ complex forms at pH values greater than 11.4; and a $Fe(OH)_4^-$ complex forms at pH values greater than 12.2.

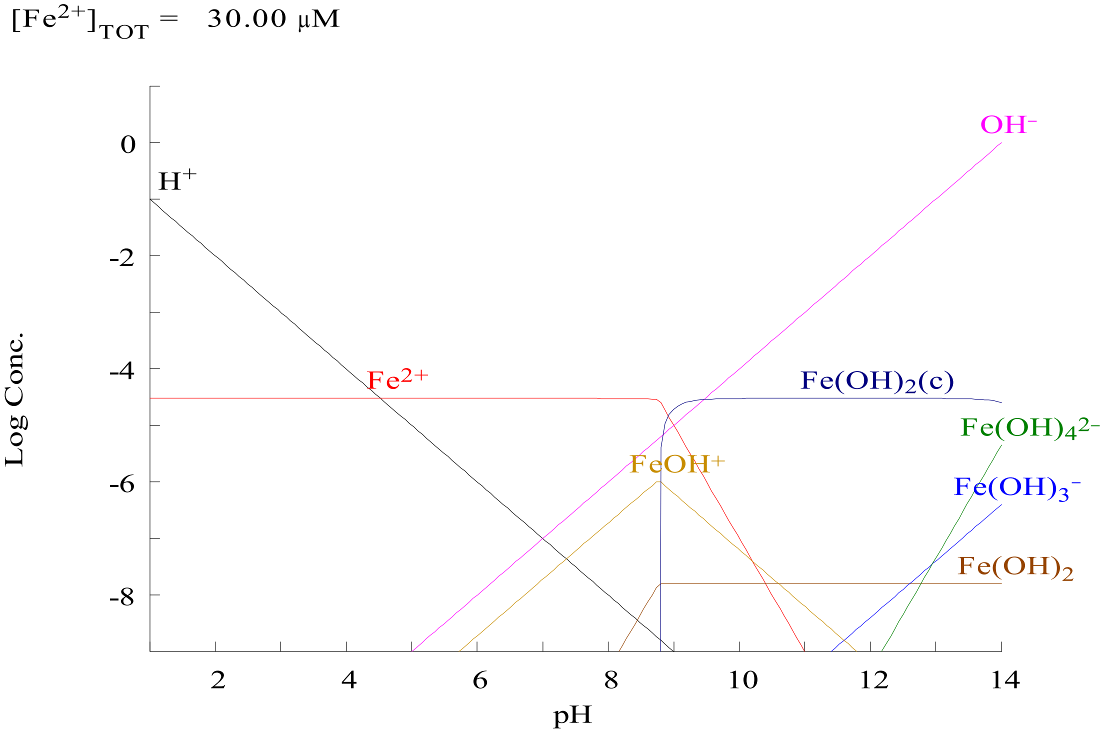


Figure 1.12. Phase diagram of hydrolysis products of Fe (II).

2.3 Partitioning, Fate, and Transport of Heavy Metals in the Environment

Water can transport metals that are associated with particles or are in dissolved forms. The major route for particulate-metal transport is overland flow. Dissolved metals are mainly transported in overland flows, however some underground transport can occur. Many dissolved metals that are carried below the land surface readily sorb to soil particles (NC State University, NCSU Water Quality Group).

Studies have been conducted on associations of heavy metals with particulates in stormwater and it was found that heavy metals are predominantly associated with particulate matter, with the exception of zinc, which is mainly associated with the filterable fraction (Morquecho 2005; US EPA 2007a; Pitt et al. 1995; Horvath 2011; Schriewer et al. 2007; Athanasiadis et al. 2004; Gromaire-Mertz et al. 1999). However, research conducted on zinc in stormwater runoff from industrial storage areas in Birmingham, AL, revealed that zinc was mostly associated with particulates that were transported by runoff coming from areas affected by heavy truck traffic and not galvanized metals (Pitt et al. 1999). Also, Tobiason (2004) found that zinc leaching from Galvalume roofing into roof runoff was strongly sorbed to sediments in open drainage channels and stormwater ponds prior to the ultimate discharge to receiving waters. Fan et al. (2001) also found that zinc in urban stormwater runoff was in particulate form, or sorbed onto particulates. Gumbs and Dierberg (1985) found that heavy metals (zinc, lead, chromium, and cadmium) are bound with particulate matter. Zobrist et al. (2000) found that Pb and Fe in tile and polyester roof runoff samples were mainly associated with particulate fraction, however Cu, Zn, Cd, Mn and Cr were chiefly associated with in the dissolved fraction. Faller and Reiss (2005) studied roof runoff from roofing materials that included copper and zinc with different surface treatment, tinned copper, galvanized steel, aluminum, stainless steel, tinned stainless steel, titanium, and lead in Dubendorf, Switzerland. Copper, zinc and lead released measurable amounts of metallic ions, however a fraction bounded with particulate matter was small.

Pollutants that are mainly associated with filterable fractions have a greater ability to contaminate groundwater and are more difficult to control with traditional stormwater control practices that usually use sedimentation and filtration techniques (Pitt, et al. 1999).

Factors that affect the behavior of metals in natural waters include the suspended sediment and substrate sediment composition, and the water chemistry. Many heavy metals readily sorb to organic and inorganic particulates which accumulate as bedded sediments. During rain events, these sediments may become resuspended and more biologically active by pollutant desorption, transformation, or particle uptake by organism ingestion (Burton and Pitt 2002). Sediment made of fine sand and silt will usually have higher levels of adsorbed metal than quartz, feldspar, and detrital carbonate-rich sediment (NC State University, NCSU Water Quality Group).

Fates of metals in the environment and effects of metals on “ecological receptors” strongly depend on the environmental chemistry of metals (US EPA 2007a). Metals do not degrade. The transformation of species from one form to another depends on the environmental chemistry of the medium. Factors that control metal sorption to sediments include chemical identity, complexation chemistry, solubility, precipitation chemistry, redox behavior, and vapor pressure (US EPA 2007a).

The mobility and bioavailability of metals greatly depends on the metal speciation, therefore the knowledge of metal speciation is very important to an understanding of metal behavior in the environment (Benjamin 2002).

Glenn et al. (2001) studied how traffic activities and winter maintenance practices influence the behavior of particulates in the runoff at highway test sites in Cincinnati, OH. The authors noted that urban snow has a much greater capacity to accumulate traffic-related pollutants when compared to stormwater, which was attributed to longer residence times before melting, and the snow's porous matrix. Factors such as residence time, solids loadings, alkalinity, hardness and pH affect the heavy metal partitioning in the snow (Glenn et al. 2001). Glenn et al. (2001) observed that Cu, Pb, Zn, Al, Fe, and Cd were mainly associated with particulate forms. Partition coefficients for most heavy metals in snowmelt water ranged from 103 to 106 L/kg.

DeCarloet al. (2004) investigated the composition of water and suspended sediment in streams of urbanized watersheds in Hawaii. It was determined that the transport of the most trace metals was influenced by suspended particles. Deletic and Orr (2005) studied sediment from a road in Aberdeen, Scotland. The authors analyzed particulate fractions of copper, zinc, lead, and cadmium. It was determined that the greatest heavy metal concentrations were associated the smallest particle size fraction examined of being less than 63 µm. Magnuson et al. (2001) obtained similar results and concluded that the fate and transport of metal contaminants through a watershed were dependent on the characteristics of the solid particles to which they are bound. It was noted that the particles most frequently associated with metal pollutants have nominal diameters of < 50 µm.

The zinc contaminants in the roof runoff originate from dissolution of the roofing and gutter material rather than from atmospheric deposition (Horvath 2011). Schriewer et al. (2008) also found that the major portion of zinc in roof runoff from zinc material exposure has been mostly bioavailable in the speciation form Zn^{2+}. After roof runoff comes in contact with other surfaces, changes in runoff properties occurs (Heijerick et al. 2002). These changes are difficult to predict and treatment for zinc roof runoff is advised in order to avoid potential detrimental effects on the ecosystem.

Sarin et al. (2004) examined iron release from the corroded pipes under flow and stagnant water conditions. Iron released from corroded iron pipes mainly in the ferrous form (Fe^{2+}). Table 1.11 summarizes metal associations from different source areas.

Table 1.11. Metal distributions in stormwater runoff from various source areas.

Metal	Source Area	Partitioning	Reference
Zinc	Zinc-based roofing materials	94.3-99.9 % dissolved	Heijerick et al. (2002)
Zinc	Zinc-galvanized metal roofs	66 to 92 % dissolved	Tobiason and Logan (2000)
Zinc	Unpainted Galvalume metal roof	86% dissolved	Tobiason (2004)
Zinc	Sawmills	85±15% Dissolved	Bailey et al. (1999)
Zinc	15 (different zinc panels or zinc coatings, which included new and naturally aged sheets) commercial zinc-based construction materials	greater than 95% dissolved	Wallinder et al. (2001) Wallinder et al. (2000) He et al. (2001)
Copper	Copper sheets as fittings around roof windows and the chimney base	1.4 ratio dissolved to particulate	Förster (1999)
Lead	Painted structures in an urban area	70% or greater) particulate	Davis and Burns (1999)
Lead	Zinc roof	0.15 ratio dissolved to particulate	Förster (1999)
Cadmium	Tar felt roof	24 ratio dissolved to particulate	Förster (1999)
Cadmium	Zinc roof	10 ratio dissolved to particulate	Förster (1999)

2.4 Speciation and Complexes

The behavior and toxicity of metals are determined by the metal speciation. Metal chemical forms may consist of free metal ions, metal complexes dissolved in a solution and sorbed on solid surfaces, and metal species that have been coprecipitated in metal solids. Besides toxicity, the speciation of a metal also influences its sorption, acid/base equilibrium, complexation, electron-transfer reactions, solubility and precipitation equilibria, and diffusivity (US EPA 2007a; Benjamin 2002.)

In most natural waters lead and copper are most often found as complexes and not as free ions (US EPA 2007a). Some elements occur in more than one oxidation state, which governs the chemical and biological behavior of the element including toxicity and mobility (Langmuir 1997).

The fate of heavy metals entering an estuary is influenced by salinity changes, physical mixing and dilution, and chemical processes such as sorption, complexation, cation exchange and redox reactions (Turner et al. 1993). Often, heavy metals in estuarine systems occur in greater concentrations in the sediments than the water column (Morse et al. 1993).

Complexes can form between metals (acids) and ligands (bases), both in solution and at the surfaces of minerals and organisms. The nature of the metal complexes formed in solution and at the surface of the organism affects the toxic reaction of organisms to metals (US EPA 2007a).

The idea of hard and soft acids and bases (HSAB) helps to describe the strength of metal complexing and metal toxicity. According to this concept, metal cations are Lewis acids and ligands are Lewis bases. The metal cation and ligand in a complex act as electron acceptor and donor, respectively. The electron cloud of soft species is deformable or polarizable, the electrons are mobile and can easily move. These soft species prefer to participate in covalent bonding. The electron cloud of hard species is comparatively rigid and non-deformable, has low polarizability. Hard species prefer to participate in ionic bonds in complex formation (Langmuir, 1997). Strong, mainly ionic bonds are formed between hard acids and hard bases. If the complex is formed by soft acids and soft bases, mainly covalent bonds are formed which are very strong. In a complex formed by hard-soft or soft-hard acids and bases, bonds are weak. Such complexes tend to be rare (US EPA 2007a). Such ions as Ag^+, Cd^{2+}, Cu^+, Hg^{2+}, and Hg^+ are soft acids; on the other hand, Al^{3+}, Co^{3+}, Cr^{3+}, Fe^{3+}, Mn^{2+}, Sr^{2+} are hard acids. Borderline (between hard and soft) acids include Co^{2+}, Cu^{2+}, Fe^{2+}, Ni^{2+}, Pb^{2+}, Zn^{2+}. Such ions as I^-, HS^-, S^{2-}, CN^-, SCN^-, Se^{2-}, $S_2O_3^{2-}$, R^- (where R is an organic molecule) C_2H_4, C_6H_6, RNC, CO, R_3P, $(RO)_3P$, R_2S, RS^- are soft bases; F^-, H_2O, OH^-, SO_4^{2-}, CO_3^{2-}, HCO_3^-, $C_2O_4^{2-}$, CrO_4^{2-}, MoO_4^{2-}, $H_nPO_4^{n-3}$, SeO_4^{2-}, NH_3, RNH_2, N_2H_4, ROH, RO^- are hard bases. Borderline (between hard and soft) bases include Cl^-, Br^-, NO_2^-, SO_3^{2-}, $H_nAsO_3^{n-3}$, $C_6H_5NH_2$, C_5H_5N.

Hard metals (acids) are the least toxic and the majority are macronutrients. Hard metals prefer to bind with hard bases which contain oxygen. When hard metals bind with soft nitrogen and sulfur species, weaker bonds are formed. The strength of bonds between hard metals and hard ligands is usually dependent on pH. Soft metals (acids) prefer to bind with soft S and N ligands, and form weaker bonds with hard bases (hydroxide, sulfate). Soft and borderline metals, and hard Mn^{2+}, binding with soft ligands such as sulfide, have bonds' strength generally in the following decreasing order: $Pb^{2+} > Cu^{2+} > Cd^{2+} > Co^{2+} – Fe^{2+} > Ni^{2+} > Zn^{2+} > Mn^{2+}$. Soft and borderline metals have the greatest tendency to bind to soft ligands or to organic substrates (which are usually soft), followed by the hard metals, usually in the order $Pb^{2+} > Cu^{2+} > Cd^{2+} > Zn^{2+} > Ca^{2+} > Mg^{2+} >> Na^+$ (US EPA 2007a).

The inclination of metals to form solid phases, such as sulfides in sediments, is also affected by their HSAB characteristics. For example, soft acid metal cations, such as Hg^{2+} or Ag^{+} form very insoluble complexes with sulfides in anoxic sediments. On the other hand, hard or borderline hard metal cations such as Mn^{2+} or Fe^{2+} form marginally more soluble, although still highly insoluble, metal sulfides.

2.4.1 Solubility Product

Solubility product (Ksp) indicates water solubility of a solid (Clark and Pitt 2012). The definition of solubility product is given by Degremont (1979) using the notion of the ionic equilibrium state of a sparingly soluble or insoluble substance:

$AC \leftrightarrow A^{-}+C^{+}$

$$[A^{-}][C^{+}] = Ksp \qquad \text{Equation 1.4}$$

Where,

$[A^{-}]$ and $[C^{+}]$ are the activities of products of the reaction

Ksp is the solubility product.

The magnitude of solubility product is constant for a given temperature and ionic strength of the solution. The less soluble the substance is, the smaller the value of the solubility product. The solutions, in which the product of activities is less than solubility product is undersaturated with respect to the solid, and in such solutions, the solid will dissolve as the system equilibrates. However, if the product of activities is greater than solubility product, the solution is said to be oversaturated with respect to the solid, and in such solutions the solid will tend to precipitate (Benjamin 2002). The activity product of the compounds is compared to the solubility products to determine whether the solution is oversaturated or undersaturated with respect to a compound.

The use of the equilibrium constants in estimating phase separation may not be accurate if the system is dynamic (Clark and Pitt 2012).

To determine the activity product of the compounds in the solution, the dissolved concentrations of constituents in the compound were multiplied by their activity coefficients.

Ionic strength is calculated using the formula (from Snoeyink and Jenkins 1980; Klyachko 1971):

$$\mu = 0.5\, \Sigma\, (C_i Z_i^2) \qquad \text{Equation 1.5}$$

Where,

Ci = concentration of ionic species i, mol/L

Zi = charge of species i

Activity coefficients in aqueous solutions are calculated using the Maclinnes assumption, which allows for the effect of the decrease in concentration of solvent in concentrated solutions (Truesdell and Jones 1974):

$$\log\gamma_i = -\, A\, Z_i^2\, \mu^{1/2} / (1 + B\, \alpha_i\, \mu^{1/2}) + b_i\, \mu \qquad \text{Equation 1.6}$$

A = a constant that relates to the solvent

B = a constant that relates to the solvent

A = 0.509 at 25 ^{o}C (Snoeyink and Jenkins, 1980)

B = $0.328 * 10^8$ at 25 ^{o}C (Snoeyink and Jenkins, 1980)

α_i = the quantity dependent upon the "effective diameter" of the ion in solution (Garrels and Christ 1990). For Ca^{2+}, α_i = 6.00E-08; for HCO_3^-, α_i = 4.00E-08 (Garrels and Christ, 1990).

b_i = an adjustable parameter, which allows for the effect of the decrease in concentration of solvent in concentrated solution (Truesdell and Jones 1974). For Ca^{2+}, b_i = 0.165; for HCO_3^-, b_i = 0 (Truesdell and Jones, 1974).

Metals of zero valence and some inorganic metal compounds are not readily soluble (US EPA 2007a). Many ligands that form solids with metals produce soluble complexes, thus metal solubility is dependent on the solubility of the ligands (Benjamin 2002).

Heavy metals can form insoluble complexes with such ions as hydroxides, carbonates, and phosphates (Stumm and Morgan, 1996). The solubility product can be used to calculate the maximum concentrations of these ions in the water at a given pH value (Clark and Pitt 2012).

Solubility is associated with surface charge (Clark and Pitt 2012).Water is a polar molecule and therefore contaminant ions, colloids, and complexes with surface charges have a tendency to dissolve in water. To remove these pollutants, other chemical properties can be used. Water solubilities of inorganic ions very widely and are influenced by the presence of other ions in the water. Such ions as hydroxides and chlorides can form complexes and increase the water solubility of metals above the value estimated using the K_{SP} (Snoeyink and Jenkins, 1980).

The formation of soluble complexes with ions can complicate the calculation of precipitation of these ions (Clark and Pitt 2012). For instance, besides precipitating, zinc can form various soluble complexes with hydroxide ions, with the valence of complexes ranging from +1 to -2 (Snoeyink and Jenkins, 1980). Complexation can provide an explanation to the discrepancy between ionic concentrations estimated using K_{SP} and the measured concentrations in the solution (Clark and Pitt 2012).

2.5 Environmental Health Risk and Aquatic Life Criteria

The toxicity of a heavy metal to an aquatic organism is influenced by the concentration and bioavailability of the metal, and the exposure duration. Metal bioavailability and toxicity depend on the chemical, physical, and biological conditions under which an organism is exposed

(US EPA 2007a). Bioavailability is controlled by speciation and partitioning of a heavy metal (Rochford 2008; US EPA 2007a; Benjamin 2002). The speciation and partitioning of heavy metals in the aquatic environment is a function of physical and chemical conditions of the system such as suspended sediment, dissolved organic matter, salinity, pH, redox potential, temperature, hardness and dissolved oxygen, inorganic and organic anionic complexation (Rochford 2008; Turner et al. 1993; Stumm and Morgan 1996; US EPA 2007a). Metals in the form of free ions are usually the most bioreactive, metals in the form of complex forms are usually much less bioavailable (US EPA 2007a). Some species of metals are more toxic than others, for example, chromium of valence IV is more toxic than chromium of valiance III (US EPA 2007a). In the environment, metals frequently exist as mixtures with other metals and organic compounds. Depending on the combinations of metals and their relative amounts, the toxicity effect can be significantly greater or lesser than the sum of the individual component effects (US EPA 2007a).

Heavy metals can be toxicants, i.e. chemical pollutants that have the potential to exert direct toxic effects on organisms by interfering with their physiological activity (Rochford 2008). Heavy metals do not degrade in the environment, and therefore have the potential to bioaccumulate (accumulate in an organism) and biomagnify (increase in concentration in a food chain) up the aquatic food chain (Rochford 2008).

The toxic effect of metals can be either mitigated or exacerbated when multiple metals are present in the mixture. The rate of uptake of one metal can be decreased at the expense of the other one if they interact. For example, such metals as cadmium or zinc interacting with a hardness cation such as calcium (US EPA 2007a). Cations also influence metal bioaccumulation and toxicity. Such dissolved cations as Na^+, K^+, Ca^{2+}, and Mg^{2+} can entirely inhibit metal uptake (US EPA 2007a).

If multiple metals are present in the mixture, this can lead to competition among the metals for the complexation capacity of the water. As a result, the complexation capacity of the water will decrease relative to what would be available if any metal would have been present alone, which will have an effect on metal availability and toxicity (US EPA 2007a).

Copper, iron and zinc are nutritionally essential elements for biological functions and the normal development of both aquatic plants and animals. These metals are required for organism health at a certain range of concentrations and can be toxic if those concentrations are exceeded. Lead has no known beneficial effects (Veleva et al. 2010; US EPA 2007a).

Metals are usually found in the environment as mixtures. Toxic effects of metals may be mitigated or enhanced by the interactions in the mixture. Risks are affected by the relative dose and mixture composition (US EPA 2007a).

Copper has toxic effects in fish, invertebrates, and amphibians. Amphibians are very susceptible to copper toxicity which can lead to many diseases, including sodium loss, adverse effects in tadpoles and embryos, and mortality. The toxic effect of copper sulfate and other copper compounds on algae ranges from retarding photosynthesis and growth to mortality. Copper bioconcentrates in different organs of mollusks and fish. Copper bioavailability is reduced when it adsorbs to carbonates, organic matter, and clay (U.S.EPA 2007a).

2.6 Copper

Copper toxicity has been noted to vary substantially due to various physicochemical factors of the exposure water that include temperature, dissolved organic compounds, suspended particles, pH, and various inorganic cations and anions, including those composing hardness and alkalinity (US EPA 2007a). Many of these physicochemical parameters influence copper speciation, and their effects on copper toxicity thus could be due to effects on copper bioavailability. Acute copper toxicity decreases as hardness increases (Burton and Pitt 2002). Copper toxicity decreases as alkalinity and total organic carbon increase. The U.S. EPA established Aquatic Life Ambient Freshwater Quality Criteria for copper. The national aquatic life criteria are a function of hardness (Burton and Pitt 2002).

2.7 Lead

High levels of lead have toxic effects on algae, invertebrates, and fish. For amphibians the adverse effect includes developmental problems and reduced learning capability, and for fish they include growth inhibition, paralysis, muscular and neurological degeneration and destruction, and mortality. Lead has negative effects on invertebrate reproduction and reduces algal growth. Lower lead levels are found as the trophic levels in freshwater habitats increase. Lead bioavailability decreases with increasing hardness, pH, and organic matter. Lead bioaccumulates in algae, macrophytes and benthic organisms, but the inorganic forms of lead do not biomagnify (US EPA 2007a).

The acute and chronic lead toxicity to freshwater animals decreases as the hardness of water increases. A national freshwater aquatic life criterion for lead established by U.S. EPA is a function of hardness. Figure G.3 (Burton and Pitt 2002).

2.8 Zinc

Elevated levels of zinc negatively affect aquatic plants and animals leading to adverse effects in growth and survival (US EPA 2007a). Ambient Aquatic Life Criteria for Zinc set by the U.S. EPA is as a function of hardness (US EPA 1986). Aquatic life criteria for several cationic metals have been expressed as a function of water hardness, however this approach doesn’t account for other important ions and ligands that can affect metals bioavailability and toxicity. To make site-specific bioavailability adjustments to criteria, the Water Effect Ratio

(WER) was developed. The WER is used to adjust the national criteria to reflect site-specific bioavailability (US EPA 2007a).

The EPA established the acute aquatic life criteria for zinc, lead, and copper. Criteria Maximum Concentration (CMC) for zinc in freshwater is 120 µg/L, for lead is 65 µg/L, and for copper 13 µg/L (US EPA, National Recommended Water Quality Criteria). Acute toxicity of copper for freshwater animals ranges between about 3 and 110,000 µg/L, and for freshwater plants between about 1 and 10,000µg/L (US EPA. 2007a). The EPA also established the continuous aquatic life criteria for metals: the Criterion Continuous Concentration (CCC) of 9.0 µg/L for copper, 2.5 µg/L for lead, 120 µg/L for zinc (Burton and Pitt 2002).

2.9 Chapter Summary

Stormwater runoff from roofs and pipes can be contaminated with high heavy metal concentrations. The dissolution of roofing and pipe material is affected by rainwater pH, and other factors. Acidic rainwater can dissolve the $CaCO_3$ content of cement roofs and drainage system, and metal ions from metal and plastic materials. These processes lead to weathering and degradation of the roofing and piping materials. Factors that affect material deterioration include the chemical composition of water and the time of contact with it. Many studies identified that the type of material influences heavy metal concentrations leaching into the water. Metal ions released from roofs are chiefly in the most bioavailable form, and therefore roof runoff can be a significant source of toxicity.

The greatest zinc concentrations were observed from exposure of zinc and galvanized materials (Förster 1999; Heijerick et al. 2002; Clark et al. 2008a, b, and 2007; Burton and Pitt 2002; Bannerman et al. 1983; Pitt et al. 1995; Good 1993; Tobiason and Logan 2000; Tobiason

2004; Veleva et al. 2007, 2010; Gromaire-Mertz et al. 1999; Schriewer et al. 2008; Wallinder et al. 2001, 2000; Gromaire, et al. 2002). Coated galvanized steel materials released lower zinc concentrations compared to un-coated galvanized metals (Clark et al. 2008a; Wallinder et al. 2001, 2000; Mendez et al. 2011). When exposed to the atmosphere, zinc material forms a protective layer (zinc oxides/hydroxides/carbonates), which serves as a physical barrier between the metal surface and the atmosphere (Legault and Pearson 1978; Zhang 1996). Clark et al. (2008a, b, and 2007) noted that there can be elevated zinc concentrations form zinc and galvanized metal materials throughout their useful life. Clark et al. (2008a), Good (1993), and Gromaire-Mertz et al. (1999) found that zinc concentrations in stormwater frequently exceed the criterion for aquatic toxicity. Heijerick et al. (2002), Clark et al. (2008a), and Wallinder et al. (2001) also determined that as the age of metal panels increased, zinc concentrations increased also.

Copper materials released high copper concentrations (Wallinder et al. 2009, 2002a; Sandberg et al. 2006; Zobrist et al. 2000; Karlen et al. 2002; Boller and Steiner 2002). Fresh copper sheets released greater copper concentrations compared to naturally patinated copper sheet (Sandberg et al. 2006). The copper concentrations from galvanized metals and vinyl materials didn’t exceed 25 µg/L (Clark et al. 2008a, b; Mendez et al. 2011). Copper-based paints are important sources of copper at marina basins (US EPA 2011). Corvo et al. (2005) observed that the metal mass loss was proportional to chloride deposition rate. However Sandberg et al. (2006) found that copper runoff rates were significantly lower at the marine site compared to data acquired in an urban environment even despite substantially higher chloride deposition rates at the marine site. Copper concentrations may continue to leach out in an acid rain environment during the material’s useful life (Clark et al. 2008b).

Galvanized steel and galvalume roofing materials were not major sources of lead (Tobiason and Logan 2000; Gromaire-Mertz et al. 1999; Förster 1999; Gumbs and Dierberg 1985; Shahmansouri et al. 2003; Mendez et al. 2011). Clark et al. (2007) determined that old galvanized metals released lead. It was found that lead was leaching out of PVC rain gutters and that lead concentrations in roof runoff samples surpassed the water quality criteria for the corresponding constituents (Good 1993). Davis and Burns (1999) found that lead can be released in stormwater runoff from painted structures. Lead concentrations were significantly affected by paint age and condition. Lead releases from washes of older paints were significantly higher than from fresh paints. It was found that old surface paints have the potential to release high masses of lead into a watershed. Such factors as stagnation time, pH of the water, pipe age, and the Cl/SO_4 ratio influence lead release from PVC, polypropylene, and galvanized iron pipes (Lasheen et al. 2008). Al-Malack (2001) also found that pH of water, time of contact, UV-radiation affected the migration of lead and other metal stabilizers from unplasticized polyvinyl chloride (uPVC) pipes. The author observed the increase of lead concentrations leaching out of uPVC pipes with the time. Gromaire-Mertz et al. (1999) found that lead concentrations in roof runoff exceeded level 2 of French water quality standards of 50 µg/L for practically all samples.

Galvanized iron and PVC can leach iron concentrations, with galvanized iron materials releasing higher concentrations compared to PVC materials (Lasheen et al. 2008; Shahmansouri et al. 2003; Wallinder et al. 2002b). Lasheen et al. (2008) found that water quality parameters (pH, Cl^-/SO_4^{2-} ratio), stagnation time, pipe age, and pipe material affect heavy metal concentrations. Stagnation time and pipe age increase iron concentrations. At low pH (pH = 6) the concentrations of iron increased. High Cl^-/SO_4^{2-} ratio increased iron concentrations in all pipes. Sarin et al. (2004) observed that when oxidants were present in water, greater iron release was noted during stagnation in comparison to flowing water conditions. Corvo et al. (2005) found that metal mass loss was proportional to chloride deposition rate.

Rainwater pH influences the degradation of roofing and gutter material. The acidic environment of the rainwater dissolves $CaCO_3$ content of cement roofs and drainage system, and metal ions from metal roofing materials. This results in corrosion and damage of the roofing and piping materials and the change of the roof runoff pH. In case of concrete and metal materials, pH of the roof runoff is usually higher than that of rainwater and attributed to the $CaCO_3$ and metal ions, but below neutral (Horvath 2011; Pitt et al. 2004; Clark et al. 2007; Clark et al. 2008 a, b; Tobiason 2004; Tobiason and Logan 2000).

Periodic spikes in nutrients were noted from galvanized roofing materials (Clark et al. 2007; Clark et al. 2008 a, b). It was found that roof runoff can be highly toxic (Good 1993; Tobiason and Logan 2000; Bailey et al. 1999; Heijerick et al. 2002).

First flush was observed for heavy metals in the stormwater runoff and was dependent on the antecedent dry period and the rain intensity (Zobrist et al. 2000; He et al. 2001a; Schriever 2008; Gromaire-Mertz et al. 1999; Horvath 2011).

Factors that affect runoff concentrations include time of exposure, runoff water composition (pH, Cl-, etc.), meteorological factors (climate, humidity etc.), and material characteristics such as composition of the metal itself, its age, condition (Faller and Reiss 2005; Schriewer et al. 2008; He et al. 2001a; He 2002; Cramer et al 2002; Veleva et al. 2010, 2007; Sarin et al. 2004; Lasheen et al. 2008; Horvath 2011).

The form of the metals affects their behavior and toxicity in natural waters. Ionic forms of metal are the most bioavailable forms.

2.10 Need for Research

Extensive prior research has been done by scientists on the contribution of rooftop materials to runoff water quality. The results show that roof runoff water quality is heavily dependent on the type of roofing material used. However, a limited number of studies have been done on how pipe and tank materials and environmental parameters influences stormwater quality. In this dissertation research, a wide variety of drainage and storage tank materials under different water quality parameters were examined to determine which materials can be used during long exposures, such as for storage tanks, and which are suitable for drainage components (short exposures) and to identify conditions under which certain materials are to be avoided. Pipe and tank material exposure is different from roofing material exposure due to the significant differences in water chemistry of the runoff water and the much longer exposure times.

Awareness of the amount of the contaminants coming from water piping and storage materials can be used to facilitate the design of stormwater drainage and water storage systems. Data on the potential pollutant release of gutter, piping, and tank materials will allow designers to make better environmental choices of these materials. Pollutant releases can be incorporated into the design of more precise models. The results of this research can assist in the development of stormwater management, control, treatment strategies and planning procedures.

2.11 Dissertation Research

The goal of this research was to determine how different drainage and storage system (pipe, gutter, and storage tank) materials and water characteristics affect water quality through a series of controlled laboratory experiments. The tests were conducted during two three month test periods by immersing sections of the test materials in large quantities of pH buffered solutions made using locally collected roof runoff, and further tests using local un-buffered waters, but having different conductivity conditions. The buffered pH tests were being performed at pH 5 and pH 8. Water samples were being periodically collected and then analyzed for a broad range of nutrients and metallic constituents. Statistical analyses were conducted to identify significant trends in the releases of these constituents from the samples as a function of time and compare the release rates from the different materials.

The dissertation research included the following:

1. Quantified the concentrations and release rates of selected metal and nutrient contaminants and toxicity from different pipe, gutter, and storage materials, and compared these with literature information for similar materials used in roofing systems.

2. Predicted the predominant forms of the measured metals and their environmental effects.

3. Determined whether the solution components reached equilibrium concentration conditions during the duration of the tests, and quantified the expected pollutant releases anticipated for different material selections for different uses (drainage system vs., storage tanks) and water types (low and high pHs, saline and non-saline waters).

3. HYPOTHESIS AND EXPERIMENTAL DESIGN

3.1 Hypothesis

The goal of this dissertation research was to determine how materials used in the construction of drainage or water storage systems can affect water quality. Factors (such as pH and salinity) causing degradation of the materials with time of contact and their interactions were also examined.

The literature review and preliminary analyses have shown that runoff water quality is greatly affected by the material it comes in contact with along with the chemical characteristics of the water. Elevated metal levels can have a detrimental effect on aquatic life and humans, yet, most runoff historically has not been treated before discharge. The emerging use of numeric discharge limits for stormwaters that usually include very low allowable concentrations for heavy metals (such as 14 µg/L for copper and 5.8 µg/L for lead at hardness of 25 mg/L as $CaCO_3$ listed in the permit for stormwater discharges from industrial activities in Nashville, TN) is resulting in more common uses of advanced treatment methods. Pollution prevention, through the use of appropriate materials coming in contact with the stormwater, can reduce these concentrations in the stormwater. The purpose of this dissertation was to quantify these pollution prevention benefits and to show how this approach can be an important part of a stormwater management plan.

The contributions of rooftop material degradation to runoff contamination have been the subject of extensive prior research. However, only a small number of studies have been conducted to determine the effect of the wide variety of drainage system and storage tank materials and influencing environmental parameters on stormwater quality. Insight into the pollutants leaching from these materials will facilitate the design of stormwater management programs and regulatory policies.

The following hypotheses for this dissertation research were developed based on the literature review and preliminary analyses.

Hypothesis:

The type of pipe and storage tank material, environmental parameters affecting degradation of the material, and time of contact, all affect runoff water quality.

Prediction: Stormwater runoff quality is affected by the composition of the material that it comes in contact with and environmental characteristics such as pH and salinity of the water. Rain naturally has an acidic pH of 5.6 and can be reduced further in areas having acid rain. Most runoff has pH values close to 7 after contacting soil (or concrete). However, roof gutter and downspout materials are usually subjected to the lower pH conditions, at least for a short period. The low pH water is more corrosive and will leach greater amount of pollutants from the material. Longer contact times, such as when water is stored in water tanks or cisterns, will cause higher concentrations of contaminants. In addition, certain major ions in the water (such as chlorides) can accelerate the degradation of the material through corrosion processes or dissolution. Sacrificial zinc anodes (such as galvanized materials) are intended to release zinc as part of the chemical reactions that protect the underlying metals (mostly iron or aluminum). Unfortunately, the zinc is much more problematic to receiving waters than the metals being protected, although structural integrity of the underlying metal is preserved.

Research Activities:

a) To determine whether piping, gutter, and storage tank materials contain heavy metals of concern, and their content, by chemically analyzing shavings of the materials.

b) To collect natural stormwater in the city of Tuscaloosa from downspouts and from storm drain inlets (sheet flow runoff) and adjust pH to different values using disodium phosphate dihydrate and potassium phosphate, monobasic, which are standard buffer chemicals. These buffered waters have pH values of 5 and 8, but have high conductivity (and phosphorus) values due to the buffering chemicals. These buffers were used during the first testing stage examining pH effects on the metal release rates with time. Conductivity could not be simultaneously tested as it was not possible to create buffers having low conductivity values.

c) To collect water from Mobile Bay (saline with high conductivity) and the Black Warrior River (non-saline with low conductivity) and to use these un-buffered natural waters to contrast high and low conductivity effects with time on metal leaching during the second testing stage.

d) To conduct static leaching factorial experimental tests with different pipe/gutter material samples at different pH values and conductivities, with water samples periodically analyzed for the parameters of interest.

e) The samples were analyzed for metal concentrations and other constituents of interest, along with toxicity screening using Microtox procedures.

f) Preliminary tests were conducted using the Microtox procedures to determine the optimal salt (NaCl) additions which adjust water sample salinity for bacterium osmotic pressure. QA/QC procedures were also developed to determine IC_{50} and IC_{20} for $ZnSO_4$ and phenol concentrations as reference toxicants to be used as standards.

g) To determine the method detection limits (MDL) for nitrogen analyses.

h) To determine metal mass released per sample surface area for the different test conditions.

i) To determine the predominant forms of metals present for the test conditions using Eh-pH diagrams.

j) To calculate Langelier Index values to determine whether the solution is oversaturated or undersatureated with respect to $CaCO_3$ and therefore whether concrete samples would deteriorate.

k) To use the Medusa water chemistry program to model metal speciation in the test solutions.

l) To develop a predictive model that can be used to compare the benefits of alternative material selections for different uses (roofing components, drainage pipes and culverts, and water storage tanks) and water chemistry conditions (contact time, pH, and conductivity).

Critical Tests:

a) Time series plots were constructed to examine the overall data patterns. The water quality parameters were plotted against exposure time to evaluate basic data behavior. These tests were used to identify the specific exposure breakpoints, lag periods, and to determine if the release rates remain constant with time.

b) Kruskall-Wallis tests were conducted for metals and toxicity to determine whether the data can be combined into replicates of short exposure vs. long exposure periods.

c) Two-way factorial analyses were conducted to identify significant effects of exposure periods and pH factors for each material during the first testing stage, and the effects of exposure periods and salinity for each material during the second testing stage. The data was combined into groups based on the calculated effects from the factorial analyses. Also Factorial analyses were performed to estimate the effect of several factors (and their interactions): exposure time (short vs. long); pH (5 vs. 8) or conductivity (bay vs. river); and material (copper vs. non copper; non-steel vs. steel materials; copper and steel materials vs. the rest of the materials) on metal releases in mg per area of material and on toxicity data in %.

d) Box and whisker plots were plotted to graphically represent the data and to illustrate the differences between the significant groupings of the data.

e) The results of the tests were compared with the information found during the literature review.

f) The strength and significance of the associations between water quality parameters and contaminants released into the water were analyzed employing Pearson correlation, principal component, and cluster analyses. Correlation coefficients helped to quantify the relationships between the variables and illustrated how strongly the contaminant concentrations were associated with the water quality characteristics.

k) A model was developed that can be used to compare different materials for different uses and water chemistries. The data were combined into groups based on the calculated effects from the factorial analyses. Based on these tests, it was determined which materials can be safely used for long term storage of water.

3.2 Methodology

3.2.1 Materials and Methods

Eight gutter and pipe materials (some also used in tank construction) were subjected to long-term static leaching tests under different water conditions: buffered low and high pH waters and natural bay and river waters having different conductivities. The gutter materials included vinyl, aluminum, copper, and galvanized steel. The pipe materials included concrete, PVC (polyvinyl chloride), HDPE (high density polyethylene), and galvanized steel. Materials that are also commonly used in water tank construction include: aluminum, galvanized steel, concrete, PVC, and HDPE. All of the material samples for these tests were obtained as new specimens from a local building material supplier. The specimens used for the two controlled pH tests and bay and river water tests were nearly identical, with the exception of the concrete pipes. The two concrete samples for the pH tests were the same, but larger than the two smaller, but identical concrete samples for the bay and river water tests.

The tests were performed in two stages. During the first testing stage, the materials were immersed into locally collected roof runoff and parking lot runoff that were adjusted to pH values of 5 and 8 using buffer chemicals added to the runoff water (disodium phosphate dehydrate $Na_2HPO_4 * 2H_2O$ and potassium phosphate monobasic KH_2PO_4). These buffered waters therefore had high phosphate concentrations (2,065 mg/L as P) and high conductivity values (greater than 10 mS/cm) that can affect the metal speciation during the tests. Each section of pipe and gutter material was submerged into the runoff water in 16 L plastic buckets, or 80 L containers for the concrete specimens. During the first test, the effects of pH, time, and material type on contaminant leaching from the drainage system materials were investigated. A second series of tests were conducted to investigate the metal releases under natural pH conditions, but with varying conductivity values associated with natural brackish bay water and river water. During the second testing stage, un-buffered waters from Mobile Bay (saline) and the Black Warrior River (non-saline) were used. Saline water was used to study the effect of salinity on metal releases, such as when pipe materials are exposed to snowmelt containing salt in stormwater runoff during spring months and for pipe crossings or outfall structures in brackish or saline waters.

The pH 5 and 8 values were chosen for the test conditions based on the studies summarized by Pitt et al. (2004). The authors found that pH varied widely for different source areas, with the pH of roof runoff being on the lower end of the reported pH range between 4.4 and 8.4, and a mean value of 6.9. The highest pH was observed for storage areas at a concrete plant with reported pH values ranging between 6.5 and 12, with a mean of 8.5. The pH 5 and 8 conditions were therefore within the ranges of the two extreme groups of sample sets and could be controlled by known buffer systems.

Each specimen of pipe and gutter material was submerged into containers with pH values of 5 and 8 during the first series of tests; the gutter materials were submerged in buffered roof runoff (at both 5 and 8 pH) and the pipe materials were submerged in the buffered parking lot runoff (also at both 5 and 8 pH). For the second series of tests, new specimens of the same samples were submerged in containers having un-buffered bay and river waters. The pH and conductivity values for the first and second series of tests at time zero (waters without specimens) are listed in Table 1.12.

Table 1.12. Initial pH and conductivity values for buffered and natural water tests.

	pH 5	pH 8	Bay	River
pH	5	8	8	8
Conductivity, mS/cm	6.1	10.1	10.1	0.4

Water samples from each leaching container were periodically collected and analyzed over a three month period for selected heavy metals, nutrients (during first stage of the experiments), toxicity (using Microtox screening methods); pH, conductivity, and Eh. Eh is the half-cell potential relative to the standard hydrogen electrode (see Langmuir 1997 and Garrels and Christ 1990 for a complete definition and descriptions of how it is used in water chemistry modeling).The samples from the first series of tests were analyzed at time 0 (water with adjusted pH without pipes), 0.5 hour, 1 hour, 27 hours, 1 month, 2 months, and 3 months for total concentrations of cadmium, chromium, lead, copper, and zinc. The samples were also analyzed for total aluminum and iron, along with filterable concentrations of lead, copper, zinc, and aluminum after 3 months of exposure. Analyzed nutrients included ammonia nitrogen, total nitrogen, and nitrate plus nitrite. Since phosphates were a major component of the buffers, they were not considered during the leaching tests (except as possible films to protect the materials). Chemical Oxygen Demand (COD) was also measured. During the second series of tests, 14 L leaching containers with un-buffered bay and river waters were sampled at time 0(natural bay or river waters without pipes), 1 hour, 27 hours, 1week, 1 month, 2 months, and 3 months for total concentrations of lead, copper, and zinc, and also screened for toxicity. Concentrations in mg/L were converted to mg of constituent per surface area of a pipe or gutter in order to account for different area surfaces of the pipes and water volumes. Water samples were also analyzed for total aluminum and iron, and filterable iron, at time zero and at 3 months. Alkalinity, total hardness as $CaCO_3$, and calcium hardness as $CaCO_3$ concentrations were measured after 3 months during first stage of the experiments and at time zero and after 3 months during the second stage of the experiments. Additionally, Cl^- and SO_4^{2-}were analyzed after 3 months of exposure during the first and the second series of tests. Bay and river waters were analyzed for fluoride, nitrate, total phosphorus, bromide, and manganese, boron as BO_3^{3-}, silicon, sodium, and potassium. Shavings from pipe and gutter materials were also analyzed for Pb, Cu, Zn, Al, and Fe. Metal analyses were performed using inductively coupled plasma mass spectroscopy (ICP-MS).The detection limits for zinc, copper, and lead concentrations were20, 2, and 5 µg/L respectively. The detection limits for cadmium and chromium were 5µg/L and 20 µg/L respectively, and for aluminum and iron 100 µg/L and 20 µg/L respectively. Analytical methods used and method detection limits are shown in Table 1.13.

Table 1.13. Analytical methods and method detection limits.

Analyte	Analytical Method	Method Detection Limit (MDL), µg/L
Zinc, Copper, Chromium, Iron, Manganese, Boron (outside laboratory*)	Inductively Coupled Plasma Mass Spectrometry (ICP-MS). EPA Method 200.8	20
Lead, Cadmium (outside laboratory)	Inductively Coupled Plasma Mass Spectrometry (ICP-MS). EPA Method 200.8	5
Aluminum (outside laboratory)	Inductively Coupled Plasma Mass Spectrometry (ICP-MS). EPA Method 200.8	100
Chloride, Sulfate, Fluoride, Nitrate, Bromide (outside laboratory)	Ion Chromatography. Standard Methods. Method 4110B	20
Phosphorus (outside laboratory)	Ascorbic Acid Method. Standard Methods. Method 4500P-E	20
Silicon (outside laboratory)	Standard Methods. Method 3111D. Metals by Flame Atomic Absorption Spectrometry	10,000
Sodium (outside laboratory)	EPA Method 273.1 Flame Atomic Emission Spectrometry	20
Potassium (outside laboratory)	EPA Method 258.1	20
Alkalinity (outside laboratory)	Standard Methods. Method 2320B Titration	100
Ca Hardness as $CaCO_3$ and Total Hardness as $CaCO_3$ (outside laboratory)	Standard Methods. Method 2340B Hardness by Calculation.	20
Ammonia Nitrogen	HACH Method 10023. Test 'N Tube	61 as N**
Total Nitrogen	HACH Method 10071 TNT Persulfate Digestion.	734 as N **
Nitrate	HACH Method 8171 Using Accuvac Ampule	95 as N**
Chemical Oxygen Demand	HACH Method 8000. Colorimetric Determination.	1,530as COD**

* the outside commercial laboratory was Stillbrook Environmental Testing Laboratory in Fairfield, AL.
** at95% confidence level

A full 2^2 factorial experiment examined the direct effects and interactions of pH and exposure time for each material for the data collected during the first testing stage and the effects and interactions of conductivity and time for each material for the data collected during the second testing stage. Also, a full 2^3 factorial experiment identified the effects and interactions of exposure time, pH, and material during the first series of tests and the effects and interactions of exposure time, conductivity and material during the second series of the experiments.

3.2.2 Detailed Pipe and Gutter Description

All samples were purchased new and were typical materials used in new construction. The gutter samples were obtained from the local Lowes store; the HDPE, PVC, and galvanized steel pipe samples were obtained from Summit Pipe and Supply Co., and the concrete pipe samples were obtained from Hanson Pipe and Precast. The gutters were rectangular in shape (with the exception of galvanized steel gutter which was rounded), while the pipes were round. All the pipe and gutter segments were new and were 30.5 cm long, with the exception of the concrete pipe samples, which were 15.3 cm long in the first testing stage (a smaller portion of the new concrete pipe was used during the second testing stage) (Figure 1.13 and 1.14). Tables 1.14 and 1.15 describe the test specimens.

Table 1.14. Round pipe section descriptions.

Material	Outer Diameter, cm	Wall thickness, cm	Length, cm	Weight, g	Surface Area, m^2
Concrete Pipe	41.2 (20% section of cylinder)	5.5	15	22,400 (4,400)	0.47 (0.10)
PVC Pipe	15.7	0.5	30.5	1,096	0.30
HDPE Pipe	17.5	1	30.5	409	0.65
Galvanized Steel Pipe	16.4	0.6	30.5	8,000	0.32

Note: the values in parenthesis are for the second testing stage

Table 1.15. Rectangular gutter section descriptions.

Material	Outer Diameter or Cross-sectional Dimensions, cm	Wall thickness, cm	Length, cm	Weight, g	Surface Area, cm^2
Galvanized Steel Gutter	15	0.05	30.5	704	0.29
Vinyl Gutter	5 x 8	0.1	30.5	100	0.07
Aluminum Gutter	8.4 x 5.6	0.05	30.5	79	0.08
Copper Gutter	10.58 x 7.2	0.07	30.5	503	0.10

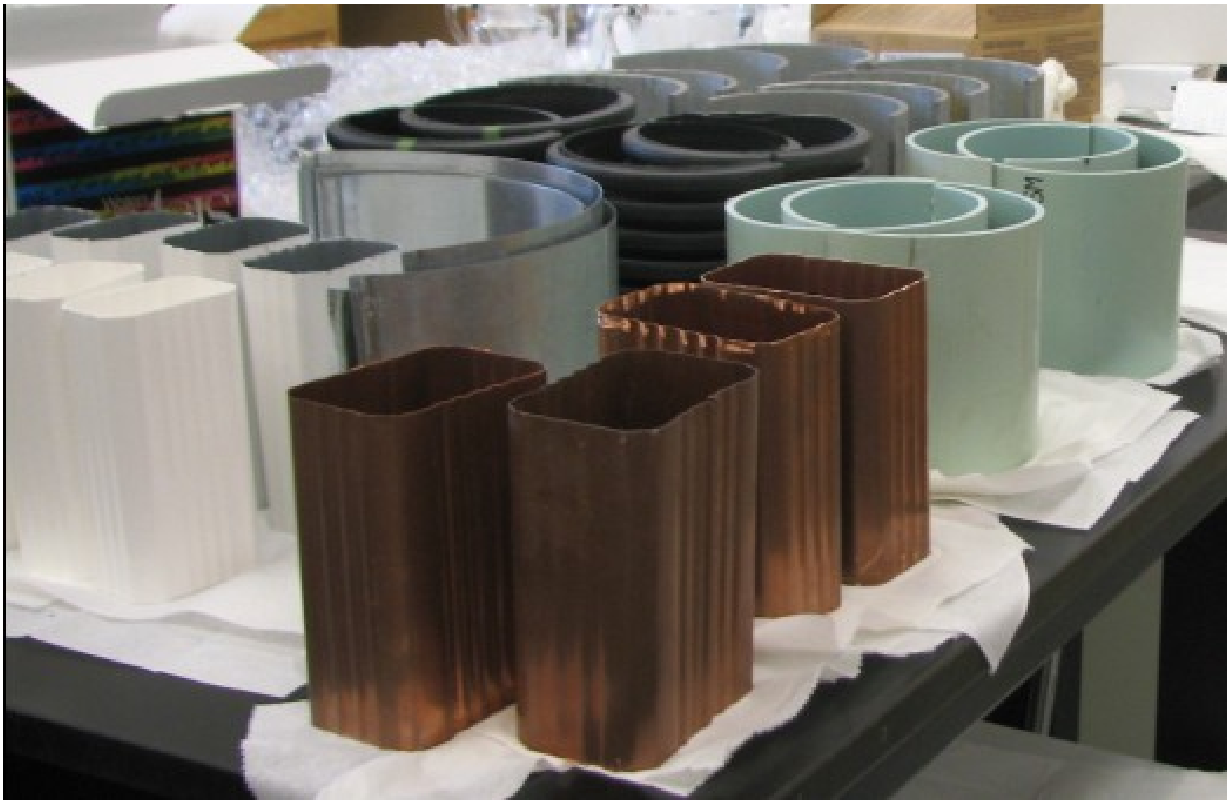


Figure 1.13. Pipe and gutter samples

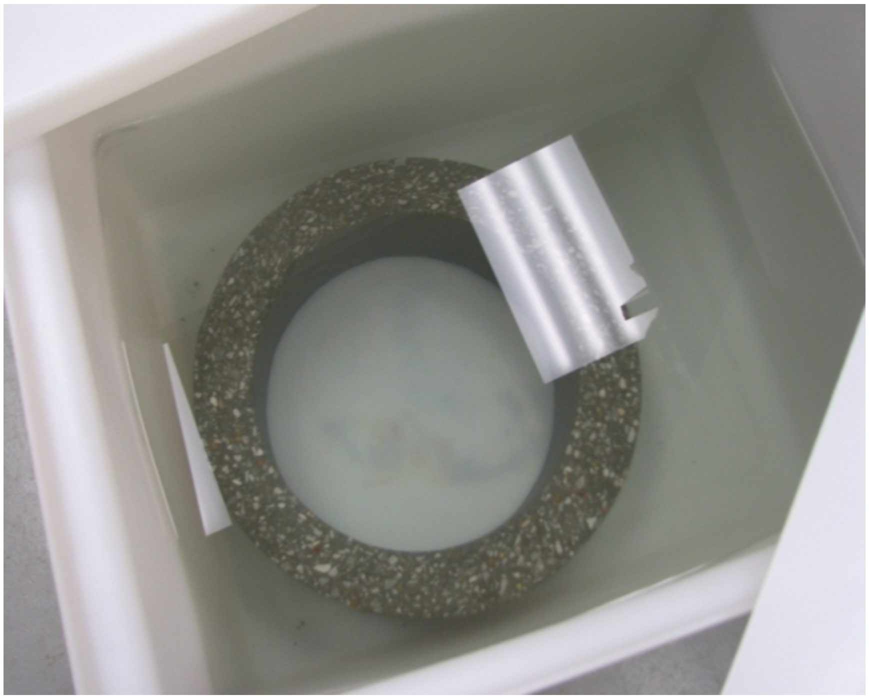


Figure 1.14. Concrete pipe sample submerged in test solution.

The shavings of the pipe and gutter materials were acquired by drilling the samples which were then chemically analyzed for lead, copper, zinc, aluminum, and iron (Table A.6.1, Appendix A).Lead was a constituent in concrete, galvanized steel, aluminum, and copper materials. Galvanized steel pipe and gutter materials had similar metal content concentrations. Galvanized steel pipes had slightly higher lead and zinc content compared to the galvanized steel gutter samples. Iron concentrations were 970 and 980 g/kg for galvanized steel pipes and gutters respectively; zinc concentrations were28 and 18 g/kg for galvanized steel pipes and gutters respectively. Copper materials had 998g/kg copper concentrations. Copper was also detected in the concrete, HDPE, galvanized steel, and aluminum materials, but the concentrations were much lower (≤0.52 g/kg).Besides galvanized steel materials, zinc was also detected as a component in concrete, aluminum, and copper materials.

3.2.3 Buffer Preparation

Roof runoff was collected from the flat roof from the H.M. Comer engineering building to use as the base for the buffer solutions for the gutter samples, while parking lot runoff from behind the building was collected to use as a base for the buffer solutions for the pipe samples. These runoff samples were used as they represented the basic types of waters that the materials would be exposed to during typical use. The following describes how the buffer solutions were prepared (very large volumes of the buffers were prepared by adjusting the quantities in the following description):

$Na_2HPO_4 * 2H_2O$ and KH_2PO_4 can be used for the buffers with the values of pH between 4.8 and 8.00:

To prepare a buffer having pH 5:

- dissolve 11.866 g of $Na_2HPO_4 * 2H_2O$ in 1 L H_2O, take 0.95 mL from the solution
- dissolve 9.073 g of KH_2PO_4 in 1L H_2O, take 99.05 mL from the solution
- combine the 0.95 mL portion from the first solution with the 99.05 mL portion from the second solution to produce 100 mL of buffer having a pH of 5

To prepare buffer having pH 8:

- dissolve 11.866 g of $Na_2HPO_4 * 2H_2O$ in 1 L H_2O, take 96.9 mL from the solution
- dissolve 9.073 g of KH_2PO_4 in 1L H_2O, take 3.1 mL from the solution
- combine the 96.9 mL portion from the first solution with the 3.1 mL portion from the second solution to produce 100 mL of buffer having a pH of 8

More than 450 liters of roof runoff and parking lot runoff buffers were prepared for the first series of tests.

3.2.4 Method Detection Limit Determination

The analytical method detection limit (MDL) for ammonia nitrogen, total nitrogen, nitrate nitrogen, and Chemical Oxygen Demand were determined in the UA lab using standards with known low concentrations (about twice the expected MDL value). Seven replicates were analyzed to determine the standard deviation of the analyses (Eaton et al., 2005). The MDL was calculated using the measured standard deviation times the value of t from a table of the one-sided t distribution for 7-1 = 6 degrees of freedom at the desired confidence level (for the 99% level t = 3.14) (Eaton et al., 2005). The calculated method detection limits are shown in Appendix H. For example, to determine the method detection limit for ammonia nitrogen, a standard having a known concentration of 1 mg/L as N was used. The expected MDL was 0.5 mg/L as N, or lower. Seven replicates of the ammonia nitrogen Standard 1 mg/L as N were analyzed. The values observed are shown in Table 1.16.

Table 1.16. Observed values for nitrogen ammonia standard with concentration 1 mg/L as N

Value Observed, mg/L as N
0.88
0.92
0.92
0.94
0.96
0.97
0.96
Standard deviation: 0.032

The standard deviation of the seven samples was 0.032 mg/L N. The MDL was the calculated standard deviation times the coefficient at the specified confidence level. The calculated MDLs at different confidence intervals are listed in the Table 1.17.

Table 1.17. Method detection limits for ammonia nitrogen at different confidence levels.

MDL	Confidence Level, %
0.099	99
0.061	95
0.045	90

HACH states that a standard deviation of 0.03 mg/L as N for ammonia nitrogen was obtained using a 1.5 mg/L as N ammonia nitrogen standard, a similar standard deviation as found during the UA lab tests. The analytical method detection limits for the rest of nutrients are shown in Appendix H.

3.3 Quality Control and Quality Assurance

QA/QC data are shown in Appendix J. Figures1.15 and 1.16 as plots of pH values with time in the containers with initial pH 5 and pH 8, respectively. The graphs show that pH values in the containers were fairly constant throughout the experiments. The pH change with time did not exceed 1 pH unit, with the exception of the containers with concrete samples and initial pH 5. In those conditions, the pH increased from 4.98 to 6.37 due to the increased alkalinity from the immersed concrete sample. Figures 1.17 and 1.18 show changes in conductivity values with time. The metal releases in the containers with immersed concrete samples were below or just above the detection limits, while the conductivity values in those containers were fairly constant with time. The increase in conductivity values with time in the rest of the containers can be explained by the increase in metal concentrations released from the immersed samples.

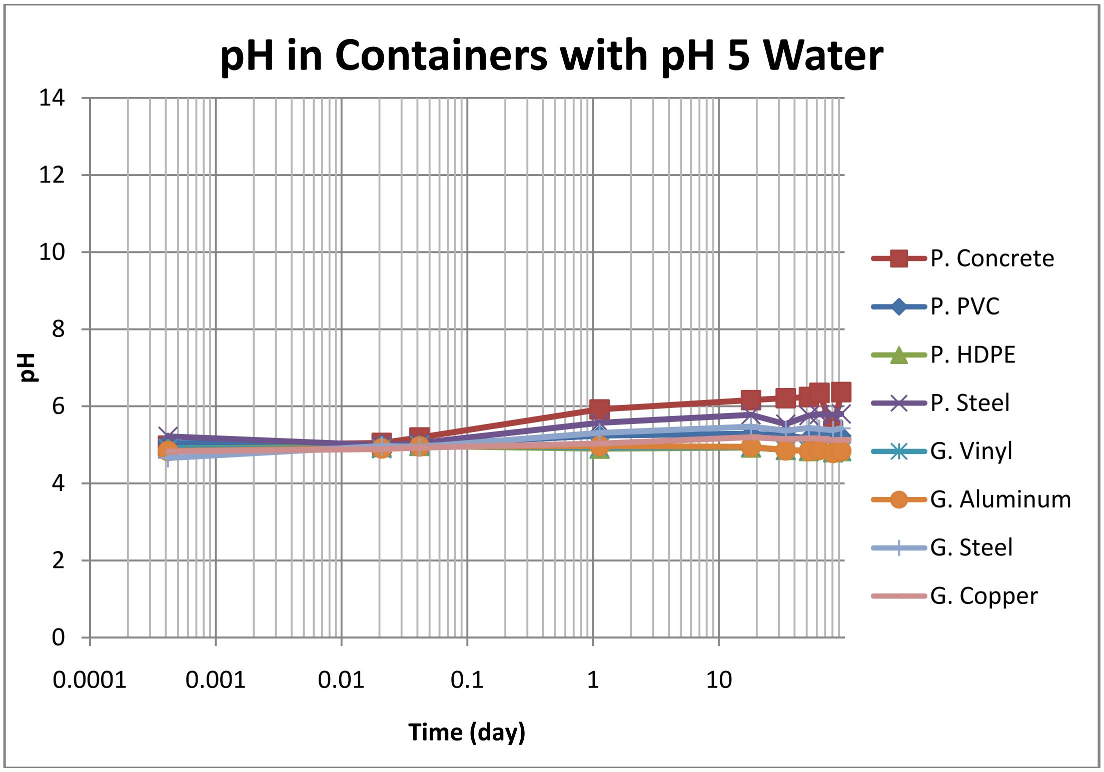


Figure 1.15. pH measurements in the containers with pH 5 water.

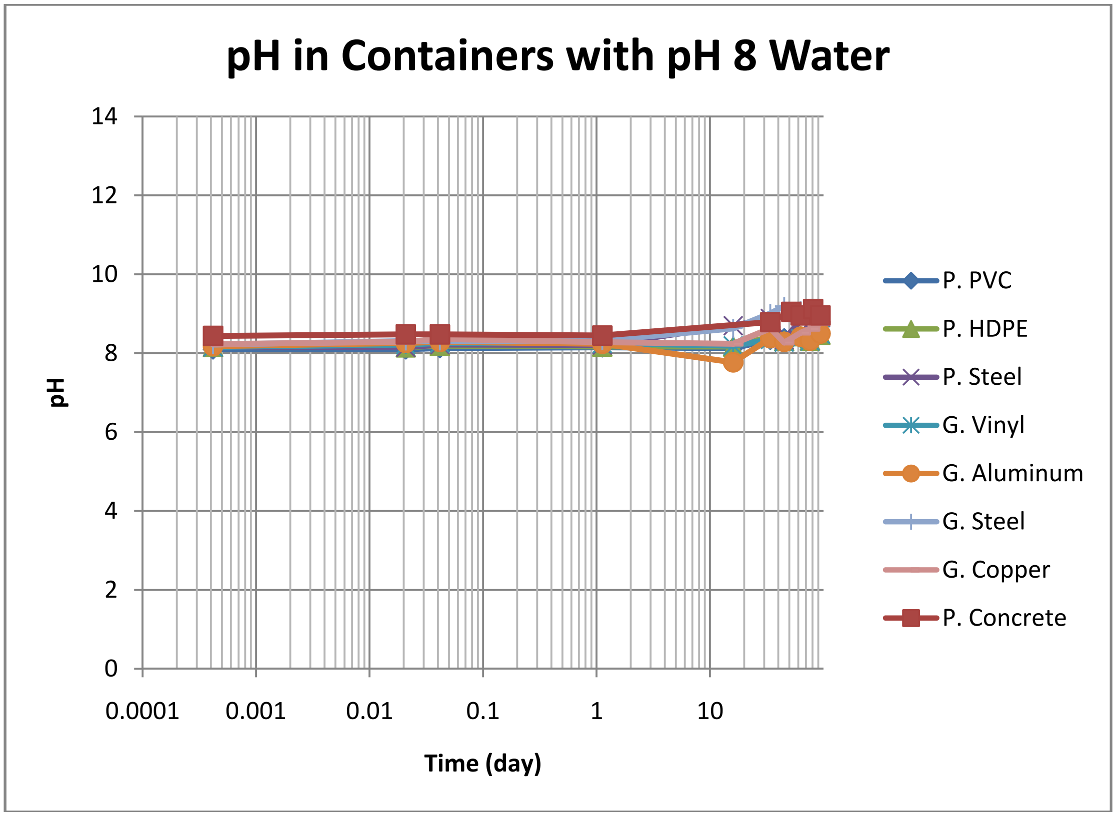


Figure 1.16. pH measurements in the containers with pH 8 water.

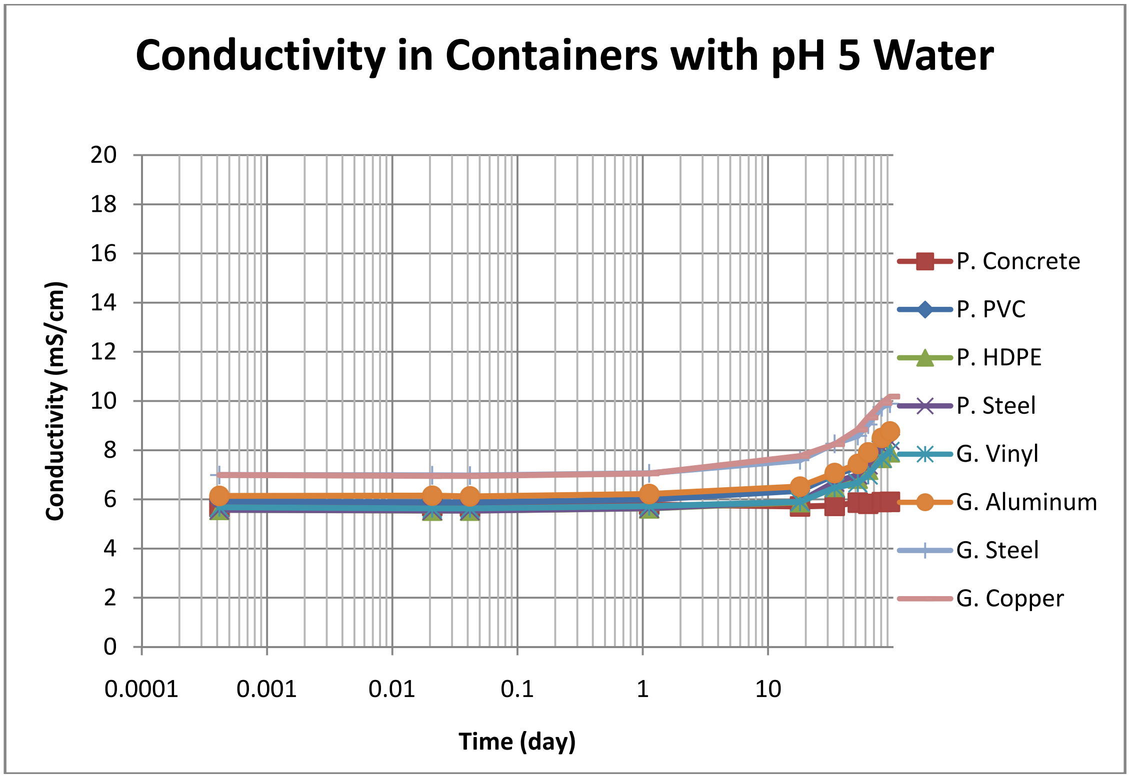


Figure 1.17. Conductivity measurements in the containers with pH 5 water.

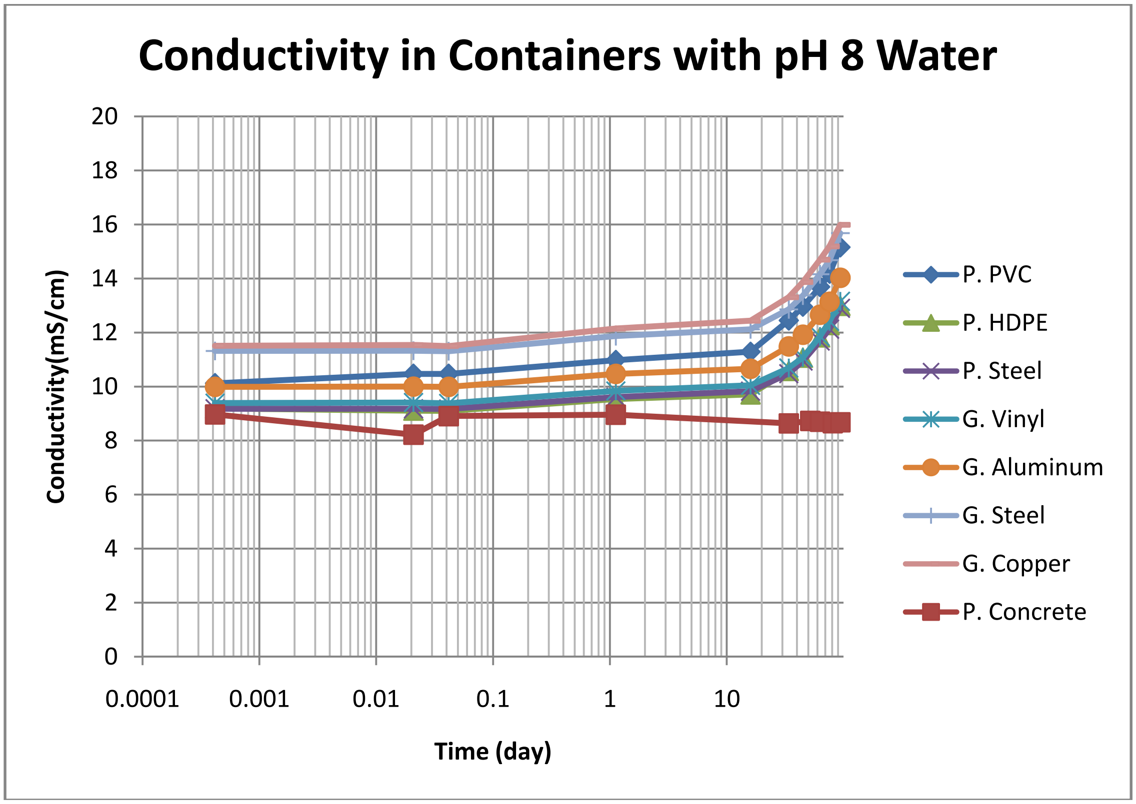


Figure 1.18. Conductivity measurements in the containers with pH 8 water.

Metal analyses and associated laboratory quality control procedures were performed by Stillbrook Environmental Lab, in Fairfield, AL using inductively coupled plasma mass spectroscopy (ICP-MS). Stillbrook Environmental Lab also conducted analyses on major constituents using analytical methods listed in Table 1.16. QA/QC results are shown in Appendix J.

The labware used for sample collection and storage was made of polyethylene and was soaked in 10% nitric acid for at least 24 hours before use and rinsed off with 18mΩ water to avoid heavy metal contamination. High-density polyethylene (HDPE) containers were used for sample storage. Leaching buckets were washed using warm tap water and laboratory phosphate-free detergent, rinsed with tap water, washed with 10% nitric acid, then distilled water, followed by 18mΩ water. Polyethylene bottles were washed using warm tap water and laboratory phosphate-free detergent, rinsed with tap water, then deionized water, soaked in a 10% solution of reagent grade nitric acid for at least 24 hours before use, and rinsed with laboratory grade 18mΩ water. The glassware used for sample collection was also cleaned with phosphate-free detergent, rinsed with tap water, deionized water, and soaked in a 10% nitric acid bath at least overnight before use and rinsed with 18mΩ water. Glassware used for toxicity analysis also was rinsed with sampled water. 18mΩ water was also used for method blanks. If not immediately analyzed, water samples were adjusted to pH <2, as required, and placed in a refrigerator at $4^{o}C$ until they were analyzed. During this research, the labware preparation and sample storage and preservations requirements that were followed were from Eaton et al (2005) and Burton and Pitt (2002).The instruments were calibrated prior to each data collection. Calibration techniques are listed in Table 1.18.

Table 1.18. Instrument calibration.

Instrument	Calibration
pH meter Model IQ 160, conductivity meter model sensION5 by HACH, DR 2010 (for nitrate, nitrogen ammonia, total nitrogen, chemical oxygen demand analysis)	used known standards
ORP meter HI 98120, salinity meter YSI 30	factory calibrated, checked with standard solution
Dissolved oxygen meter YSI Model 57	air calibration
Microtox	$ZnSO_4$ and phenol solutions used as reference toxicants

Toxicity analyses were conducted in duplicate for each water sample. Standards were run together with the samples for nutrient and toxicity analyses to confirm the instrument performance, and methods blanks were used (Appendix J). The observed nutrient values were reasonably close to the standard values. For phenol standards, the toxicity responses were generally constant with bacteria exposure time during each individual experiment. For the majority of the samples, toxicity associated with the $ZnSO_4$ standards increased with bacteria exposure time. In some cases, there was a change in the sensitivity of the bacteria that can be explained by change in Microtox reagent, as also reported by Morquecho (2005).

3.4 Analyses of the Data

The metal masses released per surface area of a pipe or gutter (expressed as mg/m^2) were calculated to account for the loss of water due to sample extraction and for varying sample specimen sizes. Eh-pH diagrams were constructed for the test water systems; the measured values of pH and Eh were placed on the diagrams to determine the predominant metal species expected. Also, log concentration – pH and fraction – pH diagrams were plotted to illustrate the concentrations of chemical species in the test waters. Other analyses of the data are described in the following subsections.

3.4.1 The Langelier Index

The Langelier Index was calculated to determine whether the leaching water for the concrete specimens is in equilibrium with $CaCO_{3(s)}$ (Snoeyink and Jenkins, 1980). The Langelier Index is the difference between the actual pH of the water and the pH the water would have if it were in equilibrium with $CaCO_{3(s)}$. If the Langelier Index has a positive value, the water is oversaturated with $CaCO_{3(s)}$ and will tend to precipitate $CaCO_{3(s)}$, with no degradation of the concrete. If the Langelier Index has a negative value, the water is undersaturated with $CaCO_{3(s)}$ and will tend to dissolve $CaCO_{3(s)}$ from the concrete. If the Langelier Index of the water is zero, it is in the equilibrium with $CaCO_{3(s)}$.

3.4.2 Toxicity

Toxicity analyses were conducted using the Microtox® Test System (Strategic Diagnostics, Inc.). In this test, bioluminescent marine bacteria (Vibrio fischeri) were exposed to water samples and the reduction of light output by the bacteria was measured at specific times. Vibrio fischeri emits light during its normal respiration. The toxicity was calculated by comparing the light output in a sample to that of a control. The bacteria have been freeze-dried, with one vial of freeze-dried reagent containing approximately one million test organisms. Reconstitution solution (specially prepared nontoxic ultra pure water) was used to rehydrate the bacteria. Zinc sulfate ($ZnSO_4$) and phenol were used as reference toxicants to check the performance of the test system.

3.5 Statistical Analyses of the Data

3.5.1 Basic Data plots

Exploratory data analyses were used to identify relationships between contaminant concentrations (metal leaching) and gutter and piping material samples, water conditions, and time. These initial tests were followed by statistical tests to determine the significance of the observations (Burton and Pitt 2002). Time series plots were constructed to examine the data. For example, Figure 1.19 shows time series plots of lead releases from different pipe and gutter materials under controlled pH 5 conditions. For containers with galvanized steel materials, detectable amounts of lead were released after 27 hours of exposure. Lead releases were greater associated with galvanized steel pipe compared to galvanized steel gutter samples. Lead was not detected in the containers having any of the other test materials the entire during three months exposure time.

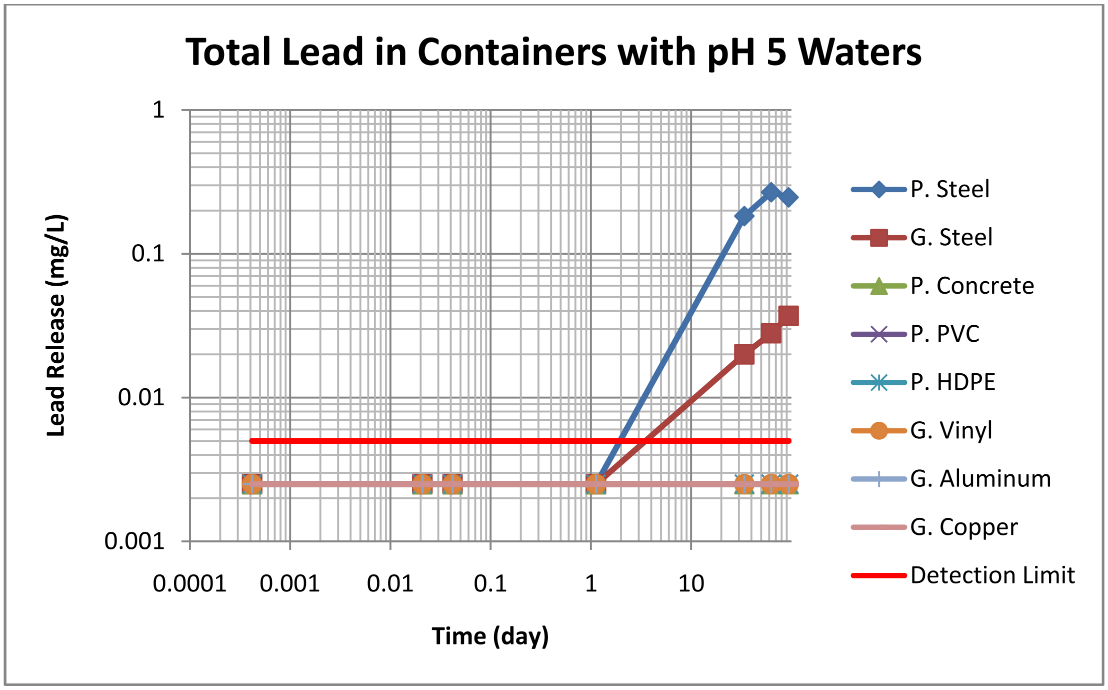


Figure 1.19. Time series of lead releases from various gutter and pipe materials under controlled pH 5 conditions.
(Ogburn et al. 2012)

The water quality parameters were plotted as a function of time for different pipe and gutter materials on the same graph. Figure 1.16 is another exploratory data analysis plot: group box and whisker plots for zinc releases from various pipe and gutter materials immersed in bay and river waters during different exposure times. The box plot for the plastic materials (vinyl, PVC, and HDPE) represent all the data combined (for bay and river waters and for short and long exposure times). As expected, zinc releases from plastic materials were significantly lower than from galvanized materials. The 75thpercentile lines of the box and whisker plot for plastic materials are located much lower than the medians of box and whisker plots for galvanized materials, therefore the pairs of groups of plastic materials and galvanized materials are likely significantly different at the 95% confidence level. However, there was no statistically significant difference between the box plots of galvanized steel pipe and gutter materials during short exposure time, and also there was no statistically significant difference between box plots of galvanized pipe and gutter materials during long exposure times. Zinc releases from galvanized materials increase with exposure time. There were statistically significant differences between zinc releases from galvanized materials during short and long exposure times, as indicated on Figure 1.20.

Probability plots show the possible range of the values expected, their likely probability distribution type, and the data variation (Burton and Pitt 2002). Figure 1.21 is a normal probability plot of zinc releases from a galvanized steel pipe section submerged in bay water. The p-value of the Anderson Darling test for normality is greater than 0.05, indicating that the data population distributions not statistically different from a normal population distribution, allowing certain categories of statistical analyses (after appropriate log transformations).

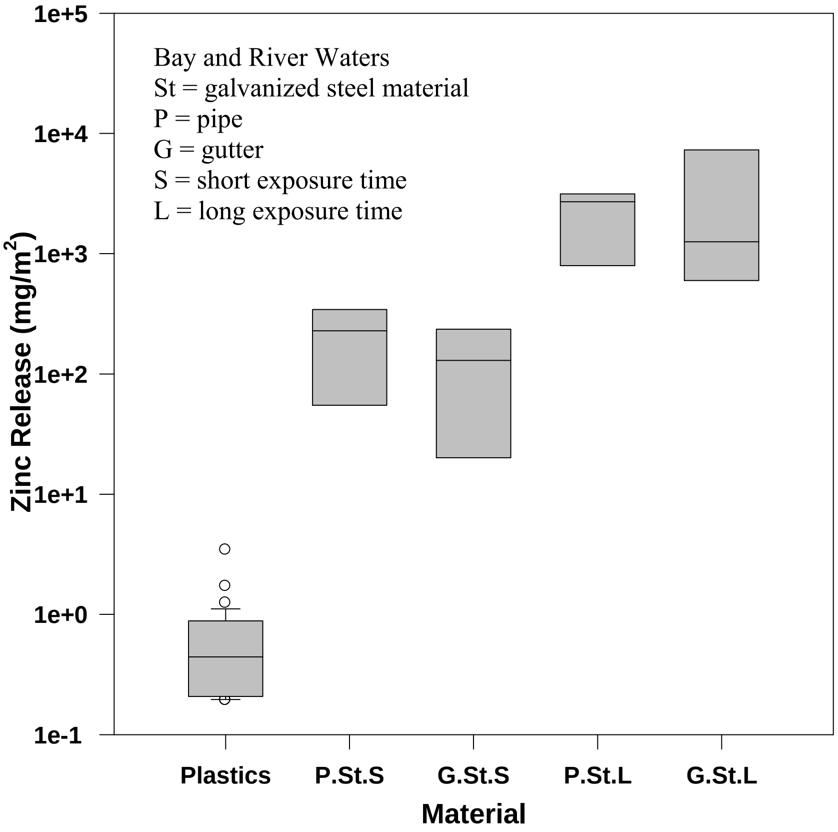


Figure 1.20. Group box plot of zinc releases from different construction materials.

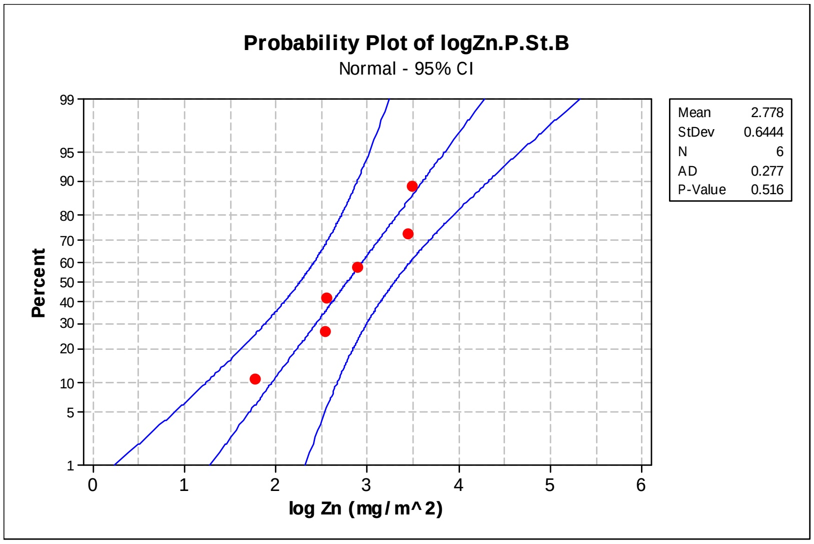


Figure 1.21. Probability plot of zinc releases from galvanized steel pipe immersed in bay water.

3.5.2 Statistical Significance Measures and Power Analysis

A Type I error refers to rejecting the null hypnosis when the null hypothesis is actually true (a false positive) (Burton and Pitt 2002, Devore 2008). The calculated alpha (α) from statistical tests is the probability of making this Type I error. The alpha value is often referred to as the significance level, or confidence, of the test. The typical alpha value of 0.05 is usually chosen, meaning accepting a 5% risk of having a Type I error. Consequently, the confidence of not having a false positive is 1 – α (or 95% if the alpha is 0.05). A Type II error is not rejecting the null hypnosis when the null hypothesis is actually false (a false negative) (Burton and Pitt 2002, Devore 2008). Beta (β) is the probability of making a Type II error. Power is the certainty of not having a false negative = 1 – β (Devore, 2008; Burton and Pitt, 2002, http://www.minitab.com/en-US/training/tutorials/accessing-the-power.aspx?id=1742&langType=1033). A common level of beta is 0.20 with a resulting power of 80%. If ignored (unfortunately common), the false negative rate then becomes 50%. The statistical power, or the sensitivity of a statistical test, is the probability that the test will detect a significant difference or an effect among the groups if a difference or effect truly exists. The closer the power is to unity, the more sensitive the test. The power is the sensitivity of the test for rejecting the hypothesis. For example, for an ANOVA test, it is the probability that the test will detect a difference amongst the groups if a difference really exists (Burton and Pitt 2002).

During a statistical test of previously obtained data, alpha and beta values cannot be distinguished: a decrease in the alpha value reduces the Type I error but also results in a larger value of beta increasing the probability of making a Type II error. Therefore α and β values need to be chosen during the experimental design phase such that to have the smallest β at the largest α values that can be tolerated (Devore 2008). The experimental design (selecting the sample numbers needed, for example), needs to ensure that both adequate confidence and power can be achieved.

A p-value reveals information about the strength of evidence against the null hypothesis and permits a conclusion at any specified level of α. If the p-value is below the specified significance level α, the null hypothesis is rejected and the results are considered to be statistically acceptable at that level of significance (Devore 2008). Failure to reject the null hypothesis does not mean that the sample sets are the same (if doing a comparison test), only that insufficient numbers of data observations are available to detect the significance difference for the conditions being examined.

3.5.3 Normality Tests

The applicability of most statistical tests is dependent on their probability distribution types. Probability plots and the Kolmogorov-Smirnov tests can be used to determine if the data are normally distributed (Systat Software, Inc., 2008) and therefore able to use a broad range of standard statistical tests. If not normally distributed, the statistical tests available are more limited. Using incorrect statistical tests results in very low power.

Data are plotted on normal probability graphs in order to visually identify whether the data are normally distributed. If the observations are roughly normal (from the normal distribution), then the points plotted on normal probability graphs will roughly plot as a straight line (Burton and Pitt, 2002). If observations do not fit reasonably well on a straight line, the data are not normally distributed. Typically, data transformations (log10) are also used to identify possible log-normal probability distributions.

The Kolmogorov-Smirnov test uses a P value to determine whether the data passes or fails the normality test (Systat Software, Inc., 2008). If the computed P value is greater than the selected alpha value (usually 0.05), the test of normality passes (the data cannot be shown to be significantly different from the normal distribution), however, if the computed P value is less than or equal to the critical alpha value, the hypothesis of normality is rejected and we can conclude with 95% confidence that the observations do not follow the normal distribution.

3.5.4 Comparison Tests with More than Two Groups using Analysis of Variance

Analysis of Variance (ANOVA) tests are used to test the hypothesis that the means among two or more groups (treatments) are equal (Systat Software, Inc., 2008; Devore 2008). This test is valid if the treatment populations are normal and have the same variance. Assumptions of normality and equal variance need to be checked. It is often recommended to transform the data to meet the ANOVA assumptions of homogeneity of variance and normality. The square root, log, and arcsin-square root transformation are used most often, with log10 transformations being most common for water quality analyses (Burton and Pitt 2002).

One-way ANOVA can be used to see if varying the levels of one factor affects the response (if the data are normally distributed) (Devore 2008). One–way ANOVA were used to determine whether the samples collected after 1, 2, and 3 month of exposure could be combined together as replicates into a single “long term” exposure group for each constituent for some of the comparison tests, and to determine if the samples collected after 0.5 hr, 1 hr, and 27 hrs of exposure during first testing stage (and after 1hr, 27 hrs, and 1 week during the second testing stage) could be combined together as replicates of “short term” exposure periods. If the normality assumption doesn’t hold, the Kruskal-Wallis test can be used. A P-value of 0.05 was used to reject the hypothesis. This test identifies if there are at least one subset that is significantly different from the other subsets. Unfortunately, the test does not identify which subgroup(s) are different from the others (Navidi 2006). Post-hoc tests are used to determine which groups are different from the others (Burton and Pitt 2002).

If the assumptions of normality and equal variance do not hold, the Kruskall-Wallis test can be used to determine if there is a statistically significant difference between the median values among the treatment groups affected by a single factor (Systat Software, Inc., 2008). The populations that samples are drawn from do not have to be normal or have equal variances. The P-value of 0.05 was used.

Two-way Analyses of Variance (ANOVA) is used to determine whether varying the levels of either the row factor, the column factor, or both factors affect the treatment means (response) (Navidi, 2006). ANOVA requires that within any treatment, the observations are a simple random sample from a normal population with roughly equal variances for all treatments. The test will tell if there are differences among the groups, i.e. if at least one group is statistically different from another one, but it will not tell which groups are different. Post-hoc procedures must be used to determine which groups are different from one another. Post-hoc tests discussion can be found in section 3.5.5.

3.5.5 Post-Hoc Tests

An ANOVA or Kruskal-Wallis tests determines whether at least one treatment statistically differs from the others; however, they do not identify which are different (Navidi 2006). Post hoc tests can be used to identify the significant treatments that are different from the others (Burton and Pitt 2002).

The Mann-Whitney test can be used as a post hoc test. The Mann-Whitney Test was performed to see if there is a statistically significant difference between the medians of two groups affected by a single factor (pairwise comparisons). This is a nonparametric test and does not require normality or equal variance (Systat Software, Inc., 2008). Group box and whisker plots were also prepared showing the ranges and comparisons between the different groups. These plots show many important characteristics of the data: center, spread, the extent of departure from symmetry (skewness), and unusual conditions. The advantage of a boxplot is that it is unsusceptible to a few unusually large values because it is based on medians and forth spread (which is the difference between the median of the largest half of the observations and the median of the smallest half of the observations) (Devore 2008). The grouped box and whisker plots were used to examine the range of water quality parameter within and between different piping/gutter/tank materials. If the 25 and 75 percentile lines of a box and whisker plot are located higher or lower than the medians of other box and whisker plots, then the groups are likely significantly different at the 95% confidence level, for moderate numbers of samples (Burton and Pitt, 2002). The group box and whisker plots were also used to examine the overlapping and separation of some groups relative to others to see if some data groups could be combined.

3.5.6 Comparison Tests with Two Groups

The paired t-test is a commonly used standard parametric statistical method that has high power if used correctly. It assumes that the observed treatment effects are normally distributed. The test examines the changes that occur before and after a treatment on the same individuals and determines whether or not the treatment had a significant effect (Systat Software, Inc., 2008). This test examines the changes rather than the values observed before and after the treatment. The paired t-test can be used to see if the effect of a single treatment on the same individual is significant. For paired t-tests, the number of data observations in each set must be the same, and they must be organized in pairs, in which there is a definite relationship between each observation in each pair of the data points (such as concurrent before and after treatment samples).

The sign test can be used as a simple paired test for non-normally distributed data (Burton and Pitt 2002). However, a test with more power is the Wilcoxon Signed Rank Test. This test is a nonparametric paired test and is used to determine whether the effect of a single treatment on the same individual is significant. As noted, this is a non-parametric test and should be used when the distribution of the observed effects are non-normal (Systat Software, Inc., 2008).

3.5.7 Regression Analyses

Regression methods use the values of one or more independent variables to predict the value of a dependent variable. The regression coefficients are determined by minimizing the sum of the squared residuals (Systat Software, Inc, 2008). Regression is a parametric statistical method that assumes that the residuals (differences between the predicted and observed values of the dependent variables) are normally distributed with constant variance. The residuals must be independent, and have zero mean, constant variance, and be normally distributed (Systat Software, Inc., 2008). The normal probability plot (and related statistical tests, such as the Anderson-Darling test (Minitab, Inc.) of the residuals can be used to determine whether the residuals are normally distributed. To determine whether the residuals have constant variance and zero mean, the scatterplots of the residuals versus the predicted values can be used and the plots need to indicate a relatively constant width of a flat band of residuals (Burton and Pitt 2002, Navidi 2006, Berthouex and Brown 2002). If the requirements of normality and constant variance hold, then the fitted model can be assumed to be correct (but only if it makes physical sense!). The coefficient of determination (R^2) is the proportion of the variance in y explained by the regression equation (Navidi 2006, Burton and Pitt 2002). ANOVA can also be used to test the significance of the regression coefficients (Burton and Pitt 2002, Berthouex and Brown 2002).

3.5.8 Factorial Experiment

Factorial experiments are used to examine a set of factors that are independent variables and identify which of them (singly or in combinations) are significant factors in explaining the magnitude of the variability produced by the experimental factors. The test results were used to build an empirical model (Berthouex and Brown 2002). The basic experimental design for testing two factors (pH and time) is shown in Table 1.19.

Table 1.19. Factorial experimental design for two factors.

Experiment No.	pH	Time	pH*Time
1	+	-	-
2	+	+	+
3	-	-	+
4	-	+	-

Full 2^2 factorial experiments will therefore require four experiments representing all combinations of conditions in order to examine the main effect and all possible interactions of those factors (only one interaction term for this simple two-way test). The plus and minus signs represent different levels (such as high and low values) for each main factor during the experiments. This table of contrasts shows the main factors and the one possible two-way interaction.

Factorial analyses are used to determine which factors and their interactions have an important effect on the outcome (are significant) (Navidi 2006). The null hypothesis for each factor was tested assuming that the effect is equal to 0. If the null hypothesis is rejected, a conclusion can be made that the factor affects the outcome (the factor is significant) (Navidi 2006, Devore 2008).

For each pipe and gutter material, full 2^2 factorial analyses were conducted for each material to determine whether exposure time (the data sorted by short and long exposure periods), pH value (5 and 8), and the interaction of these factors affect the pollutant releases in mg per area of the material(during the first stage of the experiment). Effects of pH, time, and pH x time interactions were estimated along with the pooled standard error. The two factors that were studied: pH of rain water at 2 Levels (5 -, 8 +) and time of contact at 2 Levels (short -, long +). pH values for the design were chosen based on studies summarized by Pitt et al. (2004).

The replicates for each experiment were averaged and the value entered into a table of contrast coefficients (or Yates's algorithm methods can be used) (Box et al. 1978). Two Way-ANOVA was used to determine if the effects were significant. Also, the effects can be plotted on normal probability graphs in order to identify which effects and interaction terms are significant. If the observations are roughly normal (from the normal distribution), then the points plotted on normal probability graphs will roughly plot as a straight line. If any of the extreme values plotted do not fit reasonably well on a straight line, they are likely causing significant effects on the predictions of interest, while those effects that roughly fall on the straight line are likely random noise (not causing any significant effect) (Boxet al., 1978).

Models were developed which contain the significant factors affecting the parameter outcome (Burton and Pitt 2002). Residuals were also examined to determine if the model was reasonable and met the calculation requirements. Residuals are the unexplained variation of a model and must satisfy the assumptions of being independent, having zero mean, having constant variance σ^2, and be normally distributed (Burton and Pitt 2002). Graphical analyses of model residuals were conducted to determine if these requirements are met.

The model was checked by plotting the residuals on normal probability graphs. If all the points from this residual plot lie close to a straight line, this would confirm the assumption that effects (other than those off the straight line in the normal probability plot of the effects) are readily explained by random noise (Box et al. 1978). To check if there is a trend of residuals and if the residuals are homoscedastic and have zero mean, the graph of residuals vs. fitted (predicted) values were also constructed. To check the independence of the residuals, the plot of residuals vs. order in which the observations were made is necessary (Navidi 2006). The models can be used to predict the contaminant concentration for each pipe and gutter material by focusing on the significant factors.

If a factor does not interact with another one(s), then the main effect of that factor will be considered individually. However, if one factor interacts with another one(s), then the factors with interactions will be interpreted jointly. The effects of the row levels depend on which column levels they are paired with, and vice versa, and the main effects can be misleading (Navidi 2006, p. 669).

The standard errors were also calculated as estimates of the standard deviation of the effects under consideration and were used to help identify the significant effects (Box et al. 1978).The pooled estimate of run variance were calculated using the following formulas (Box et al. 1978):

$$S^2 = (\nu_1 * S_1^2 + \nu_2 * S_2^2 + \ldots + \nu_g * Sg^2) / (\nu_1 + \nu_2 + \ldots + \nu_g) =$$

$$= ((n_1 - 1) * S_1^2 + (n_2 - 1) * S_2^2 + \ldots + (n_g - 1) * Sg^2) / ((n_1 - 1) + (n_2 - 1) + \ldots + (n_g - 1))$$

with $\nu = \nu_1 + \nu_2 + \ldots + \nu g$ degrees of freedom

Where:

g = the number of sets of experimental conditions that were replicated.

ni = the number of replicate runs made at the ith set yield an estimate si^2 of σ^2 having

νi = ni-1 degrees of freedom.

di = the difference between the duplicate observation for the ith set of conditions.

If there are two replicates (ni = 2, νi = 2 – 1 = 1), the equation for ith variance:

$Si^2 = di^2/2$

Si^2=ith variance, then

$S^2 = \Sigma\ di^2/2g$

S = sqrt (S^2) = (the pooled estimate of run standard error) with ν degrees of freedom

The variance of each effect was calculated using the formula:

V (effect) = $4*\sigma^2/N$

σ^2 will be estimated with S^2

N = the number of runs

The estimated standard error of an effect was calculated using the formula:

St. error = sqrt (V (effect))

Using the P-value of the ANOVA Analysis (or Factorial Effect/Pooled Standard Error Ratio of the Factorial Analysis), the observations were combined into groups for each pipe and gutter according to whether there was or was not an effect of pH, time, and interaction of those factors.

3.5.9 Correlation Analyses

Simple correlation analyses (such as the Pearson correlation matrix) measure the strength of association between two variables, and can be a measure of the certainty of prediction. The correlation coefficient r is a number between -1 and +1 (Navidi 2006). A correlation of -1 indicates that there is a perfect negative relationship between the two variables, with one always decreasing as the other increases. A correlation of +1 indicates there is a perfect positive relationship between the two variables, with both always increasing simultaneously. A correlation of 0 indicates no relationship between the two variables (Systat Software, Inc., 2008).

Pearson product moment correlations were used to determine the strength of the associations between pairs of variables without regard to which variable is dependent or independent. This is a parametric test that assumes a normal distribution and constant variance of the residuals. This procedure was used to evaluate the strength of association between water quality characteristics and released contaminant concentrations. High correlation coefficients between variables indicate that one variable can be predicted by the other one (Systat Software, Inc., 2008).

Spearman rank order correlations were used to determine the strength of association between pairs of variables without regard to which variable is dependent or independent. This is a nonparametric association test that does not require data normality or constant variance of the residuals. The Pearson product moment correlation test is slightly more sensitive (has greater power) than the nonparametric Spearman rank order correlation test (Systat Software, Inc., 2008).

3.5.10 Cluster and Principal Component Analyses

Cluster and principal component analyses were used to examine associations between independent and dependent variables in groupings (not constrained to pairs of data) to investigate likely cause and effect relationships. Hierarchical cluster analyses were used to investigate associations between observed water quality parameters and contaminant concentrations released into the water. Factors connected together with short lines have higher correlation than factors that are linked by longer lines. Figure 1.22 is a dendrogram from a cluster analysis for water quality parameters from the concrete pipe material tests under natural pH conditions. This figure shows that Pb, Cu, and Zn concentrations were highly correlated with pH and conductivity. The toxicity was affected by the metal releases, conductivity, pH, and time of exposure. There were also correlations between metal releases and exposure time. Conductivity was closely associated with metal releases.

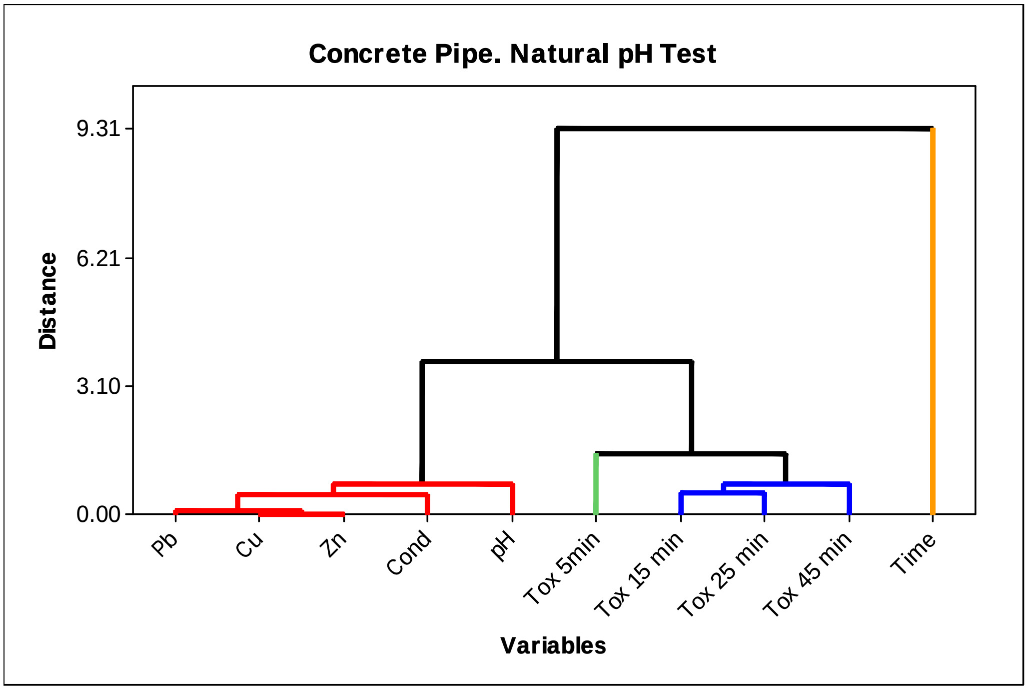


Figure 1.22 Dendrogram from cluster analysis for water quality parameters. Concrete pipe. Natural pH tests

Principal component analysis is a technique that has the ability to reduce the number of variables (Jensen 2005, Johnson and Wichern 2007). During this analysis, the original dataset is converted into a smaller set of uncorrelated variables that represents most of the information existing in the original dataset. First principal component accounts for the maximum proportion of the variance in the original dataset. The succeeding components explain the maximum percentage of the remaining variance (Jensen 2005; Johnson and Wichern 2007

3.5.11 Model

To build an empirical model, factorial experiments were utilized to determine the significant factors, materials, exposure times, and their combinations affecting contaminant concentrations. The data were combined into groups based on the calculated effects from the factorial analysis. Based on this test, materials were identified that can be used for long term storage of water and for short term exposures such as for roof gutters and piping of water. Also, cluster and principal component analyses were performed on raw data to determine associations between different materials and water quality conditions and contaminant loads. Pearson correlations were calculated to quantify associations between significant materials and water quality parameters and contaminant concentrations. Finally, regressions were performed on time series plots to predict pollutant release with time. A model identifying critical materials and exposure conditions or critical combinations of materials and exposure conditions was finally developed based on these prior analyses.

3.6 Chapter Summary

A spreadsheet model was developed to allow users to predict and examine the pros and cons of various materials being considered for applications such as roofing components, drainage pipes, culverts, and water storage tanks and for water chemistry conditions such as time of contact, pH, conductivity and aggressiveness.

4. HEAVY METAL RELEASES

4.1 Introduction

This chapter describes metal releases from different pipe and gutter materials subjected to different water conditions. For metal releases that were below the detection limit, values were substituted with half of the detection limit values for all analyses or plots with the exception of Medusa modeling. For all chemical components in Medusa files, only the concentrations at and above the detection limit were used. In the graph legends, P stands for pipe, G stands for gutter. For the first series of tests, the data for 0.5 h, 1 h and 27 h were defined as short exposure periods, and for 1 month, 2 months and 3 months as long term exposure periods, based on results of statistical grouping analyses described later. For the second series of the experiments, the data for 1 h, 27 h and 1 week were defined as short exposure periods, and for 1 month, 2 months and 3 months as long term exposure periods. Statistical analyses were performed to determine the effect of time, pH, and salinity on the releases of the metals for each type of material. Model fitting was performed on the time series plots to predict the release rates of the metals as a function of exposure time and surface area. Chemical speciation modeling was performed to determine the forms of heavy metals in solution in order to identify their toxicity effects and treatability. Part of this chapter contains information presented by Ogburn et al, (2013).

4.2 Results and Discussions

These tests showed that pipe and gutter materials can release substantial amounts of metals and can be a significant source of toxicity. The highest lead and zinc concentrations were observed for galvanized steel samples under buffered and natural pH conditions during both short and long exposure. The greatest copper release was, unsurprisingly, observed from copper materials. Cadmium and chromium were not detected in any of the containers with controlled pH values.

4.2.1 Zinc Releases during Controlled pH Tests

During short term exposures, zinc was released from the galvanized steel pipe and gutter at both low and high pH conditions, as well as from the copper and HDPE gutter samples at pH 5, and from vinyl and aluminum gutters at pH 8. For other materials, zinc releases were noted after 1 or 2 months of exposure. After the first day of exposure, the galvanized steel pipes and gutters had very high levels of zinc concentrations (1 mg/L to >14 mg/L; 45-720 mg/m^2), with greater and faster releases observed under the lower pH conditions. These concentrations exceeded the aquatic life freshwater criteria of 120 µg/L established by the US Environmental Protection Agency (US EPA) by 8 to 116 times. Zinc releases were the highest from galvanized steel materials. During long term exposures (after 1 month), zinc concentrations in the samples with galvanized metals under pH 8 conditions were >90 mg/L (4200 mg/m^2), compared with 14 mg/L (640 mg/m^2) values under the pH 5 conditions. Higher zinc losses at pH 8 compared to pH 5 can be attributed to zinc being an amphoteric species which dissolves well in acidic environments (with the formation of zinc salts). It also dissolves well in basic environments (with the formation of divalent zincate-anion (i.e. $CaZnO_2$) or complex tetrahedral zincate ion (i.e. $Na_2[Zn(OH)_4]$)) (Klinskiy and Skopinzev 2001). Typically, zinc releases were greater in galvanized steel gutter samples compared to samples with galvanized pipes. The second highest sources of zinc were the copper gutters; greater releases occurred under pH 5 conditions (>0.13 mg/L, 8 mg/m^2). Zinc was also released from plastic materials, but the resultant concentrations were much lower. The smallest sources of zinc were concrete (<30 µg/L; 5 mg/m^2) and plastic materials (for PVC pipes ≤680 µg/L (22 mg/m^2), for HDPE pipes ≤60 µg/L (1 mg/m^2), and for vinyl gutters ≤40 µg/L (3.47 mg/m^2)).

Zinc concentrations resulting from different gutter and pipe materials during the tests with buffered waters are shown in Figures 4.1 and 4.2. Figures 4.3 and 4.4 show the corresponding zinc releases in mg/m^{2}normalized for pipe or gutter surface area. These graphs show that zinc releases from galvanized steel pipes and gutters were very similar; other zinc sources included plastic, aluminium, and copper materials, but they released much smaller amounts of zinc.

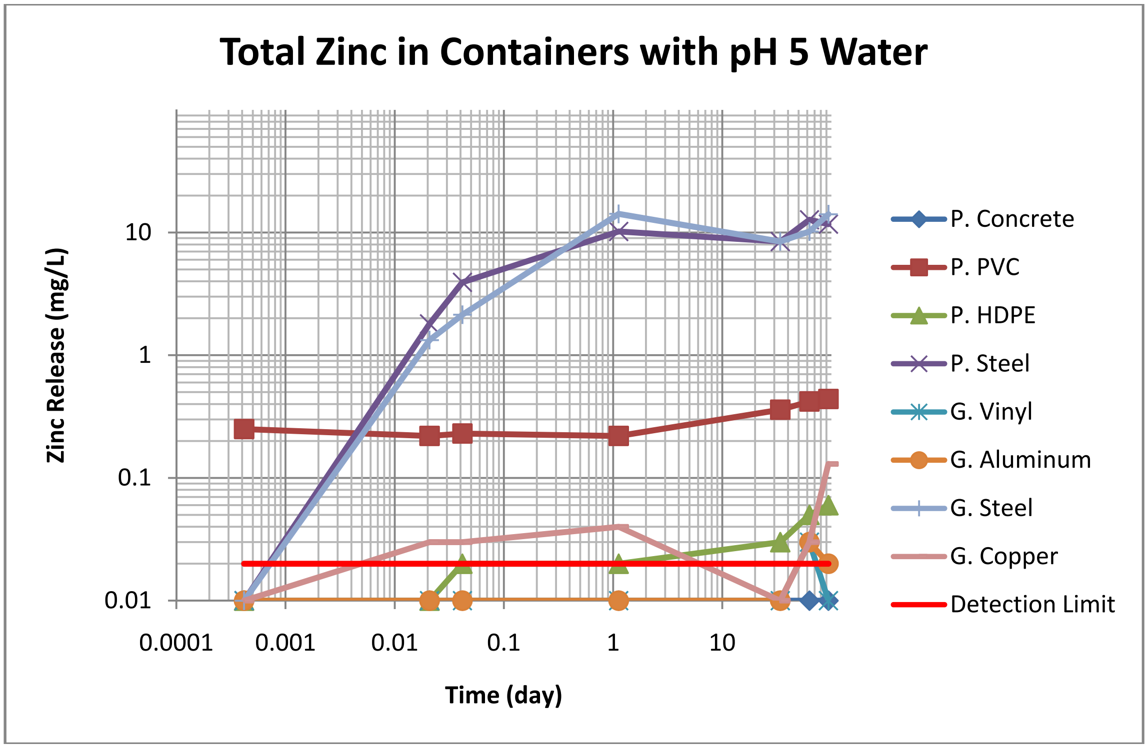


Figure 4.1. Total zinc concentrations in containers with pH 5 water.
Footnote: P. = Pipe, G. = Gutter

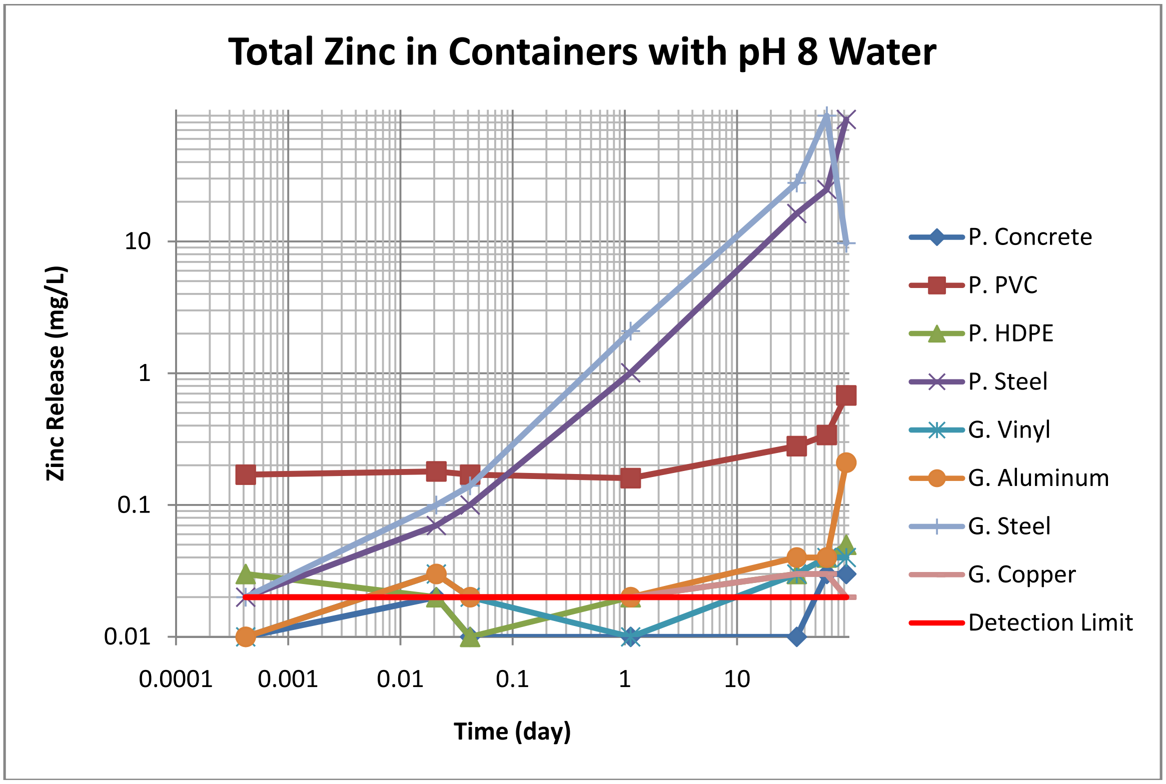


Figure 4.2. Total zinc concentrations in containers with pH 8 water.
Footnote: P. = Pipe, G. = Gutter

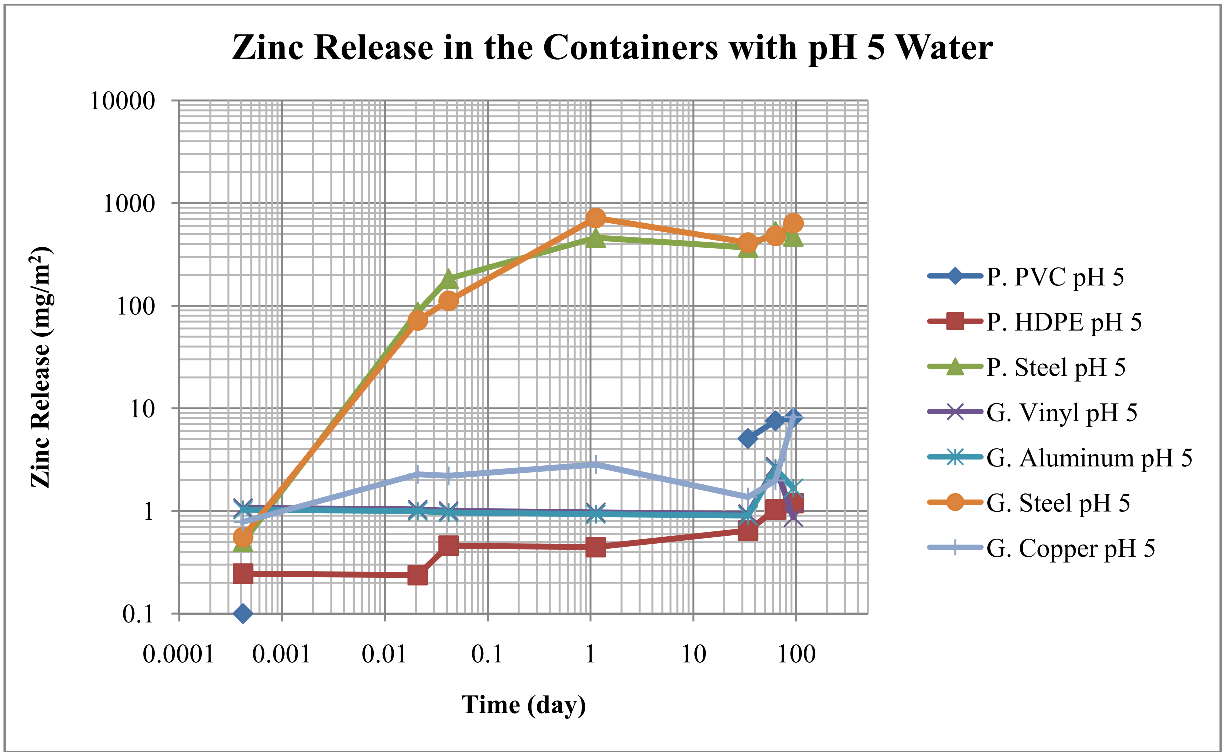


Figure 4.3. Total zinc losses in containers with pH 5 water.
Footnote: P. = Pipe, G. = Gutter

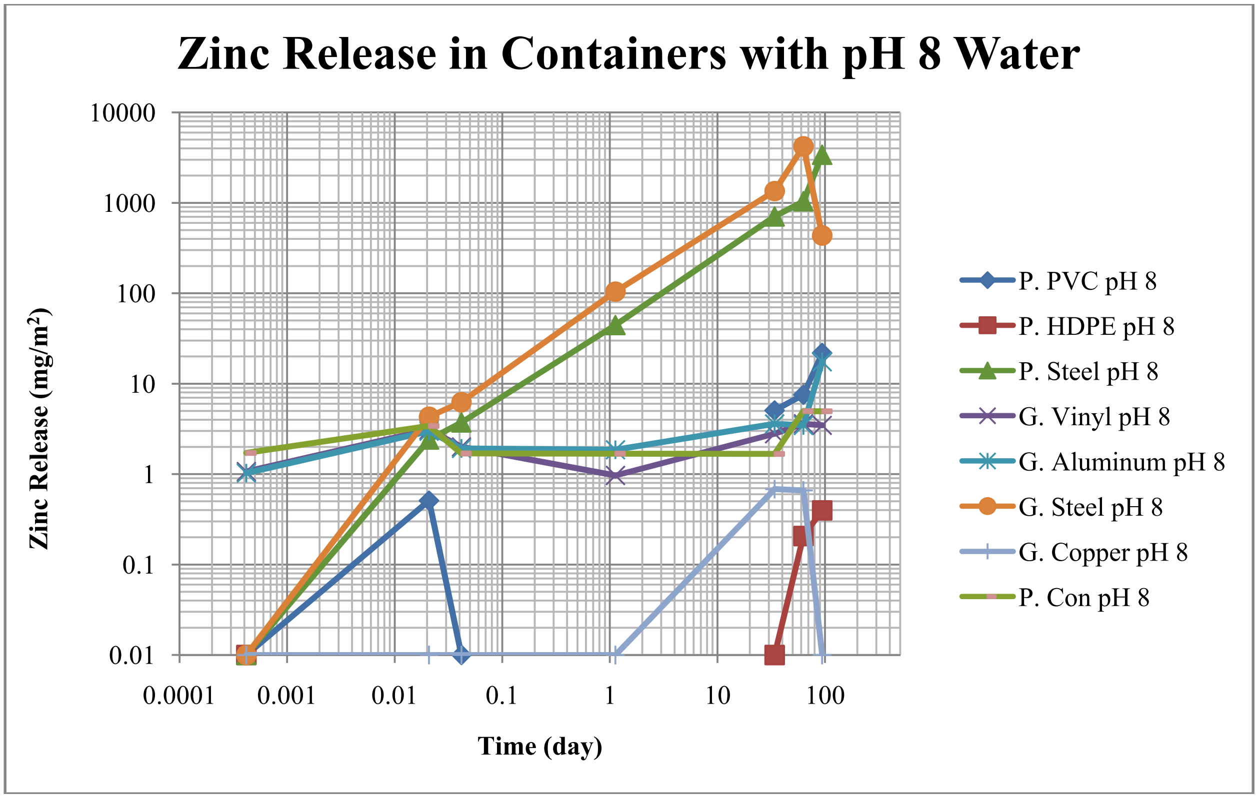


Figure 4.4. Total zinc losses in containers with pH 8 water.
Footnote: P. = Pipe, G. = Gutter

4.2.2 Zinc Releases during Natural pH Tests

Short term exposures (≤1 week) resulted in zinc releases from the galvanized steel pipe and gutter materials immersed in both bay and river water and from copper gutter materials immersed in bay water. Zinc losses from the other materials were noted after 1 or 2 months of exposure. As for controlled pH conditions, galvanized steel materials in the containers under natural pH conditions were the greatest sources of zinc releases. The samples with galvanized steel gutters and pipes had very high levels of zinc concentrations (5 mg/L to >8 mg/L; 230 mg/m^2 to 350 mg/m^2) after the first day of exposure, with greater releases observed for samples immersed into bay water. These concentrations exceeded the aquatic freshwater toxicity criteria of 120 µg/L established by the US EPA by more than 40 times. However, after one day of exposure, these concentrations were lower than the zinc concentrations in containers at controlled pH 5 conditions (>14 mg/L; 720 mg/m^2) and greater than zinc releases in containers at controlled pH 8 tests (>2 mg/L; 100 mg/m^2).

For galvanized pipes, zinc concentrations in bay water samples were generally higher than samples in river water samples. After long term exposures (approaching 3 months), galvanized steel pipe samples immersed into bay waters resulted in zinc concentrations >70 mg/L (3070 mg/m^2). However, galvanized gutter materials indicated a different trend and after 1 week exposure, zinc releases from galvanized gutters immersed in containers with river water exceeded those in bay water. After long term exposures, zinc losses from galvanized gutters in river water reached 190 mg/L (8,310 mg/m^2) compared to 40 mg/L (1,610 mg/m^2) in bay water. The higher zinc releases from the galvanized gutter specimen immersed in river water compared to the bay water can be explained by the lower pH and higher fluoride concentration in the river water sample. The different trends in the zinc releases from pipes and gutters are explained by different material compositions. The second highest sources of zinc releases were the copper materials, with higher concentrations observed in containers with river water samples (0.48 mg/L; 30 mg/m^2) compared to bay samples. Plastic and aluminum materials had much lower zinc releases. Zinc was not detected in concrete pipe samples with either bay or river waters. Due to the high chloride content of the bay water, the zinc releases from galvanized steel pipe tended to be greater in bay water samples compared to river water samples. Figures 4.5 and 4.6 show zinc concentrations released from various gutter and pipe materials during the un-buffered experiments. Figures 4.7 and 4.8 show the corresponding zinc releases in mg per m^2 pipe/gutter surface area. Similar to the controlled pH tests, during natural pH tests, the zinc releases from galvanized steel pipes and gutters tracked each other very closely; copper, aluminium, and plastics showed much smaller zinc releases.

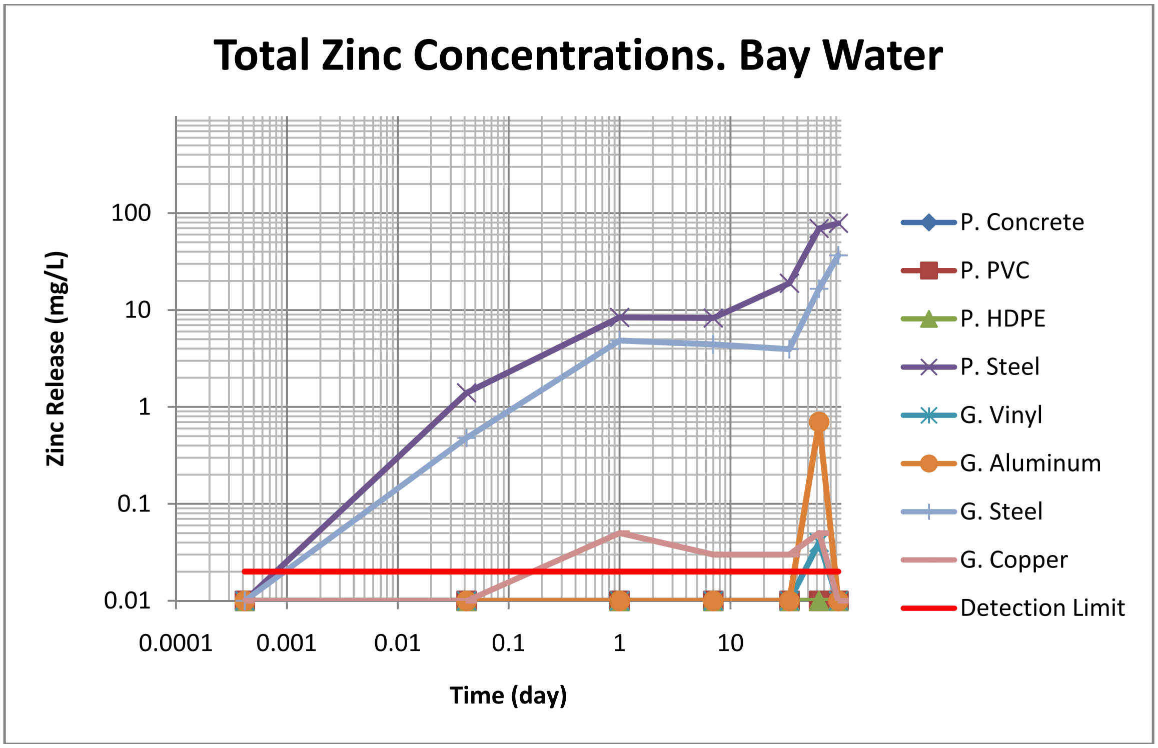


Figure 4.5. Total zinc concentrations in containers with bay water.
Footnote: P. = Pipe, G. = Gutter

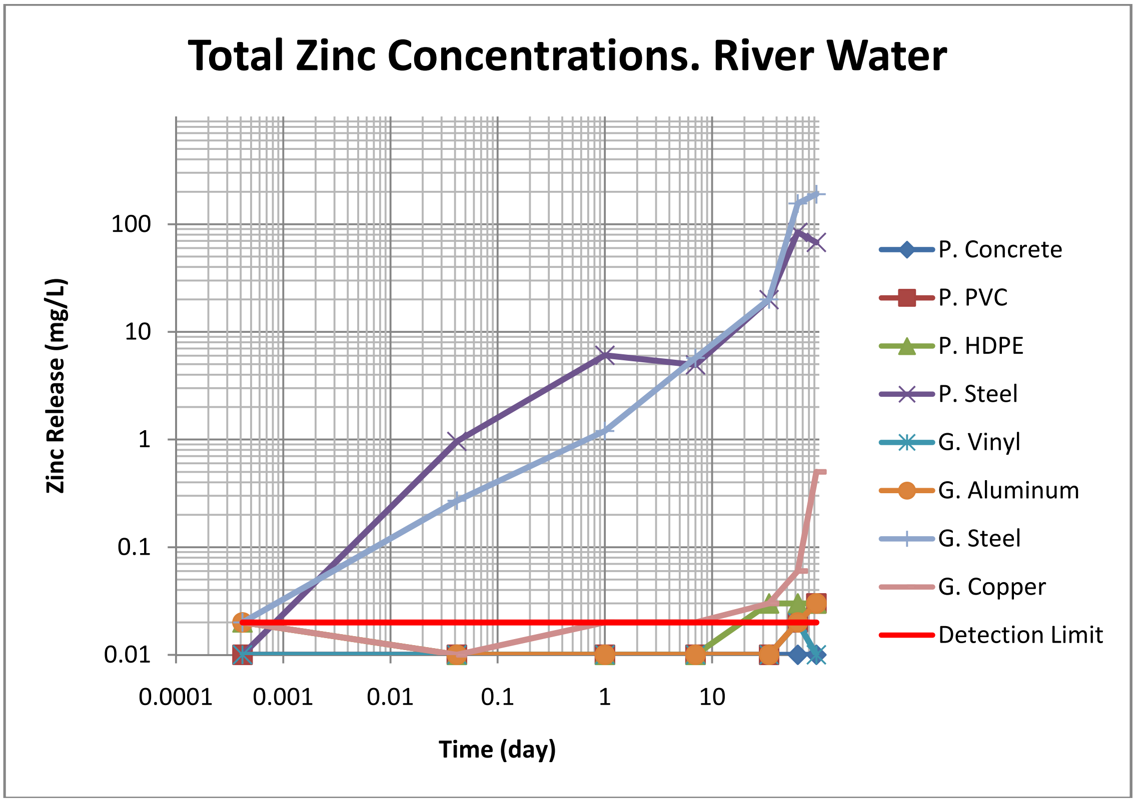


Figure 4.6. Total zinc concentrations in containers with river water.
Footnote: P. = Pipe, G. = Gutter

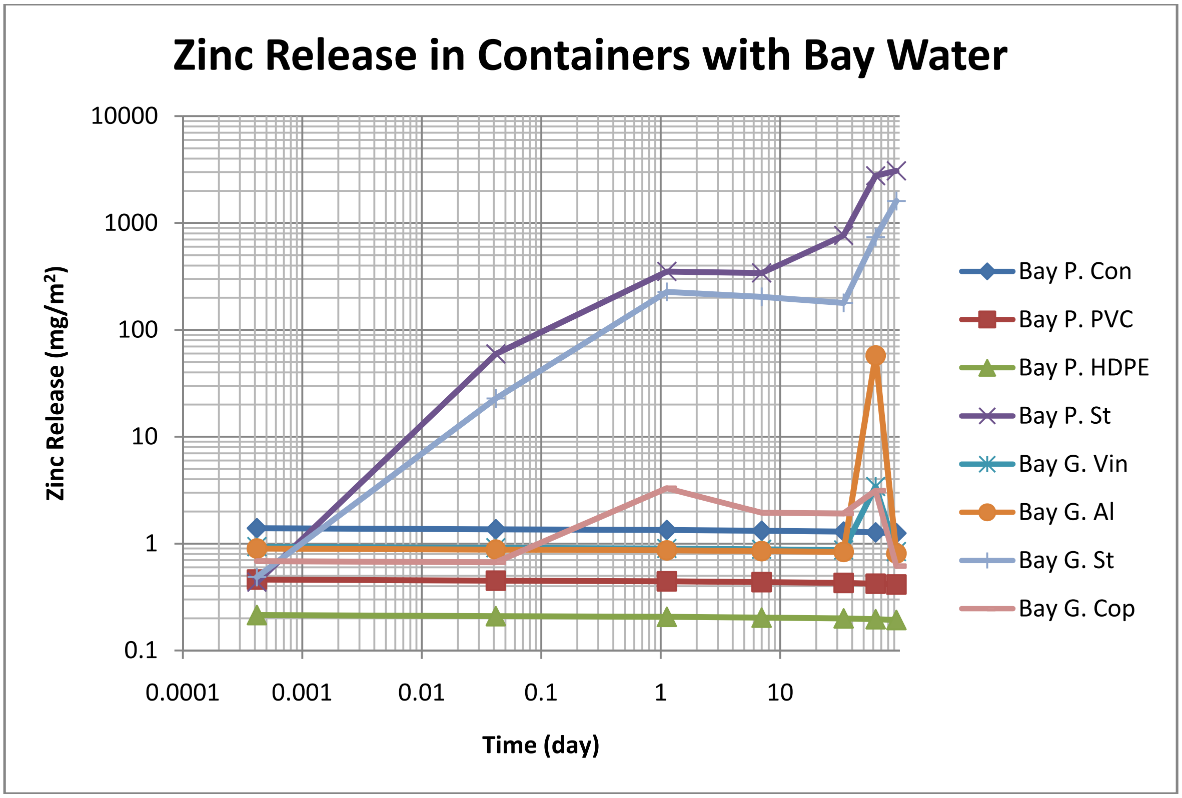


Figure 4.7. Total zinc losses in containers with bay water.
Footnote: P. = Pipe, G. = Gutter

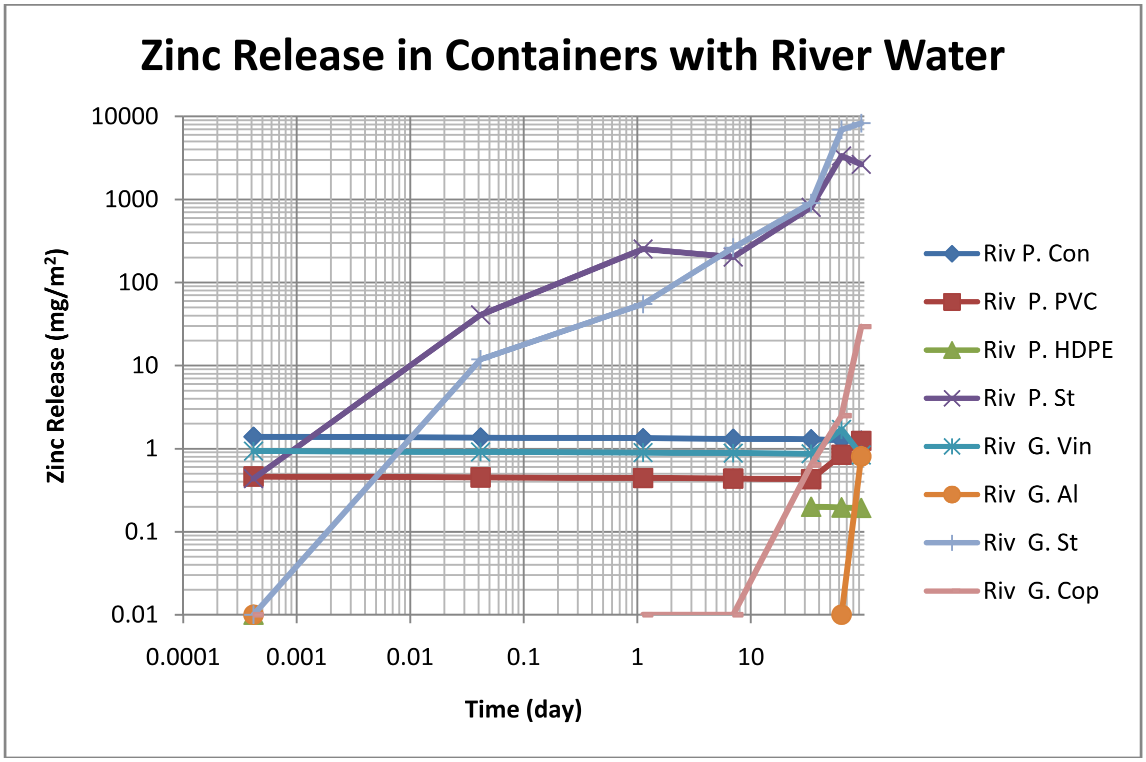


Figure 4.8. Total zinc losses in containers with river water.
Footnote: P. = Pipe, G. = Gutter

4.2.3 Copper Releases during Controlled pH Tests

Copper materials were the greatest source of copper under controlled pH conditions, as expected. During short term exposure times, copper was released only in the copper gutter samples under both low and high pH values. Copper releases from most of the other materials were detected after 1 or 2 months of exposure.

After the first day of exposure, copper concentrations in copper test containers were about 7 mg/L (480 mg/m^2) under pH 5 conditions (exceeding the mean acute toxicity value for certain freshwater animals; US EPA, 2007b) and <1 mg/L (21 mg/m^2) under pH 8 conditions. Greater and faster releases occurred at lower pH conditions. Copper concentrations >5 mg/L (320 mg/m^2) were detected in the copper gutter sample container under pH 5 conditions after long term exposure, compared to 2 mg/L (135 mg/m^2) values under the pH 8 conditions. The greatest copper releases (>6 mg/L, 480 mg/m^2) were detected from copper sample containers after 27 h exposure before they started to level off. Some of the plastic, aluminum and galvanized steel materials also released copper, but the concentrations were much lower. After the copper materials, PVC pipe samples had the highest copper releases of about 5 mg/m^2 after long exposure periods. Copper releases were detected from galvanized steel gutter and pipe samples under pH 8 conditions. However, under pH 5 conditions, the copper release was detected only at 1 month exposure for steel pipes. HDPE and galvanized steel materials had the lowest copper releases of ≤60 µg/L (1.24 mg/m^2) and ≤30 µg/L (1.36 mg/m^2) respectively. Copper releases were not detected in the concrete pipes samples at both pH 5 and pH 8 values.

Copper concentrations resulting from different materials during the buffered tests are shown in Figures 4.9 and 4.10. The corresponding copper releases in mg per m^2 pipe surface area during the buffered tests are shown in Figures 4.11 and 4.12. The general shapes of the metal releases expressed in mg/L are similar to the releases expressed in mg/m^2.

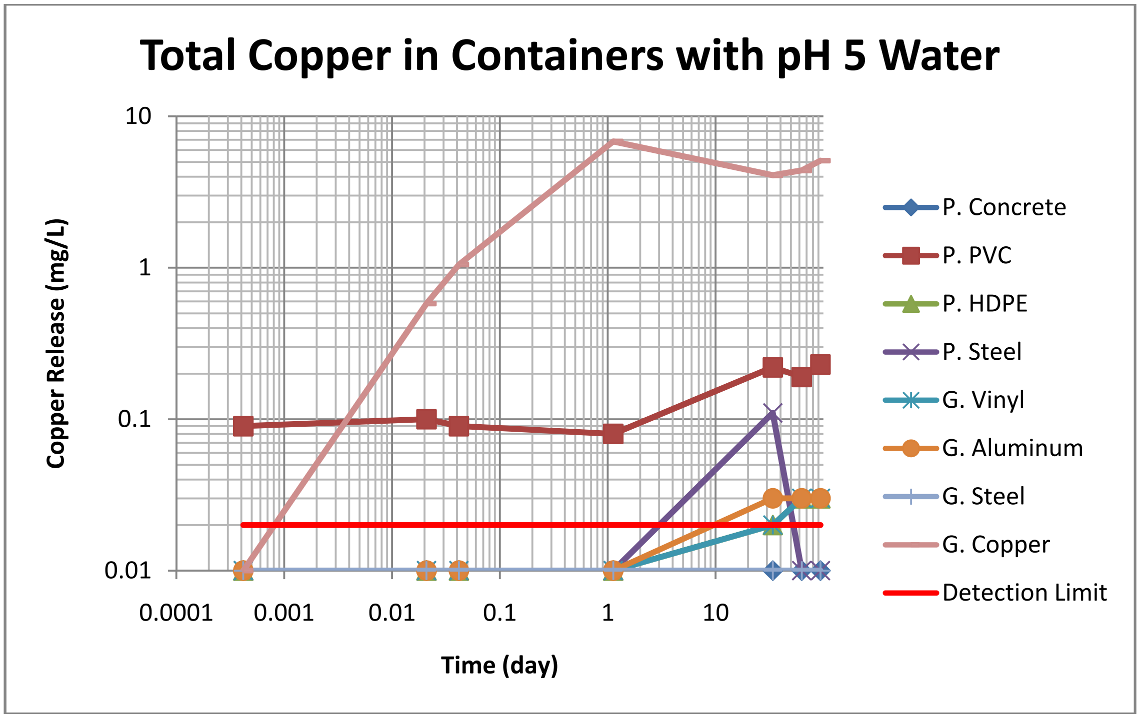


Figure 4.9. Total copper concentrations in containers with pH 5 water.
Footnote: P. = Pipe, G. = Gutter

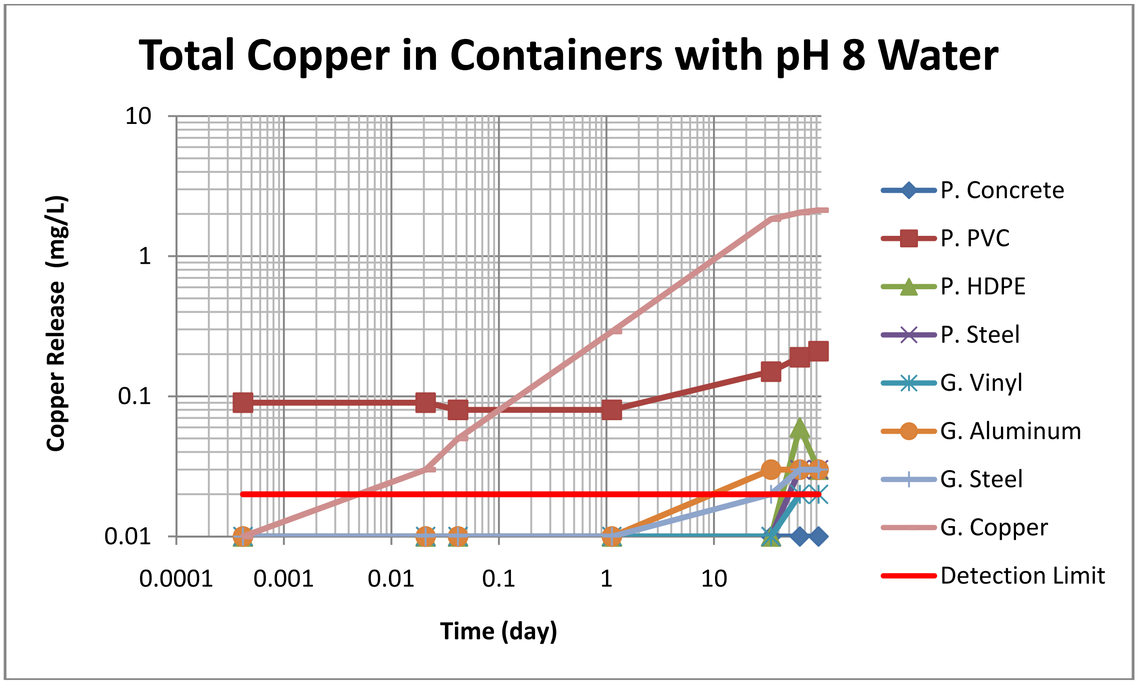


Figure 4.10. Total copper concentrations in containers with pH 8 water.
Footnote: P. = Pipe, G. = Gutter

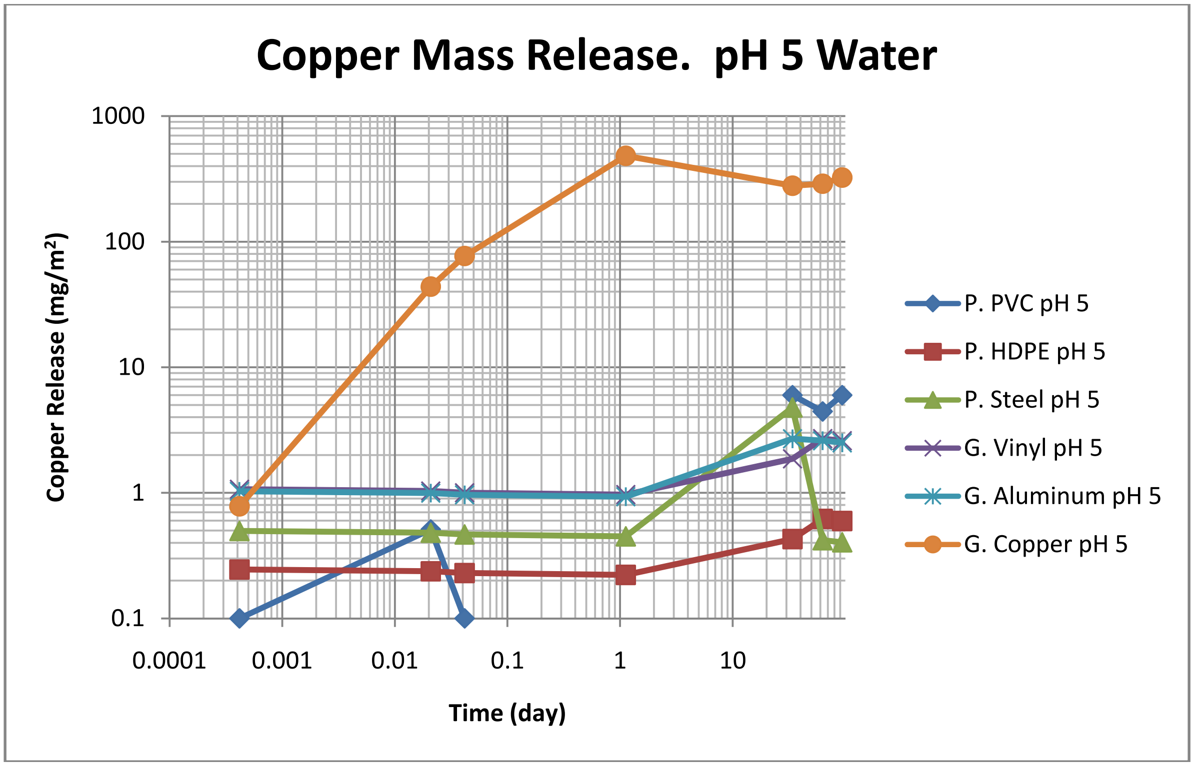


Figure 4.11. Total copper losses in containers with pH 5 water.
Footnote: P. = Pipe, G. = Gutter

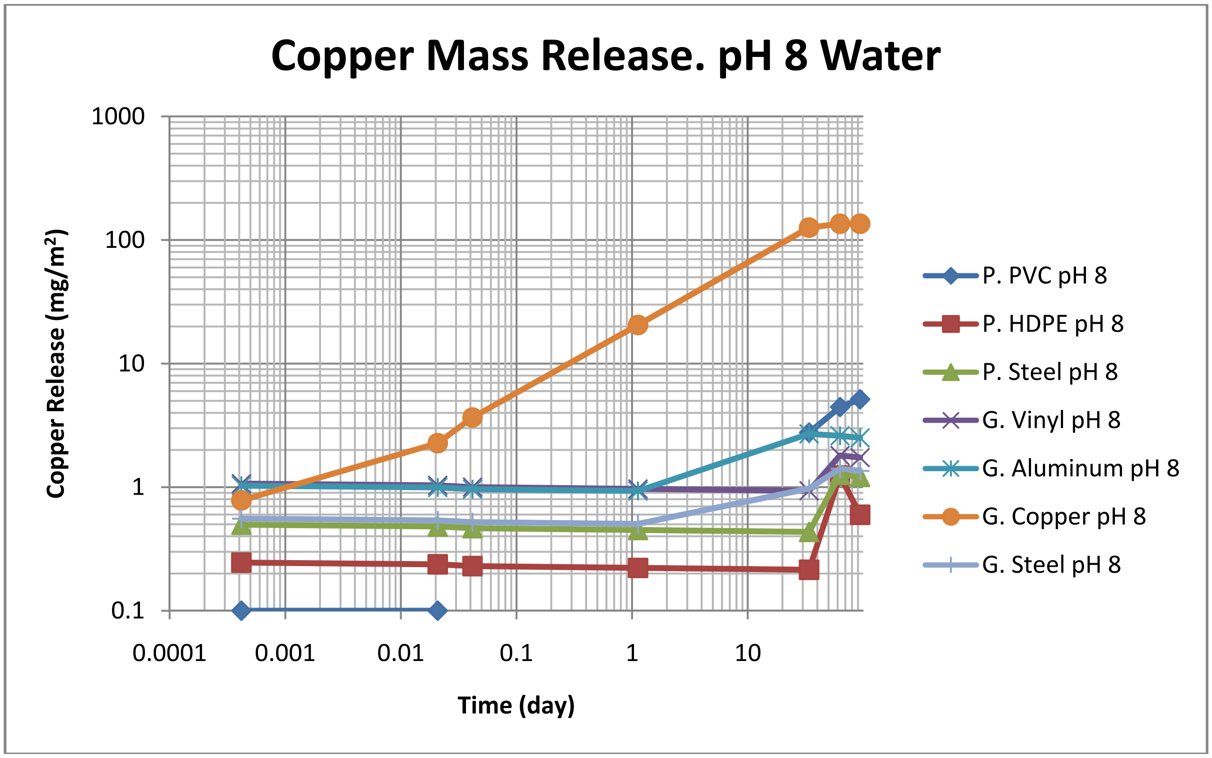


Figure 4.12. Total copper losses in containers with pH 8 water.
Footnote: P. = Pipe, G. = Gutter. (Ogburn and Pitt 2011)

4.2.4 Copper Releases during Natural pH Tests

Copper releases were detected only from copper materials during both short and long exposure periods under natural pH conditions in the river and saline bay sample test containers.

For both bay and river waters, copper releases were observed after 1 h exposure. Copper materials immersed into bay water had slightly greater copper releases compared to containers with river water samples. After the first day of exposure, copper releases in bay water samples exceeded 2 mg/L (140 mg/m^2).

After long term exposures (3 months), the greatest copper releases were noted from copper gutter sections immersed in bay water and reached 36 mg/L (2,200 mg/m^2), compared to 5.5 mg/L (340 mg/m^2) from copper gutter sections immersed in river water, 5.1 mg/L (320 mg/m^2) from copper gutter sections under pH 5 conditions, and 2.1 mg/L (135 mg/m^2) from copper sections under pH 8 conditions. Copper releases were greater under pH 5 conditions compared to pH 8 conditions and could be explained by the more acidic environment. Higher copper releases in bay water compared to river water are attributed to the more aggressive environment due to the high chloride content (3,350 mg/L).

Figures 4.13 and 4.14 show copper concentrations in containers with various materials during the un-buffered tests. Copper releases in mg per m^2 pipe surface area during the un-buffered tests are shown in Figures 4.15 and 4.16.

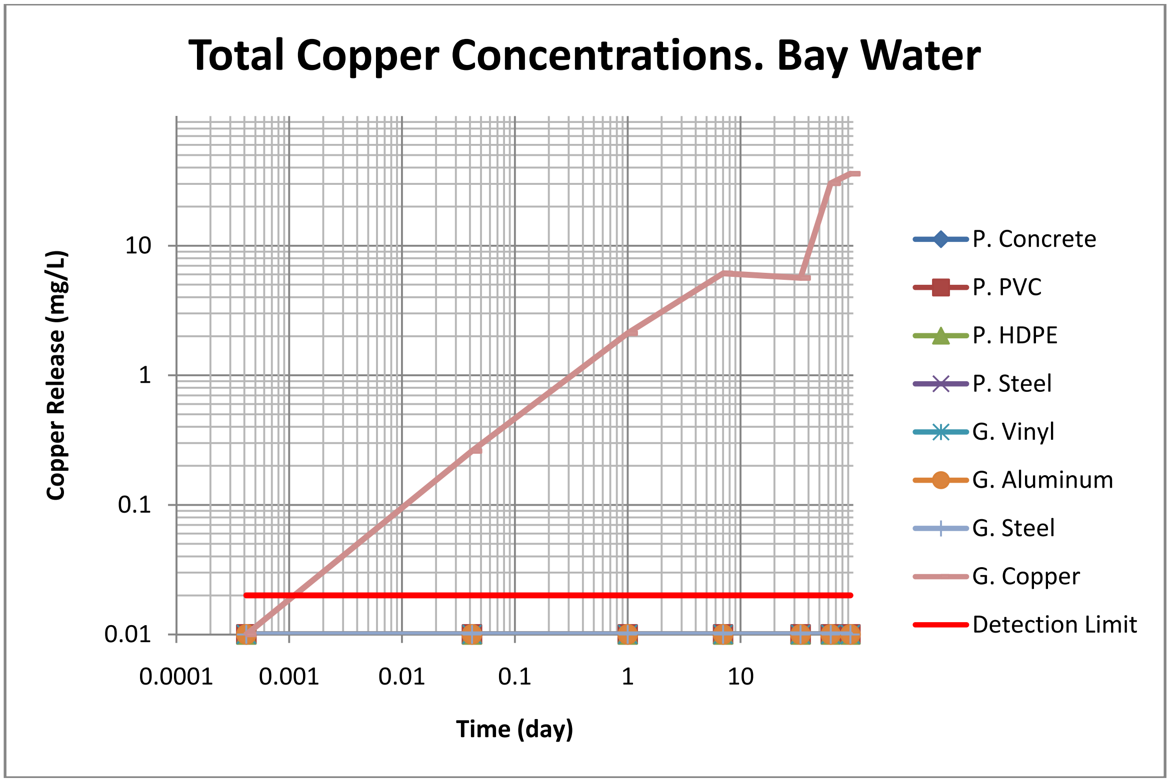


Figure 4.13. Total copper concentrations in containers with bay water.
Footnote: P. = Pipe, G. = Gutter

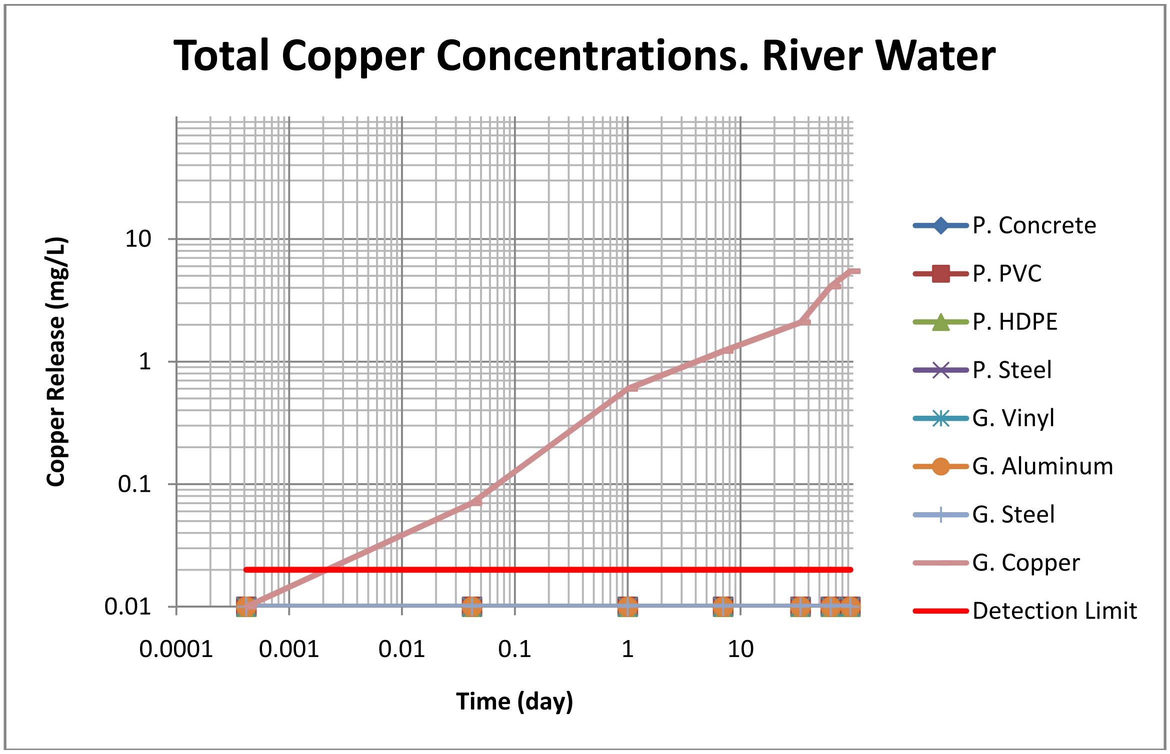


Figure 4.14. Total copper concentrations in containers with river water.
Footnote: P. = Pipe, G. = Gutter

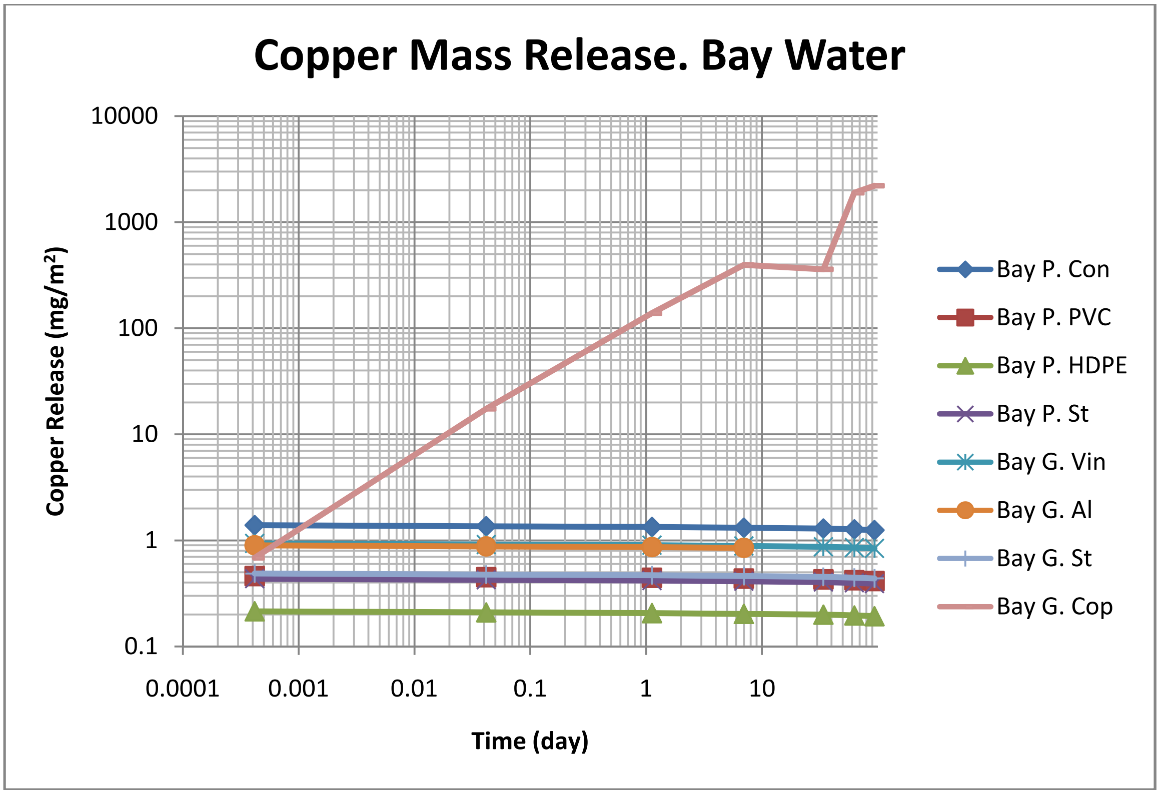


Figure 4.15. Total copper losses in containers with bay water.
Footnote: P. = Pipe, G. = Gutter

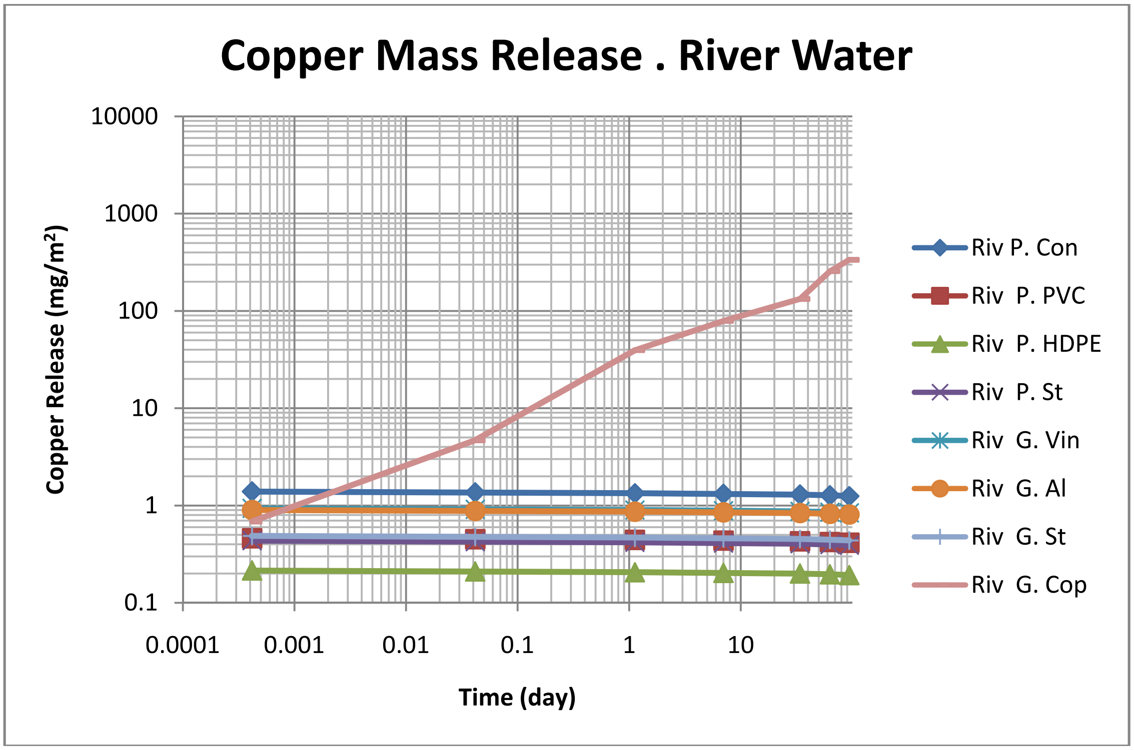


Figure 4.16. Total copper losses in containers with river water.
Footnote: P. = Pipe, G. = Gutter

4.2.5 Lead Releases during Controlled pH Tests

Only galvanized materials were a source of lead releases during both short (0.5 h to 27 h) and long (1 month to 3 months) exposure periods for the samples tested.

During short exposure times, lead was not detected in any of the containers having galvanized steel, with the exception of the galvanized steel gutter sample under the pH 8 conditions. This sample had a lead concentration of 8 µg/L (0.4 mg/m^2) at 27 h exposure and didn't exceed the aquatic toxicity criteria of 65 µg/L established by the US EPA. For the steel pipe and gutter specimens exposed at pH 5, lead was detected after 1 month exposure, while the steel pipe sample exposed to pH 8 conditions released lead after 2 months. Under both pH 5 and pH 8 conditions, the release of lead was greater for steel pipe samples than for steel gutter samples probably due to different material compositions. For a given material, the releases of lead were greater at high pH conditions compared to low pH conditions and can be explained by lead amphoteric properties; lead can dissolve well in acidic environments with the formation of salts in which lead is a divalent cation; lead can also dissolve well in alkaline solutions and form complexes (i.e. $Na_2[Pb(OH)_4]$ (Klinskiy and Skopinzev 2001).

The greatest lead releases were observed for the galvanized steel pipe sample at pH 8 which reached lead concentrations of 600 µg/L to 700 µg/L (25 mg/m^2 to30 mg/m^2), followed by the galvanized steel pipe sample at pH 5 with concentrations of 250 µg/L (9.98 mg/m^2) after 3 months exposure. Samples with aluminum, copper, and plastic materials did not contain any detectable lead concentrations. Figures 4.17 and 4.18 show lead concentrations released from different materials under controlled pH conditions. Corresponding lead releases in mg per m^2 pipe/gutter surface area are shown in Figures 4.19 and 4.20.

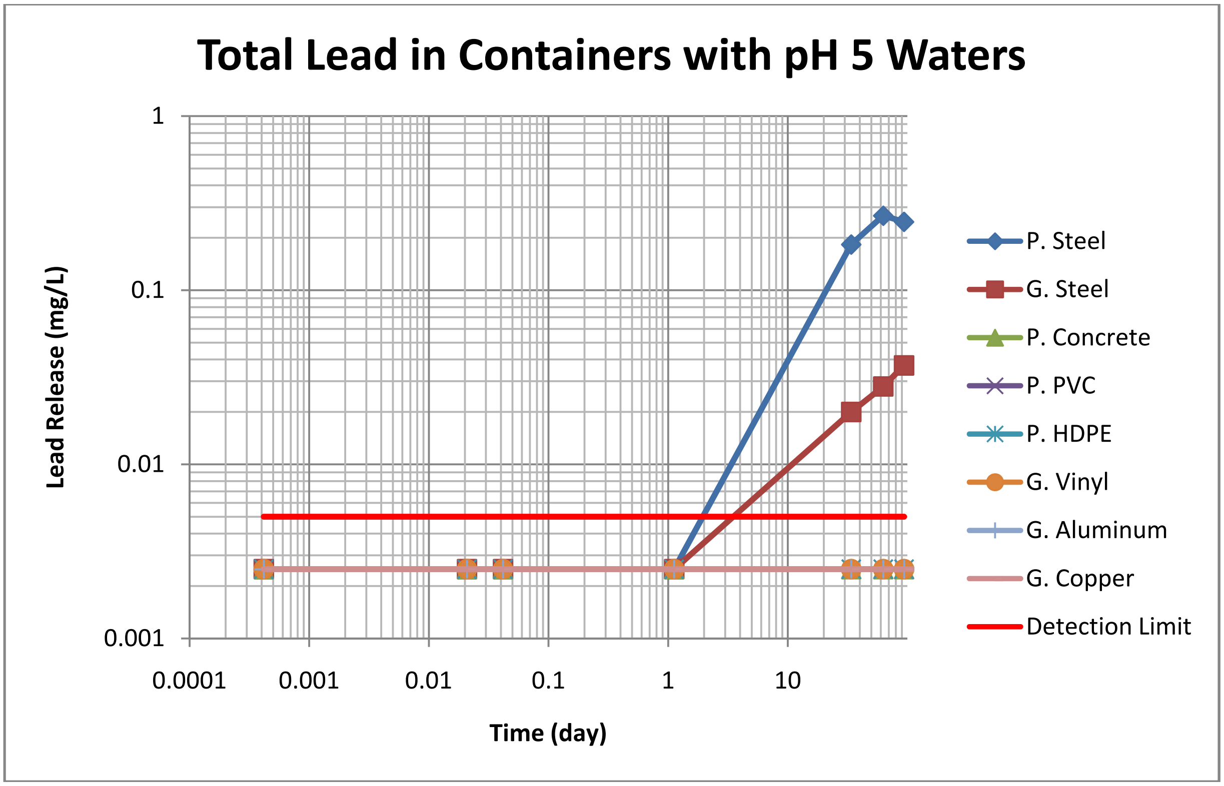


Figure 4.17. Total lead concentrations in containers with pH 5 water.
Footnote: P. = Pipe, G. = Gutter

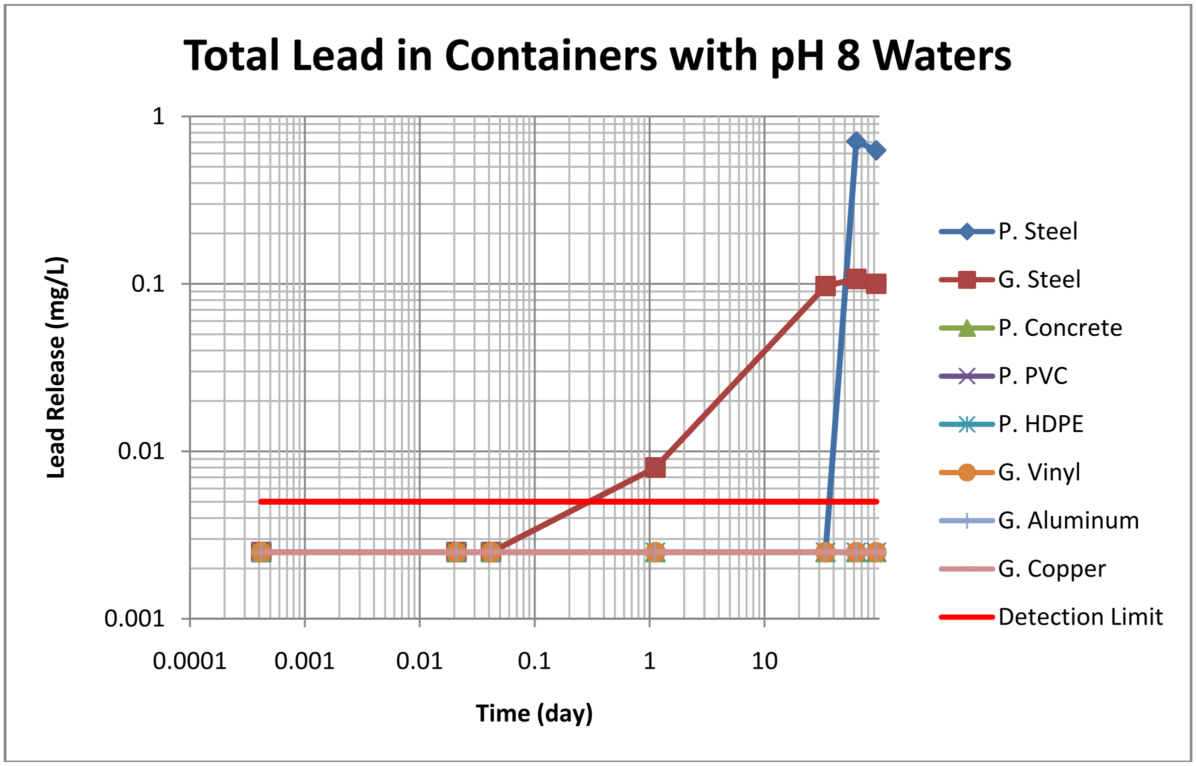


Figure 4.18. Total lead concentrations in containers with pH 8 water.
Footnote: P. = Pipe, G. = Gutter

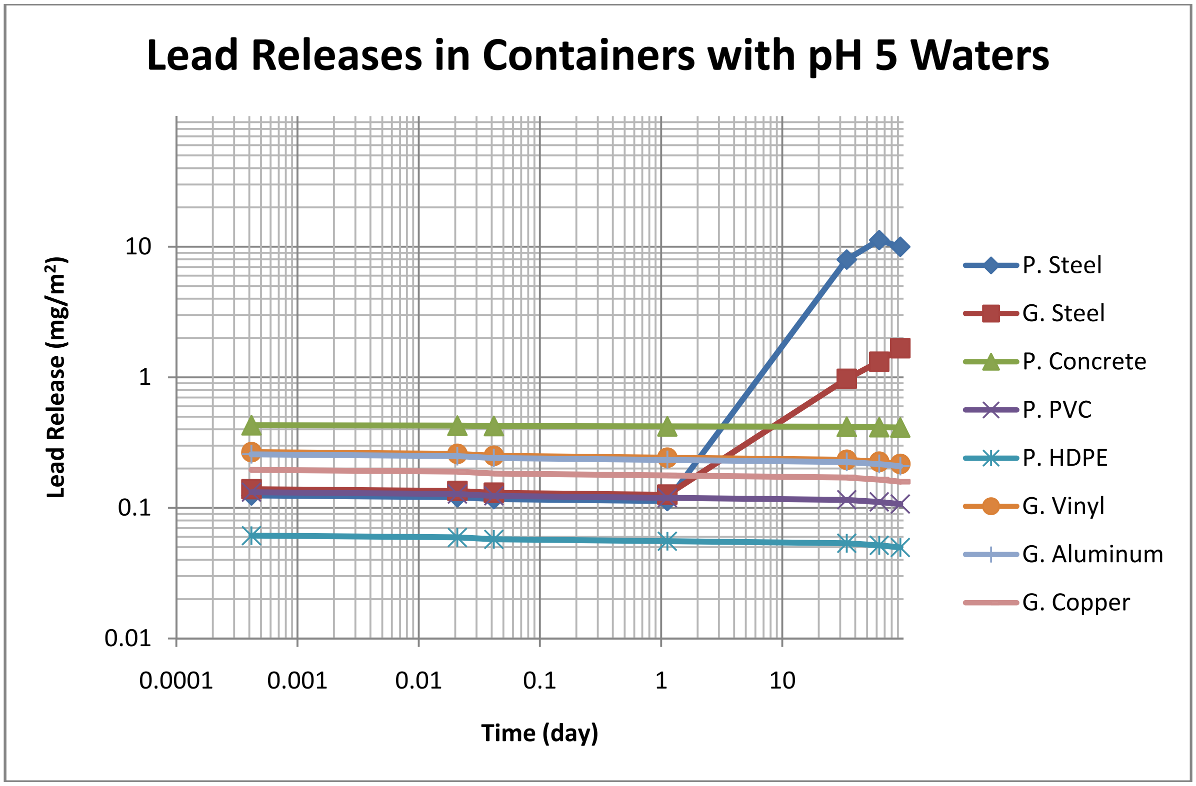


Figure 4.19. Total lead losses in containers with pH 5 water.
Footnote: P. = Pipe, G. = Gutter

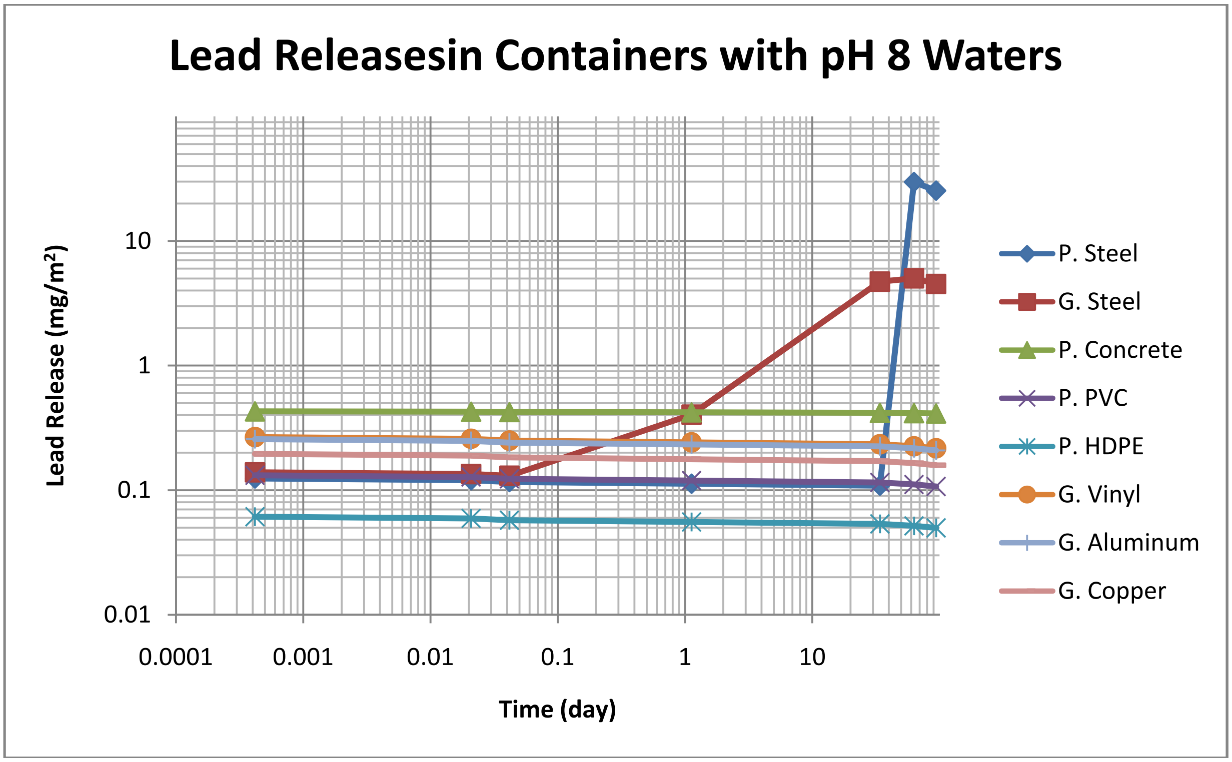


Figure 4.20. Total lead losses in containers with pH 8 water.
Footnote: P. = Pipe, G. = Gutter

4.2.6 Lead Releases during Natural pH Tests

As during the controlled pH conditions, lead releases were detected only for galvanized steel materials during both short and long exposures for the bay and river waters under natural pHs. During short exposure periods (1 h to 1 week), there were elevated lead concentrations noted from the galvanized steel materials immersed in bay and river waters. For example, a lead concentration of 0.012 mg/L (0.5 mg/m^2) was detected for the galvanized steel pipe section immersed into the bay water after 27 h exposure.

During long exposure periods (1 to 3 months), periodic lead concentrations were detected only for galvanized steel materials immersed in containers having either bay or river waters. The greatest lead release of 0.058 mg/L (2.54 mg/m^2) was observed after 3 months exposure of the steel gutter sample with river water. For galvanized steel materials, lead releases were greater in samples under controlled pH conditions compared to samples under natural pH conditions. Figures 4.21 and 4.22 show lead concentrations released from different pipe and gutter materials under un-controlled pH conditions. Figures 4.23 and 4.24 show the corresponding lead releases in mg per m^2 pipe/gutter surface area during these tests.

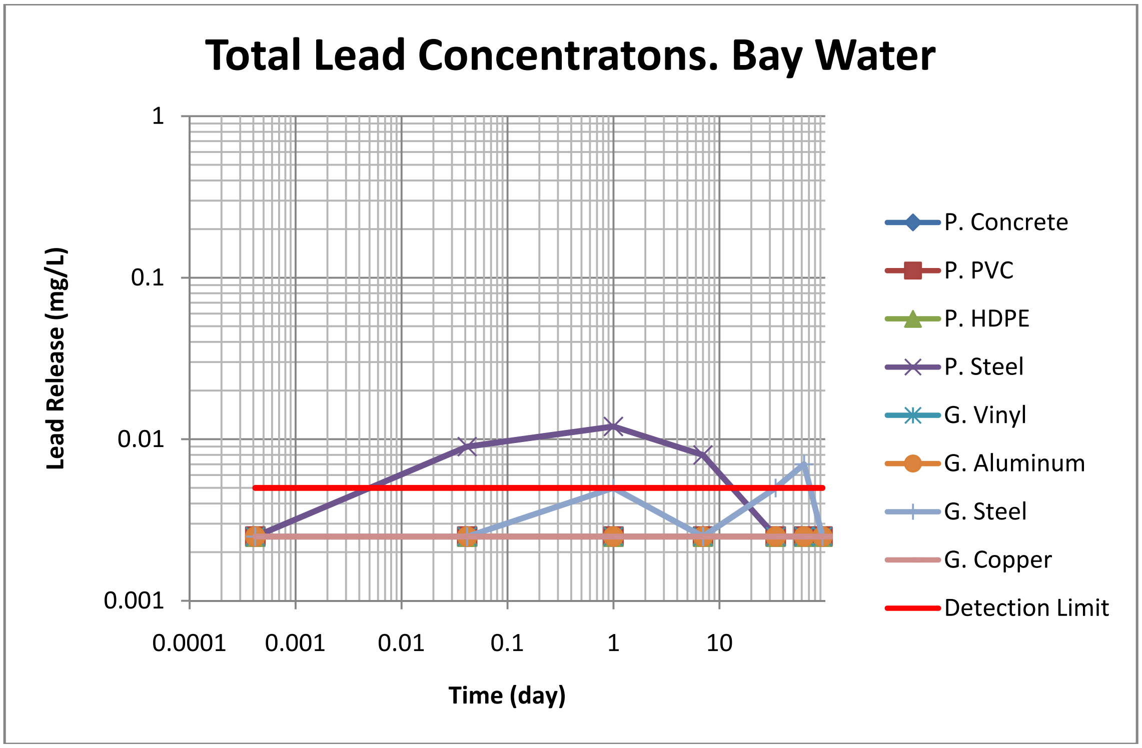


Figure 4.21. Total lead concentrations in containers with bay water.
Footnote: P. = Pipe, G. = Gutter

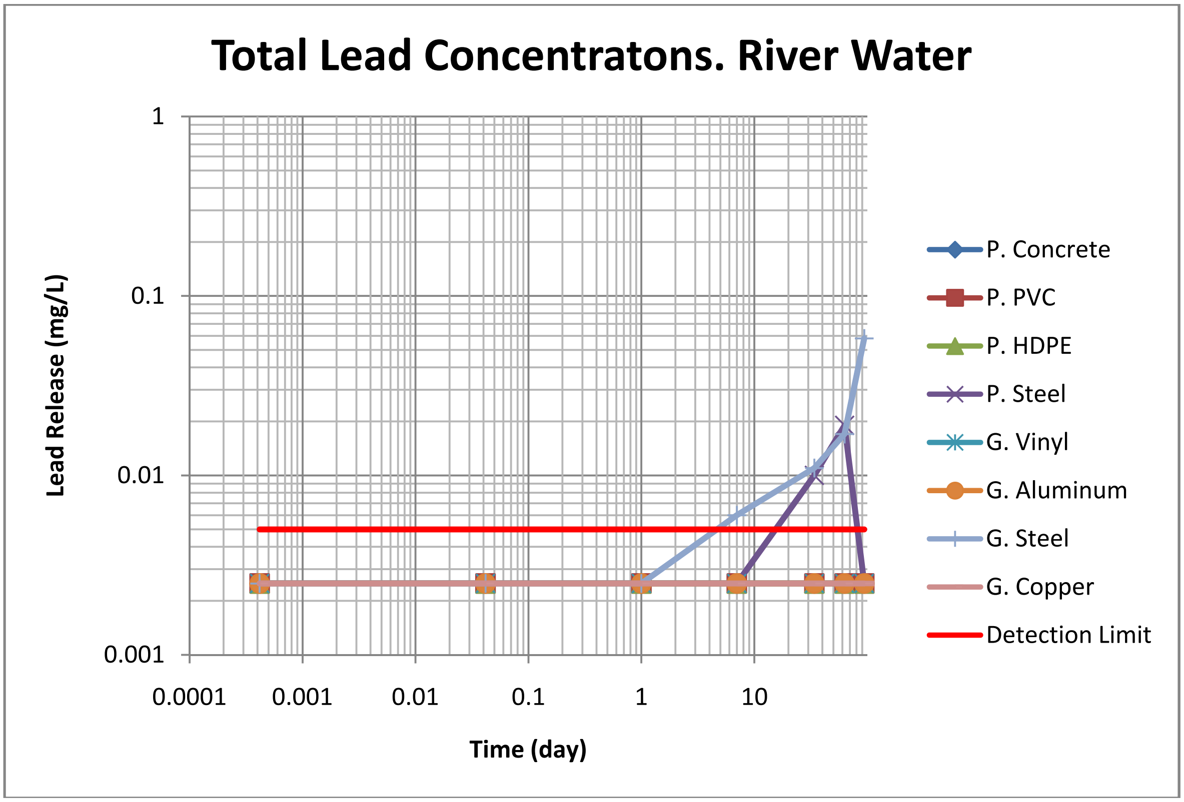


Figure 4.22. Total lead concentrations in containers with river water.
Footnote: P. = Pipe, G. = Gutter

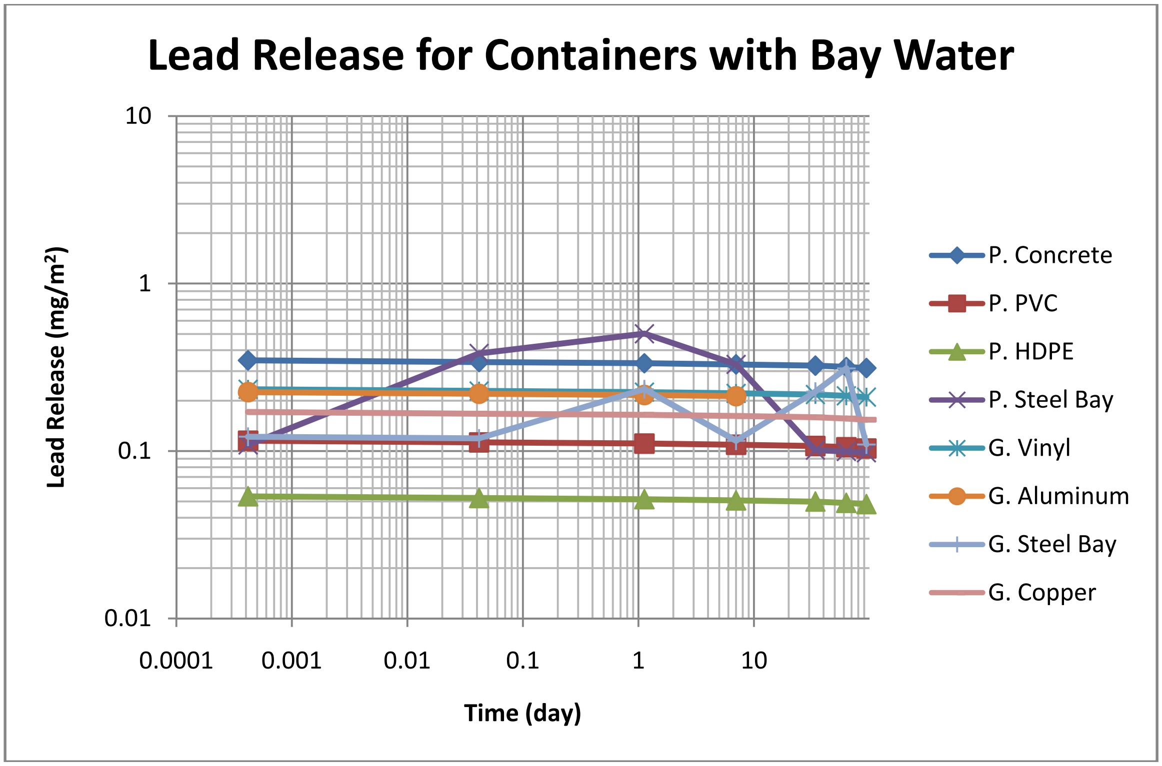


Figure 4.23. Total lead losses in containers with bay water.
Footnote: P. = Pipe, G. = Gutter

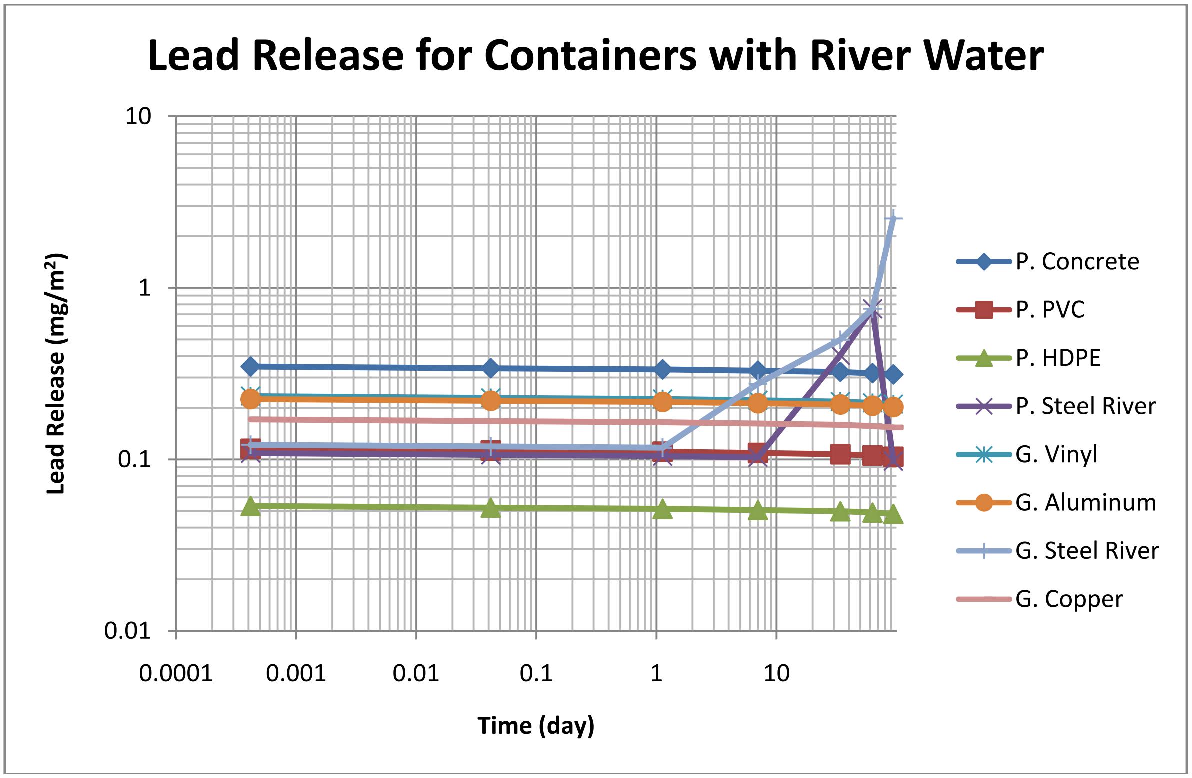


Figure 4.24. Total lead losses in containers with river water.
Footnote: P. = Pipe, G. = Gutter

Table 4.1 lists zinc, lead and copper releases from the most significant sources under various water conditions after three months exposure. The details of metal releases can be found in Appendix A.

Table 4.1. Final zinc, lead, and copper releases (mg/m^{2}after 3 months of exposure).

Metal	Material	pH 5	pH 8	Bay	River
Zn	P. Galv. Steel	470	3,400	3,100	2,600
Zn	G. Galv. Steel	640	4,200*	1,600	8,300
Pb	P. Galv. Steel	10	25	ND	ND
Pb	G. Galv. Steel	1.7	4.5	ND	2.5
Cu	G. Copper	320	140	2,200	340

* After 2 months exposure

4.2.7 Aluminum and Iron Releases during Controlled and Natural pH Tests

Iron releases from galvanized steel materials exceeded those from other materials and were greater under pH 5 conditions than under pH 8 conditions. At pH 5 the releases ranged between 6 mg/L and 22 mg/L (260 mg/m2 and 850 mg/m2) and around 1 mg/L (<45 mg/m2) at pH 8. Iron releases from the galvanized steel specimens submerged into bay and river water were between 1 and 2 mg/L (<66.49 mg/m2) and were similar to iron releases at pH 8 values. Iron concentrations leached from concrete pipes in bay water (>2 mg/L; 68.3 mg/m2) were greater than those in river water (<1 mg/L; 25 mg/m2). The highest concentrations of aluminum were detected in the containers having aluminum materials and were ≤1 mg/L (<80 mg/m2) for all conditions and did not exceed the aquatic freshwater toxicity criteria for aluminum of 750 µg/L established by the US EPA. For pH 5 tests, aluminum was detected in the samples with aluminum and PVC materials. Under pH 8 conditions materials that released aluminum included aluminum, PVC, HDPE, vinyl, and steel gutter.

4.3 The Effect of Pipe and Storage Tank Materials, Exposure Time, pH, and Salinity on Heavy Metal Releases

Statistical analyses were conducted to determine the behavior of pollutant leaching from the gutter and piping materials depending on exposure time and pH (during the first test series) and on exposure time and salinity (during the second series of tests). The heavy metal releases per unit area (shown in Appendix A) were compared for the various gutter and pipe materials.

Kruskal–Wallis tests were performed on the metals data (zinc, copper and lead) for each of the test series after 1, 2, and 3 months exposure to determine if there was a statistically significant difference between these data points. The tests showed that the data for these exposure periods can be combined as replicates of long term exposure times. Also, Kruskal–Wallis tests were conducted on the metal data after 0.5, 1, and 27 h exposures during the first test series, and on the metal data after 1 and 27 h, and 1 week exposures during the second series of the experiments. These tests also showed that these data can be combined as replicates of short term exposure times at the 0.05 significance level.

Next, 2^2 factorial analyses were performed to evaluate the effects of exposure times (short vs. long) and pH (low vs. high) and the interactions of those factors on the metal releases in mg/m^2 surface area for each pipe and gutter material during the first series of tests. During the second test series, 2^2 factorial analyses were conducted to estimate the effect of exposure time and salinity (high vs. low), and the interaction of those factors. The results of 2^2 factorial analyses are shown in Appendix A.7.

By using the P-values (0.05) and the factorial effect/pooled standard error ratios of the factorial analysis (shown in Table A.7.3 - Table A.7.6, Appendix A.7), a determination was made as to whether or not the data could be combined into groups for each pipe and gutter material based on the effect (or absence of effect) of the factors and their interactions. Table 4.2 shows significant groupings for each sample type for the different exposure conditions for zinc, lead, and copper releases according to the separate 2^2 factorial analyses.

Table 4.2. Significant groups for lead, copper and zinc releases.

Material	Constituent	Varying pH Conditions	Varying Conductivity Conditions
Concrete (pipe sample)	Pb	ND	ND
	Cu	ND	ND
	Zn	all combined into one group	ND
PVC (pipe sample)	Pb	ND	ND
	Cu	short* vs. long** exp periods	ND
	Zn	short vs. long exp periods	all combined into one group
HDPE (pipe sample)	Pb	ND	ND
	Cu	short vs. long exp periods	ND
	Zn	pH 5 vs. pH 8; and short vs. long exp. periods	Short bay vs. short river vs. long bay vs. long river
Galvanized steel (pipe sample)	Pb	short vs. long exp periods	Short bay vs. short river vs. long bay vs. long river
	Cu	all combined into one group	ND
	Zn	all combined into one group	short vs. long exp periods
Vinyl (gutter sample)	Pb	ND	ND
	Cu	Short at pH 5 vs. short at pH 8 vs. long at pH 5 vs. long at pH 8	ND
	Zn	pH 5 vs. pH 8	all combined into one group
Aluminum (gutter sample)	Pb	ND	ND
	Cu	short vs. long exp periods	ND
	Zn	all combined into one group	all combined into one group
Galvanized steel (gutter sample)	Pb	short at pH 5 vs. short at pH 8 vs. long at pH 5 vs. long pH 8	all combined into one group
	Cu	Short at pH 5 vs. short at pH 8 vs. long at pH 5 vs. long at pH 8	ND
	Zn	all combined into one group	short vs. long exp periods
Copper (gutter sample)	Pb	ND	ND
	Cu	pH 5 vs. pH 8	short vs. long exp periods
	Zn	pH 5 vs. pH 8	all combined into one group

* Short exposure period (0 h to 27 h) for the varying pH tests, and short exposure period (0 week to 1 week) for varying conductivity tests.

** Long exposure period (27 h to 3 months) for the varying pH tests, and long exposure period (1 week to 3 months) for varying conductivity tests.

ND: the concentrations in the test solutions were mostly non-detected, therefore statistical analyses were not possible for these conditions.

Mann–Whitney tests were performed next to determine whether there were any statistically significant differences between the groups at a chosen significance level. These tests were performed as a pairwise comparison. The Mann–Whitney test was used because some of the data did not meet the assumptions of normality and equal variance (log transformations of the data also did not result in normally distributed values). The results for Mann-Whitney tests are shown in Appendix A.8. As an example, the Mann-Whitney Test P-values for zinc releases from different pipe and gutter materials under controlled pH conditions are shown in the Table A.8.1, Appendix A.8 (Con = concrete; St = galvanized steel; Alum = Aluminum; Cop = copper; S = short exposure time; L = long exposure time; 5 = pH 5; 8 = pH 8; P = pipe; G = gutter). The results showed that there was a difference (at 0.05 significance level) between the majority of the groups. The exception included the difference between HDPE groups and copper pH8 group. Also, there was no difference between steel pipe and steel gutter groups.

For zinc releases from different materials under natural pH conditions, pairwise comparison of the groups indicated that there were differences between the majority of the groups; the exceptions included the differences between HDPE groups and aluminum and steel gutter (short exposure time) groups. There was no difference between steel gutter (short exposure) and steel pipe (short exposure) groups; also, there was no difference between steel gutter (long exposure) and steel pipe (long exposure) groups. However, there was a difference between the groups of steel gutter (short exposure) and steel gutter (long exposure), as well as between the groups of steel pipe during short exposure and the same material during the long exposure times.

For copper releases during buffered tests, there was a statistically significant difference between the majority of copper groups and groups with the other materials. There was no difference between copper releases from copper materials at pH 5 and pH 8 conditions. For copper releases under natural pH conditions, there was a statistically significant difference between the copper groups the groups with other materials. There was a difference between copper material (short exposure time) group and copper material (long exposure time) group.

For lead releases during controlled pH conditions, there were no statistically significant differences between short and long exposure releases for steel pipe; no differences between short and long exposure releases for steel gutter at pH 5 conditions; and no differences between short and long exposure releases for steel gutter at pH 8 conditions. Also, there were no differences between lead releases from steel gutter during short term exposure at pH 5 and at pH 8 conditions; and there were no differences between lead releases from steel gutter during long exposure time at pH 5 and pH 8 conditions. However there was a statistically significant difference (at 0.05 significance level) between the majority of the steel gutter groups and the groups of the other materials.

For lead releases during the natural pH tests, there were no statistically significant differences for steel pipe during short exposure time in bay and river waters; no differences between steel pipes during long exposure in bay and river waters. Also, there were no differences between lead releases from steel pipe submerged in bay water during short and long exposure times; no difference between lead releases from steel pipe immersed into river water during short and long exposure times. However, there was a statistically significant difference between releases from steel pipe immersed into bay water during short exposure and the groups of materials other than steel. Also, there was a statistically significant difference between steel gutter group and the groups of materials other than-steel.

Group box plots were plotted on a log scale for each metal constituent to illustrate the variations and differences between each group. Figure 4.25 is a group box plot of copper releases from copper materials under pH 5 vs. pH 8 conditions. Low pH conditions and exposure time increased released copper. The 75th percentile of the box plot for copper releases under pH 5 conditions during short time exposure is higher than that of copper releases under the same conditions during long exposure time and was an unusually high value.

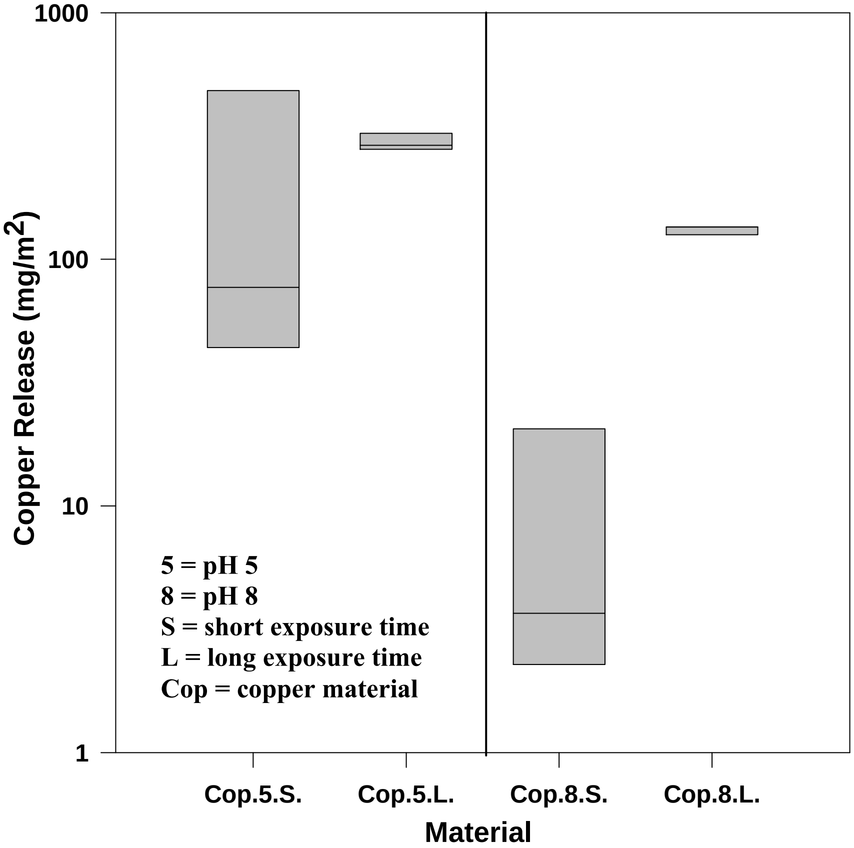


Figure 4.25 Group box plot for copper release in mg/m^2 for copper materials immersed in pH 5 and pH 8 waters.

Figure 4.26 shows copper releases from copper materials in bay and river waters. The copper releases increased with the exposure time; greater concentrations were observed for the samples in the bay water possibly due to the higher content of the chloride ion which causes corrosion (Corvo 2005; Gabriel and Moran 1998).

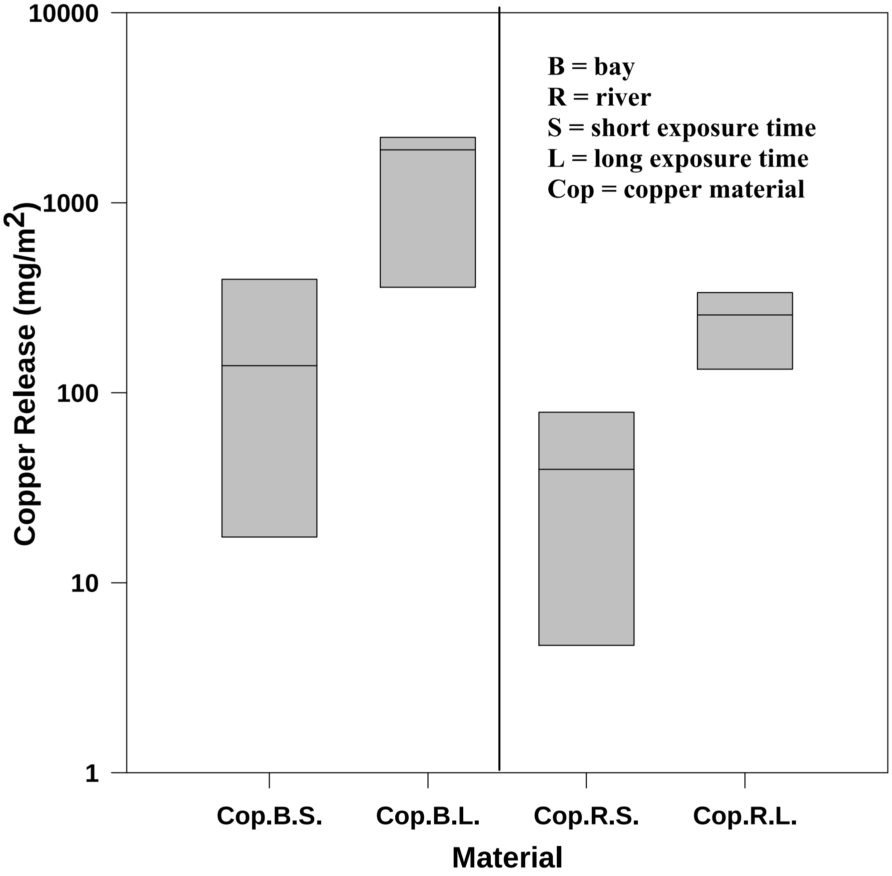


Figure 4.26 Group box plot for copper release in mg/m^2 for copper materials immersed in bay and river waters.

Figure 4.27 shows zinc releases from various gutter and pipe materials under controlled pH conditions. Concrete, galvanized steel and aluminum material box plots represent all the data combined (short and long exposure times for both pH 5 and pH 8 conditions). Box plots for PVC and HDPE materials show the data during long term exposure, with both pH 5 and pH 8 combined. Box plots for vinyl and copper materials represent the data with short and long exposure times combined. Galvanized steel materials have significantly higher zinc releases compared to the rest of materials.

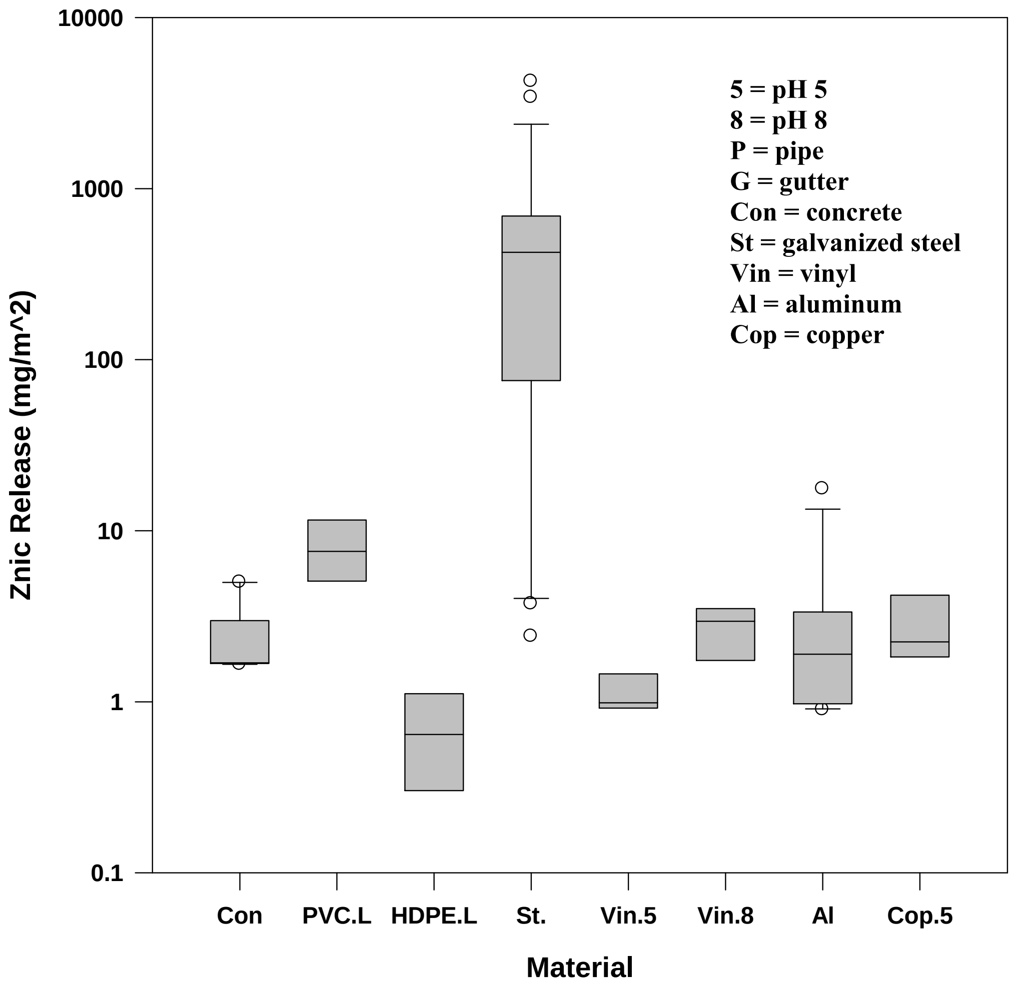


Figure 4.27 Group box plot for zinc release in mg/m^2 for different gutter and pipe materials immersed in pH 5 and pH 8 waters.

Figure 4.28 shows zinc releases for the materials exposed to bay and river waters. The box plots for plastics represents all the data combined (for bay and river waters and for short and long exposure times). As the exposure time increased, the zinc releases also increased.

Figure 4.29 shows lead releases from galvanized steel materials under controlled pH conditions. Box plots for lead releases from galvanized steel pipes during short exposure times at pH 5 and 8, as well as from galvanized steel gutters during short exposure times at pH 5, were below detection limits. As can be seen from the figure, exposure time increased lead releases.

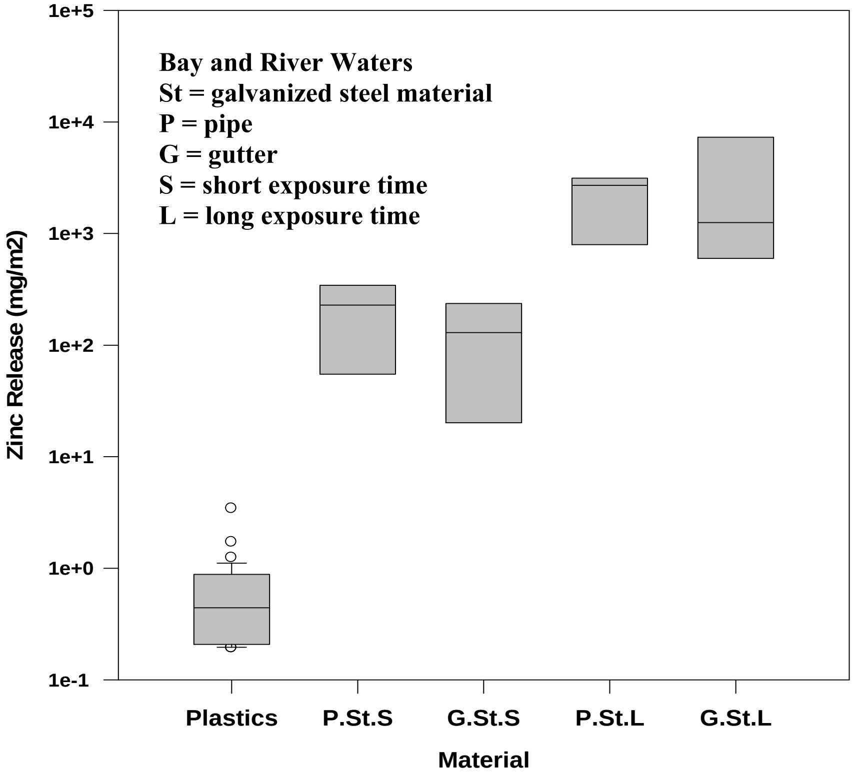


Figure 4.28 Group box plot for zinc release in mg/m^2 for various gutter and pipe materials immersed in bay and river waters.

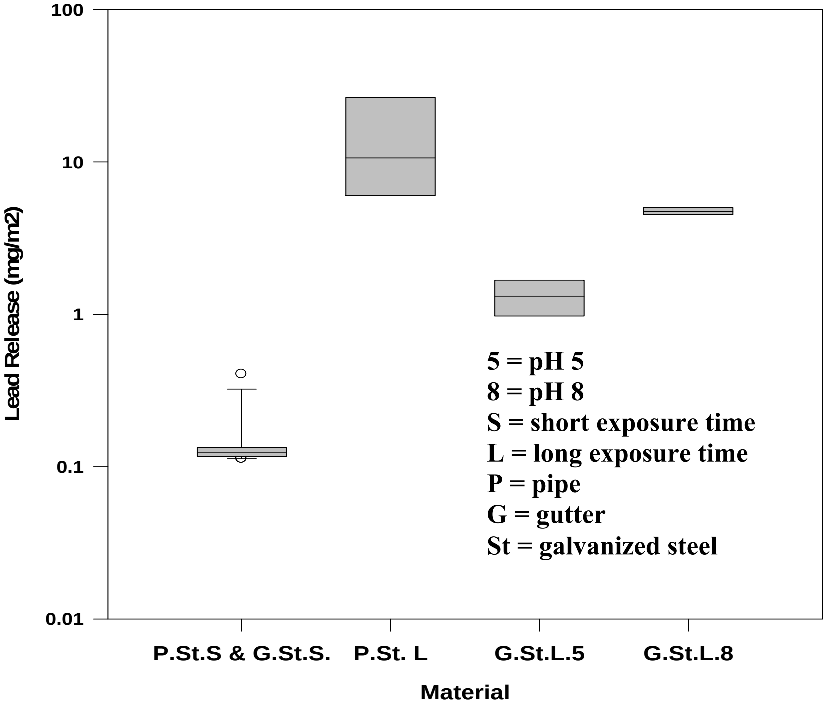


Figure 4.29 Group box plot for lead release in mg/m^2 for galvanized steel materials immersed in pH 5 and pH 8 waters.

Figure 4.30 shows lead releases from galvanized steel materials under natural pH conditions. Lead releases during both short and long exposure times and under both bay and river conditions do not differ significantly between the groups, with the group of lead releases from galvanized steel gutters immersed into river water during long exposure times being slightly higher than the rest of the groups.

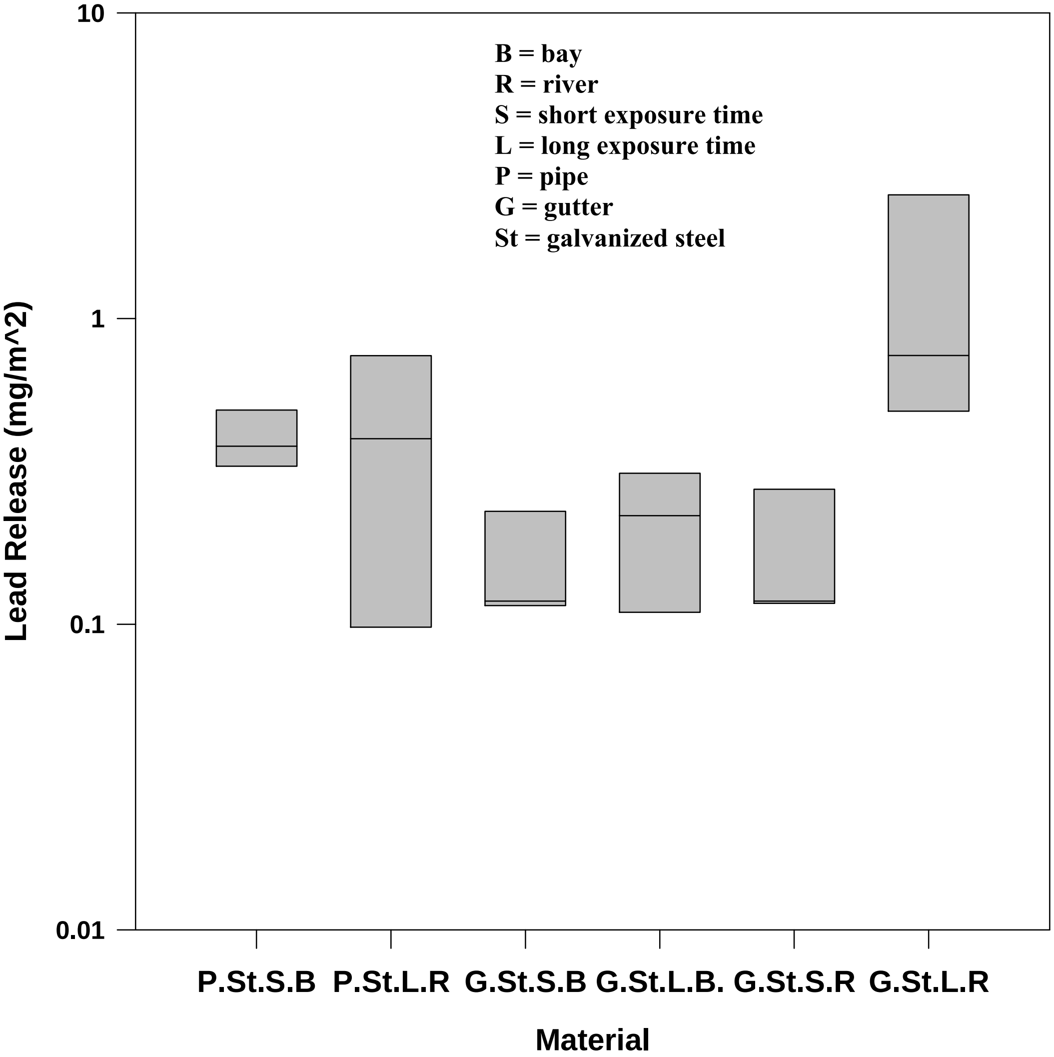


Figure 4.30 Group box plot for lead release in mg/m^2 for galvanized steel materials immersed in bay and river waters.

4.4 Model Fitting

Linear regression was conducted on time series plots of log-transformed metal releases per pipe surface area vs. log time for different pipe and gutter materials under controlled and natural pH conditions. The regression analyses results are shown in Tables 4.3through 4.5. There were six time series data points for each plot. The majority of the scatterplots revealed that first order polynomials can be fitted to the log of metal releases vs. log of time.

The time series of lead releases from steel gutters at pH 5 and of steel pipes at pH 8 were not fitted with linear equations due to initial lag periods before releases were observed. In the container with steel gutters at pH 5, no lead was detected until after 1 month exposure: after 1 month exposure, the lead release reached 0.97 mg/m^2 (0.02 mg/L) and after 2 months exposure, the lead release exceeded 1 mg/m2 (0.028 to 0.037 mg/L). There were only three detected lead concentrations in the data series. In the containers with steel pipe at pH 8, lead releases were detected after 2 months exposure and exceeded 29 mg/m^2 (0.71 mg/L). Two concentration values above the detection limits were available.

Time series for copper releases from copper gutters under pH 5 conditions showed an apparent increase in the copper concentrations after 0.5 h exposure, and, after 27 h exposure, reached 970 mg/m^2 (6.8 mg/L). However, after 27 h exposure, copper concentrations leveled off. The linear regression equation fitted to this data was not significant (p-value for regression equation is greater than 0.05 and is highlighted in red in Table 4.3).These copper data were therefore fitted using first order polynomial and 2 segment liner equations due to the obvious change in release rate after 27 hrs. The numbers of data points in these time series were limited and the high concentration observed after 27 h exposure could have been an unusually high value. On the other hand, cupric ions could have been combined with the orthophosphate from the solution and thereby reducing copper solubility. Edwards (2002) observed that higher doses of orthophosphate tend to decrease solubility of copper.

The statistical software packages Minitab 16 (Minitab, Inc.) and Sigmaplot 11 (Systat Software, Inc.) were used to perform analyses and to check the assumptions. Pearson product moment correlations or Spearman rank order correlations were computed to determine if the data were significantly correlated at the 0.05 level. The majority of the data were not statistically significantly correlated (indicated by p-values greater 0.05). The data that were correlated (p-values less than 0.05) are highlighted in red in Table 4.3. To investigate the goodness of model fit, residual plots were inspected to determine if the least squares assumptions for errors were met. To check the constant variance assumption, the plots of residuals vs. the fitted values were inspected and the Levene median test was conducted to detect the differences in the variance values. To evaluate the normality of the residuals, normal probability plots and histograms of the residuals were also constructed. The Anderson–Darling test statistic was also calculated to check for normality. This test showed that all the data for regression analysis were normally distributed with the exception of lead releases from galvanized pipe under controlled pH 5 conditions (Table 11.4). The zero mean of the residuals assumption was checked by examining the descriptive statistics and graphs of the residuals vs. fitted values and vs. the order of the observations. To determine if the residuals were independent from each other, graphs of the residual vs. observation number were examined and the Durbin–Watson statistic was calculated.

ANOVA tables were used to determine if the regression coefficients were not equal to zero and were statistically significant, and to evaluate if the overall regression equations were significant. The regression coefficients that were not significantly different from zero and the overall regression equations that were not statistically significant are highlighted in red (Table 4.3). The coefficient of determination (R^2) was also calculated for each regression.

The residuals for most of the regression equations met the assumptions of normality, constant variance, zero mean, and independence. P-values for some regression analyses were lower than desired (P values ranged from 0.04 to 0.008, as shown in Table 4.3) which could have been explained by the fact that there were few data observations available for some conditions. The examination of the residual values vs. fitted values for some of the samples showed that there was more spread in the residuals for the higher fitted values, but the assumption of the constant variance of the residuals was not rejected because of the few data points available. The Spearman rank correlations between the absolute values of the residuals and the observed value of the dependent variable were calculated to test the assumption of constant variance, which may be violated if the Spearman rank correlation was statistically significant. Levene's test was also used to determine if the residuals have constant variance. The results of Levene's test showed that the assumption of equal variance was met for most of the data, and for the rest of the time series the hypothesis of equal variances was not rejected due to the limited data. The results of the Durbin-Watson statistic indicated that the majority of the residuals were independent from each other (Durbin-Watson statistic was in the range 1.5-2.5), and for the remaining data the hypothesis of independent residuals was not rejected because of the few data points.

The majority of the models had histograms of the residuals that were approximately bell shaped; the residuals were normally distributed and had zero mean, and are independent of each other.

In the ANOVA tests of the regression equations, the significance of the regression coefficients is strongly affected by the number of data observations. A high R^2 value can be observed with insignificant equation coefficients if there are only a few data available, such as in the time series of copper released from copper gutters under pH 5 conditions. An important and strong association may not appear to be significant if there are only a few data observations available (Berthouex and Brown, 1994).

The standard error of the estimate was used to evaluate the ability of the model to predict (rather than relying only on R^2). Using the model, the standard error of the estimate was calculated utilizing the variance of the predicted values and was found to be a more precise indicator of the capability of the model to accurately predict dependent variables (Burton and Pitt, 2002).

For all of the regression equations, the constant term (intercept) was significant, with an exception for zinc releases from galvanized steel gutters in river water (P-value = 0.079) and therefore in this case the regression was done without the intercept term. Additionally, ANOVA tables indicated that the slope terms were significant for all regression equations. The regression analysis results for zinc and lead releases from galvanized materials and copper releases from copper materials under controlled and natural pH conditions are shown in Tables 4.2 through 4.4 (G = gutter; P = pipe; St = steel; Cop = copper; B = bay waters; R = River waters; 5 = pH 5 waters; 8 = pH 8 waters). An example set of plots are shown in Figure 4.31, a linear regression of zinc losses from a galvanized steel gutter sample submerged in bay water vs. exposure time. Linear regression results are shown in Appendix B.

Table 4.3. Regression analysis results for zinc, lead, and copper releases under controlled and natural pH conditions.

Linear Regression equation: log(Conc., mg/m^2) = m + b log(Time, hr)

2 Segment Linear Regression for Cu.G.Cop.5:
t1 = min(logTime); t2 = max(logTime)
Segment 1(logTime): log(Conc., mg/m^2) = (y1*(T1-logTime) + y2*(logTime-t1))/(T1-t1)
Segment 2(logTime):log(Conc., mg/m^2) = (y2*(t2-logTime) + y3*(logTime-T1))/(t2-T1)
f = if(logTime<= T1, Segment1(logTime), Segment2(logTime))

Metal, Pipe, Condition	**Data Correl., r, (P-Value)**	**Data Normality AD statistic (P-Value)**	**Coeff. m (P-Value)**	**Coeff. b (P-Value)**	**Regress. (P-Value)**	**R^2 adj., %**	**Stand Error of the Estimate, S**
Cu.G.Cop.B	0.855 (0.065)	0.281 (0.509)	1.245 (0.003)	0.587 (0.002)	0.002	91.4	0.2288
Cu.G.Cop.R	0.966 (0.008)	0.318 (0.409)	0.725 (0.001)	0.525 (0.000)	0.000	98.0	0.0950
Cu.G.Cop.5 (Linear)	0.499 (0.392)	0.507 (0.118)	1.916 (0.000)	0.202 (0.053)	0.053	56.0	0.2716
Cu.G.Cop.5 (2 Segments)	0.499 (0.392)	0.507 (0.118)	-	-	0.0123	97.95	0.0586
Cu.G.Cop.8	0.887 (0.045)	0.534 (0.098)	0.552 (0.000)	0.499 (0.000)	0.000	99.2	0.0746
Zn.P.St.B	0.838 (0.076)	0.277 (0.516)	1.736 (0.001)	0.477 (0.004)	0.004	87.7	0.2264
Zn.G.St.B	0.592 (0.293)	0.304 (0.446)	1.435 (0.006)	0.438 (0.017)	0.017	74.5	0.3179
Zn.P.St.R	0.800 (0.104)	0.227 (0.678)	1.528 (0.003)	0.535 (0.006)	0.006	85.1	0.282
Zn.G.St.R	0.831 (0.376)	0.278 (0.486)	-	1.131 (0.000)	0.000	96.3	0.5819
Zn.P.St.5	0.766 (0.131)	0.526 (0.104)	2.181 (0.000)	0.165 (0.025)	0.025	69.4	0.1713
Zn.G.St.5	0.521 (0.368)	0.497 (0.124)	2.095 (0.000)	0.216 (0.036)	0.036	63.3	0.2541
Zn.P.St.8	0.920 (0.027)	0.340 (0.355)	0.569 (0.004)	0.812 (0.000)	0.000	98.7	0.1521
Zn.G.St.8	0.752 (0.142)	0.263 (0.550)	0.878 (0.028	0.717 (0.003)	0.003	88.7	0.4118
Pb.G.St.R	0.939 (0.018)	0.239 (0.631)	-1.1566 (0.010)	0.3439 (0.028)	0.028	67.3	0.293538
Pb.P.St.5	(>0.05)	0.830 (0.013)	-1.029 (0.020)	0.598 (0.007)	0.007	82.8	0.4365
Pb.G.St.8	0.807 (0.099)	0.627 (0.053)	- 0.852 (0.001)	0.472 (0.000)	0.000	96.1	0.1544

Footnote: data that are correlated or not normally distributed are highlighted in red. Also regression coefficients and regression equations that are not significant are also highlighted in red.

Table 4.4. Examination of the residuals of the regression analysis for zinc, lead, and copper releases under controlled and natural pH conditions.

Metal, Pipe, Condition	**Resid. Normality AD statistic (P-Value)**	**Resid. Constant Variance P Value**	**Resid. Indep. Durbin- Watson statistic**
Cu.G.Cop.B	0.678 (0.037)	0.060	2.4974
Cu.G.Cop.R	0.182 (0.845)	0.060	2.3095
Cu.G.Cop.5 (Linear)	0.846 (0.012)	0.059	1.9746
Cu.G.Cop.5 (2 Segments)	0.295 (0.471)	0.0600	1.7820
Cu.G.Cop.8	0.118 (0.974)	0.060	1.1108
Zn.P.St.B	0.532 (0.100)	0.060	1.7010
Zn.G.St.B	0.292 (0.481)	0.060	1.8208
Zn.P.St.R	0.386 (0.264)	0.060	1.8546
Zn.G.St.R	0.328 (0.350)	N/A	1.3176
Zn.P.St.5	0.167 (0.887)	0.060	2.0350
Zn.G.St.5	0.829 (0.013)	0.060	2.2657
Zn.P.St.8	0.363 (0.307)	0.040	1.6505
Zn.G.St.8	0.313 (0.421)	0.008	2.0137
Pb.G.St.R	0.384 (0.267)	0.060	1.40583
Pb.P.St.5	0.858 (0.011)	0.060	2.2959
Pb.G.St.8	0.203 (0.772)	0.060	2.3248

Footnote: data that are not normally distributed are highlighted in red. Data that do not have constant variance or are not independent are also highlighted in red.

Table 4.5 Segment linear regression coefficients for copper releases under controlled pH 5 conditions.

Metal, Pipe, Condition	**Coeff. y1 (P-Value)**	**Coeff. y2 (P-Value)**	**Coeff. y3 (P-Value)**	**Coeff. T1 (P-Value)**
Cu.G.Cop.5 (2 Segments)	1.6428 (0.0013)	2.7152 (0.0007)	2.4546 (0.0002)	1.0247 (0.1059)

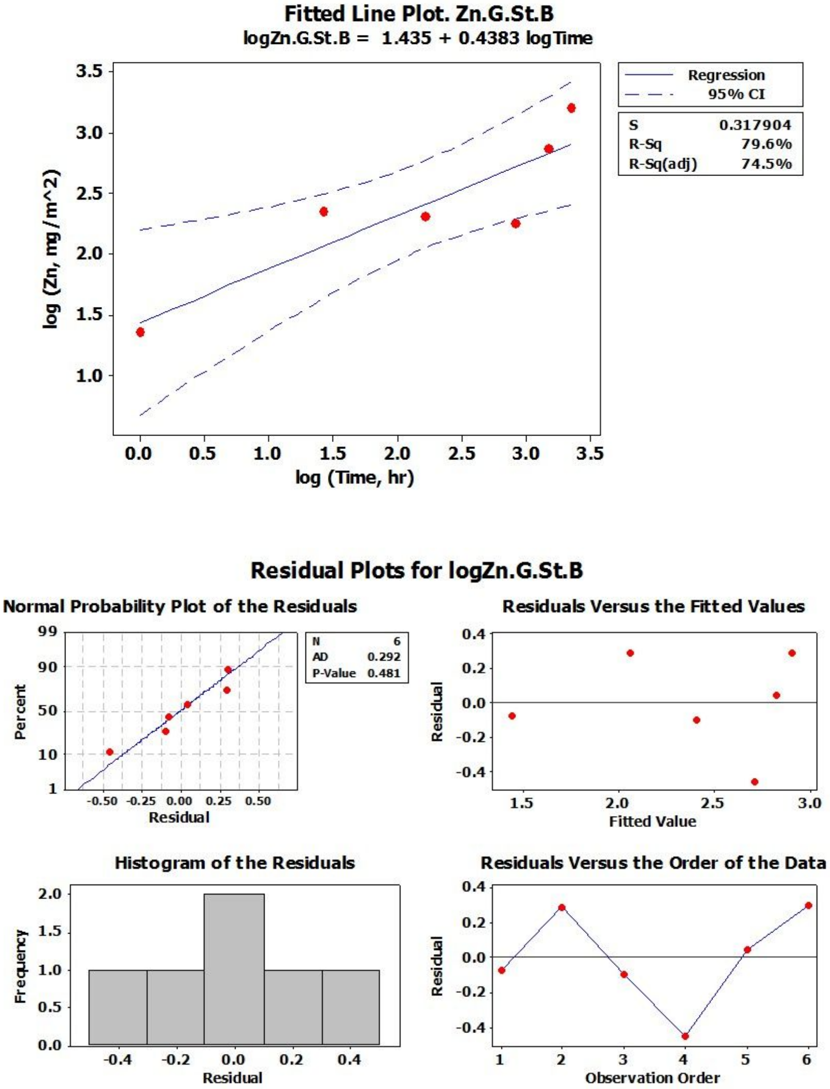


Figure 4.31 Empirical estimation (linear equation) of zinc release from galvanized steel gutter section submerged into bay waters as a function of time.

4.5 Chemical Speciation Modeling (Medusa)

In stormwater, many heavy metals can sorb to inorganic and organic particulate matter that accumulate as bed sediments. Water chemistry, the suspended sediment and substrate sediment composition influence the behavior of heavy metals in natural waters. The sorption of heavy metals to particulates is affected by chemical identity, redox conditions, water pH, and complexation and precipitation chemistry (Clark and Pitt 2012). The forms of metal species present in the environment will affect toxicity and treatability of heavy metals. Comprehensive water chemistry modeling was conducted to predict the forms of the measured metals. Medusa software (Medusa, KTH, available at http://www.kemi.kth.se/medusa/) was used. Phase, Fraction, and Pourbaix diagrams show the predominant species of metals and their concentrations. For all chemical components in Medusa files, only the concentrations at and above the detection limit were used. The diagrams and summary tables were made for the zinc, copper, and lead contaminants. Phase, Fraction, and Pourbaix diagrams and the predominant species tables were constructed for time zero, one day of exposure (representing rainstorm event and applicable to gutter and pipe materials) and three months of exposure times (for tank materials) and are shown in Appendix C. The pH values of the samples are marked with a red vertical line on the Phase and Fraction diagrams. For the Pourbaix diagrams, the pH and E_{SHE} values of the samples are shown with a red cross.

For Medusa input files, an assumption was made that equilibrium was reached during the static experiments. For the buffered test, total hardness and calcium hardness, chloride, and sulfate were measured after 3 months of exposure and were assumed to be representative of conditions during the whole time of the experiment. In the buckets with copper gutter at pH 5 and with aluminum gutter at pH 8, Ca hardness was less than the detection limit of 0.02 mg/L as CaCO3. For the un-buffered test, total hardness and calcium hardness were measured at time zero and after 3 months of exposure, therefore the hardness values after one day of exposure and was assumed to be equal to those measured at time zero. Since only one form of phosphorus species can be included into a Medusa file, $H_2PO_4^-$ was used for solutions with pH 5 since at this pH, $H_2PO_4^-$ is the predominant phosphorus species, and HPO_4^{2-} for solutions with pH 8 since at pH 8, HPO_4^{2-} is a predominant phosphorus species (Golubzov 1966). Other major ions (fluoride, nitrate, total phosphorus, bromide Br^-, manganese, Boron, silicon, sodium, potassium, chloride, and sulfate) for un-buffered tests were measured in the source water were assumed to be the same for all the containers during the whole duration of the experiment.

The tables with predominant species (Appendix C) include the concentrations of the metal species in mol/L which were converted to mg/L of a compound, and then converted to the concentration of heavy metal of interest in mg/L. The cumulative percentage of a heavy metal was calculated in mg/L as a heavy metal constituent and was based on the sorted concentration of the corresponding compounds in mg/L. The predominant species tables show the predominant forms of heavy metal species that account for 99.9% of total metal concentration.

For example, Figure 4.32 is the phase diagram for steel pipe sample submerged into bay water after three months of exposure. In this water sample, the pH is 7 and zinc is predominantly in the free ion form (Zn^{2+}). Full phase diagrams that contain information for a wide range of pH values and contain information for large numbers of potential species in the diagram look overwhelming. Therefore, the phase diagrams for the study area were constructed that showed a smaller portion of full phase diagrams and included the pH values observed during these experiments and a few metal species of interest that had the greatest concentrations (shown in

Appendix C). Figure 4.33 is the Fraction diagram of zinc shows the distribution of zinc species in this sample and also confirms that at pH 7 zinc is mainly in Zn^{2+} form. The Pourbaix diagram Figure 4.34 also shows that at pH 7 and Eh = -0.18V, free ion Zn^{2+} is the predominant species. This information is important in assessing the water toxicity which is greatly affected by the species of heavy metals in the water. Phase, Fraction, and Pourbaix diagrams for the other samples are shown in Appendix C.

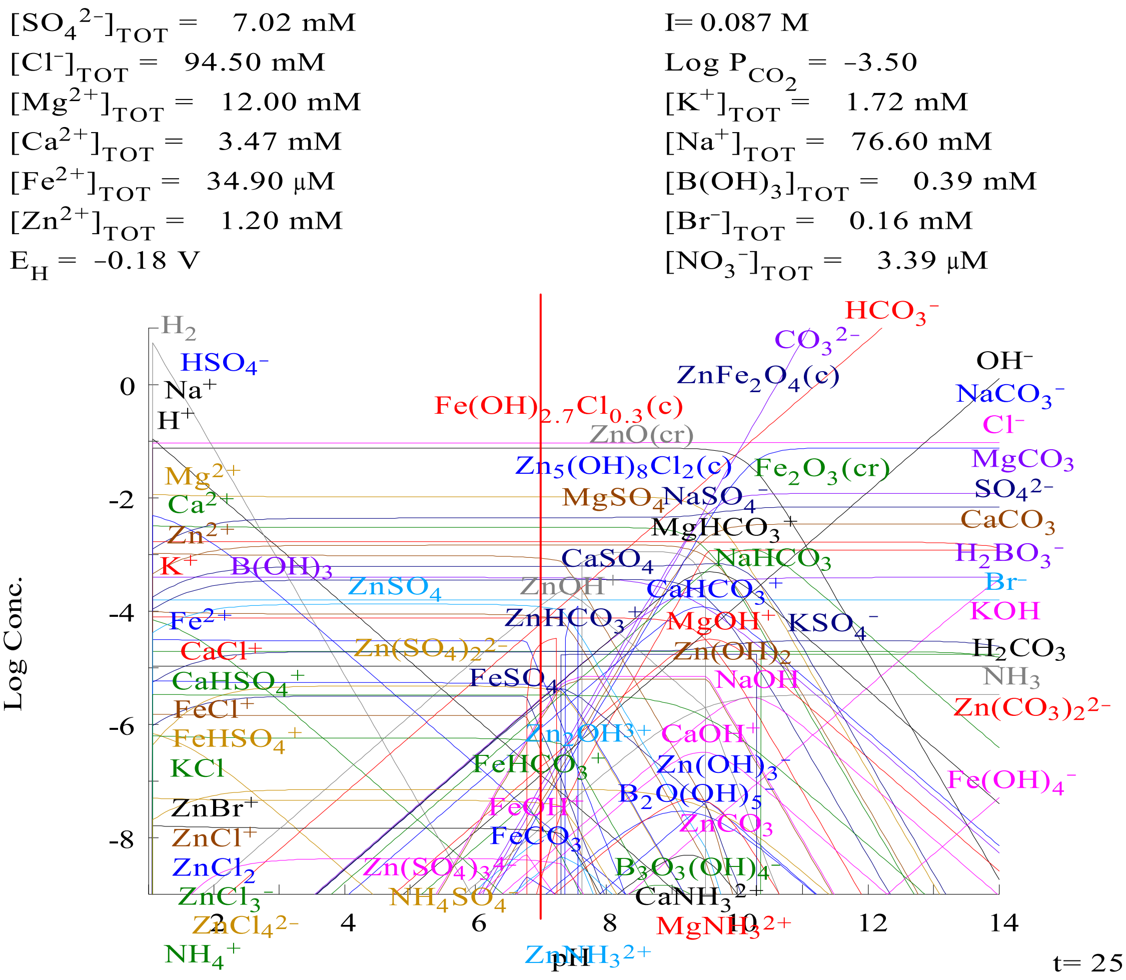


Figure 4.32. Phase diagram for steel pipe section immersed into bay water after three months of exposure.

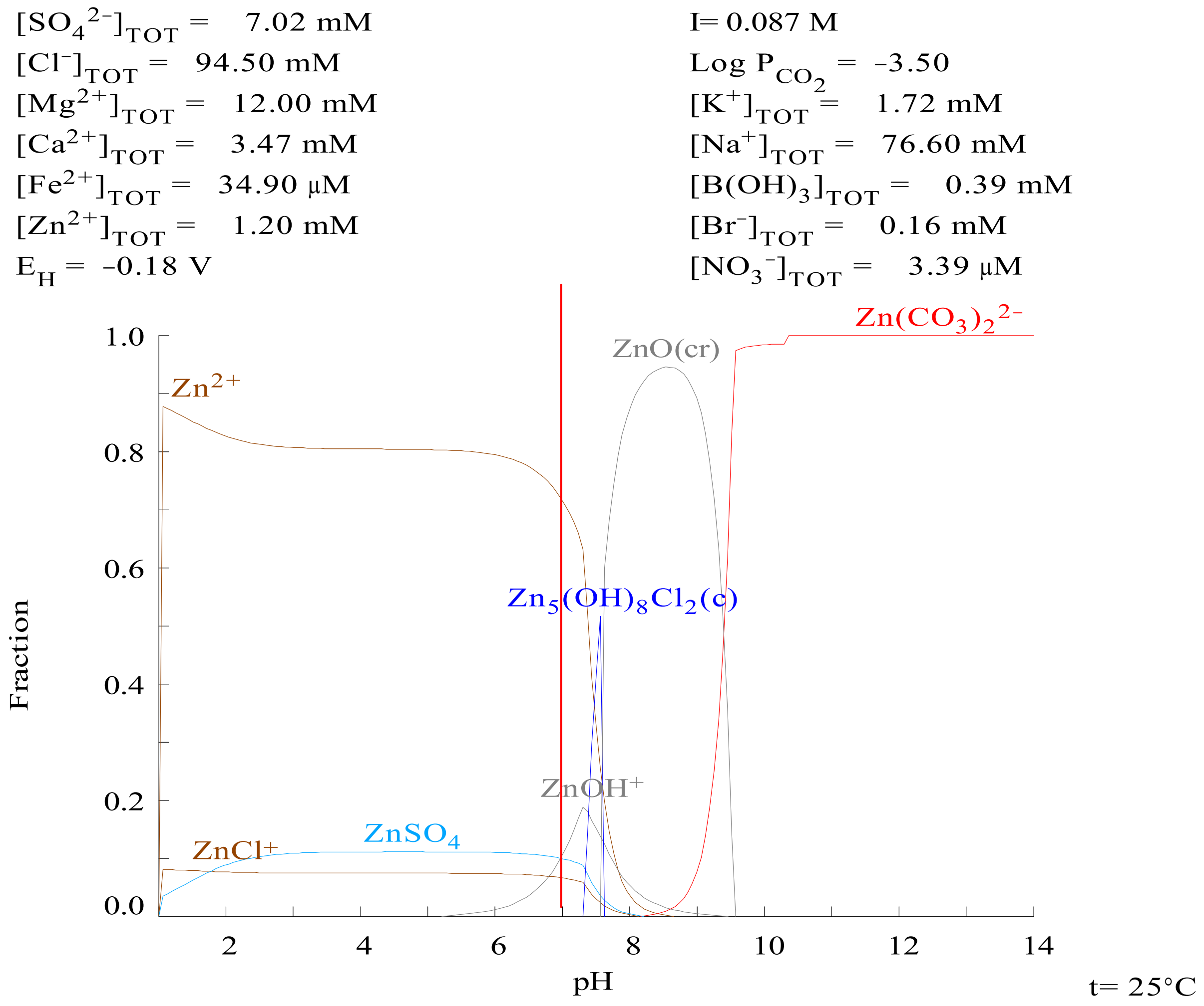


Figure 4.33. Fraction diagram of zinc for steel pipe section immersed into bay water after three months of exposure.

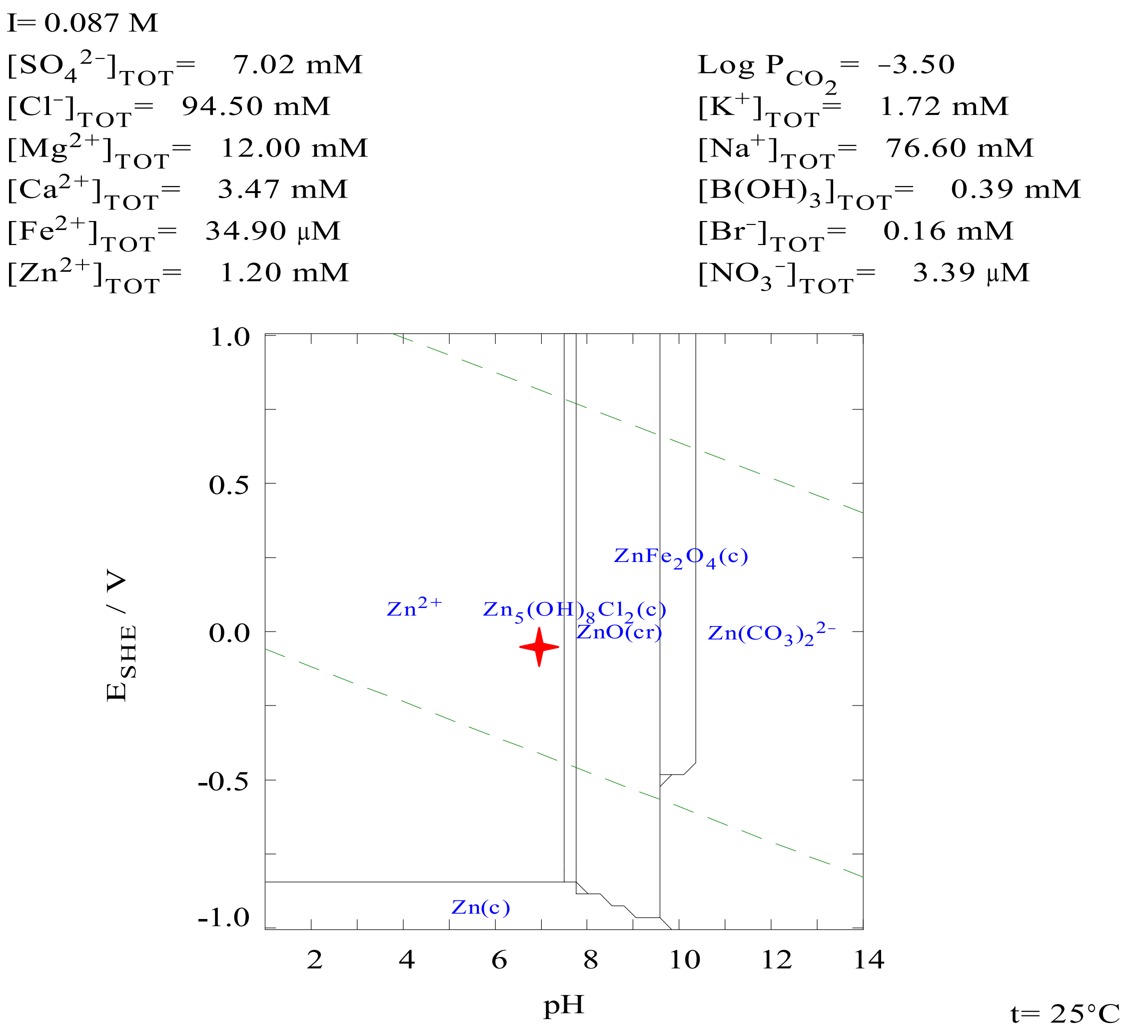


Figure 4.34. Pourbaix diagram of zinc for steel pipe section immersed into bay water after three months of exposure.
Note: the symbol is located at the conditions measured during these tests

The modeled concentrations of zinc and copper compounds in the containers were examined and compared with the theoretical maximum possible solubility of those compounds to determine if zinc and copper would have continued to dissolve in the water if the experiment had continued for a longer time (Tables 4.5.2 through 4.5.13). The calculations were performed for the solubility of those zinc and copper compounds which had the greatest concentrations in those containers. During these calculations, the assumption was made that those zinc and copper compounds are dissolved in pure water (Kreshkov 1971).

The solubility of several compounds:

$$\text{Solubility } CuH_2(PO_4)_2^{2-} = (\text{Solubility Product}/(108\ \gamma_{Cu}^{2+}\ (\gamma_H^{+})^2\ (\gamma_{PO4}^{2-})^2))^{1/5}$$

Equation 4.5.1

$$\text{Solubility } CuH_3(PO_4)_2^{-} = (\text{Solubility Product}/(108\ \gamma_{Cu}^{2+}\ (\gamma_H^{+})^3\ (\gamma_{PO4}^{2-})^2))^{1/6}$$

Equation 4.5.2

$$\text{Solubility } Zn_5(OH)_6(CO_3)_2 = (\text{Solubility Product}/(0.48\ (\gamma_{Zn}^{2+})^5\ (\gamma_{OH}^{-})^6\ (\gamma_{CO3}^{2-})^2))^{1/13}$$

Equation 4.5.3

The solubility of compounds with the KtAn formula (Kreshkov 1971):

$$\text{Solubility KtAn} = (\text{Solubility Product}_{KtAn}/(\gamma_{Kt}\gamma_{An}))^{1/2}$$

Equation 4.5.4

Where,

Kt = cation

An = anion

γ = activity coefficient of cation or anion.

The solubility of compounds with the $KtAn_2$formula (Kreshkov 1971):

$$\text{Solubility } KtAn_2 = (\text{Solubility Product}_{KtAn2}/(4\ \gamma_{Kt}\ (\gamma_{An})^2))^{1/3}$$

Equation 4.5.5

The solubility of compounds with the Kt_2Anformula (Kreshkov 1971):

$$\text{Solubility } Kt_2An = (\text{Solubility Product}_{Kt2An}/(4(\gamma_{Kt})^2\gamma_{An}))^{1/3}$$

Equation 4.5.6

The solubility of compounds with the Kt_3An_2formula (Kreshkov 1971):

Solubility Kt_3An_2= (Solubility Product$_{Kt3An2}$/$(108(\gamma_{Kt})^3 (\gamma_{An})^2))^{1/5}$ Equation 4.5.7

The solubility formulas of other compounds can be found in Kreshkov 1971.

Table 4.5.1 shows solubility products for some reactions. The rest of the solubility products were taken from Medusa. Medusa is available from http://www.kemi.kth.se/medusa/.

Table 4.5.1. Solubility products

Equation	Solubility Product, K_{sp}	Reference
$Zn(OH)_2 \leftrightarrow Zn^{2+} + 2OH^-$	$1.4 * 10^{-17}$	(Lurie 1989)
$ZnCO3 \leftrightarrow Zn^{2+} + CO_3^{2-}$	$1.45 * 10^{-11}$	(Lurie 1989)

Medusa results showed that during the buffered pH tests, $Zn_3(PO_4)_2{:}4H_2O$(c) precipitated in the containers with galvanized steel pipe immersed in pH 5 and pH 8 waters after three months of exposure (Table 4.5.2 and Table 4.5.4). The solubility product for $Zn_3(PO_4)_2{:}4H_2O$(c) is very small ($K_{sp} = 9.1 * 10^{-33}$ (Lurie 1989)) and $Zn_3(PO_4)_2{:}4H_2O$(c) easily precipitates. In pure water, not taking into consideration hydrolysis of phosphoric acid and complex formation, the amount of $Zn_3(PO_4)_2{:}4H_2O$ that can dissolve in water is 5.6E-07mol/L (0.11 mg/L as Zn), however due to hydrolysis and complexation the amount of dissolved $Zn_3(PO_4)_2{:}4H_2O$ was greater that the theoretical value and reached 3.37E-05 mol/L (6.62 mg/L as Zn) in the container with galvanized steel pipe immersed into pH 5 water. Golubzov (1966) pointed out that hydrolysis increases the solubility of insoluble salts in the solution. If the experiment had continued for a longer time, the increase in the concentrations of zinc compounds would not be expected to be large due to the formation of $Zn_3(PO_4)_2{:}4H_2O$ which act as a protective layer (Aramaki, 2003)

Table 4.5.2. The modeled equilibrium concentrations and theoretical maximum possible solubility of zinc species after three months exposure. Galv. steel pipe immersed in pH 5 water.

Compound	Concentration in the water as compound (mol/L)	Concentration in the water as Zn (mg/L)	Solubility of a compound (mol/L)	Amount of Zn from Solubility of a compound (mg/L)
$Zn_3(PO_4)_2{:}4H_2O(c)$	3.37E-05	6.62	5.6E-07	0.11
Zn^{2+}	7.69E-05	5.03	2.32E-06	0.15
$ZnOH^+$	7.80E-07	5.10E-02	9400	6.2 E+08
Sum		11.7		6.2 E+08

In the containers with steel gutter immersed in pH 5 water and steel pipe immersed in bay water, there were zinc complexes and zinc compounds that have high solubility (such as ZnSO4 with solubility of 57.7 g/100g H2O at 25^{o}C and ZnCl2 with solubility of 408 g/100g H2O at 25^{o}C (Lide 2001)), precipitation of zinc compounds was not observed in Medusa results after three months of exposure. The comparison of concentrations of zinc compounds in the containers with the theoretical maximum possible solubility of those compounds showed that if the experiment had continued for a longer time, concentrations of zinc compounds would have continued to dissolve in the water (Table 4.5.3 and Table 4.5.8).

Table 4.5.3. The modeled equilibrium concentrations and theoretical maximum possible solubility of zinc species after three months exposure. Galv. steel gutter immersed in pH 5 water.

Compound	Concentration in the water as compound (mol/L)	Concentration in the water as Zn (mg/L)	Solubility of a compound (mol/L)	Amount of Zn from Solubility of a compound (mg/L)
Zn^{2+}	2.15E-04	14.06	2.32E-06	1.52E-01
$ZnOH^+$	8.92E-07	5.83E-02	9443	$617653*10^3$
$ZnSO_4$	1.41E-07	9.22E-03	1.5E-01	10045
Sum		14.1		6.2E+08

The amount of $Zn_3(PO_4)_2{:}4H_2O(c)$ that had precipitated in the container with galvanized steel pipe immersed in pH 8 water and exceeded the theoretical maximum possible amount after three months of exposure and can be explained by hydrolysis and complexation (Table 4.5.4). Modeled $Zn(CO_3)_2^{2-}$ concentration in the water was smaller the calculated maximum possible concentration indicating that dissolution of that compound in the water is possible, but since protective film of $Zn_3(PO_4)_2:4H_2O(c)$ precipitated, concentration of zinc compounds in the water will not increase. The calculated thickness of $Zn_3(PO_4)_2:4H_2O(c)$ film was 0.5 μm, assuming that the density of that compound is equal to that of zinc.

Table 4.5.4. The modeled equilibrium concentrations and theoretical maximum possible solubility of zinc species after three months exposure. Galv. steel pipe immersed in pH 8 water.

Compound	Concentration in the water as compound (mol/L)	Concentration in the water as Zn (mg/L)	Solubility of a compound (mol/L)	Amount of Zn from Solubility of a compound (mg/L)
$Zn_3(PO_4)_2:4H_2O(c)$	4.19E-04	82.28	9.5E-07	0.19
$Zn(CO_3)_2^{2-}$	1.61E-05	1.06	1.3E-03	84
Sum		83.34		84.19

There was a precipitation of that $Zn_5(OH)_6(CO_3)_2(c)$ and $ZnFe_2O_4(c)$ compounds in the container with galvanized steel gutter immersed in pH 8 water after three months of exposure (Table 4.5.5), indicating that higher concentrations of zinc compounds in the water would not be expected beyond three months period. $Zn_5(CO_3)_2(OH)_6$ and $ZnCO_3$ are the most common compounds in the carbonate films. $Zn_5(CO_3)_2(OH)_6$ (hydrozincate) compound is often found in abundance in protective rust layers of zinc surfaces. This compound is comprised of a combination of $Zn(OH)_2$ and zinc carbonate: $3Zn(OH)_2 + 2Zn(CO_3)_2 \rightarrow Zn_5(CO_3)_2(OH)_6$ (Zaki Ahmad, 2006). It was assumed that modeled $ZnFe_2O_4(c)$ concentration in the water is equal to the maximum possible equilibrium concentration. Theoretically, zinc concentration that could dissolve into the water was 832,220 mg/L, but dissolved only 9.5 mg/L likely due to the protective film of $Zn_5(OH)_6(CO_3)_2(c)$.

Table 4.5.5. The modeled equilibrium concentrations and theoretical maximum possible solubility of zinc species after three months exposure. Galv. steel gutter immersed in pH 8 water.

Compound	Concentration in the water as compound (mol/L)	Concentration in the water as Zn (mg/L)	Solubility of a compound (mol/L)	Amount of Zn from Solubility of a compound (mg/L)
$Zn_5(OH)_6(CO_3)_2(c)$	1.96E-05	6.42	12.72	832135
$Zn(CO_3)_2^{2-}$	4.21E-05	2.75	1.3E-03	84
$ZnFe_2O_4(c)$	2.81E-06	0.18	2.81E-06	0.18
$ZnCO_3$	1.78E-06	0.12	1.2E-05	0.8
Sum		9.5		832220

There was $CuFeO_2$(c) precipitation noted in the container with copper gutter immersed in pH 5 water (0.17 mg/L as Cu and constituted about 3 % from total copper concentration, not shown in the table), and therefore further increase in the concentration of copper compounds in the water would not have been expected. Copper concentration in the container with copper gutter immersed in pH 5 water was greater than the calculated maximum possible copper concentration (Table 4.5.6) due to hydrolysis of phosphate ions and complexation with phosphate ions.

Table 4.5.6. The modeled equilibrium concentrations and theoretical maximum possible solubility of zinc species after three months exposure. Copper gutter immersed in pH 5 water.

Compound	Concentration in the water as compound (mol/L)	Concentration in the water as Zn (mg/L)	Solubility of a compound (mol/L)	Amount of Zn from Solubility of a compound (mg/L)
$CuH_2PO_4^+$	2.16E-05	1.37	3.1E-11	2.0E-06
$CuHPO_4$	2.15E-05	1.37	1.4E-08	8.9E-04
$CuH_2(PO_4)_2^{2-}$	1.98E-05	1.26	4.9E-07	3.1E-02
Cu^{2+}	1.06E-05	0.67	4.19E-07	2.66E-02
Sum		4.67		0.058

For the container with the copper gutter sample immersed in pH 8 water, it was assumed that the calculated maximum possible concentrations of CuO(cr) and $CuFeO_2$(c) were equal to the modeled concentrations in the water. CuO is insoluble in water (Lide 2001). The total copper concentrations of modeled copper species exceed the calculated total maximum possible copper concentration likely due to the hydrolysis of phosphate ions and their complexation. Also, CuO(cr) and $CuFeO_2$(c) formed protective film on the metal surface (Table 4.5.7) and therefore the concentrations of copper compounds in the water would not likely to have increased after three months exposure period.

Table 4.5.7. The modeled equilibrium concentrations and theoretical maximum possible solubility of zinc species after three months exposure. Copper gutter immersed in pH 8 water.

Compound	Concentration in the water as compound (mol/L)	Concentration in the water as Zn (mg/L)	Solubility of a compound (mol/L)	Amount of Zn from Solubility of a compound (mg/L)
CuO(cr)	2.89E-05	1.84	2.89E-05	1.84
$CuFeO_2$(c)	2.69E-06	0.17	2.69E-06	0.17
$CuH_2(PO_4)_2^{2-}$	1.79E-06	0.11	7.6E-07	4.9E-02
Sum		2.12		2.06

No precipitates were formed in the container with the galvanized steel pipe immersed in bay water after three months exposure period (Table 4.5.8). Theoretical calculations of the maximum possible zinc concentrations showed that zinc concentration could further increase in the water after three months of exposure.

Table 4.5.8. The modeled equilibrium concentrations and theoretical maximum possible solubility of zinc species after three months of exposure. Galv. steel pipe immersed in bay water.

Compound	Concentration in the water as compound (mol/L)	Concentration in the water as Zn (mg/L)	Solubility of a compound (mol/L)	Amount of Zn from Solubility of a compound (mg/L)
Zn^{2+}	8.64E-04	56.48	2.40E-06	0.16
$ZnOH^+$	1.22E-04	7.96	9857	$644707*10^3$
$ZnSO_4$	1.20E-04	7.86	0.17	10839
Sum		72.3		6.4E+08

For the container with galvanized steel gutter immersed in bay water, it was assumed that the calculated maximum possible concentration of ZnO and $ZnFe_2O_4$(c) was equal to the modeled concentrations in the water (Table 4.5.9). ZnO is insoluble in water (Lide 2001). Because protective film of ZnO and $ZnFe_2O_4$(c) were formed, further increase of zinc concentration in the water after three months exposure period would not have been likely.

Table 4.5.9. The modeled equilibrium concentrations and theoretical maximum possible solubility of zinc species after three months exposure. Galv. steel gutter immersed in bay water.

Compound	Concentration in the water as compound (mol/L)	Concentration in the water as Zn (mg/L)	Solubility of a compound (mol/L)	Amount of Zn from Solubility of a compound (mg/L)
ZnO(cr)	3.04E-04	19.92	3.04E-04	19.92
Zn^{2+}	9.93E-05	6.49	2.40E-06	0.16
$ZnOH^+$	9.67E-05	6.33	9859	$644859*10^3$
$ZnFe_2O_4$(c)	2.06E-05	1.35	2.06E-05	1.35
Sum		34.1		6.4E+08

For the container with galvanized steel pipe immersed in river water, it was assumed that the calculated maximum possible concentration of $ZnFe_2O_4$(c) was equal to the modeled concentration of $ZnFe_2O_4$(c) in the water. The theoretical maximum possible $Zn(CO3)_2^{2-}$ concentration in the water was 37 mg/L, however its solubility was restricted by the formation of protective films of $Zn_5(OH)_6(CO_3)_2$ (c) and $ZnFe_2O_4$(c) (Table 4.5.10). The calculations showed that theoretical maximum possible concentration of $Zn_5(OH)_6(CO_3)_2$ (c) in the protective film was 489,433 mg/L as Zn.

Table 4.5.10. The modeled equilibrium concentrations and theoretical maximum possible solubility of zinc species after three months exposure. Galv. steel pipe immersed in river water.

Compound	Concentration in the water as compound (mol/L)	Concentration in the water as Zn (mg/L)	Solubility of a compound (mol/L)	Amount of Zn from Solubility of a compound (mg/L)
$Zn_5(OH)_6(CO_3)_2$ (c)	2.0E-04	66.41	7.48	489,433
$ZnFe_2O_4$(c)	1.3E-05	0.83	1.3E-05	0.83
$Zn(CO3)_2^{2-}$	6.7E-06	0.44	5.6E-04	37
Sum		67.68		489,471

The theoretical maximum possible Zn^{2+} concentration in the container with galvanized steel gutter immersed in river water were lower than the modeled concentrations due to the complexation which increases the solubility of compounds, however the solubility of zinc in the water was restricted by the formation of protective film of $Zn_5(OH)_6(CO_3)_2$ (c) (Table 4.5.11).

Table 4.5.11. The modeled equilibrium concentrations and theoretical maximum possible solubility of zinc species after three months exposure. Galv. steel gutter immersed in river water.

Compound	Concentration in the water as compound (mol/L)	Concentration in the water as Zn (mg/L)	Solubility of a compound (mol/L)	Amount of Zn from Solubility of a compound (mg/L)
$Zn_5(OH)_6(CO_3)_2$(c)	3.60E-04	1.18E+02	7.74	506,515
Zn^{2+}	8.20E-04	53.6	1.89E-06	0.12
$ZnOH^+$	1.61E-04	10.5	7365	$481764*10^3$
Sum		182		4.8E+08

It was assumed that the theoretical maximum equilibrium concentrations of Cu(c) and $CuFeO_2$(c) were equal to the modeled concentrations in the water for containers with copper gutter immersed in bay and river waters (Tables 4.5.12 and 4.5.13). Because of the formation of the protective film of $CuFeO_2$(c), the copper concentration would not have been expected to increased in the water after three months of exposure period.

Table 4.5.12. The modeled equilibrium concentrations and theoretical maximum possible solubility of zinc species after three months exposure. Copper gutter immersed in bay water.

Compound	Concentration in the water as compound (mol/L)	Concentration in the water as Zn (mg/L)	Solubility of a compound (mol/L)	Amount of Zn from Solubility of a compound (mg/L)
Cu(c)	5.27E-04	33.51	5.27E-04	33.51
$CuFeO_2$(c)	3.76E-05	2.39	3.76E-05	2.39
Sum		35.9		35.9

Table 4.5.13. The modeled equilibrium concentrations and theoretical maximum possible solubility of zinc species after three months exposure. Copper gutter immersed in river water.

Compound	Concentration in the water as compound (mol/L)	Concentration in the water as Zn (mg/L)	Solubility of a compound (mol/L)	Amount of Zn from Solubility of a compound (mg/L)
Cu(c)	5.42E-05	3.44	5.42E-05	3.44
$CuFeO_2$(c)	3.19E-05	2.03	3.19E-05	2.03
Sum		5.47		5.47

Tables 4.5.14 through 4.5.21 show total measured metal concentrations and modeled metal species at time zero, after one day of exposure and after three months of exposure. The

total percent of compound valence doesn't always add up to 100 due to the rounding. At time zero (water without pipes and gutters), zinc and zinc compounds were predominantly in valence two state in the containers with pH 5 water, and were mostly in valence one state in the containers with pH 8 water. At time zero, copper and copper compounds in the buckets with pH 5 and 8 waters were mainly in valence two state.

After one day of exposure, zinc and zinc compounds were predominantly in valence two state in the samples with steel, copper, and plastic materials immersed in pH 5 water, and mainly in zero and one valence states in the samples with steel, copper, aluminum, and plastic materials immersed in pH 8 water. After one day of exposure, copper and copper compounds in containers with copper materials immersed into pH 5 water were approximately equally distributed between valence states of two, one, and zero, however for the buffered pH 8 waters, copper compounds in containers with copper gutters were predominantly in valence two state which can be explained by the formation of copper complexes with phosphate and other ions. Copper was generally in valence zero state in the samples with copper materials immersed in bay and river waters.

Sandberg et al. (2006) examined corrosion-induced copper runoff from copper sheet, naturally patinated copper and pre-patinated copper in a chloride-rich marine environment during one year. The bioavailable concentration (the portion that is available for uptake by an organism) of released copper comprised a small fraction (14–54%) of the total copper concentration due to complexation towards organic matter in impinging seawater aerosols (Sandberg, et. al., 2006). The authors concluded that released copper is complexed with other ligands which reduce the bioavailability. Factors that influence the bioavailability of copper include alkalinity, hardness, pH and dissolved organic matter. Seawater contains organic matter that is primarily of biotic origin, and a significant portion of copper is most likely complexed with these ligands, which leads to reduction of the bioavailability (Sandberg, et. al., 2006). In this research, the results from Medusa modeling showed that copper released in the containers with copper gutter materials immersed into bay water was almost all in valence zero state. For containers with galvanized steel materials immersed into buffered pH 8 and bay waters, lead was mainly in valence zero after one day of exposure.

After three months of exposure, zinc and zinc compounds in the containers with galvanized steel, copper, aluminum, and plastic materials immersed into buffered pH 5 water were mainly in valence two state after; for galvanized steel, copper, aluminum, concrete, and plastic materials immersed into buffered pH 8, bay, and river waters, zinc was in one or zero valence states. For containers with copper materials immersed into pH 5 water, the valence state of copper and cooper compounds was approximately equally distributed between two, one, and zero and for copper materials submerged into buffered pH 8, bay, and river waters copper was predominantly in zero valence state after three months of exposure. Lead in containers with galvanized steel materials immersed into pH 5, pH 8, bay and river waters was mainly in zero valence state after three months of exposure.

Table 4.5.14. Total measured copper concentrations and modeled species after time zero.

Sample	Total Measured Cu Concentration (mg/L as Cu)	Compound Valence, mg/L as Cu			Compound Valence, %		
		Two or greater	**One**	**Zero**	**Two or greater**	**One**	**Zero**
pH 5 P. PVC	0.09	3.3E-02 $CuH_2(PO_4)_2^{2-}$ Cu^{2+} $CuH_3(PO_4)_2^{2-}$	3.3E-02 $CuH_2PO_4^+$ $CuH_3(PO_4)^{2-}$ Cu^+	2.4E-02 $CuHPO_4$ CuH_2PO_4 $Cu(H_2PO_4)_2$	37	36	27
pH 8 P. PVC	0.09	8.8E-02 $CuH_2(PO_4)_2^{2-}$ $CuH_3(PO_4)_2^{2-}$ Cu^{2+}	1.2E-04 Cu^+ $Cu(OH)_2^-$ $CuOH^+$	1.8E-03 $CuHPO_4$ $CuCO_3$ $Cu(OH)_2$	98	0.14	2.0

Table 4.5.15. Total measured zinc concentrations and modeled species at time zero.

Sample	Total Measured Zn Concentration (mg/L as Zn)	Compound Valence, mg/L as Zn			Compound Valence, %		
		Two or greater	One	Zero	Two or greater	One	Zero
pH 5 P. PVC	0.25	0.25 Zn^{2+} $Zn(SO_4)_2^{2-}$ Zn_2OH^{3+}	4.2E-04 $ZnOH^+$ $ZnHCO_3^+$	1.1E-03 $ZnSO_4$ $ZnCO_3$ $Zn(OH)_2$	99	0.17	0.45
pH 8 P. PVC	0.17	6.0E-02 Zn^{2+} $Zn(CO_3)_2^{2-}$ $Zn(SO_4)_2^{2-}$	8.2E-02 $ZnOH^+$ $ZnHCO_3^+$ $Zn(OH)_3^-$	2.8E-02 $ZnCO_3$ $Zn(OH)_2$ $Zn_3(PO_4)_2{:}4H_2O(c)$	35	48	17
pH 8 P. HDPE	0.03	1.0E-02 Zn^{2+} $Zn(CO_3)_2^{2-}$ $Zn2OH^{3+}$	1.6E-02 $ZnOH^+$ $ZnHCO_3^+$ $Zn(OH)_3^-$	4.2E-03 $ZnCO_3$ $Zn(OH)_2$	34	52	14
pH 8 P. Steel	0.02	6.8E-03 Zn^{2+} $Zn(CO_3)_2^{2-}$ $Zn(SO_4)_2^{2-}$	1.0E-02 $ZnOH^+$ $ZnHCO_3^+$ $Zn(OH)_3^-$	2.8E-03 $ZnCO_3$ $Zn(OH)_2$	34	52	14
pH 8 G. Steel	0.02	6.3E-03 Zn^{2+} $Zn(CO_3)_2^{2-}$ Zn_2OH^{3+}	1.0E-02 $ZnOH^+$ $ZnHCO_3^+$ $Zn(OH)_3^-$	3.3E-03 $ZnCO_3$ $Zn(OH)_2$	31	52	17
pH 8 G. Copper	0.02	6.3E-03 Zn^{2+} $Zn(CO_3)_2^{2-}$ $Zn(SO_4)_2^{2-}$	1.0E-02 $ZnOH^+$ $ZnHCO_3^+$ $Zn(OH)_3^-$	3.3E-03 $ZnCO_3$ $Zn(OH)_2$	31	52	17
River P. HDPE	0.02	3.8E-03 Zn^{2+} $Zn(CO_3)_2^{2-}$ $Zn(SO_4)_2^{2-}$	1.2E-02 $ZnOH^+$ $ZnHCO_3^+$ $ZnCl^+$	4.4E-03 $ZnCO_3$ $Zn(OH)_2$ $ZnSO_4$	19	59	22
River G. Alum	0.02	3.8E-03 Zn^{2+} $Zn(CO_3)_2^{2-}$ $Zn(SO_4)_2^{2-}$	1.2E-02 $ZnOH^+$ $ZnHCO_3^+$ $ZnCl^+$	4.4E-03 $ZnCO_3$ $Zn(OH)_2$ $ZnSO_4$	19	59	22
River G. Steel	0.02	3.4E-03 Zn^{2+} $Zn(CO_3)_2^{2-}$ $Zn(SO_4)_2^{2-}$	1.2E-02 $ZnOH^+$ $ZnHCO_3^+$ $ZnCl^+$	4.9E-03 $ZnCO_3$ $Zn(OH)_2$ $ZnSO_4$	17	59	25
River G. Copper	0.02	3.8E-03 Zn^{2+} $Zn(CO_3)_2^{2-}$ $Zn(SO_4)_2^{2-}$	1.2E-02 $ZnOH^+$ $ZnHCO_3^+$ $ZnCl^+$	4.3E-03 $ZnCO_3$ $Zn(OH)_2$ $ZnSO_4$	19	59	22

Table 4.5.16. Total measured zinc concentrations and modeled species after one day.

Sample	Total Measured Zn Concentration (mg/L as Zn)	Compound Valence, mg/L as Zn			Compound Valence, %		
		Two or greater	One	Zero	Two or greater	One	Zero
pH 5 P. PVC	0.22	2.2E-01 Zn^{2+} $Zn(SO_4)_2^{2-}$	5.9E-04 $ZnOH^+$ $ZnHCO_3^+$	10E-04 $ZnSO_4$ $ZnCO_3$ $Zn(OH)_2$	99	0.27	0.45
pH 5 P. HDPE	0.02	2.0E-02 Zn^{2+}	2.6E-05 $ZnOH^+$	1.0E-05 $ZnSO_4$	100	0.13	0.05

		$Zn(SO_4)_2^{2-}$	$ZnHCO_3^+$	$ZnCO_3$ $Zn(OH)_2$			
pH 5. P. Steel	10.20	10 Zn^{2+} $Zn(SO_4)_2^{2-}$	5.8E-02 $ZnOH^+$ $ZnHCO_3^+$	1.7E-02 $ZnSO_4$ $ZnCO_3$ $Zn(OH)_2$	99	0.57	0.17
pH 5. G. Steel	14.20	14 Zn^{2+} Zn_2OH^{3+}	4.4E-02 $ZnOH^+$ $ZnHCO_3^+$	9.3E-03 $ZnSO_4$ $ZnCO_3$ $Zn(OH)_2$	100	0.31	0.07
pH 5. G. Copper	0.04	4.0E-02 Zn^{2+} $Zn(SO_4)_2^{2-}$	7.0E-05 $ZnOH^+$ $ZnHCO_3^+$	3.5E-05 $ZnSO_4$ $ZnCO_3$ $Zn(OH)_2$	100	0.17	0.09
pH 8 P. PVC	0.16	0.054 Zn^{2+} $Zn(CO_3)_2^{2-}$	0.083 $ZnOH^+$ $ZnHCO_3^+$	0.023 $ZnCO_3$ $Zn(OH)_2$ $ZnSO_4$	34	52	14
pH 8 P. HDPE	0.02	2.0E-02 Zn^{2+} $Zn(SO_4)_2^{2-}$	3.4E-05 $ZnOH^+$ $ZnHCO_3^+$	1.6E-06 $ZnSO_4$ $ZnCO_3$ $Zn(OH)_2$	100	0.17	0.01
pH 8. P. Steel	1.01	5.4E-02 Zn^{2+} $Zn(CO_3)_2^{2-}$	9.0E-02 $ZnOH^+$ $ZnHCO_3^+$	8.7E-01 $Zn_3(PO_4)_2{:}4H_2O(c)$ $ZnCO_3$ $Zn(OH)_2$	5.3	8.8	86
pH 8. G. Alum	0.02	6.3E-03 Zn^{2+} $Zn(CO_3)_2^{2-}$	1.0E-02 $ZnOH^+$ $ZnHCO_3^+$	3.3E-03 $ZnCO_3$ $Zn(OH)_2$ $ZnSO_4$	31	52	17
pH 8. G. Steel	2.09	5.8E-02 Zn^{2+} $Zn(CO_3)_2^{2-}$	9.9E-02 $ZnOH^+$ $ZnHCO_3^+$ $Zn(OH)_3^-$	1.9 $Zn_3(PO_4)_2{:}4H_2O(c)$ $ZnCO_3$ $Zn(OH)_2$	2.8	4.7	93
pH 8. G. Copper	0.02	5.9E-03 Zn^{2+} $Zn(CO_3)_2^{2-}$	1.0E-02 $ZnOH^+$ $ZnHCO_3^+$	3.8E-03 $ZnCO_3$ $Zn(OH)_2$, $ZnSO_4$	30	52	19
Bay P. Steel	8.4	0.2 Zn^{2+} $Zn(CO_3)_2^{2-}$ $Zn(SO_4)_2^{2-}$	0.42 $ZnOH^+$ $ZnCl^+$ $ZnHCO_3^+$	7.8 $Zn_5(OH)_6(CO_3)_2(c)$ $ZnFe_2O_4(c)$ $ZnCO_3$	2.3	5.0	93
Bay G. Steel	4.8	0.20 Zn^{2+} $Zn(CO_3)_2^{2-}$ $Zn(SO_4)_2^{2-}$	0.42 $ZnOH^+$ $ZnCl^+$ $ZnHCO_3^+$	4.2 $Zn_5(OH)_6(CO_3)_2(c)$ $ZnFe_2O_4(c)$ $ZnCO_3$	4.1	8.7	87
Bay G. Copper	0.05	1.4E-02 Zn^{2+} $Zn(CO_3)_2^{2-}$ $Zn(SO_4)_2^{2-}$	2.6E-02 $ZnOH^+$ $ZnCl^+$ $ZnHCO_3^+$	1.0E-02 $ZnCO_3$ $Zn(OH)_2$ $ZnSO_4$	28	52	20
River P. Steel	6.1	0.25 $Zn(CO_3)_2^{2-}$ Zn^{2+} $Zn(SO_4)_2^{2-}$	0.17 $ZnOH^+$ $ZnHCO_3^+$ $Zn(OH)_3^-$	5.6 $Zn_5(OH)_6(CO_3)_2(c)$ $ZnCO_3$ $ZnFe_2O_4(c)$	4.2	2.8	93
River G. Steel	1.20	0.19 $Zn(CO_3)_2^{2-}$ Zn^{2+} $Zn(SO_4)_2^{2-}$	0.20 $ZnOH^+$ $ZnHCO_3^+$ $Zn(OH)_3^-$	0.82 $Zn_5(OH)_6(CO_3)_2$ $ZnCO_3$ $ZnFe_2O_4(c)$	16	16	68
River G. Copper	0.02	3.2E-03 Zn^{2+} $Zn(CO_3)_2^{2-}$ $Zn(SO_4)_2^{2-}$	1.1E-02 $ZnOH^+$ $ZnHCO_3^+$ $ZnCl^+$	5.4E-03 $ZnCO_3$ $Zn(OH)_2$ $ZnSO_4$	16	57	27

Table 4.5.17. Total measured copper concentrations and modeled species after one day.

Sample	Total Measured Cu Concentration (mg/L as Cu)	Compound Valence, mg/L as Cu			Compound Valence, %		
		Two or greater	One	Zero	Two or greater	One	Zero
pH 5 P. PVC	0.08	3.7E-02 $CuH_2(PO_4)_2^{2-}$ Cu^{2+} $CuH_3(PO_4)_2^{2-}$	2.1E-02 $CuH_2PO_4^{+}$ $CuH_3(PO_4)_2^{-}$ Cu^{+}	2.3E-02 $CuHPO_4$ CuH_2PO_4 $Cu(H_2PO_4)_2$	46	26	28
pH 5 G. Copper	6.82	2.5 $CuH_2(PO_4)_2^{2-}$ Cu^{2+} $CuH_3(PO_4)_2^{2-}$	2.5 $CuH_2PO_4^{+}$ $CuH_3(PO_4)_2^{-}$ Cu^{+}	1.8 $CuHPO_4$ $Cu(H_2PO_4)_2$ CuH_2PO_4	37	36	27
pH 8 P. PVC	0.08	7.8E-02 $CuH_2(PO_4)_2^{2-}$ $CuH_3(PO_4)_2^{2-}$ Cu^{2+}	1.2E-04 $Cu(OH)_2^{-}$ Cu^{+} $CuOH^{+}$	1.7E-03 $CuHPO_4$ $CuCO_3$ $Cu(OH)_2$	98	0.15	2.1
pH 8 G. Copper	0.29	2.8E-01 $CuH_2(PO_4)_2^{2-}$ Cu^{2+} $CuH_3(PO_4)_2^{2-}$	2.5E-04 $Cu(OH)_2^{-}$ $CuOH^{+}$ Cu^{+}	6.5E-03 $CuHPO_4$ $CuCO_3$ $Cu(OH)_2$	98	8.8E-02	2.2
Bay G. Copper	2.11	1.1E-04 $CuCl_3^{2-}$ $Cu_2Cl_4^{2-}$ Cu^{2+}	3.2E-03 $CuCl_2^{-}$ Cu^{+} $Cu(OH)_2^{-}$	2.1 Cu(c) $CuFeO_2$(c) $CuSO_4$	5.0E-03	0.15	100
River G. Copper	0.60	5.5E-09 $CuCl_3^{2-}$ Cu^{2+} $Cu(CO_3)_2^{2-}$	1.9E-05 $CuCl_2^{-}$ $Cu(OH)_2^{-}$ Cu^{+}	0.6 Cu(c) $CuFeO_2$(c) $CuCO_3$	9.2E-07	3.2E-03	100

Table 4.5.18. Total measured lead concentrations and modeled species after one day.

Sample	Total Measured Pb Concentration (mg/L as Pb)	Compound Valence, mg/L as Pb			Compound Valence, %		
		Two or greater	One	Zero	Two or greater	One	Zero
pH 8 G. Steel	0.008	5.9E-05 $Pb(CO_3)_2^{2-}$ Pb^{2+}	1.8E-05 $PbOH^{+}$ $PbHCO_3^{+}$	8.0E-03 $Pb_3(PO_4)_2$(c) $PbCO_3$ $PbHPO_4$	0.73	0.22	99
Bay P. Steel	0.012	1.1E-03 $Pb(CO_3)_2^{2-}$ Pb^{2+} $Pb(SO_4)_2^{2-}$	4.6E-04 $PbOH^{+}$ $PbCl^{+}$ $PbHCO_3^{+}$	1.1E-02 $PbCO_3$ $PbSO_4$ $Pb(OH)_2$	9.3	3.8	87
Bay G. Steel	0.005	4.7E-04 $Pb(CO_3)_2^{2-}$ Pb^{2+} $Pb(SO_4)_2^{2-}$	1.9E-04 $PbOH^{+}$ $PbCl^{+}$ $PbHCO_3^{+}$	4.4E-03 $PbCO_3$ $PbSO_4$ $Pb(OH)_2$	9.3	3.8	87

Table 4.5.19. Total measured zinc concentrations and modeled species after three months of exposure.

Sample	Total Measured Zn Concentration (mg/L as Zn)	Compound Valence, mg/L as Zn			Compound Valence, %		
		Two or greater	One	Zero	Two or greater	One	Zero
pH 5 P. Steel	11.70	5.03 Zn^{2+} $Zn(SO_4)_2^{2-}$ Zn_2OH^{3+}	0.05 $ZnOH^+$ $ZnHCO_3^+$	6.6 $Zn_3(PO_4)_2{:}4H_2O(c)$ $ZnSO_4$ $ZnCO_3$ $Zn(OH)_2$	43	0.44	57
pH 5 G. Steel	14.10	14.1 Zn^{2+} Zn_2OH^{3+} $Zn(SO_4)_2^{2-}$	0.06 $ZnOH^+$ $ZnHCO_3^+$	0.01 $ZnSO_4$ $ZnCO_3$ $Zn(OH)_2$	100	0.42	0.07
pH 8 P. Steel	84.30	1.1 $Zn(CO_3)_2^{2-}$ Zn^{2+} $Zn(OH)_4^{2-}$	0.17 $ZnOH^+$ $ZnHCO_3^+$ $Zn(OH)_3^-$	83 $Zn_3(PO_4)_2{:}4H_2O(c)$ $ZnFe_2O_4(c)$ $ZnCO_3$ $Zn(OH)_2$	1.3	0.17	99
pH 8 G. Steel	9.69	2.8 $Zn(CO_3)_2^{2-}$ Zn^{2+} $Zn(OH)_4^{2-}$	10E-02 $ZnOH^+$ $ZnHCO_3^+$ $Zn(OH)_3^-$	6.8 $Zn_5(OH)_6(CO3)_2(c)$ $ZnFe_2O_4(c)$ $ZnCO_3$ $Zn(OH)_2$	29	1.0	70
pH 5 PVC	0.44	0.44 Zn^{2+} $Zn(SO4)_2^{2-}$ $Zn2OH^{3+}$	1.2E-03 $ZnOH^+$ $ZnHCO_3^+$ $Zn(OH)_3$-	2.0E-03 $ZnSO_4$ $ZnCO_3$ $Zn(OH)_2$	99	0.27	0.45
pH 8 PVC	0.68	8.4E-02 $Zn(CO_3)_2^{2-}$ Zn^{2+} $Zn(SO_4)_2^{2-}$	1.1E-01 $ZnOH^+$ $ZnHCO_3^+$ $Zn(OH)_3^-$	0.49 $Zn_3(PO_4)_2{:}4H_2O(c)$ $ZnCO_3$ $Zn(OH)_2$ $ZnSO_4$	12	16	72
pH 5 HDPE	0.06	6.0E-02 Zn^{2+} $Zn(SO_4)_2^{2-}$	6.6E-05 $ZnOH^+$ $ZnHCO_3^+$	3.1E-05 $ZnSO_4$ $ZnCO_3$ $Zn(OH)_2$	100	0.11	5.2E-02
pH 8 HDPE	0.05	1.7E-02 $Zn(CO_3)_2^{2-}$ Zn^{2+} Zn_2OH^{3+}	2.1E-02 $ZnOH^+$ $ZnHCO_3^+$ $Zn(OH)_3^-$	1.2E-02 $ZnCO_3$ $Zn(OH)_2$ $ZnSO_4$	33	43	25
pH 5 Alum	0.02	2.0E-02 Zn^{2+} $Zn(SO_4)_2^{2-}$ Zn_2OH^{3+}	2.2E-05 $ZnOH^+$ $ZnHCO_3^+$ $Zn(OH)_3^-$	1.2E-05 $ZnSO_4$ $ZnCO_3$ $Zn(OH)_2$	100	0.11	0.06
pH 8 Alum	0.21	4.9E-02 $Zn(CO_3)_2^{2-}$ Zn^{2+} Zn_2OH^{3+}	6.4E-02 $ZnOH^+$ $ZnHCO_3^+$ $Zn(OH)_3^-$	9.7E-02 $ZnFe_2O_4(c)$ $ZnCO_3$ $Zn(OH)_2$ $ZnSO_4$	23	30	46
pH5 Copper	0.13	0.13 Zn^{2+} $Zn(SO_4)_2^{2-}$ Zn_2OH^{3+}	2.6E-04 $ZnOH^+$ $ZnHCO_3^+$ $Zn(OH)_3^-$	1.1E-04 $ZnSO_4$ $ZnCO_3$ $Zn(OH)_2$	100	0.20	0.09
pH 8 Copper	0.02	1.2E-02 $Zn(CO_3)_2^{2-}$ Zn^{2+}	3.9E-03 $ZnOH^+$ $ZnHCO_3^+$	4.1E-03 $ZnCO_3$ $Zn(OH)_2$	60	19	20

		$Zn(OH)_4^{2-}$	$Zn(OH)_3^-$	$ZnSO_4$			
pH 8 Vinyl	0.04	1.3E-02 $Zn(CO_3)_2^{2-}$ Zn^{2+} Zn_2OH^{3+}	1.7E-02 $ZnOH^+$ $ZnHCO_3^+$ $Zn(OH)_3^-$	9.8E-03 $ZnCO_3$ $Zn(OH)_2$ $ZnSO_4$	33	43	25
pH 8 Concrete	0.03	2.4E-02 $Zn(CO_3)_2^{2-}$ Zn^{2+} $Zn(OH)_4^{2-}$	2.1E-03 $ZnOH^+$ $ZnHCO_3^+$ $Zn(OH)_3^-$	3.5E-03 $ZnCO_3$ $Zn(OH)_2$ $ZnSO_4$	81	7.1	12
Bay P. Steel	78.6	57 Zn^{2+} $Zn(SO_4)_2^{2-}$ $ZnCl_4^{2-}$ Zn_2OH^{3+}	13 $ZnOH^+$ $ZnCl^+$ $ZnHCO_3^+$ $ZnCl_3^-$	8.3 $ZnSO_4$ $ZnCl_2$ $ZnCO_3$ $Zn(OH)_2$	72	17	11
Bay G. Steel	36.7	6.6 Zn^{2+} $Zn(SO_4)_2^{2-}$ $Zn(CO_3)_2^{2-}$	7.1 $ZnOH^+$ $ZnCl^+$ $ZnHCO_3^+$	23 $ZnO(cr)$ $ZnFe_2O_4(c)$ $ZnSO_4$	18	19	63
River P. PVC	0.03	4.9E-03 Zn^{2+} $Zn(CO_3)_2^{2-}$ $Zn(SO_4)_2^{2-}$	1.5E-02 $ZnOH^+$ $ZnHCO_3^+$ $ZnCl^+$	9.6E-03 $ZnCO_3$ $Zn(OH)_2$ $ZnSO_4$	16	51	32
River P. HDPE	0.03	4.7E-03 Zn^{2+} $Zn(CO_3)_2^{2-}$ $Zn(SO_4)_2^{2-}$	1.6E-02 $ZnOH^+$ $ZnHCO_3^+$ $ZnCl^+$	9.0E-03 $ZnCO_3$ $Zn(OH)_2$ $ZnSO_4$	16	55	30
River P. Steel	68	0.44 $Zn(CO_3)_2^{2-}$ $Zn(SO4)_2^{2-}$ $Zn(OH)_4^{2-}$	0.13 $ZnOH^+$ Zn^{2+} $ZnHCO_3^+$	67 $Zn_5(OH)_6(CO_3)_2$ $ZnFe_2O_4(c)$ $ZnCO_3$	0.65	0.18	99
River G. Alum	0.03	4.7E-03 Zn^{2+} $Zn(CO_3)_2^{2-}$ $Zn(SO_4)_2^{2-}$	1.6E-02 $ZnOH^+$ $ZnHCO_3^+$ $ZnCl^+$	9.0E-03 $ZnCO_3$ $Zn(OH)_2$ $ZnSO_4$	16	55	30
River G. Steel	190	54 Zn^{2+} $Zn(SO_4)_2^{2-}$ Zn_2OH^{3+}	11 $ZnOH^+$ $ZnCl^+$ $ZnHCO_3^+$	126 $Zn_5(OH)_6(CO_3)_2(c)$ $ZnSO_4$ $ZnFe_2O_4(c)$	28	5.8	66
River G. Copper	0.5	7.9E-02 Zn^{2+} $Zn(CO_3)_2^{2-}$ $Zn(SO_4)_2^{2-}$	2.8E-01 $ZnOH^+$ $ZnHCO3^+$ $ZnCl^+$	1.4E-01 $ZnCO_3$ $Zn(OH)_2$ $ZnSO_4$	16	56	29

Table 4.5.20. Total measured copper concentrations and modeled species after three months of exposure.

Sample	Total Measured Cu Concentration (mg/L as Cu)	Compound Valence, mg/L as Cu			Compound Valence		
		Two or greater	One	Zero	Two or greater	One	Zero
pH 8 P. Steel	0.03	7.3E-12 $Cu(CO_3)_2^{2-}$ $CuH_3(PO_4)_2^{2-}$ Cu^{2+}	1.0E-11 $Cu(OH)_2^-$ Cu^+ $CuOH^+$ $CuHCO_3^+$ $Cu(OH)_3^-$	0.03 $CuFeO_2(c)$ $CuH_2(PO_4)_2^{2-}$ $CuCO_3$ $CuHPO_4$ $Cu(OH)_2$	2.4E-08	3.4E-08	100
pH 8 G. Steel	0.03	2.4E-10 $CuH_2(PO_4)_2^{2-}$	1.6E-11 $Cu(OH)_2^-$	3.0E-02 $CuFeO_2(c)$	8.1E-07	5.3E-08	100

		$Cu(CO_3)_2^{2-}$ $Cu^{\ 2+}$ $CuH_3(PO_4)_2^{2-}$	$CuOH^+$ Cu^+ $Cu(OH)_3^-$ $CuHCO_3^+$	$CuCO_3$ $CuHPO_4$ $Cu(OH)_2$			
pH 5 PVC	0.23	0.04 $CuH_2(PO_4)_2^{2-}$ $Cu^{\ 2+}$ $CuH_3(PO_4)_2^{2}$	0.02 $CuH_2PO_4^+$ $CuH_3(PO_4)_2^-$ Cu^+	0.16 $CuFeO_2(c)$ $CuHPO_4$ CuH_2PO_4 $Cu(H_2PO_4)_2$	19	11	71
pH 8 PVC	0.21	6.0E-02 $CuH_2(PO_4)_2^{2-}$ $Cu(CO_3)_2^{2-}$ $CuH_3(PO_4)_2^{2}$ $Cu^{\ 2+}$	2.4E-04 $Cu(OH)_2^-$ Cu^+ $CuOH^+$	0.15 $CuFeO_2(c)$ $CuHPO_4$ $CuCO_3$ $Cu(OH)_2$	28	0.11	71
pH 5 HDPE	0.03	3.6E-06 Cu^{2+} $CuH_2(PO_4)_2^{2-}$ $CuH_3(PO_4)_2^{2-}$	5.1E-06 $CuH_2PO_4^+$ $CuH_3(PO_4)_2^-$ Cu^+	0.03 $CuFeO_2(c)$ $CuHPO_4$ CuH_2PO_4	1.2E-02	1.7E-02	100
pH 8 HDPE	0.03	4.4E-10 $CuH_2(PO_4)_2^{2-}$ $Cu(CO_3)_2^{2-}$ $CuH_3(PO_4)_2^{2-}$ $Cu^{\ 2+}$	1.8E-12 $Cu(OH)_2^-$ Cu^+ $CuOH^+$	0.03 $CuFeO_2(c)$ $CuHPO_4$ $CuCO_3$ $Cu(OH)_2$	1.5E-06	5.9E-09	100
pH 5 Alum	0.03	2.9E-06 $Cu^{\ 2+}$ $CuH_2(PO_4)_2^{2-}$ $CuH_3(PO_4)_2^{2-}$	4.8E-06 $CuH_2PO_4^+$ $CuH_3(PO_4)_2^-$ Cu^+ $Cu(H_2PO_4)_2^-$	0.03 $CuFeO_2(c)$ $CuHPO_4$ CuH_2PO_4 $Cu(H_2PO_4)_2$	1.6E-02	2.3E-02	100
pH 8 Alum	0.03	7.1E-10 $CuH_2(PO_4)_2^{2-}$ $Cu(CO_3)_2^{2-}$ Cu^{2+} $CuH_3(PO_4)_2^{2-}$	2.3E-12 $Cu(OH)_2^-$ $CuOH^+$ Cu^+	0.03 $CuFeO_2(c)$ $CuHPO_4$ $CuCO_3$ $Cu(OH)_2$	2.4E-06	7.7E-09	100
pH 5 Copper	5.10	1.9 $CuH_2(PO_4)_2^{2-}$ $Cu^{\ 2+}$ $CuH_3(PO_4)_2^{2-}$	1.6 $CuH_2PO_4^+$ $CuH_3(PO_4)_2^-$ Cu^+ $Cu(H_2PO_4)_2^-$ $CuOH^+$	1.6 $CuHPO_4$ $CuFeO_2(c)$ $Cu(H_2PO_4)_2$ CuH_2PO_4	38	32	30
pH 8 Copper	2.13	0.12 $CuH_2(PO_4)_2^{2-}$ $Cu(CO_3)_2^{2-}$ $Cu^{\ 2+}$	4.3E-04 $Cu(OH)_2^-$ $CuOH^+$ $CuHCO_3^+$ Cu+ $Cu(OH)_3^-$ $CuH_3(PO_4)_2^-$ $CuH_2PO_4^+$	2.0 CuO(cr) $CuFeO_2(c)$ $CuCO_3$ $CuHPO_4$ $Cu(OH)_2$	5.4	0.02	95
pH 5 Vinyl	0.03	4.7E-06 $Cu^{\ 2+}$ $CuH_2(PO_4)_2^{2-}$ $CuH_3(PO_4)_2^{2-}$	6.8E-06 $CuH_2PO_4^+$ $CuH_3(PO_4)_2^-$ Cu^+	0.03 $CuFeO_2(c)$ $CuHPO_4$ CuH_2PO_4 $Cu(H_2PO_4)_2$	1.6E-02	2.3E-02	100
pH 8 Vinyl	0.02	4.8E-10 $CuH_2(PO_4)_2^{2-}$ $Cu(CO_3)_2^{2-}$ $CuH_3(PO_4)_2^{2-}$ $Cu^{\ 2+}$	1.8E-12 $Cu(OH)_2^-$ Cu^+ $CuOH^+$	0.02 $CuFeO_2(c)$ $CuHPO_4$ $CuCO_3$	2.4E-06	8.9E-09	100
Bay G. Copper	35.90	9.4E-05 $CuCl_3^{2-}$ $Cu_2Cl_4^{2-}$	2.8E-03 $CuCl_2^-$ Cu^+	36 Cu(c) $CuFeO_2(c)$	2.6E-04	7.8E-03	100

		Cu^{2+}	$Cu(OH)_2^-$	CuCl			
River G. Copper	5.47	4.4E-08 $CuCl_3^{2-}$ Cu^{2+} $Cu(CO_3)_2^{2-}$	1.4E-04 $Cu(OH)_2^-$ $CuCl_2^-$ Cu^+	5.5 Cu(c) $CuFeO_2$(c) $CuCO_3$	8.0E-07	2.5E-03	100

Table 4.5.21. Total measured lead concentrations and modeled species after three months of exposure.

Sample	**Total Measured Pb Concentration (mg/L as Pb)**	**Compound Valence, mg/L as Pb**			**Compound Valence**		
		Two or greater	**One**	**Zero**	**Two or greater**	**One**	**Zero**
pH 5 P. Steel	0.247	9.3E-04 Pb^{2+} $Pb(SO_4)_2^{2-}$ Pb_2OH^{3+}	7.5E-04 $PbH_2PO_4^+$ $PbOH^+$ $PbHCO_3^+$	0.24 $PbHPO_4$(c) $PbHPO_4$ $PbSO_4$	0.38	0.30	99
pH 5 G. Steel	0.037	2.2E-03 Pb^{2+} $Pb(SO_4)_2^{2-}$ Pb_2OH^{3+}	1.8E-03 $PbH_2PO_4^+$ $PbOH^+$ $PbHCO_3^+$	3.3E-02 $PbHPO_4$(c) $PbHPO_4$ $PbSO_4$ $PbCO_3$	5.8	4.9	89
pH 8 P. Steel	0.628	2.7E-03 $Pb(CO_3)_2^{2-}$ Pb^{2+}	2.6E-05 $PbOH^+$ $PbHCO_3^+$ $Pb(OH)_3^-$ $PbH_2PO_4^+$	0.63 $Pb_3(PO_4)_2$(c) $PbCO_3$ $PbHPO_4$ $Pb(OH)_2$ $PbSO_4$	0.43	4.2E-03	100
pH 8 G. Steel	0.100	1.2E-02 $Pb(CO_3)_2^{2-}$ Pb^{2+} $Pb(OH)_4^{2-}$	3.0E-05 $PbOH^+$ $PbHCO_3^+$ $Pb(OH)_3^-$	8.8E-02 $Pb_3(PO_4)_2$(c) $PbCO_3$ $PbHPO_4$ $Pb(OH)_2$	12	3.0E-02	88
River G. Steel	0.058	3.4E-02 Pb^{2+} $Pb(SO_4)_2^{2-}$ $Pb(CO_3)_2^{2-}$	7.8E-03 $PbOH^+$ $PbCl^+$ $PbHCO_3^+$	1.7E-02 $PbSO_4$ $PbCO_3$ $PbCl_2$	58	13	29

4.5.1 Heavy Metal Treatability

The form of the pollutant species plays an important role in selecting an appropriate treatment technology (Clark and Pitt 2012). Many heavy metals are associated predominantly with particulates, and therefore their treatability is influenced by the removal of the associated particulates. The association of heavy metals with particulates depends on pH, oxidation-reduction potential, particulate organic matter. The treatability of stormwater solids and associated heavy metals is dependent on their size (Morquecho et al., 2005; House et al., 1993;

Li et al., 2005; Kim and Sansalone, 2008). Sedimentation and physical filtration can be used to remove the particulates with the attached pollutants from stormwater (Pitt et al., 1996). For sedimentation, the median suspended solids removal efficiency is between 70 and 80% (Clark and Pitt 2012; Hossain et al., 2005; International Stormwater BMP Database 2011). The sedimentation effectiveness is dependent upon the size of suspended solids. The removal of large suspended solids is efficient; however the suspended solids removal diminishes with the increase of content of smaller particulates (Clark and Pitt 2012; Greb and Bannerman, 1997). The heavy metal removal by sedimentation is very efficient at locations where the particulates are large (highways, for example) and the heavy metals are predominantly associated with the larger particulates (Clark and Pitt 2012; Kim and Sansalone, 2008)

Effectively designed wet detention ponds have restricted short-circuiting and low surface overflow rates (SOR). The sedimentation basins are not very effective for the removal of very small particles (< 2 μm) due to the repulsive forces caused by the negative charges on colloids and clay-sized particles that keep solids in suspension and prevent the particles from settling (Clark and Pitt 2012). The sedimentation can be improved by coagulation/flocculation that neutralized the electrical charges on the particles and causes the solids to settle out. Testing will be necessary since it is impossible to predict the settling of the floc theoretically (Clark and Pitt 2012; Metcalf and Eddy, 2003). For metals that are predominantly associated with particles in the range of colloidal and clay particles (< 1 μm), filtration with a chemically-active media may be necessary if low numeric discharge limits must be met (Clark and Pitt 2012; Pitt and Clark, 2010). Sand with oxide coatings can be used to remove colloidal pollutants (Clark and Pitt, 2012, Sansalone and Kim, 2006).

The removal of dissolved contaminants may be needed due to their high mobility and to meet permit requirements and reduce surface and ground water contamination potential (Pitt et al., 1996; Clark and Pitt 2012). Heavy metals in ionic forms are the most bioavailable. The toxicity of a heavy metal is affected by metal bioavailability which is controlled by speciation and partitioning of a metal. Metals in ionic forms are generally more bioreactive than metal complexes. Treatment techniques for metals associated with dissolved fractions include chemical treatment. To remove dissolved metals from stormwater, organic filter media (such as compost or peat), a mix of peat moss and sand, zeolite, and compost can be used. Zn^{2+} is highly reactive and is more amenable to ion exchange.

In physisorption reactions, the electrical bonds between the contaminants and the media are reversible and weak. On the other hand, during chemisorption and precipitation reactions stronger bonds are formed and the pollutant retention is permanent if the solution pH and dissolved oxygen level do not change significantly (Evangelou, 1998; Watts, 1998; Clark and Pitt 2012). Sorption and ion exchange remove pollutants through electrostatic interactions between the media and contaminants (Clark and Pitt 2012). The high sodium content during the snowmelt can regenerate the ion exchanging media and release the already retained heavy metals back into the effluent (Clark and Pitt 2012). Granular activated carbon (GAC) technology is costly and therefore is not regularly used for stormwater applications, but is used when very low permit limits must be met (Pitt and Clark 2012).

Valence charge of a metal and its complexation, among other contaminant properties, influence the choice of stormwater treatment technology (Clark and Pitt 2012). Strongly charged, small molecules can be removed effectively by zeolites (Clark and Pitt 2011 and 2012). Zeolites are not effective in the removal of compounds of zero valence and compounds with large size

(Clark and Pitt 2012). Peat, compost and soils remove pollutants by chemisorption that is generally irreversible (Watts, 1998; Evangelou, 1998). Peat can be used as a filtration media for treatment of heavy metals and likely their complexes (Clark and Pitt 2012, 1999). Peat's effectiveness is due to the wide range of binding sites (carboxylic acid, etc.) present in the humic materials and ligands in the peat (Cohen et al., 1991; Sharma and Foster, 1993; Clark and Pitt 2012). An advantage of peat media is that it can treat many heavy metals during relatively short (10 minutes) contact times (Pitt and Clark 2010; Clark and Pitt 2012). The peat's drawbacks (especially for Sphagnum peat) includes the leaching of colored humic and fulvic acids and the release of hydronium ions (H_3O^+) in exchange for metals which can lower the pH of the treated water by as much as 1 to 2 pH units and increase the solubility of the metals that were associated with stormwater runoff solids or media (Clark and Pitt 2012, 1999). Another disadvantage of using peat is the release of nutrients from the filter during the first flush under micro anaerobic conditions in the media which may occur between storms (Clark and Pitt 2009b), although this is not as problematic as for compost media. Compost (including municipal leaf waste compost) can also be used to treat metals (Sharma and Foster, 1993; Guisquiani et al., 1995). The advantage of compost is that it is not likely to reduce the pH of the treated water (Clark and Pitt, 1999). However, the disadvantage is that it can release nutrients, depending on the compost's source material, during the first few years of its life (Hathaway et al., 2008, Pitt et al., 1999; Pitt and Clark, 2010). Treatment trains, like the multi-chambered treatment train (MCTT) can be effectively used for metal treatment and include catch basins for retaining the largest sediment, settling chambers for retaining fine sediment and particle-bound pollutants, and an sorption/ion exchange chamber with mixed media (peat moss, sand) for capturing filterable contaminants through sorption/ion-exchange (Pitt et al., 1999). The upflow filter was also found to be an effective method for controlling stormwater and uses sedimentation, screens for floatable solids, sorption, and ion exchange (Togawa and Pitt, available online). Grass swales may be effective for removing metals. They capture heavy metals by sedimentation, infiltration/sorption, and biological uptake, can treat high volumes of water and are relatively inexpensive (Johnson et al, 2003).

The data for total and filtered metal concentrations of lead, copper, zinc, and aluminum analyzed after three months of exposure during the buffered tests was compared to estimate metal association with the particulate matter (Tables A.1.9, A.2.9, A.3.9, A.4.9, Appendix A). Analytical methods having smaller detection limits are necessary to account for non-detected values. Tables 4.5.22 and 4.5.23 summarize particulate and filterable lead and zinc fractions in different samples during the buffered pH tests. Generally, most of the lead was associated with the particulate fraction under pH 5 conditions and with the dissolved fraction (> 76%) under pH 8 conditions during the buffered tests after three months of exposure. For pH 5 waters, no detectable concentrations of lead were associated with the dissolved fraction. Under pH 8 conditions, most of the lead was associated with the dissolved fraction, while24% of the lead was associated with particulates for galvanized steel pipe, and only 4% for galvanized steel gutter.

Practically all copper was associated with the dissolved fraction (>67 %) for all the pipes under pH 5 and pH 8 conditions after three months of exposure. The exception was for copper gutter samples under pH 8 conditions for which the filtered copper concentration was 83%.

For plastic PVC and HDPE pipes immersed in the pH 5 water, almost all of the zinc concentrations were in dissolved forms. For metal pipes under pH 5 conditions, from 49% to more than 92% of the zinc was associated with particulates, with the exception of the aluminum gutter sample where all zinc was associated with the filterable fraction. For HDPE, vinyl, and copper materials under pH 8 conditions, all zinc was associated with the dissolved fraction. For the rest of the materials (concrete, PVC, aluminum, and galvanized steel pipe and gutter) immersed into pH 8 water, from 67% to practically 100% of zinc was associated with particulates. Under both pH 5 and 8 conditions, aluminum was predominantly associated with the dissolved fraction (from 50 to 100%).

Table 4.5.22 Filterable and particulate fractions of lead and zinc in buffered waters after three months of exposure

Water	Material	% Filterable Pb	% Particulate Pb	% Filterable Zn	% Particulate Zn
pH 5	Concrete Pipe	n/a	n/a	n/a	n/a
	PVC Pipe	n/a	n/a	89	11
	HDPE Pipe	n/a	n/a	83	17
	Steel Pipe	< 2.02	> 97.98	24	76
	Vinyl Gutter	n/a	n/a	n/a	n/a
	Aluminum Gutter	n/a	n/a	100	0
	Steel Gutter	< 13.51	> 86.49	51	49
	Copper Gutter	n/a	n/a	< 15.38	> 84.62
pH 8	Concrete Pipe	n/a	n/a	< 66.67	> 33.33
	PVC Pipe	n/a	n/a	18	82
	HDPE Pipe	n/a	n/a	100	0
	Steel Pipe	76	24	0.34	99.66
	Vinyl Gutter	n/a	n/a	100	0
	Aluminum Gutter	n/a	n/a	24	76
	Steel Gutter	96	4	1.7	98.3
	Copper Gutter	n/a	n/a	100	0

Table 4.5.23 Filterable and particulate fractions of copper and aluminum in buffered waters after three months of exposure

Water	Material	% Filterable Cu	% Particulate Cu	% Filterable Al	% Particulate Al
pH 5	Concrete Pipe	n/a	n/a	n/a	n/a
	PVC Pipe	96	4	100	0
	HDPE Pipe	100	0	n/a	n/a
	Steel Pipe	n/a	n/a	n/a	n/a
	Vinyl Gutter	100	0	n/a	n/a
	Aluminum Gutter	133	0	100	0
	Steel Gutter	n/a	n/a	n/a	n/a
	Copper Gutter	100	0	n/a	n/a
pH 8	Concrete Pipe	n/a	n/a	n/a	n/a
	PVC Pipe	71	29	< 100	> 0
	HDPE Pipe	100	0	100	0
	Steel Pipe	67	33	n/a	n/a
	Vinyl Gutter	100	0	50	50
	Aluminum Gutter	100	0	100	0
	Steel Gutter	100	0	50	50
	Copper Gutter	17	83	n/a	n/a

Table 4.5.24 summarizes particulate and filterable iron fractions during natural pH tests. After three months of exposure during natural pH tests, iron in containers with PVC and HDPE pipes and with vinyl and aluminum gutters were associated predominantly with dissolved fraction (70% and greater), while iron in containers with the rest of the materials were mainly associated with particulates.

Table 4.5.24 Filterable and particulate fractions of iron in natural pH waters after three months of exposure

Water	**Material**	**% Filterable Fe**	**% Particulate Fe**
Bay	Concrete Pipe	29	71
	PVC Pipe	90	10
	HDPE Pipe	84	16
	Steel Pipe	49	51
	Vinyl Gutter	92	8
	Aluminum Gutter	88	12
	Steel Gutter	41	59
	Copper Gutter	43	57
River	Concrete Pipe	18	82
	PVC Pipe	73	27
	HDPE Pipe	77	23
	Steel Pipe	6	94
	Vinyl Gutter	69	31
	Aluminum Gutter	70	30
	Steel Gutter	19	81
	Copper Gutter	16	84

Morquecho et al., 2005 studied the percent of pollutant reductions that were associated with removal of particulates of different sizes. It was found the tin sheet flow samples collected in Tuscaloosa, AL, a large percentage of copper (> 60%) was associated with particles smaller than 0.45 µm and are not removed by sedimentation and physical filtration techniques (Morquecho et al., 2005; Clark and Pitt 2012). For these samples, lead was reduced on the average by 62% and zinc by 70% by removing the particles greater than 5µm and lead was reduced by 76% and zinc by 70% by removing the particles greater than 1 µm, indicating that sedimentation and physical filtration would be an appropriate pretreatment technologies since it is considered that the reliable sedimentation is occurring for particles in the range of 2 to 5 μm (Camp, 1952; Clark and Pitt 2012). Frequently, lead that is in ionic form (approximately < 0.45 μm) is in very low quantities, but if necessary, it can be treated with ion exchange technology using zeolites (Clark and Pitt 2012). Chemically-active media filtration using compost, peat, and soil can be used to treat lead complexes formed with hydroxides and chlorides (Clark and Pitt 2012).

Zero-valent iron (ZVI) was found to be an efficient medium for treating stormwater heavy metal ions as Cu^{2+} and Zn^{2+}(Rangsivek and Jekel 2005, Shokes and Moller, 1999; Wilkinan and McNeil, 2003). Rangsivek and Jekel (2005) found that a significant fraction of Cu^{2+} is transformed to insoluble CuO and Cu_2O species. Zn^{2+} is removed by adsorption and co-precipitation with iron oxides. Zero-valent iron removes inorganic pollutants via cementation (reduction of redox sensitive compounds to insoluble forms, for example, $Cu^{2+}+Fe^0 \rightarrow Cu^0+Fe^{2+}$), adsorption and metal hydroxide precipitation (Rangsivek and Jekel 2005, Cantrell et al., 1995; Shokes and Moller, 1999; Blowes et al., 2000; Naftz et al., 2002; Wilkin and McNeil, 2003). Higher values of water pH, dissolved oxygen (DO), temperature, and ionic strength increased the removal rates of Zn^{2+}. At higher pH values and in the presence of dissolved oxygen (DO), adsorption and co-precipitation with iron oxide are predominantly occur (Rangsivek and Jekel 2005). On the other hand, at low pH values in the absence of DO, the cementation is very effective (Rangsivek and Jekel 2005; Strickland and Lawson, 1971; Ku and Chen, 1992).

ZVI was found to have capacity comparable to a commercial adsorbent granular ferric hydroxide (GFH). The advantages of zero-valent iron (ZVI) are that it is inexpensive and can provide environmental benefits when used in the reclamation of solid waste (Rangsivek and

Jekel 2005). Also, ZVI can be installed in an on-site remediation system as a fixed-bed barrier (Morrison et al., 2002). Drawbacks of ZVI include the release of dissolved iron and complexes of iron oxides with other heavy metals. Therefore, a post-treatment process that includes aeration and a sand filtration may be necessary. The removal of such substances as oil from iron’s surfaces may be required if iron was acquired as solid waste.

A virgin coconut hull granular activated carbon (GAC), which has a limited chemical capacity, can be used for nitrate (NO_3^-) treatment (Pitt and Clark, 2010). To remove nitrate and nitrite, vegetated systems can be utilized (Baker and Clark 2012; Lucas and Greenway 2008, 2011; Hunt et al, 2006; Hunt et al, 2008). For nitrogen removal, zeolites, commercial resins, and some native soils may be used.

Sedimentation can be utilized to treat particulate bound phosphorus. To remove phosphorus associated with colloids or are in dissolved forms, vegetative systems may be used (Clark and Pitt 2012).

Ionic fractions for zinc, copper, and cadmium can range from 25 to 75% (Clark and Pitt 2012). Sedimentation and physical filtration can be used to treat metals that are bound to particles. These metals can be associated with very small particles, therefore the efficiency of physical filtration to remove metals will depend on size of associated particulates. Treatment technologies for metals associated with dissolved fraction include chemical methods. To remove dissolved metals from stormwater, peat moss, mixtures of peat moss and sand, zeolite, and compost can be used, especially with long contact times. These metals can form soluble complexes with different inorganic and organic ligands. The complex valence can range from -2 to +2. Organic and inorganic complexes may be treated by chemically active filtration through compost, peat, and soil. Also, granular activated carbon (GAC) can be used to remove complexes with organic matter.

The choice of treatment methods depends on form of heavy metals and desired level of metal removal. If high degree of metal reduction is required, it is necessary to use multiple techniques (Clark and Pitt 2012). Generally, low numeric discharge limits can be met through combinations of pre-treatment by sedimentation and filtration with a chemically and biologically active media.

4.6 Langelier Index

The Langelier Index was calculated to determine whether the leaching water for the concrete materials was in equilibrium, oversaturated, or undersaturated with respect to $CaCO_{3(s)}$. Langelier Index indicates whether concrete samples will deteriorate as a result of $CaCO_{3(s)}$ dissolution from the concrete. Also, the Langelier Index can indicate whether $CaCO_{3(s)}$ that is present in the water will precipitate and form scale that may protect pipe material from corrosion. The Langelier Index was calculated for the samples at 3 months of exposure. $H_2PO_4^-$ and HPO_4^{2-} concentrations were calculated from weighed chemicals. During the calculations of ionic strengthμ, $H_2PO_4^-$ and HPO_4^{2-} concentrations were assumed to be in ionic form.

The Langelier Index was calculated twice: once utilizing the activity coefficients in aqueous solution determined using the DeBye-Huckel equation, and second time using the Maclinnes assumption to estimate the activity coefficients. Both methods produced the same results (Tables 4.6.1 and 4.6.2). The Langelier Index showed that all samples with buffered pH 5 and pH 8 waters were undersaturated with respect to $CaCO_{3(s).}$ Therefore, the water in the containers with concrete pipes had a tendency to dissolve $CaCO_{3(s)}$ from the concrete. The water in the containers with the remaining pipe and gutter materials didn't have a tendency to precipitate $CaCO_{3(s)}$ from the solution. During the second testing stage, the samples with galvanized steel pipe and gutter materials immersed into bay and river waters were undersaturated with respect to $CaCO_{3(s).}$ However the samples with the rest of the materials (including concrete) were oversaturated with $CaCO_{3(s)}$ indicating the water in these samples had a tendency to precipitate $CaCO_{3(s)}$ from the solution and there was no degradation of the concrete pipe after 3 months of exposure.

Table 4.6.1. Langelier Index. Buffered pH 5 and pH 8 Waters.

				γ:DeBye-Huckel Equation			**γ: The Maclinnes Assumption**		
		μ	**pHa**	**pHs**	**L.I.**	**Water with respect to CaCO3**	**pHs**	**L.I.**	**Water with respect to CaCO3**
pH 5	**P. Concrete**	0.069	6.37	12.59	-6.22	undersaturated	12.61	-6.24	undersaturated
	P. PVC	0.070	5.23	11.81	-6.58	undersaturated	11.82	-6.59	undersaturated
	P. HDPE	0.068	4.84	13.66	-8.82	undersaturated	13.67	-8.83	undersaturated
	P. Steel	0.069	5.80	13.04	-7.24	undersaturated	13.05	-7.25	undersaturated
	G. Vinyl	0.068	4.83	13.89	-9.06	undersaturated	13.90	-9.07	undersaturated
	G. Aluminum	0.068	4.84	14.10	-9.26	undersaturated	14.11	-9.27	undersaturated
	G. Steel	0.068	5.43	13.36	-7.93	undersaturated	13.37	-7.94	undersaturated
	G. Copper	0.068	5.13	15.79	-10.66	undersaturated	15.81	-10.68	undersaturated
pH 8	**P. Concrete**	0.196	8.96	12.90	-3.94	undersaturated	12.93	-3.97	undersaturated
	P. PVC	0.196	8.50	12.01	-3.51	undersaturated	12.04	-3.54	undersaturated
	P. HDPE	0.196	8.47	12.79	-4.32	undersaturated	12.83	-4.36	undersaturated
	P. Steel	0.196	8.90	13.13	-4.23	undersaturated	13.16	-4.26	undersaturated
	G. Vinyl	0.196	8.48	12.98	-4.50	undersaturated	13.01	-4.53	undersaturated
	G. Aluminum	0.196	8.50	14.68	-6.18	undersaturated	14.72	-6.22	undersaturated
	G. Steel	0.196	9.07	13.04	-3.97	undersaturated	13.07	-4.00	undersaturated
	G. Copper	0.196	8.76	13.52	-4.76	undersaturated	13.55	-4.79	undersaturated

Footnote: pH_a = actual pH of water; pH_s = pH of water if it were in equilibrium with $CaCO_{3(s)}$ at the existing solution concentrations of HCO_3^- and Ca^{2+}. L.I. = Langelier Index.

Table 4.6.2. Langelier Index. Natural Bay and River Waters.

				γ: DeBye-Huckel Equation			**γ: The Maclinnes Assumption**		
		µ	**pHa**	**pHs**	**L.I.**	**Water with respect to CaCO3**	**pHs**	**L.I.**	**Water with respect to CaCO3**
Bay	**P. Concrete**		8.39	7.49	0.90	oversaturated	7.50	0.89	oversaturated
	P. PVC		7.90	7.82	0.08	oversaturated	7.83	0.07	oversaturated
	P. HDPE		7.84	7.80	0.04	oversaturated	7.82	0.02	oversaturated
	P. Steel		7.00	8.72	-1.72	undersaturated	8.73	-1.73	undersaturated
	G. Vinyl		7.97	7.72	0.25	oversaturated	7.73	0.24	oversaturated
	G. Aluminum		8.00	7.60	0.40	oversaturated	7.62	0.38	oversaturated
	G. Steel		7.84	8.44	-0.60	undersaturated	8.45	-0.61	undersaturated
	G. Copper		8.01	7.75	0.26	oversaturated	7.76	0.25	oversaturated
River	**P. Concrete**		8.74	8.12	0.62	oversaturated	8.12	0.62	oversaturated
	P. PVC		8.43	7.84	0.59	oversaturated	7.84	0.59	oversaturated
	P. HDPE		8.35	7.94	0.41	oversaturated	7.94	0.41	oversaturated
	P. Steel		8.87	9.06	-0.19	undersaturated	9.07	-0.20	undersaturated
	G. Vinyl		8.31	7.97	0.34	oversaturated	7.97	0.34	oversaturated
	G. Aluminum		8.34	7.93	0.41	oversaturated	7.93	0.41	oversaturated
	G. Steel		6.93	9.02	-2.09	undersaturated	9.02	-2.09	undersaturated
	G. Copper		8.31	7.93	0.38	oversaturated	7.93	0.38	oversaturated

4.7 Chapter Summary

This chapter examined metal releases from different stormwater drainage and tank materials under various water conditions. It was found that galvanized steel materials released the largest amounts of lead, zinc, and iron, while copper materials were the most significant sources of copper. Zinc and lead releases from galvanized steel materials were observed during both short and long exposure times. During controlled pH tests, zinc releases in the samples with galvanized steel materials exceeded those at higher pH values during long exposure times. During short exposure times, zinc releases from galvanized materials were lower in river water samples compared to the bay water samples; however, during long time exposures, zinc concentrations in the river water samples were greater than in the bay water samples. Plastic and concrete materials were the least sources of zinc. Galvanized pipes and gutters were found to be the only source of lead releases. During short exposure times, copper releases were noted only for copper materials at both low and high pH for controlled pH conditions and for bay and river water during un-controlled pH tests. During the first series of tests, copper releases from copper gutters increased as pH decreased. During the second test series copper losses were greater in containers with bay water compared to containers with river water. The smallest copper release was noted from HDPE and galvanized materials. The highest aluminum concentrations were released from aluminum materials.

Linear regressions were conducted on the time series plots of log metal releases per pipe surface area vs. log time for different stormwater drainage materials under various water conditions.

2^2 factorial analyses examined the effects of exposure times and pH and the interactions of those factors on the metal releases in mg/m^2 surface area for each pipe and gutter material during the first series of tests. During the second test series, 2^2 factorial analyses estimated the effect of exposure time and salinity, and the interaction of those factors.

Medusa software was used to perform water chemistry modeling with the test data. Eh-pH and log Concentration-pH diagrams were constructed and metal forms present were determined. The results showed that metal releases range in form from being strongly charged (valence state +2 and -2) to zero valence. In some of the containers zinc (copper) compounds precipitated and formed protective film, therefore zinc (copper) concentration in those waters would not be expected to increase since there would be equilibrium between ions dissolved in the water and the precipitated compounds. Langelier Index calculated for the containers with concrete pipes immersed in pH 5 and pH 8 waters indicated that the waters were undersaturated with respect to $CaCO_{3(s)}$ and the waters would have a tendency to dissolve $CaCO_{3(s)}$ from the concrete. The samples with concrete pipes immersed in bay and river waters were oversaturated with respect to $CaCO_{3(s)}$ indicating that waters in these samples had a tendency to precipitate $CaCO_{3(s)}$ from the solution and there was no degradation of the concrete pipe after 3 months of exposure.

5. TOXICITY RELEASES

This chapter describes the observed toxicity of water samples that had different pipe and gutter materials exposed under different water conditions. Toxicity analyses were performed on the samples collected during controlled pH tests and during natural pH experiments. The toxicity tests were conducted using a Microtox model 500Analyzer and Microtox Omni^{TM} software to investigate how water samples that were in contact with different gutter and pipe materials may affect a biological system of receiving waters and to what degree. Methods used were taken from Microtox Acute Toxicity basic test procedures by Microbics Corporation and Manual on Microtox Model 500 Analyzer. Toxicity Effect (%) at time t was calculated using the formula:

Toxicity Effect = (Control – Sample)/Control x 100% Equation 5.1

Where,

Control = average light level of the control samples at t

Sample = light level of sample at t

Initially, tests were performed to determine the salt concentrations required to adjust water samples to optimum salinity conditions for Vibrio Fischeri osmotic pressure. Also, preliminary tests were conducted to determine $IC_{50}$and IC_{20} concentrations for the reference toxicants of $ZnSO_4$ and phenol to be used as standards to confirm the instrument performance. Three replicates of standards were used. Each water sample was analyzed in duplicate.

5.1 Osmotic Pressure (Salinity) Adjustment

Granular NaCl was used to adjust the salinity (osmotic pressure) of the samples. Previously developed protocols used granular NaCl to adjust the salinity of the samples to 2%. This protocol recommended 0.2g of NaCl per 10mL sample. Tests were conducted to determine if there was a difference in illuminescence of the test bacteria with changing NaCl concentration and to determine the optimum concentration of NaCl required when adjusting to acceptable range of salinity of a sample. These toxicity tests were conducted by adding eight different concentrations of NaCl to a composite of three stormwater samples. NaCl concentrations were 0.1, 0.2, 0.3, 0.4, 0.5, 0.6, 0.7, and 0.8 mg per 10 ml of sample. Figure 5.1.1 shows the bacteria response to these eight NaCl concentrations at 5, 15, 25, and 45 min of exposure times.

The graphs show the fluorescence of the bacteria is significantly influenced by changing the osmotic pressure of the samples. The previously developed protocol recommended adjusting the salinity to 2%. According to the graph 2% salinity corresponds to 33%-46% reduction in fluorescence during 5 to 45 min exposure. Figure 5.1.1 shows that the minimum light reduction is at 0.3 g which corresponds to 3% salinity. The percent of toxicity effect was the smallest for the NaCl concentration of 0.3 g per 10 ml of sample and the data points for this concentration at different exposure times are very close together. The toxicity effect is nearly the same for 5, 15, 25, and 45 minutes for all the NaCl concentrations with the exception 0.4 mg of NaCl per 10 ml of sample, for which the toxicity effect ranged approximately between 35 to 37% at 5 min of exposure and 56 to 61% at 45 min of exposure. Slight change in quantities of salt added has an effect of the osmotic pressure and results in reduction of light output, therefore precision is necessary weighing salt additions. Because 0.3 g of NaCl per 10 mL corresponded to a minimum fluorescence reduction, this concentration was used for future experiments.

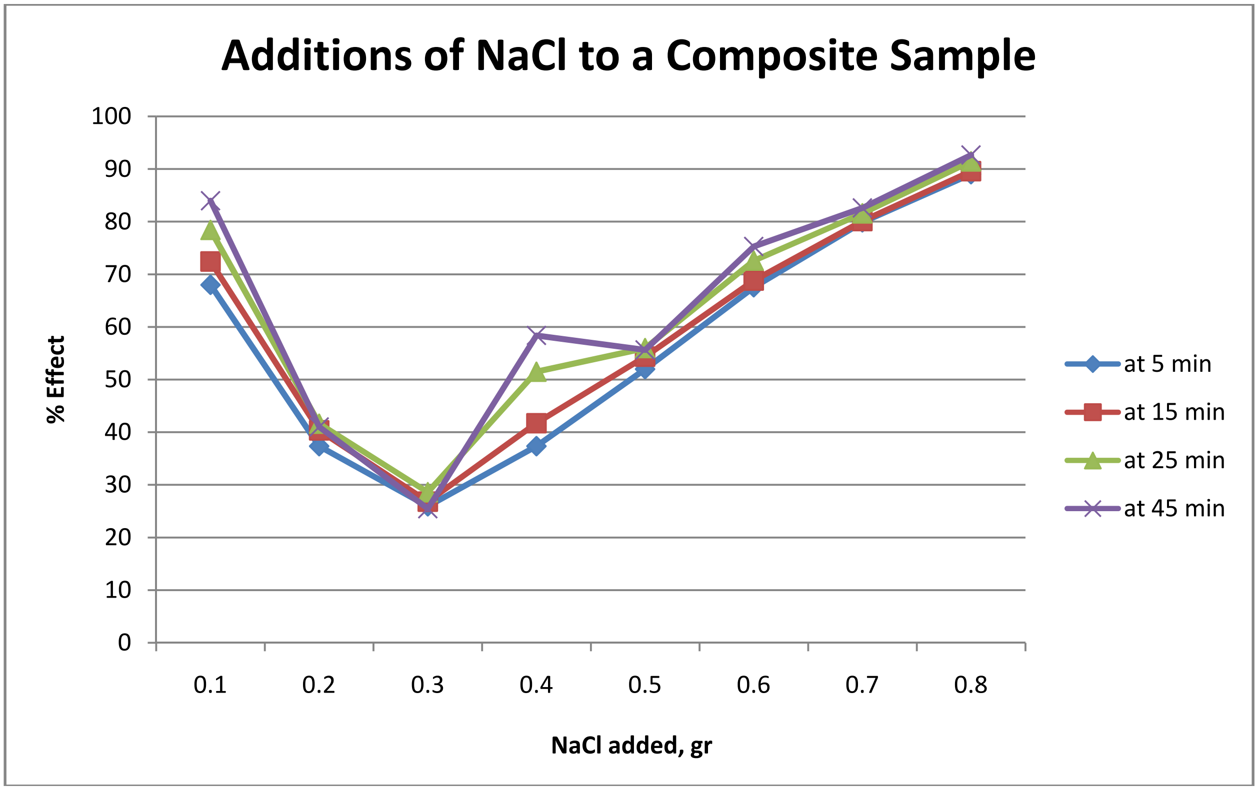


Figure 5.1.1 Toxicity effect (%) after additions of eight different NaCl concentrations to a composite sample. (X-axis: grams of NaCl per 10 ml of sample. Each point is an average of 2 replicates.)

5.2. $ZnSO_4$ and Phenol Toxicity Standards

Figures 5.2.1 and 5.2.2 show the toxicity effects of two replicates of varying $ZnSO_4$ and phenol concentrations. As can be seen from the graphs, $ZnSO_4$ has an IC_{50} (inhibition concentration resulting in 50% inhibition) at approximately 0.7 mg/L, while phenol has an IC_{20} of approximately 5 mg/L at 15 min. All further tests used ZnSO4 and phenol as reference toxicants at concentrations of 0.7 mg/L and 5 mg/L, respectively, which were analyzed along with each sample batch. Figure 5.2.1 shows that toxicity associated with ZnSO4 increases more with bacteria exposure time compared to toxicity associated with phenol in Figure 5.2.2.

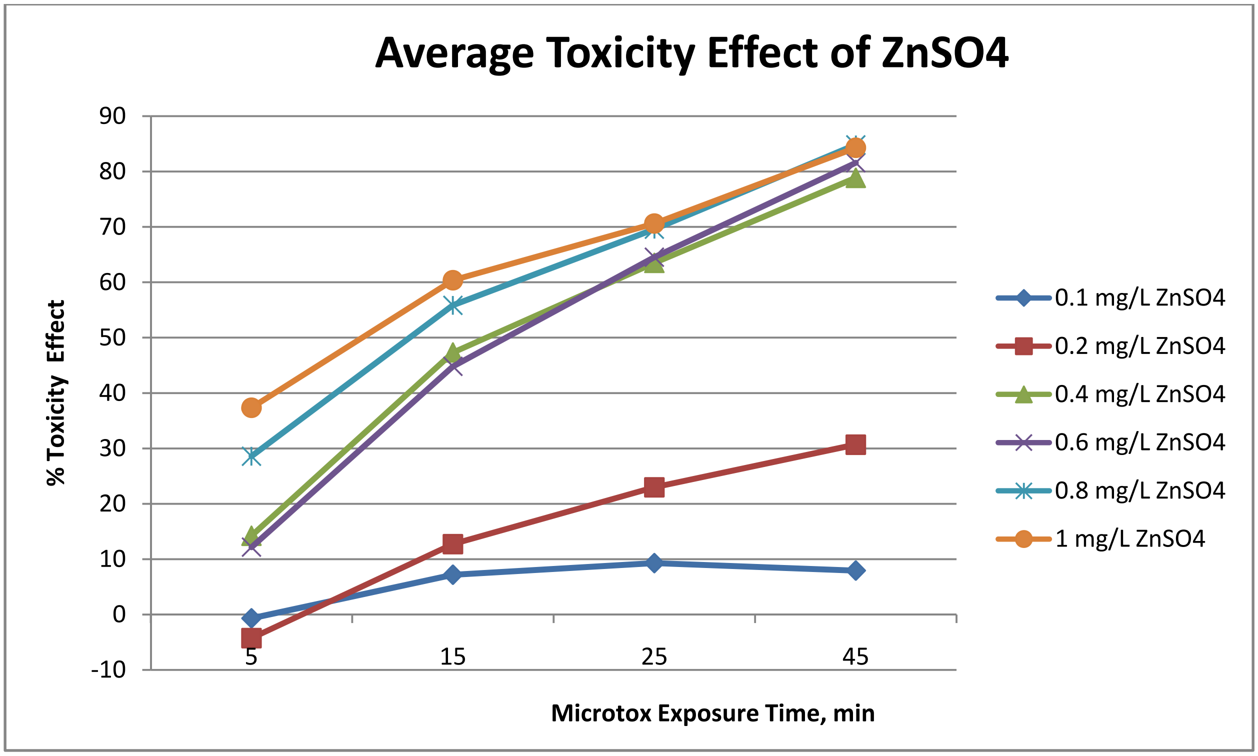


Figure 5.2.1 Toxicity effect (%) of different $ZnSO_4$ concentrations at various exposure times. (Each point is an average of 2 replicates.)

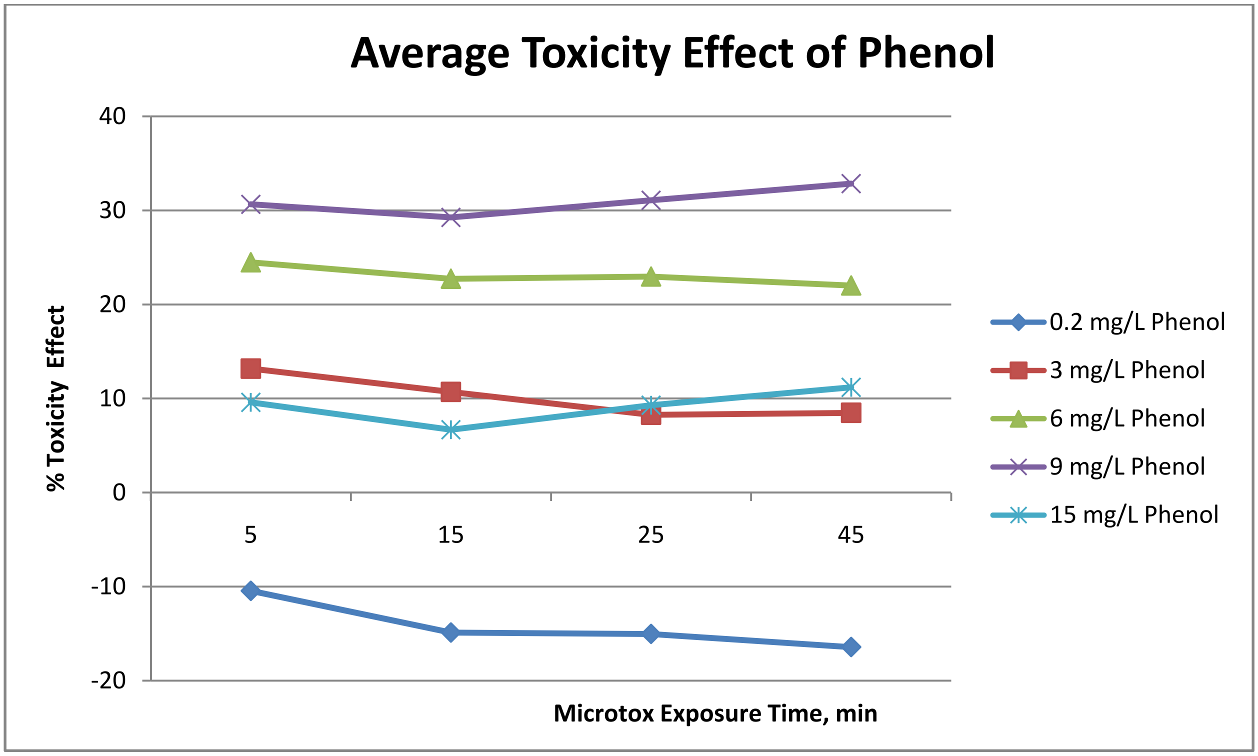


Figure 5.2.2. Toxicity effect (%) of different phenol concentrations at various exposure times. (Each point is an average of 2 replicates.)

5.3 Results and Discussion

5.3.1 Controlled pH Tests

Figures5.3.1.1 through 5.3.1.4 are plots of toxicities of the samples with different drainage materials under controlled pH conditions after 15 minutes of bacteria exposure. Similar toxicity plots for 5, 25, and 45 minute exposure times are included in Appendix E (Figures E.1.1. through E.1.16). The toxicities of the water from the roof and pipe materials were much greater for lower pH conditions than for higher pH conditions.

During the controlled pH 5 tests, the highest toxicities were found for copper, aluminum, and HDPE material exposures; the samples from concrete containers were the least toxic. High toxicity of copper, alumina, and HDPE samples are explained by low pH values that are outside of optimum range for the bacteria. Concrete pipes raised the pH values in the containers from 5 to above 6 and therefore reduced the sample toxicities.

For the controlled pH 8 conditions, copper materials were found to be most toxic, followed by PVC materials. Concrete pipes and vinyl roofing materials were found to be least toxic.

The toxicity of copper gutters was greater during controlled pH 5 tests compared to controlled pH 8 experiments. Similar results were obtained by Ho et al (1999) who found that for the Microtox solid phasetest, as the pH decreased, the toxicity for Cu increased. The toxicity of galvanized steel pipes and gutters, which released the greatest concentrations of zinc and lead, was also higher at pH 5 conditions than at pH 8 conditions, however Ho et al (1999) observed the toxicity of Pb and Zn decreased as pH decreased. The increase in toxicity of galvanized materials at low pH values can be explained bythe test pH values beingbelow the optimum pH range for Vibrio Fischeri bacteria; minimal pH effect on Vibrio Fischeri bacteria is observed in the range from 6 to 8 (Microbics Corporation, 1995. ACUTE User's Manual. Microtox Acute Toxicity. Basic Test Procedures.)

Under controlled pH 5 conditions, generally for all pipe and gutter materials, toxicity decreased with time. The toxicity of copper materials at pH 5 gradually decreased with time, however for galvanized steel materials at pH 5, the decrese of toxicity with time was more abrupt. The decrease of toxicity with time corresponds to the slow increase in pH of the buffered solutions from pH 5 to pH 6. There was a general tendency in the toxicity increase for copper and galvanized steel materials for samples buffered at pH 8 during the first series of tests**.** The toxicity increase can be explained by the slow increase in pH values of the containers from pH 8 to pH 9, with pH 9 being out of the natural habitat value. The toxicity values of less than zero may be explained by the presence organic matter that may provide a second food source for the bacteria (Burton and Pitt 2002).

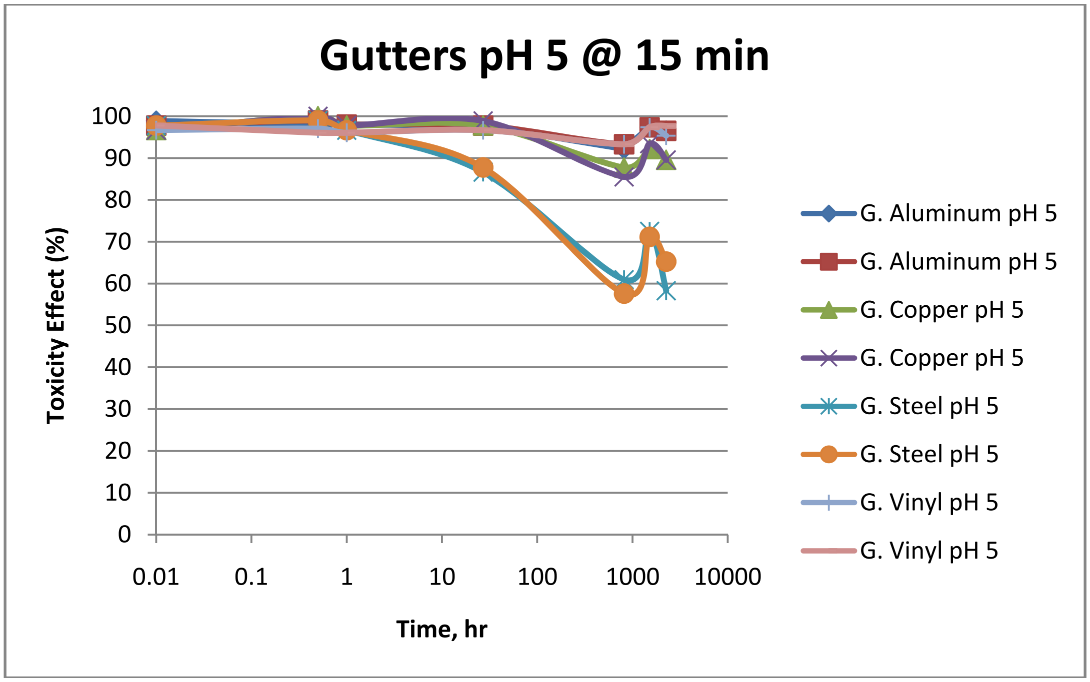


Figure 5.3.1.1 Toxicity effect in samples with gutter materials under pH 5 conditions at 15 min Microtox exposure time.

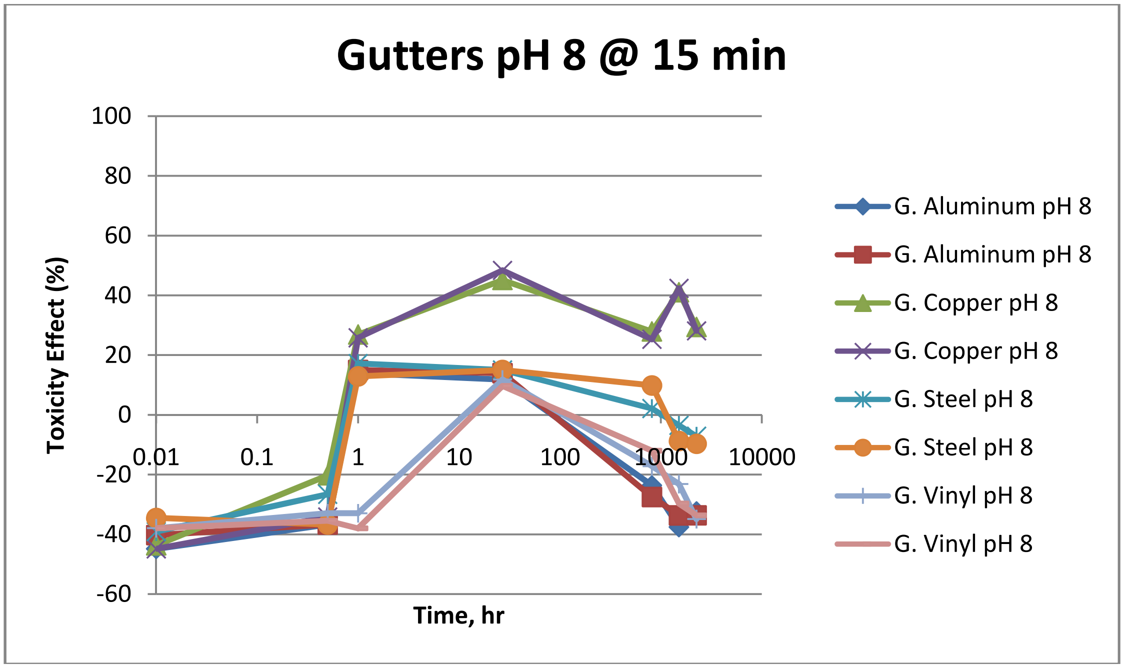


Figure 5.3.1.2 Toxicity effect in samples with gutter materials under pH 8 conditions at 15 min Microtox exposure time.

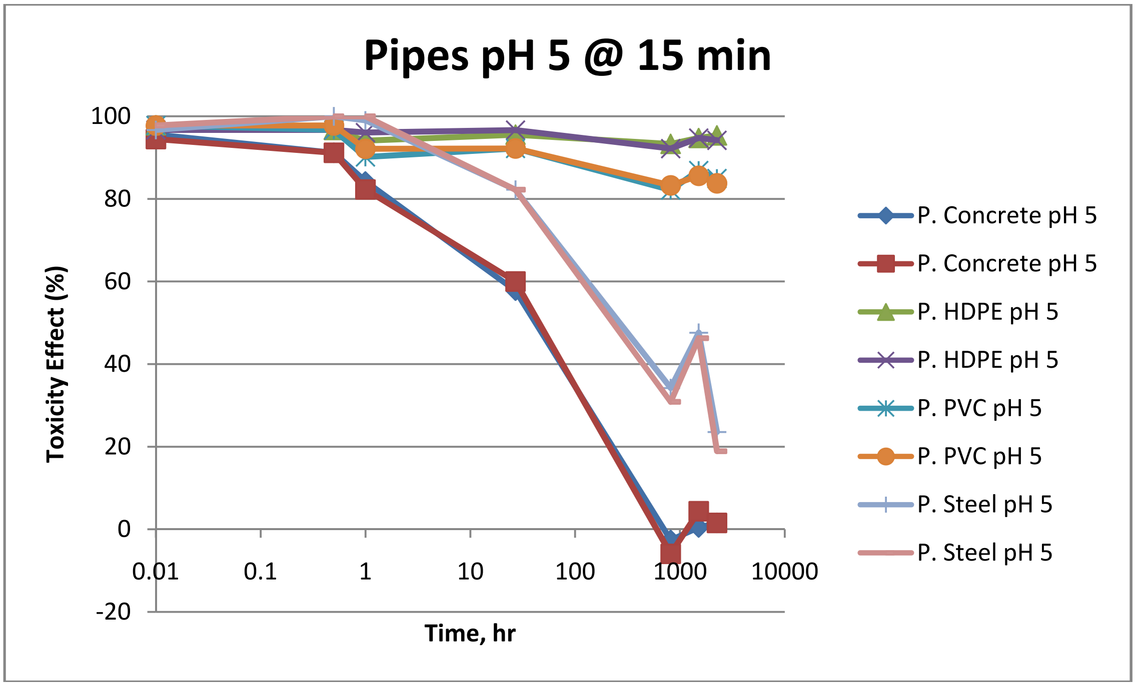


Figure 5.3.1.3 Toxicity effect in samples with pipe materials under pH 5 conditions at 15 min Microtox exposure time.

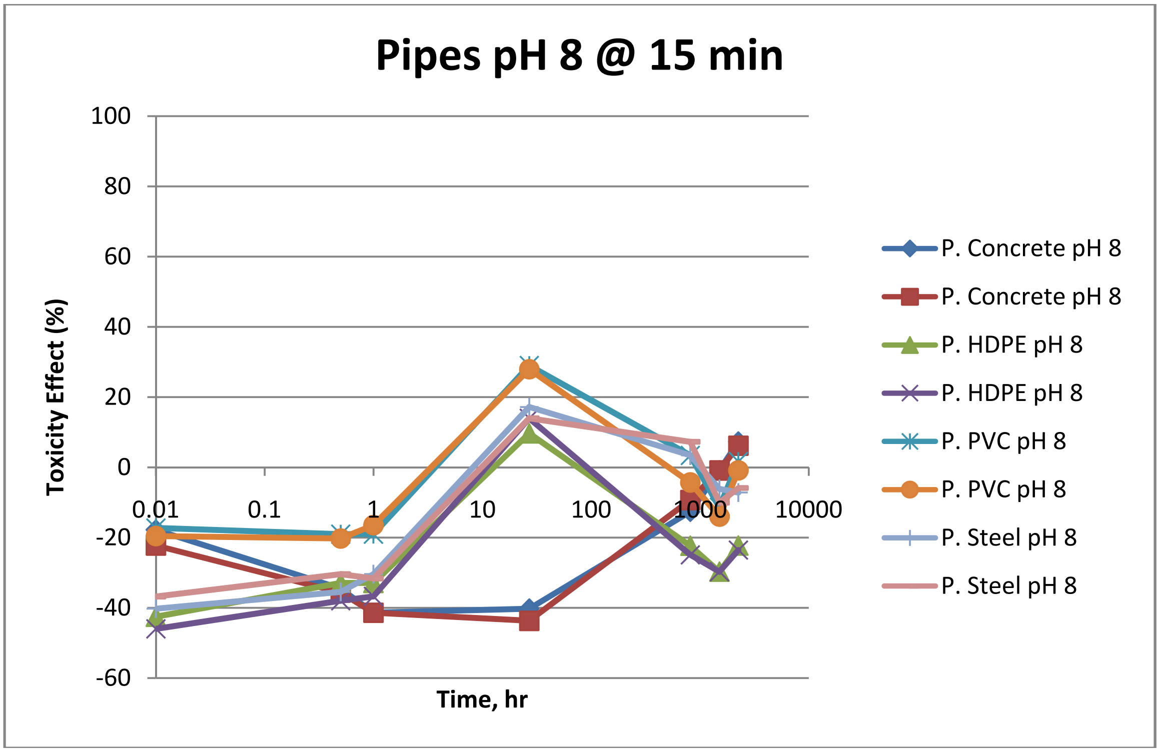


Figure 5.3.1.4 Toxicity effect in samples with pipe materials under pH 8 conditions at 15 min Microtox exposure time.

5.3.2 Natural pH Tests

Figures 5.3.2.1 through 5.3.2.4 show toxicities of the samples with different drainage materials under natural pH conditions after 15 minutes of bacteria exposure to the samples. The toxicities after 5, 25, and 45 minutes of exposure are shown in Appendix E (Figures E.2.1 through E.2.15).Aluminum and vinyl gutters and concrete, PVC, and HDPE pipes were not a source of toxicity, as the heavy metal concentrations were very low, barely detected, or below the detection limits. In containers with bay and river waters, copper materials had the highest toxicity values, followed by galvanized steel materials. The toxicity of the samples with copper and galvanized steel materials increased with exposure time and was likely due to the increase in metal concentrations and increases in pH values that were outside of the optimum pH range for bacteria. For copper gutters and galvanized steel pipes, the increase in toxicity with exposure time was greater and faster for bay water than for river water (Figures 5.3.2.5through 5.3.2.8) and can be explained by greater metal concentrations for bay waters than for river waters. For example, for galvanized steel pipe immersed in bay water, total zinc concentration after 3 months of exposure was 78 mg/L with 72% being of valence 2 state. However for galvanized steel pipe immersed in river water, total zinc concentration after 3 months of exposure was 67 mg/L with 99% of valence 0. For galvanized steel gutters, after about 2 months of exposure, the toxicity in river water samples were higher than in bay water samples and can be explained by 34% being valence of 1 and greater and the pH values outside of optimum pH range for toxicity.

For the copper and galvanized steel materials, the measured Microtox toxicity was greater when measured at 45 min compared to 15 min, as expected when heavy metals are the likely source of the toxicity. As an example, Figure 5.3.2.9shows the Microtox toxicity values for the steel gutter sample immersed in bay water for different Microtox test periods. The longer sample exposure periods (27 hr, 34 days, and 64 days) all had increasing toxicity indications with longer Microtox exposure times. The 94 day sample reached maximum toxicity after 5 min of Microtox exposure period due to the very high zinc concentrations (37 mg/L). The short sample exposure time samples (0.01 and 1 hour) were never toxic, due to their much lower metal concentrations (< 0.02 and 0.48 mg/L for 0.01 and 1 hour respectively).

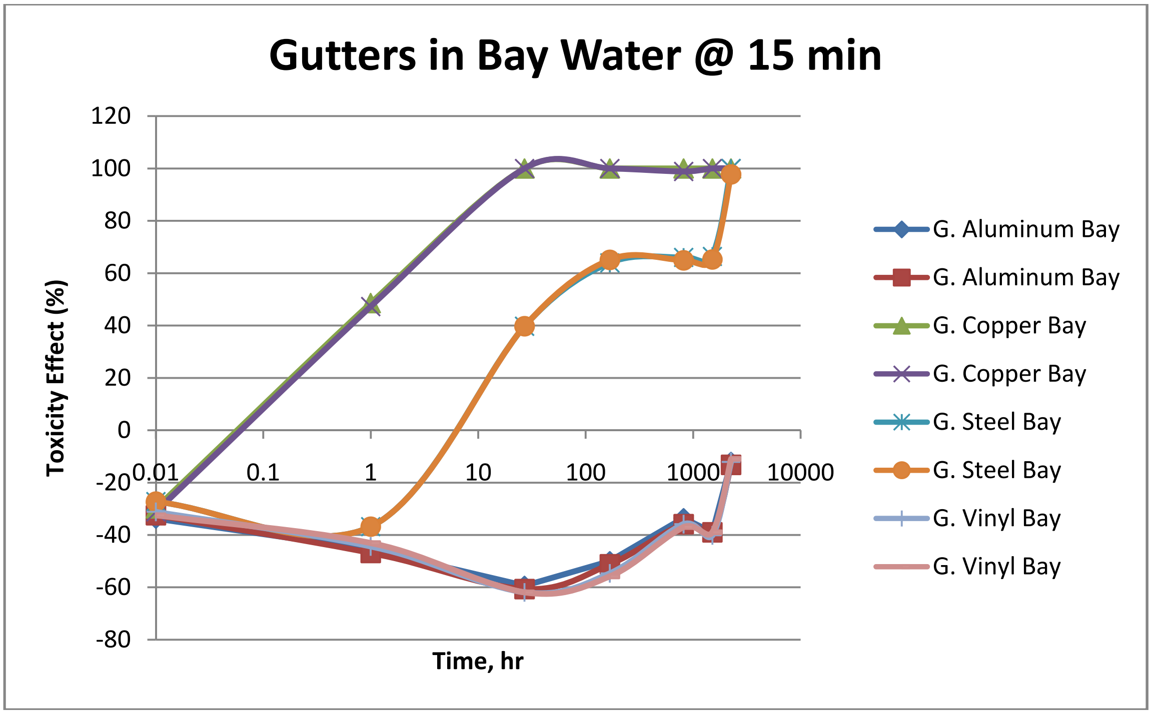


Figure 5.3.2.1 Toxicity effect in samples with gutter materials. Bay water at 15 min Microtox exposure time.

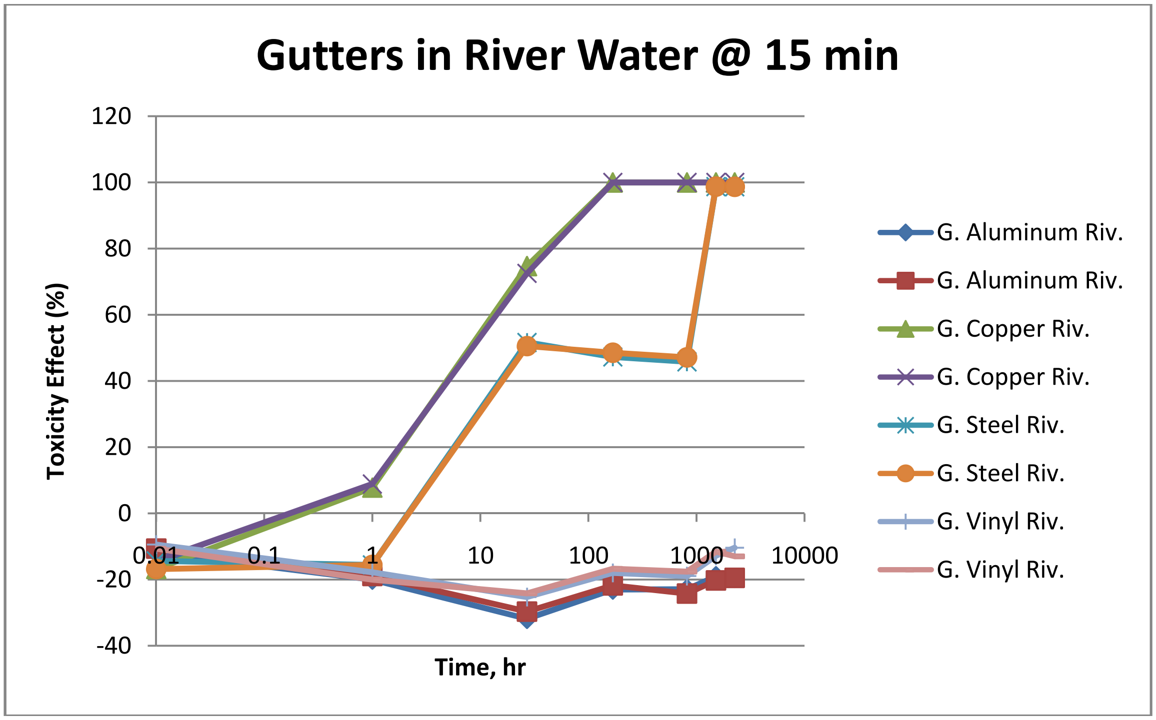


Figure 5.3.2.2 Toxicity effect in samples with gutter materials. River water at 15 min Microtox exposure time.

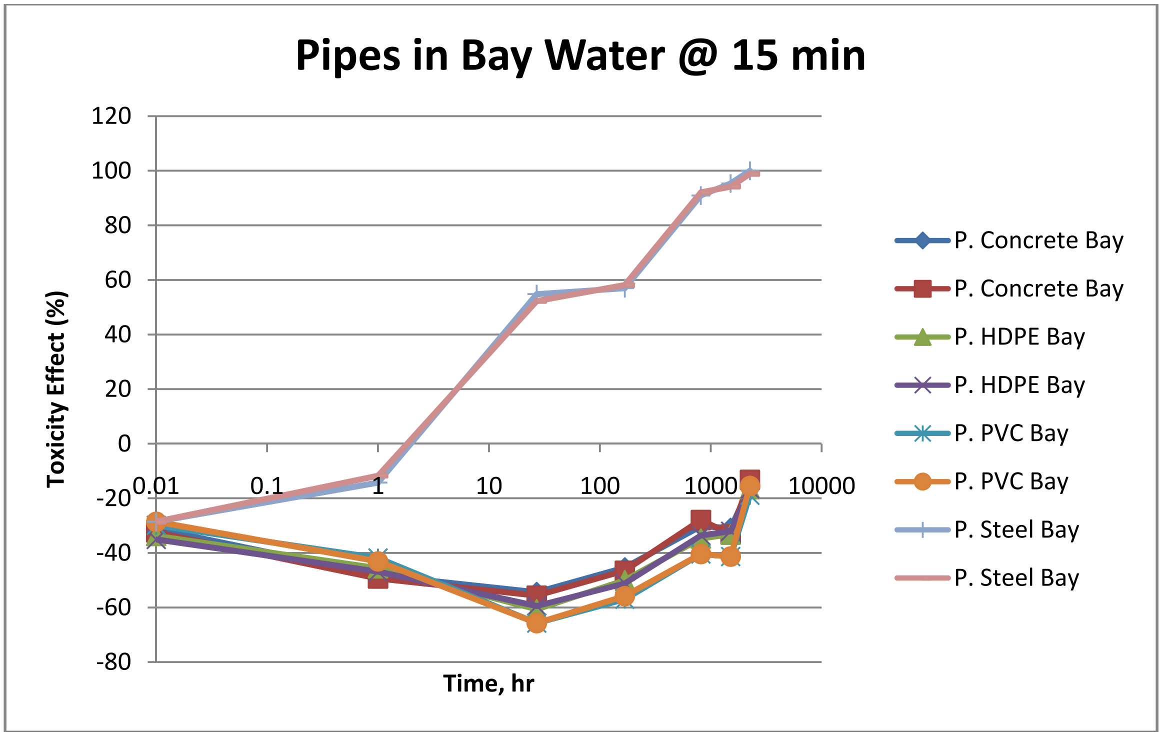


Figure 5.3.2.3 Toxicity effect in samples with pipe materials. Bay water at 15 min Microtox exposure time.

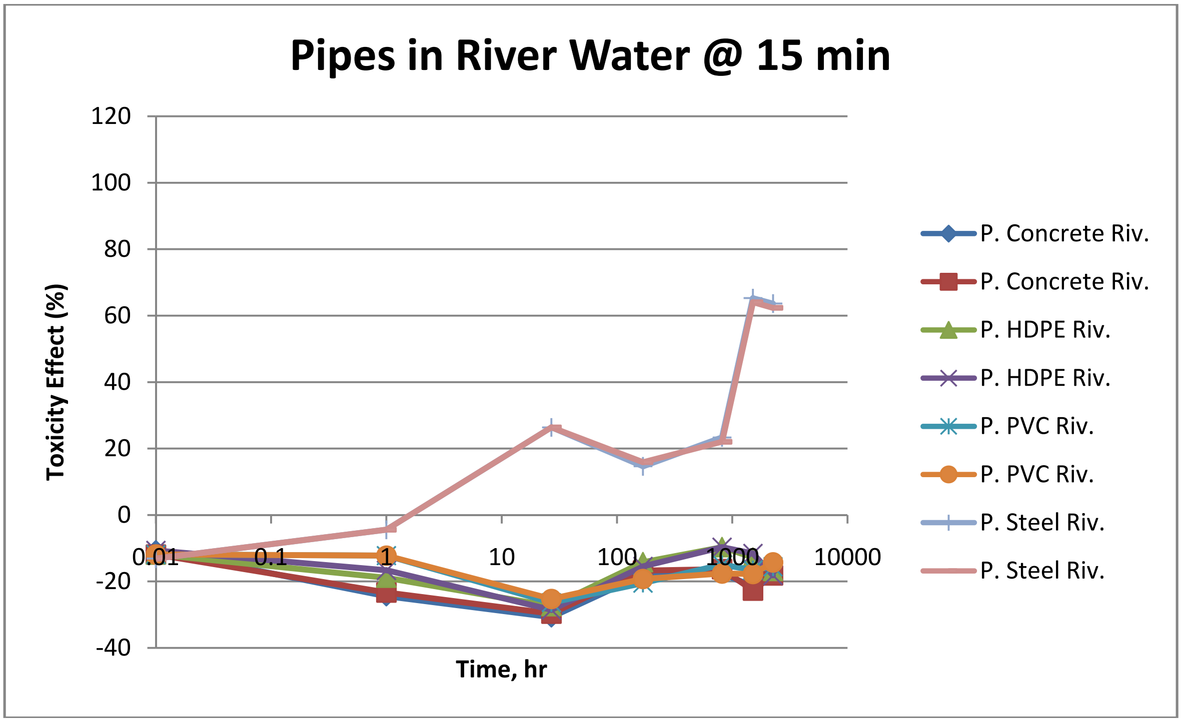


Figure 5.3.2.4 Toxicity effect in samples with pipe materials. River water at 15 min Microtox exposure time.

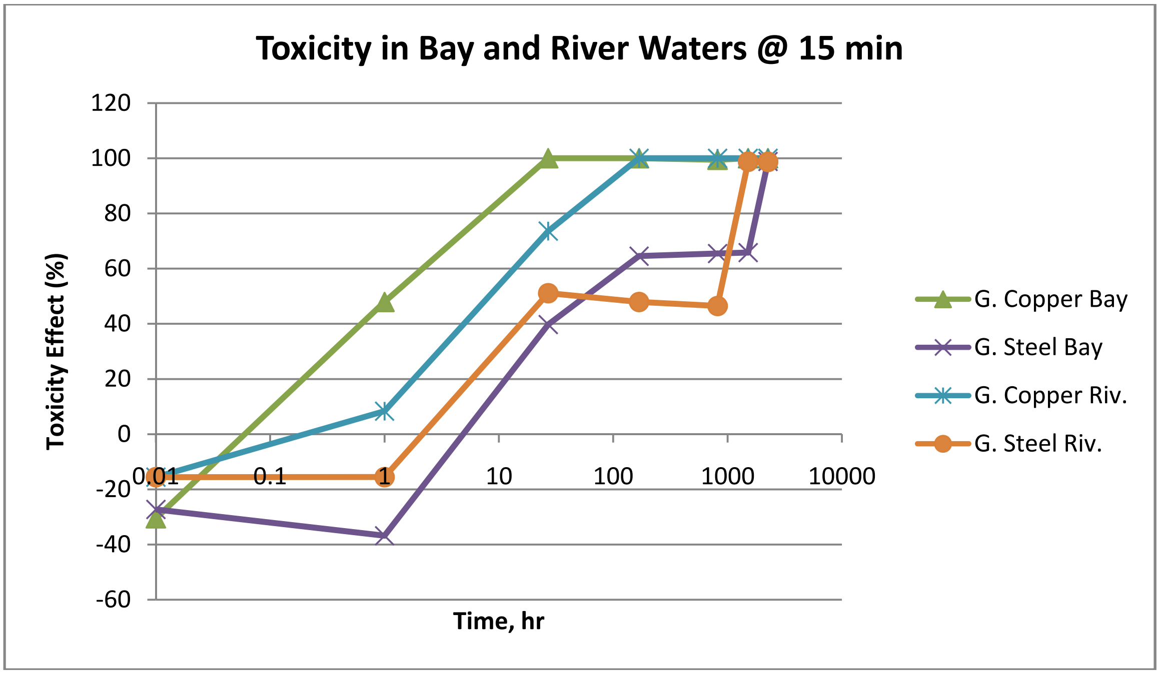


Figure 5.3.2.5 Toxicity effect in samples with copper and galvanized steel gutters immersed in bay and river water at 15 min Microtox exposure time.
(Each point is an average of 2 replicates.)

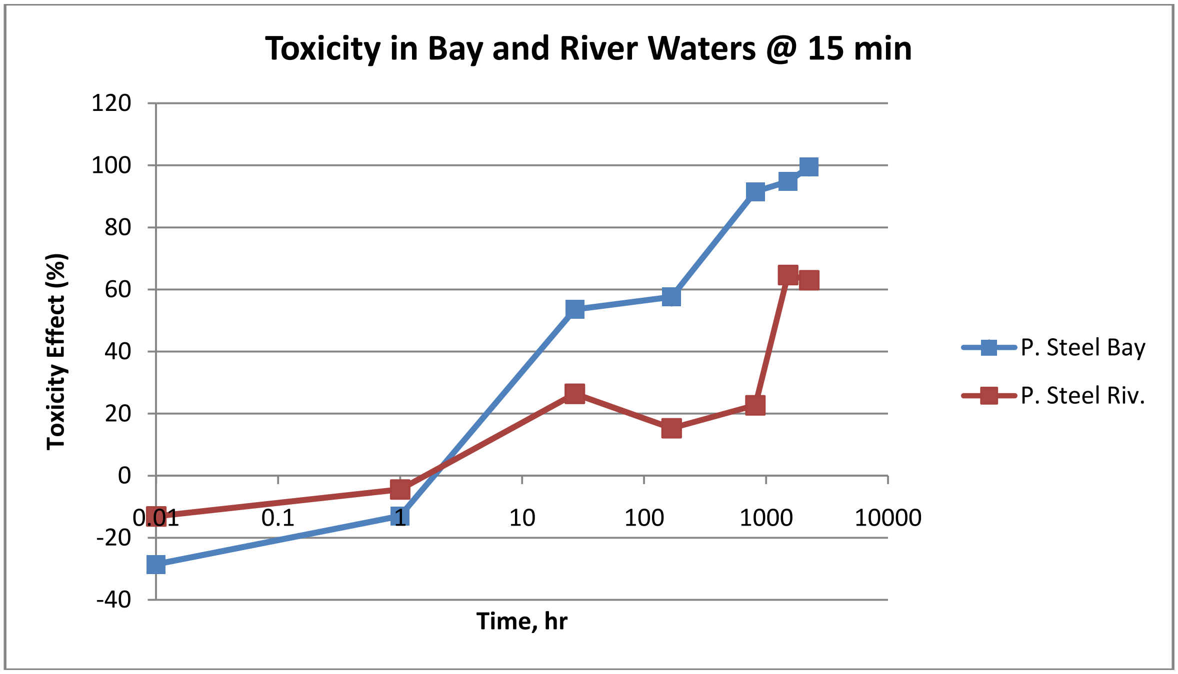


Figure 5.3.2.6 Toxicity effect in samples with galvanized steel pipes immersed in bay and river water at 15 min Microtox exposure time.
(Each point is an average of 2 replicates.)

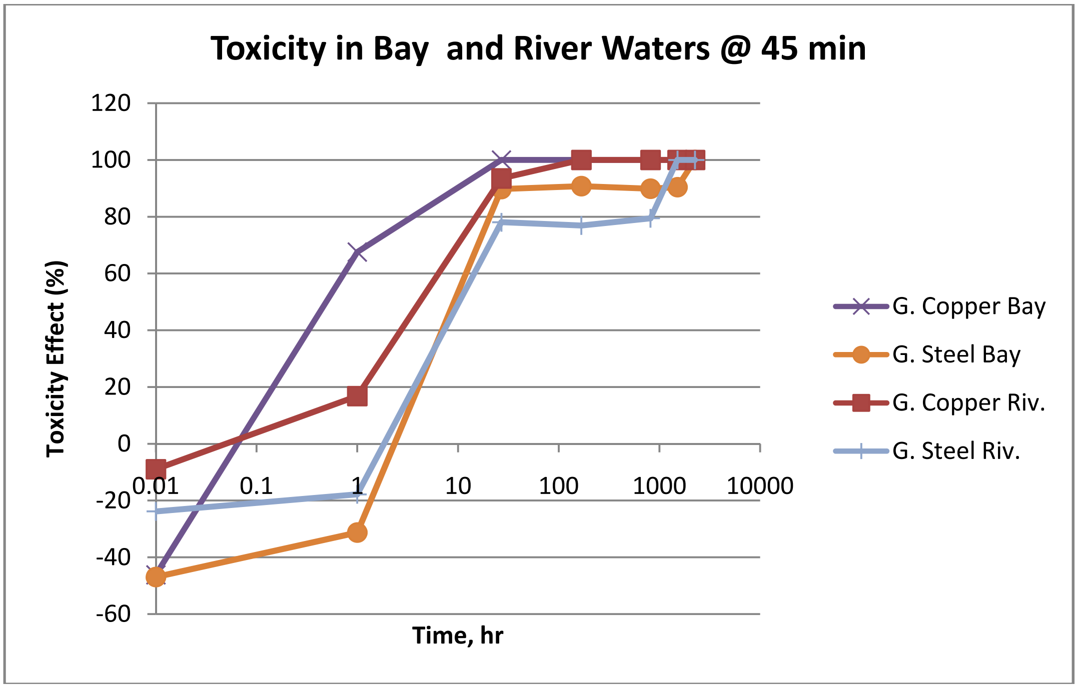


Figure 5.3.2.7 Toxicity effect in samples with copper and galvanized steel gutters immersed in bay and river water at 45 min Microtox exposure time.
(Each point is an average of 2 replicates.)

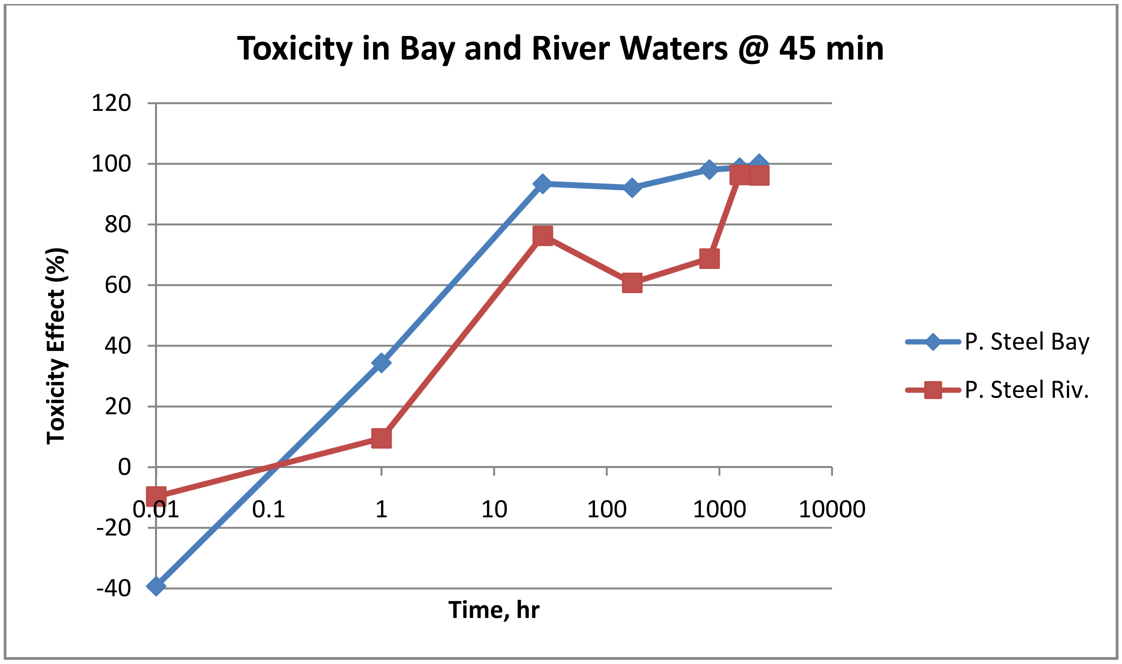


Figure 5.3.2.8 Toxicity effect in samples with galvanized steel pipes immersed in bay and river water at 45 min Microtox exposure time.
(Each point is an average of 2 replicates.)

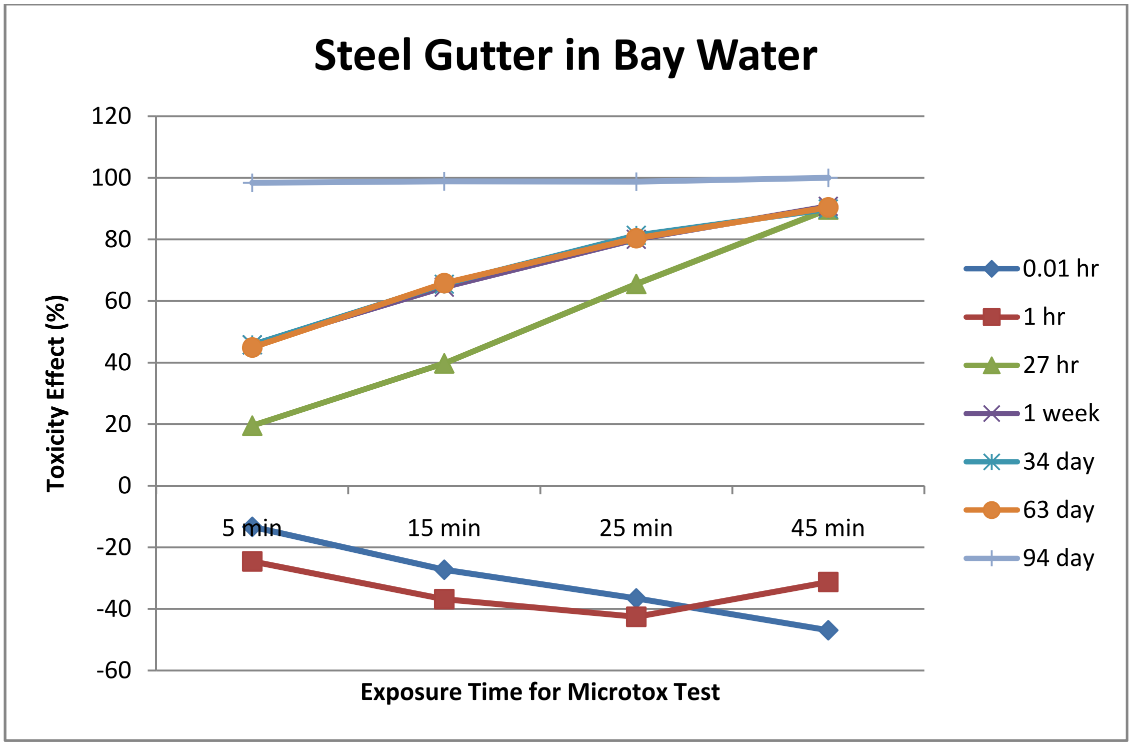


Figure 5.3.2.9 Toxicity effect in samples with galvanized steel gutter immersed in bay water for different Microtox exposure times. (Each point is an average of 2 replicates.)

5.4 Chapter Summary

Under the controlled pH 8 conditions, samples with pipes and roofing materials were found to be less toxic compared to the same materials at controlled pH 5 conditions during the buffered experiments. Copper materials were the most toxic. The concrete pipes were least toxic under both high and low pH conditions during buffered and natural pH tests.

At pH 5, samples with copper, aluminum, vinyl, and HDPE materials resulted in the highest toxicities and were attributed to low pH values. Under buffered pH 8 conditions copper, materials were the most toxic. PVC and galvanized steel materials were slightly toxic. Under natural pH conditions, only the samples with copper and galvanized steel materials were a source of toxicity. Copper and galvanized steel materials caused high toxicity during all tests with buffered and natural conditions.

Based on the toxicity analyses, copper materials should be avoided, and the use of galvanized materials should be limited. Concrete pipes can be used with a wide range of water pH values. In natural water environments with pH values from 7 to 8 and with low and high salinity values, PVC, HDPE, vinyl, aluminum materials also can be used with minimal toxicity issues.

High concentrations of heavy metals leaching out of pipe and gutter materials are toxic to the bacteria. However, the pH of the test water may also interfere with the tests. The pH of storm water can change as it comes in contact with different drainage and roofing materials and may affect the water toxicity. In the next chapter, correlation matrices, Cluster and Principal analyses will examine simple and complex correlations between toxicity and other water chemistry parameters and full Factorial analyses will evaluate the effect of the water pH, time of contact, material, and interactions of those factors during the first test series; and the effect of water conductivity, time of contact, material, and interactions of those factors during the second test series.

6. MODELING THE EFFECTS OF MATERIAL TYPE, EXPOSURE TIME, pH, AND SALINITY ON METAL RELEASES AND TOXICITY

6.1 Introduction

A model was developed to evaluate the effects of different materials available for various applications (roofing components, drainage pipes, culverts, and rainwater storage tanks) on runoff water quality for a range of field conditions, such pH, conductivity, and time of contact. To build an empirical model, Spearman correlation, Cluster, Principal Component and Factorial analyses were used to identify the significant water quality parameters, material and exposure time factors, and their interactions that influence pollutant releases and toxicity.

Spearman correlation analysis was performed to determine the association between constituents and the degree of that association, while cluster analyses were conducted to identify more complex relationships between the parameters. Principle component analyses were conducted to identify groupings of parameters having similar characteristics. The significant factors determined from the factorial analyses were used to combine the data into groups. The final model can be used to determine which materials can be safely used for short contact times such as for gutters and pipes, and for longer term storage, such as for tanks.

The Spearman correlation matrices were constructed using the statistical software Sigma Plot 11.0 (Systat Software, Inc). The cluster analyses were conducted using the statistical software Minitab 16 (Minitab, Inc). Principle component analyses were also conducted using Minitab 16 (Mintab, Inc).

6.2 Spearman Correlation Analyses

Spearman correlation analyses were conducted to measure the degree of association between water quality parameters, toxicity of the samples, time of exposure and the material type. Nonparametric Spearman correlation tests were used because some of the data were not normally distributed (a requirement for the similar Pearson correlation analyses). Parameters examined were Pb, Cu, and Zn concentrations, pH, conductivity, and toxicity at 5, 15, 25, and 45 minutes of bacteria exposure, plus the time of material exposure to the experimental water. Metal concentrations that were below detection limit were substituted with half of the detection limit. Tables G.1 through G.16 (Appendix G) show the correlation matrix for the associations between these parameters for different drainage materials during the buffered and natural pH tests. High spearman correlation coefficients (at or above 0.75) are highlighted in bold.

For all materials during the buffered pH tests, toxicity was negatively correlated with water pH (toxicity increased as the pH decreased). However during the natural pH experiments, positive correlations were observed (toxicity increased as the pH increased) for all the materials, with the exception of galvanized steel pipes and gutters. These toxicity relationship results are likely associated with the pH values being outside of the optimum range for the test bacteria for many of the test conditions and are not related to other experimental factors. For galvanized steel materials under natural pH conditions, there was a strong positive correlation between the toxicity and zinc releases, and for copper materials the toxicity was associated with copper losses. It was found that for majority of the materials (galvanized steel, copper, PVC, aluminum) under controlled pH conditions the toxicity is highly correlated with water conductivity. Toxicities at different times of bacteria exposure were highly correlated to each other, with no apparent change in toxicity mechanism with exposure time (as sometimes occurs if both organic and metallic toxicants are present). For galvanized steel materials, zinc concentrations were strongly associated with the exposure time, and similarly, for copper materials, the copper concentrations were also highly correlated with exposure times. Spearman correlation analyses showed that for galvanized steel materials under natural pH conditions, zinc releases were responsible for most of the toxicity (correlation coefficient >0.77). For the copper materials immersed into natural pH bay and river waters, the toxicity was mainly associated with copper releases.

The identified correlations between pH and metal releases, pH and toxicity, conductivity and metal releases, conductivity and toxicity, exposure time and metal releases, and exposure time and toxicity, were used in empirical model building covering all of the experimental and exposure conditions.

6.3 Cluster Analyses

Cluster analyses were performed to further investigate how pH, conductivity, material, and time of exposure affect the metal releases and toxicity of the samples. This analysis was conducted to examine complex associations between these parameters. The variables were standardized to a common scale to diminish the effects of scale range differences. Figures G.1 through G.17 (Appendix G) show the results of the cluster analyses.Figure6.3.1 is a dendrogram prepared from the cluster analyses for different water quality parameters for steel pipe sections during buffered pH tests (pH 5 and 8 test conditions).This figure shows that lead and copper concentrations were highly correlated with pH and conductivity. Metal releases, pH, and conductivity influenced the toxicity. The toxicity was also affected by time of exposure. Conductivity was closely associated with pH and metal releases.

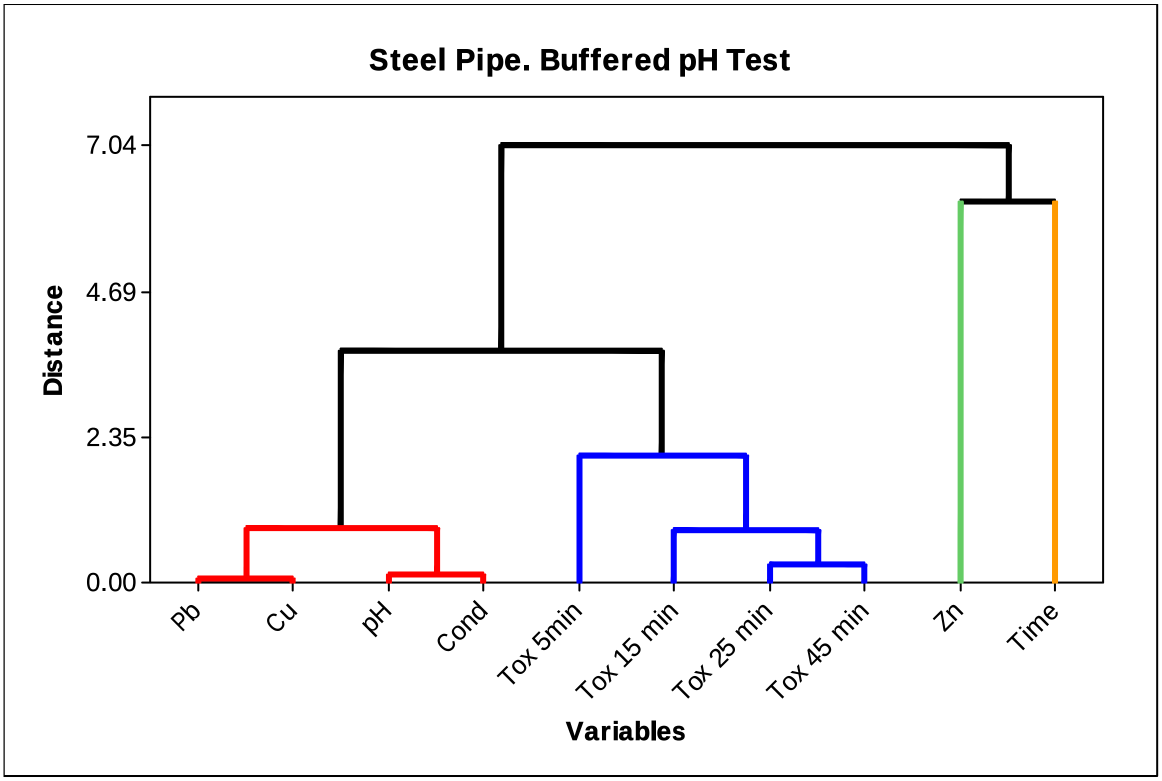


Figure 6.3.1 Dendrogram from cluster analysis for water quality parameters. Galvanized steel pipe. Buffered tests.

Cluster analyses were performed for each gutter and pipe material examining the data for buffered and natural pH tests. The dendrograms (Figures G.1 through G.16, Appendix G) were constructed for the same data that were used to compute the correlation matrices. Spearman correlation analyses confirmed that metal releases, conductivity, pH, and time of exposure all influence the toxicity. There were also high correlations between toxicity and pH, toxicity and metal releases, toxicity and conductivity, metal releases, and time of exposure. Cluster analyses showed that pH also affected the metal releases. The toxicities measured at 5, 15, 25, and 45 min of bacteria exposure to the sample water were closely related, as expected, due to the toxicity being mainly associated with heavy metals. Pb, Cu, and Zn concentrations were highly correlated with pH and conductivity for all materials, with the exception of galvanized materials for which zinc was in a separate cluster. The correlations between toxicities and pH and metal concentrations were greater for galvanized steel materials compared to the other materials.

Also, cluster analyses were used to determine groups of similar materials. These analyses were performed for all pipe and gutter materials using buffered and natural pH test results (Figure 6.3.2). Materials of galvanized steel pipe were similar to galvanized steel gutter, as expected. Generally, PVC, HDPE, vinyl, and aluminum materials also were closely associated; concrete and copper materials were in separate groups from the rest of the materials.

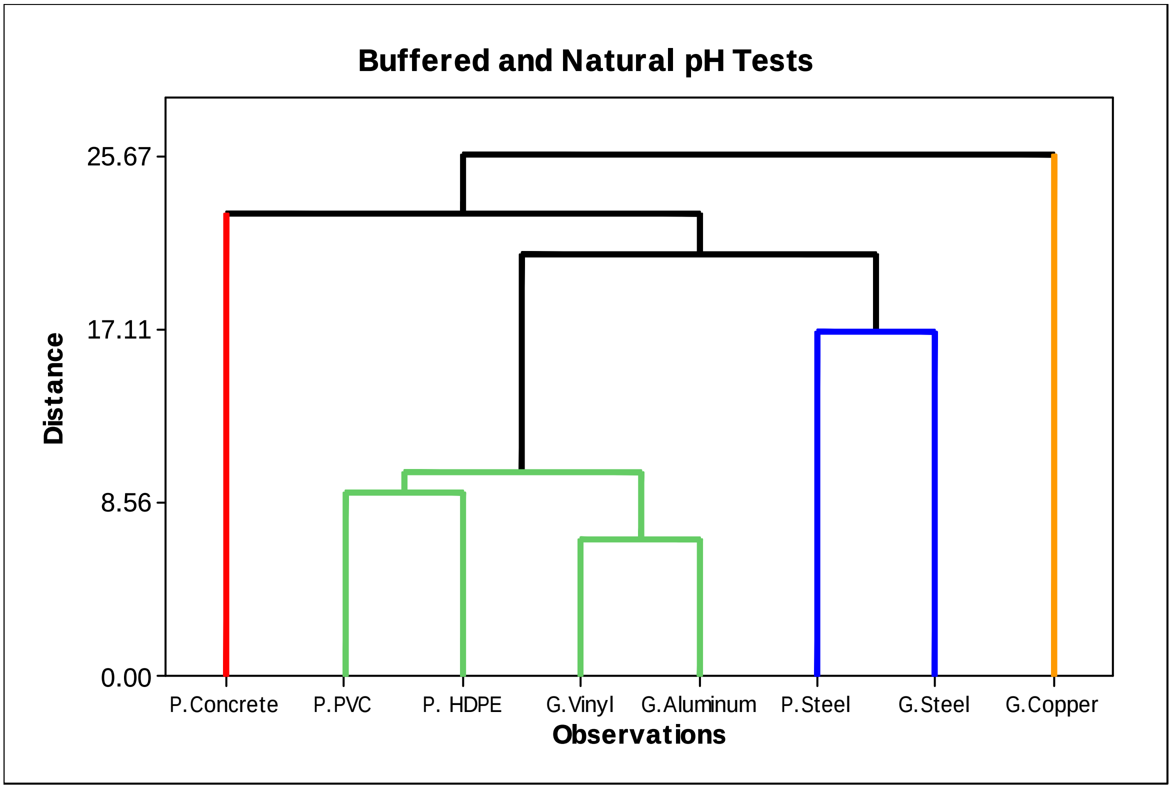


Figure 6.3.2 Dendrogram from cluster analysis for pipe and gutter materials. Buffered and Natural pH Tests.

The influence of pH, conductivity, and time of contact on toxicity and metal concentrations, as well as groupings of similar materials, resulted in supporting their use in model building.

6.4 Principal Component Analyses

Next, Principal Component Analyses (PCA) were performed to identify groupings of samples having similar characteristics. PCA transforms the original set of variables into a smaller set of variables that represents most of the information present in the original dataset (Jensen 2005). Principal components are derived from the original variables such that the first principal component explains the largest proportion of the variance of the data, with subsequent components explaining smaller fractions of the data variance. PCA was conducted on the data on all pipe and gutter materials under buffered and natural pH conditions. Minitab 16 (Minitab, Inc.) software was used for these analyses.

Scree plots (Figure 6.4.1) show eigenvalues of the correlation matrix of eleven sample variables, while Table 6.4.1 shows how much of the total variance is explained by each principal component group. The first four principal components accounts for about 78% of the total variance and can reasonably represent the data set. The fifth principal component explains another 8% of the total variance. Table 6.4.2 shows loadings of the first four principal components. Toxicity values have high loadings on the first principal component. The second principal component has high loadings of time, Pb, and Zn. Copper and Zn have large loading on the third principal component, while pH, conductivity, and material type are included in the fourth principal component.

The relationships between loadings of the first two principal components (that account for approximately 57% of the total variance) are shown in Figure 6.4.2.The vectors on this plot correspond to examined parameters. A vector’s length is comparable to its component loading.

Figure 6.4.2 shows that the first principal component has a large loading associated with toxicity. The second principal component has high loadings associated with time, lead, and zinc, and accounts for exposure time, lead and zinc releases. High loadings of principal components are highlighted in bold. Score plots of the first two principal components (Figures 6.4.3 and 6.4.4) show groupings of samples with comparable principal component loadings and similar water quality characteristics. The group "other materials" on the graphs includes concrete, PVC, HDPE, vinyl, and aluminum materials. The circled group on Figure 6.4.3represents mostly concrete, PVC, HDPE, vinyl, and aluminum materials under controlled pH 8 water conditions. The circled group of data on Figure 6.4.4 is mostly comprised of the samples with all materials that are exposed to pH 5 water conditions and is located in the upper corner of the graph indicating large loadings of toxicity and pH associated with the first principal component.

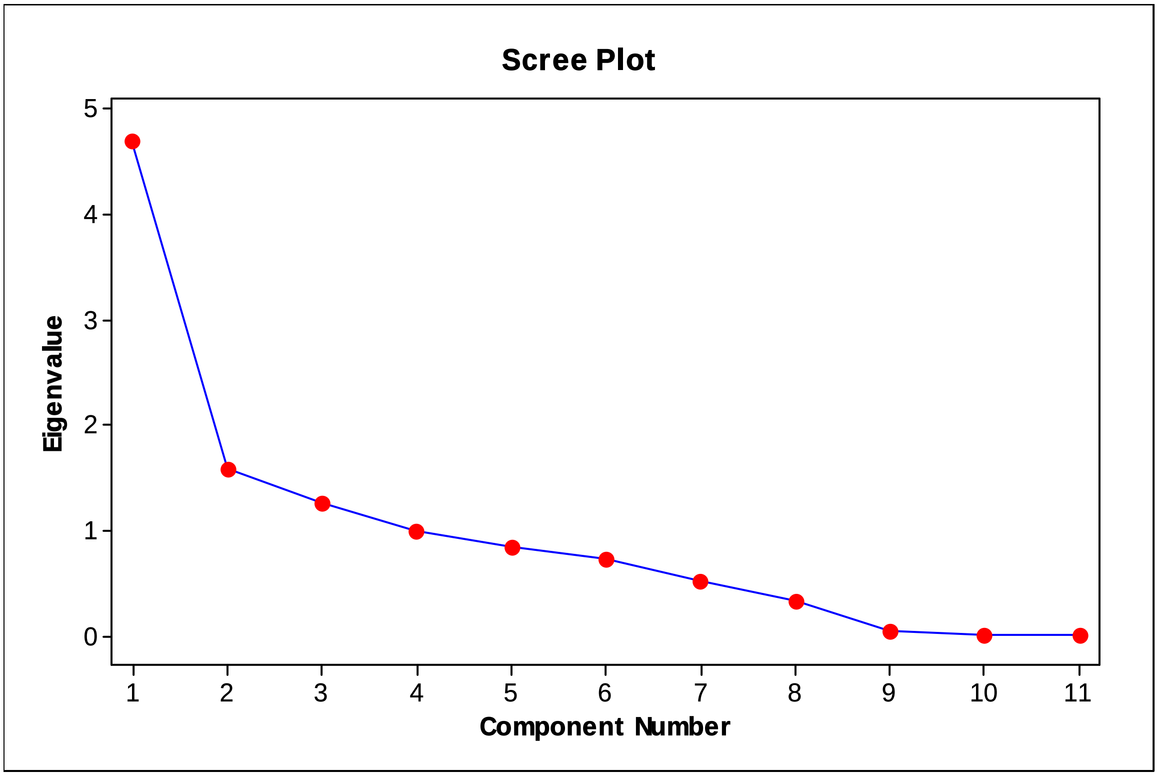


Figure 6.4.1. Scree plot of sample characteristics. All samples combined.

Table 6.4.1. Percent of total variance explained by the first six principal components.

Principal Component	Eigenvalue	Variance Explained by a Component, %	Cumulative Variance, %
1	4.7	42.8	42.8
2	1.57	14.3	57.1
3	1.26	11.5	68.6
4	1.00	9.1	77.6
5	0.84	7.7	85.3
6	0.72	6.6	91.9

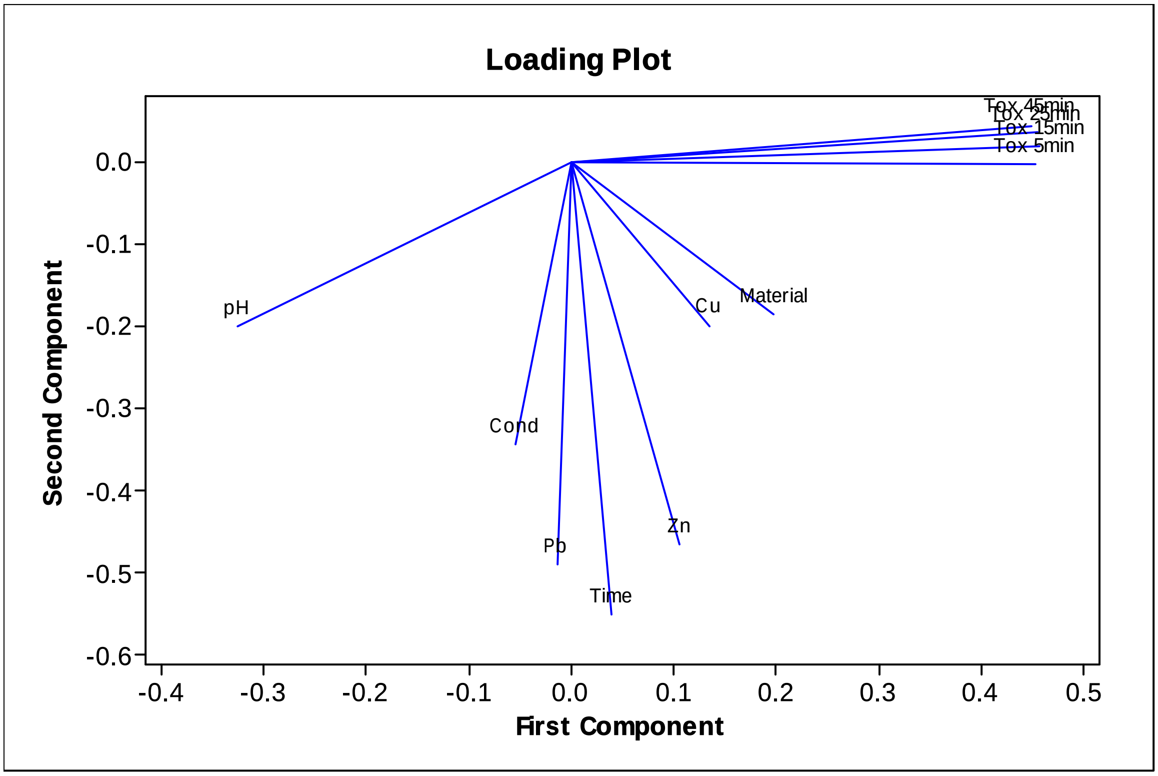


Figure 6.4.2. Principal component loadings for sample characteristics. All samples combined.

Table 6.4.2. Loadings of the principal components. All samples combined.

Variable	PC1	PC2	PC3	PC4
Pb	-0.013	**-0.491**	0.318	0.110
Cu	0.135	-0.199	**-0.606**	-0.181
Zn	0.106	**-0.467**	**0.426**	-0.352
pH	-0.325	-0.201	-0.127	**-0.474**
Cond	-0.055	-0.344	**-0.425**	**0.561**
Tox at 5min	**0.452**	-0.003	0.002	0.096
Tox at 15min	**0.457**	0.019	0.024	0.025
Tox at 25 min	**0.454**	0.036	0.040	-0.023
Tox at 45 min	**0.448**	0.045	0.048	-0.045
Time	0.039	**-0.552**	0.023	0.242
Material	0.198	-0.186	-0.385	**-0.470**

Footnote: High principal component loadings are highlighted in bold.

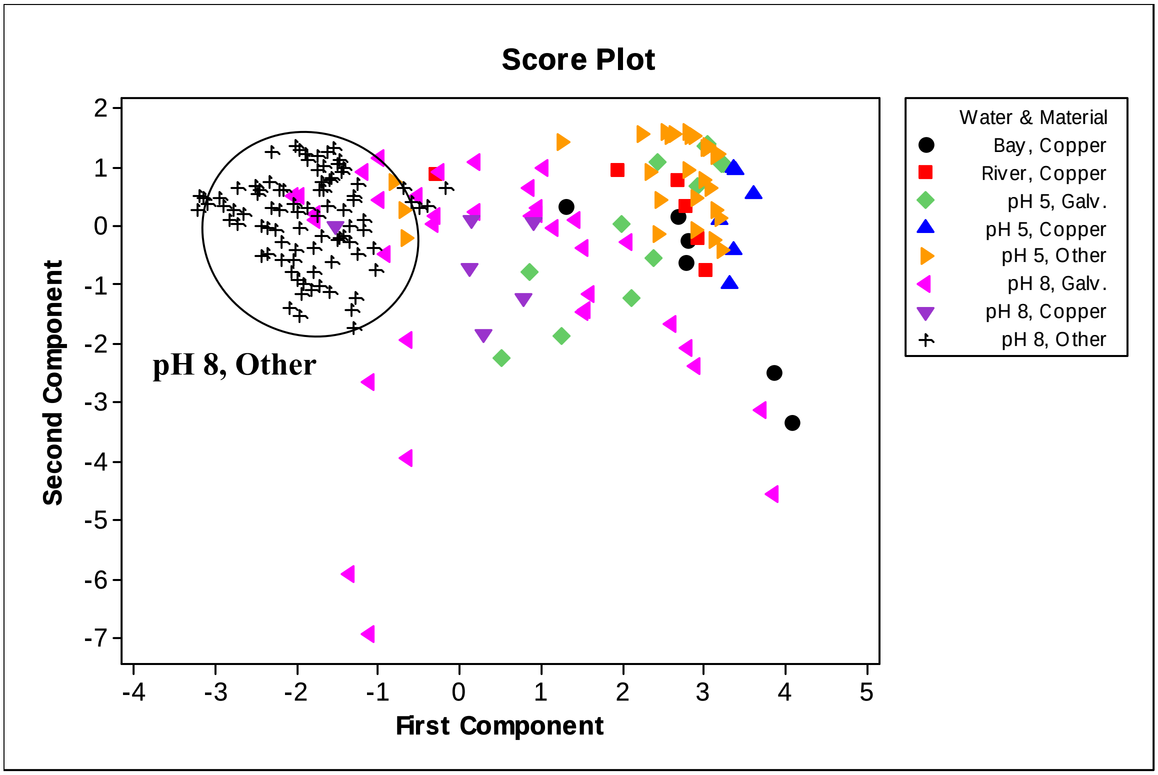


Figure 6.4.3. Score plot of principal components for sample characteristics. All samples combined.

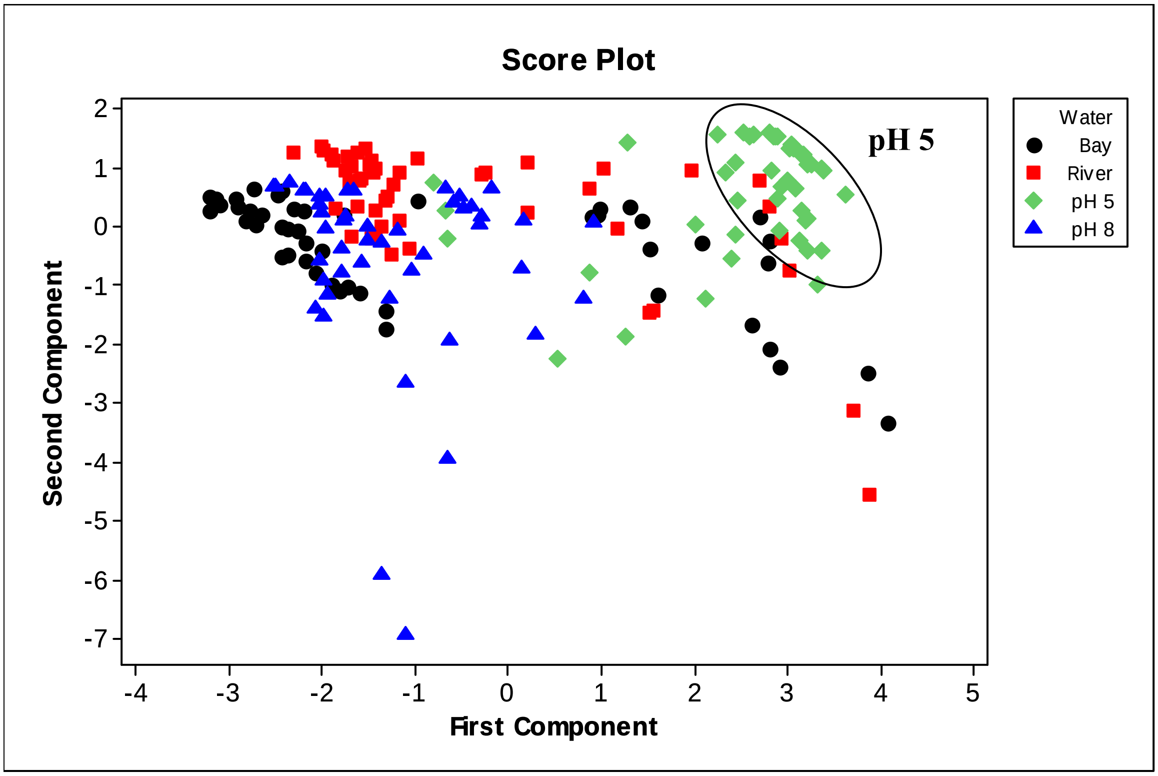


Figure 6.4.4. Score plot of principal components for sample characteristics. All samples combined.

Principal component analysis helped to indentify groupings of samples with similar characteristic. Samples with concrete, plastic, and aluminum materials under controlled pH 8 conditions had low lead and zinc releases and low toxicities. On the other hand, the samples with controlled pH 5 waters were associated with high toxicity.

6.5. Full 2^3 Factorial Analyses

Full 2^3factorial analyses were performed on Cu, Zn, Pb constituents (using the release rates of mg per $m^2$of surface area of exposed materials) and toxicities in percent light reductions at 15 and 45 min of Microtox bacteria exposure times. These analyses therefore examined the effects of time, pH, and material and their interactions for the first testing series data and the effects of time, conductivity, and material and their interactions during for the second testing series data. Table 6.5.1 shows the levels for the different factors defining how the data were sorted. The data from the first and the second testing stages were not combined into a single 2^3factorial analysis because of the lack of data having pH 5 with low conductivity conditions. As described earlier, Kruskal-Wallis tests were performed for each constituent to determine if the data for 1, 2, and 3 months of pipe and gutter exposure could be combined as replicates representing long term exposure times. The tests indicated that there were no statistically significant differences (at 0.05 significance level) between these data so they were combined into one data category. Kruskal–Wallis tests were also conducted for each constituent on the data after 0.5 and 1h of exposure to indicate if they could be combined to represent short exposure periods. These tests similarly showed that these data could be combined into one category for short term exposure times.

Table 6.5.1. 2^3 Factorial Experiment. Factors and levels.

Constituent	Factors and levels		
	Time	pH or Conductivity	Material
Cu (mg/m^2)	short (0.5h, 1h) (-) vs. long (1mo, 2mo,3mo) (+)	pH 5 (-) vs. pH8 (+)	copper (-) vs. the rest of the materials (+)
Cu (mg/m^2)	short (1h) (-) vs. long (1mo, 2mo,3mo) (+)	high cond. (-) vs. low cond. (+)	copper (-) vs. the rest of the materials (+)
Zn (mg/m^2)	short (0.5h, 1h) (-) vs. long (1mo, 2mo,3mo) (+)	pH 5 (-) vs. pH8 (+)	galv. steel (-) vs. the rest of the materials (+)
Zn (mg/m^2)	short (1h) (-) vs. long (1mo, 2mo,3mo) (+)	high cond. (-) vs. low cond. (+)	galv. steel (-) vs. the rest of the materials (+)
Pb (mg/m^2)	short (0.5h, 1h) (-) vs. long (1mo, 2mo,3mo) (+)	pH 5 (-) vs. pH8 (+)	galv. steel (-) vs. the rest of the materials (+)
Pb (mg/m^2)	short (1h) (-) vs. long (1mo, 2mo,3mo) (+)	high cond. (-) vs. low cond. (+)	galv. steel (-) vs. the rest of the materials (+)
Tox @15 min (%)	short (0.5h, 1h) (-) vs. long (1mo, 2mo,3mo) (+)	pH 5 (-) vs. pH8 (+)	metal (-) vs. non-metal (+)
Tox @15 min (%)	short (0.5h, 1h) (-) vs. long (1mo, 2mo,3mo) (+)	pH 5 (-) vs. pH8 (+)	copper and galv. steel (-) vs. the rest of the materials (+)
Tox @15 min (%)	short (1h) (-) vs. long (1mo, 2mo,3mo) (+)	high cond. (-) vs. low cond. (+)	copper and galv. steel (-) vs. the rest of the materials (+)
Tox @45 min (%)	short (0.5h, 1h) (-) vs. long (1mo, 2mo,3mo) (+)	pH 5 (-) vs. pH8 (+)	metal (-) vs. non-metal (+)
Tox @45 min (%)	short (0.5h, 1h) (-) vs. long (1mo, 2mo,3mo) (+)	pH 5 (-) vs. pH8 (+)	copper and galv. steel (-) vs. the rest of the materials (+)
Tox @45 min (%)	short (1h) (-) vs. long (1mo, 2mo,3mo) (+)	high cond. (-) vs. low cond. (+)	copper and galv. steel (-) vs. the rest of the materials (+)

The results of the 2^3factorial analyses are shown in Appendix F. Figure F.1 (Appendix F) shows normal probability plots of the effects and their interactions. The factorial effect/pooled standard error ratio of the factorial analysis (shown in Tables 6.5.2 and 6.5.3) were used to determine whether or not the data could be combined into groups for each constituent based on the effect (or absence of effect) of the factors and their interactions. The ratios of Effect/SE that were greater than three are highlighted in red, and those that are greater than five are highlighted in bold red, indicating likely significant factors and interactions. For each constituent, effects and their interactions were sorted into significant, marginally significant, and not significant groups, according to the absolute values of their effects (Tables 6.5.4 and 6.5.5). Tables 6.5.6 and 6.5.7 show the statistical findings and significant groupings for each constituent for the different exposure conditions for each constituent according to these results.

Table 6.5.2. 2^3 Factorial effect/standard error of the effect ratio (Controlled pH tests).

		Effect/Pooled Standard Error of the Effect						
Constituent	**2^3 Factorial**	**pH**	**Material**	**Time**	**pH x Material**	**pH x Time**	**Material x Time**	**pH x Material x Time**
Cu	pH: 5 vs. 8 M: Cop vs. the rest[1] T: Short vs. Long[4]	**-49.79**	**-108.74**	**82.24**	**49.61**	**-24.12**	**-81.10**	**24.01**
Zn	pH: 5 vs. 8 M: Galv. vs. the rest[2] T: Short vs. Long	3.44	**-6.64**	**6.04**	-3.42	4.03	**-6.01**	-4.02
Pb	pH: 5 vs. 8 M: Galv. vs. the rest[2] T: Short vs. Long	1.91	**-5.21**	**5.30**	-1.91	1.91	**-5.33**	-1.91
Tox. At 15 min	pH: 5 vs. 8 M: Cop, Galv. vs. the rest[3] T: Short vs. Long	**-26.77**	-2.36	-1.72	-3.34	**6.29**	0.25	-1.99
Tox. At 45 min	pH: 5 vs. 8 M: Cop, Galv. vs. the rest[3] T: Short vs. Long	**-25.78**	-2.41	-1.74	-3.23	4.46	-0.82	-1.86

[1] The rest = all the materials excluding copper: concrete, PVC, HDPE, and galv. steel pipes, and vinyl, aluminum, and galv. steel gutters.

[2] The rest = = all the materials excluding galvanized steel: concrete, PVC, HDPE pipes, and vinyl, aluminum, and copper gutters.

[3] The rest = all the materials excluding copper and galvanized steel: concrete, PVC, HDPE pipes, and vinyl and aluminum gutters.

[4] Short, long exposure times

The ratios of Effect/SE of the effect that were greater than three are highlighted in red, and those that are greater than five are highlighted in bold red, indicating likely significant factors and interactions.

Table 6.5.3. 2^3 Factorial effect/pooled standard error of the effect ratio (Natural pH tests).

		Effect/Standard Error of the Effect						
Constituent	**2^3 Factorial**	**Cond.**	**Material**	**Time**	**Cond. x Material**	**Cond. x Time**	**Material x Time**	**Cond. x Material x Time**
Cu	Cond.: High vs. Low M: Cop vs. the rest[1] T: Short vs. Long[4]	**-6.59**	**-9.15**	**8.94**	**6.59**	**-6.45**	**-8.94**	**6.45**
Zn	Cond.: High vs. Low M: Galv. vs. the rest[2] T: Short vs. Long	2.29	**-5.41**	**5.28**	-2.29	2.32	**-5.27**	-2.32
Pb	Cond.: High vs. Low M: Galv. vs. the rest[2] T: Short vs. Long	2.00	-2.34	2.24	-2.00	3.01	-2.41	-3.01
Tox. At 15 min	Cond.: High vs. Low M: Cop.& Galv. vs. the rest[3] T: Short vs. Long	2.04	**-24.72**	**17.31**	**5.08**	-2.27	**-13.94**	-0.42
Tox. At 45 min	Cond.: High vs. Low M: Cop.& Galv. vs. the rest[3] T: Short vs. Long	3.04	**-41.68**	**20.99**	**8.79**	1.32	**-17.19**	-2.56

[1] The rest = all the materials excluding copper: concrete, PVC, HDPE, and galv. steel pipes, and vinyl, aluminum, and galv. steel gutters.

[2] The rest = all the materials excluding galvanized steel: concrete, PVC, HDPE pipes, and vinyl, aluminum, and copper gutters.

[3] The rest = all the materials excluding copper and galvanized steel: concrete, PVC, HDPE pipes, and vinyl and aluminum gutters.

[4] Short, long exposure times

The ratios of Effect/SE of the effect that were greater than three are highlighted in red, and those that are greater than five are highlighted in bold red, indicating likely significant factors and interactions.

Table 6.5.4. 2^3 Factorial significant effects and their interactions (Buffered pH Tests).

Constituent	**2^3 Factorial**	Effect		
		Significant	Marginally Significant	Not Significant
Cu	pH: 5 vs. 8 M: Cop vs. the rest T: Short vs. Long	pH, material, time, pH x material, pH x time, material x time, pH x material x time.		
Zn	pH: 5 vs. 8 M: Galv. vs. the rest T: Short vs. Long	material, time, material x time	pH, pH x material, pH x time, pH x material x time.	
Pb	pH: 5 vs. 8 M: Galv. vs. the rest T: Short vs. Long	material, time, material x time,		pH, pH x material, pH x time, pH x material x time.
Tox. At 15 min	pH: 5 vs. 8 M: Cop, Galv. vs. the rest T: Short vs. Long	pH, pH x time,	pH x material,	material, time, material x time, pH x material x time.
Tox. At 45 min	pH: 5 vs. 8 M: Cop, Galv. vs. the rest T: Short vs. Long	pH,	pH x material, pH x time,	material, time, material x time, pH x material x time.

Table 6.5.5. 2^3 Factorial significant effects and their interactions (Natural pH Tests).

Constituent	**2^3 Factorial**	Effect		
		Significant	Marginally Significant	Not Significant
Cu	Cond.: High vs. Low M: Cop vs. the rest T: Short vs. Long	cond., material, time, cond. x material, cond. x time, material x time, cond. x material x time.		
Zn	Cond.: High vs. Low M: Galv. vs. the rest T: Short vs. Long	material, time, material x time,		cond., cond. x material, cond. x time, cond. x material x time.
Pb	Cond.: High vs. Low M: Galv. vs. the rest T: Short vs. Long		cond. x time, cond. x material x time.	Cond., material, time, cond. x material, material x time,
Tox. At 15 min	Cond.: High vs. Low M: Cop.& Galv. vs. the rest T: Short vs. Long	material, time, cond. x material, material x time,		cond., cond. x time, cond. x material x time.
Tox. At 45 min	Cond.: High vs. Low M: Cop.& Galv. vs. the rest T: Short vs. Long	material, time, cond. x material, material x time,	cond.,	cond. x time, cond. x material x time.

Table 6.5.6. 2^3 Factorial significant groups for constituents (Buffered pH tests).

Constituent	**2^3 Factorial**	**Groups**
Cu	pH: 5 vs. 8 M: Cop vs. the rest[1] T: Short vs. Long[4]	Short exp. period at pH 5 copper vs. Short exp. period at pH5 the rest vs. Long exp. period at pH 5 copper vs. Long exp. period at pH 5 the rest vs. Short exp. period at pH 8 copper vs. Short exp. period at pH 8 the rest vs. Long exp. period at pH 8 copper vs. Long exp. period at pH 8 the rest
Zn	pH: 5 vs. 8 M: Galv. vs. the rest[2] T: Short vs. Long	Short exp. period at pH 5, galv. vs. Short exp. period at pH5, the rest vs. Long exp. period at pH 5, galv. vs. Long exp. period at pH 5 the rest vs. Short exp. period at pH 8, galv. vs. Short exp. period at pH 8, the rest vs. Long exp. period at pH 8, galv. vs. Long exp. period at pH 8, the rest
Pb	pH: 5 vs. 8 M: Galv. vs. the rest[2] T: Short vs. Long	Galv. at short exp. period (pH 5 and 8 combined) vs. The rest at short exp. period (pH 5 and 8 combined) vs. Galv. at long exp. period (pH 5 and 8 combined) vs. The rest at long exp. period (pH 5 and 8 combined)
Tox. At 15 min	pH: 5 vs. 8 M: Cop, Galv. vs. the rest[3] T: Short vs. Long	Short exp. period at pH 5 (all materials combined) vs. Short exp. period at pH 8 (all materials combined) vs. Long exp. period at pH 5 (all materials combined) vs. Long exp. period at pH 8 (all materials combined) vs. Cop, galv., at pH 5 (short and long exp. periods combined) vs. Cop, galv., at pH 8 (short and long exp. periods combined)vs. The rest at pH 5 (short and long exp. periods combined) vs. The rest at pH 8 (short and long exp. periods combined)
Tox. At 45 min	pH: 5 vs. 8 M: Cop, Galv. vs. the rest[3] T: Short vs. Long	Short exp. period at pH 5 (all materials combined) vs. Short exp. period at pH 8 (all materials combined) vs. Long exp. period at pH 5 (all materials combined) vs. Long exp. period at pH 8 (all materials combined) vs. Cop, galv., at pH 5 (short and long exp. periods combined) vs. Cop, galv., at pH 8 (short and long exp. periods combined) vs. The rest at pH 5 (short and long exp. periods combined) vs. The rest at pH 8 (short and long exp. periods combined)

[1] The rest = all the materials excluding copper: concrete, PVC, HDPE, and galv. steel pipes, and vinyl, aluminum, and galv. steel gutters.

[2] The rest = = all the materials excluding galvanized steel: concrete, PVC, HDPE pipes, and vinyl, aluminum, and copper gutters.

[3] The rest = all the materials excluding copper and galvanized steel: concrete, PVC, HDPE pipes, and vinyl and aluminum gutters.

[4] Short, long exposure times

Table 6.5.7. 2^3 Factorial significant groups for constituents (Natural pH tests).

Constituent	2^3 Factorial	Groups
Cu	Cond.: High vs. Low[5] M: Cop vs. the rest[1] T: Short vs. Long[4]	Low cond. at short exp. period copper vs. Low cond. at short exp. period the rest vs. High cond. at short exp. period copper vs. High cond. at short exp. period the rest vs. Low cond. at long exp. period copper vs. Low cond. at long exp. period the rest vs. High cond. at long exp. period copper vs. High cond. at long exp. period the rest
Zn	Cond.: High vs. Low M: Galv. vs. the rest[2] T: Short vs. Long	Galv. at short exp. period (low and high cond. combined) vs. The rest at short exp. period (low and high cond. combined) vs. Galv. at long exp. period (low and high cond. combined) vs. The rest at long exp. period (low and high cond. combined) vs.
Pb	Cond.: High vs. Low M: Galv. vs. the rest[2] T: Short vs. Long	Low cond. at short exp. period, galv. vs. Low cond. at short exp. period the rest vs. High cond. at short exp. period, galv. vs. High cond. at short exp. period the rest vs. Low cond. at long exp. period, galv. vs. Low cond. at long exp. period the rest vs. High cond. at long exp. period, galv. vs. High cond. at long exp. period the rest
Tox. At 15 min	Cond.: High vs. Low M: Cop.& Galv. vs. the rest[3] T: Short vs. Long	Cop, galv. at short exp. period (low and high cond. combined) vs. The rest at short exp. period (low and high cond. combined)vs. Cop, galv. at long exp. period (low and high cond. combined) vs. The rest at long exp. period (low and high cond. combined) vs. Cop, galv. at low cond. (short and long exp. periods combined) vs. The rest at low cond. (short and long exp. periods combined) vs. Cop, galv. at high cond. (short and long exp. periods combined) vs. The rest at high cond. (short and long exp. periods combined)
Tox. At 45 min	Cond.: High vs. Low M: Cop.& Galv. vs. the rest[3] T: Short vs. Long	Cop, galv. at short exp. period (low and high cond. combined) vs. The rest at short exp. period (low and high cond. combined) vs. Cop, galv. at long exp. period (low and high cond. combined) vs. The rest at long exp. period (low and high cond. combined) vs. Cop, galv. at low cond. (short and long exp. periods combined) vs. The rest at low cond. (short and long exp. periods combined) vs. Cop, galv. at high cond. (short and long exp. periods combined) vs. The rest at high cond. (short and long exp. periods combined)

[1] The rest = all the materials excluding copper: concrete, PVC, HDPE, and galv. steel pipes, and vinyl, aluminum, and galv. steel gutters.

[2] The rest = = all the materials excluding galvanized steel: concrete, PVC, HDPE pipes, and vinyl, aluminum, and copper gutters.

[3] The rest = all the materials excluding copper and galvanized steel: concrete, PVC, HDPE pipes, and vinyl and aluminum gutters.

[4] Short, long exposure times

[5] High (bay water), low (river water) conductivity

Retrospective sensitivity analyses for two full 2^3factorial experiments were performed to determine what differences could be detected with acceptable power and confidence given the available sample sizes. An assumption was made that the standard deviation of the sample was equal to the standard deviation of the population. Minitab 16 software was used. The analyses were conducted at power 80% and at two alpha levels of 0.05 and 0.1 for copper, zinc, lead, and toxicities (Table 6.5.8).

Table 6.5.8. Sensitivity analyses for full 2^3 Factorial experiments. (Power 0.8)

Constituent and Conditions	St. Dev.	Sample Size	Difference (mg/m^2 for metals, % for toxicity)	
			α = 0.05	α = 0.1
Cu Releases (mg/m^2). Buffered pH Waters	61.47	2	709.972	356.084
		3	200.641	141.213
		14	49.800	43.154
		21	39.510	34.541
Cu Releases (mg/m^2). Natural pH Waters	364.2	3	1188.76	836.667
		7	463.47	388.468
		21	234.09	204.653
Zn Releases (mg/m^2). Buffered pH Waters	634.5	4	1350.18	1046.74
		6	910.22	752.37
		12	563.85	486.27
		18	444.61	387.60
Zn Releases (mg/m^2). Natural pH Waters	1498	2	17301.7	8677.62
		6	2148.9	1776.29
		18	1049.7	915.08
Pb Releases (mg/m^2). Buffered pH Waters	4.678	4	9.95455	7.71736
		6	6.71080	5.54704
		12	4.15712	3.58516
		18	3.27798	2.85764
Pb Releases (mg/m^2). Natural pH Waters	0.3243	2	3.74563	1.87861
		6	0.46522	0.38455
		18	0.22724	0.19810
Toxicity (%) at 15 min. Buffered pH Waters	53.57	12	47.6052	41.0553
		18	37.5377	32.7242
		20	35.3799	30.9047
		30	28.3512	24.9065
Toxicity (%) at 45 min. Buffered pH Waters	61.16	12	54.3501	46.8722
		18	42.8562	37.3606
		20	40.3926	35.2834
		30	32.3681	28.4353
Toxicity (%) at 15 min. Natural pH Waters	51.25	6	73.5204	60.7708
		10	51.0451	43.7069
		18	35.9120	31.3069
		30	27.1233	23.8278
Toxicity (%) at 45 min. Natural pH Waters	59.17	6	84.8820	70.1621
		10	58.9334	50.4612
		18	41.4618	36.1450
		30	31.3149	27.5101

The sample sizes for the full 2^3factorial experiments were used. Figures 6.5.1 and 6.5.2 are examples of power curves for copper releases under controlled pH conditions at different alpha levels (0.05 and 0.1). The retrospective sensitivity analyses showed that for copper releases under these controlled pH conditions, the full 2^3factorial analysis with a sample size of 2 can detect difference among mean copper releases of 700 mg/m^2 at an alpha of 0.05; increasing the alpha to 0.1 will allow detecting a difference of 350 mg/m^2. With the sample size of 21, differences of 50 and 43 mg/m^2 for alpha levels of 0.05 and 0.1 respectively could be detected. The increase in standard deviation in copper releases under natural pH conditions compared to the buffered pH tests, increased the difference that could be detected (230 and 200 mg/m^2 for alpha levels of 0.05 and 0.1 respectively). Similar data are shown for zinc releases.

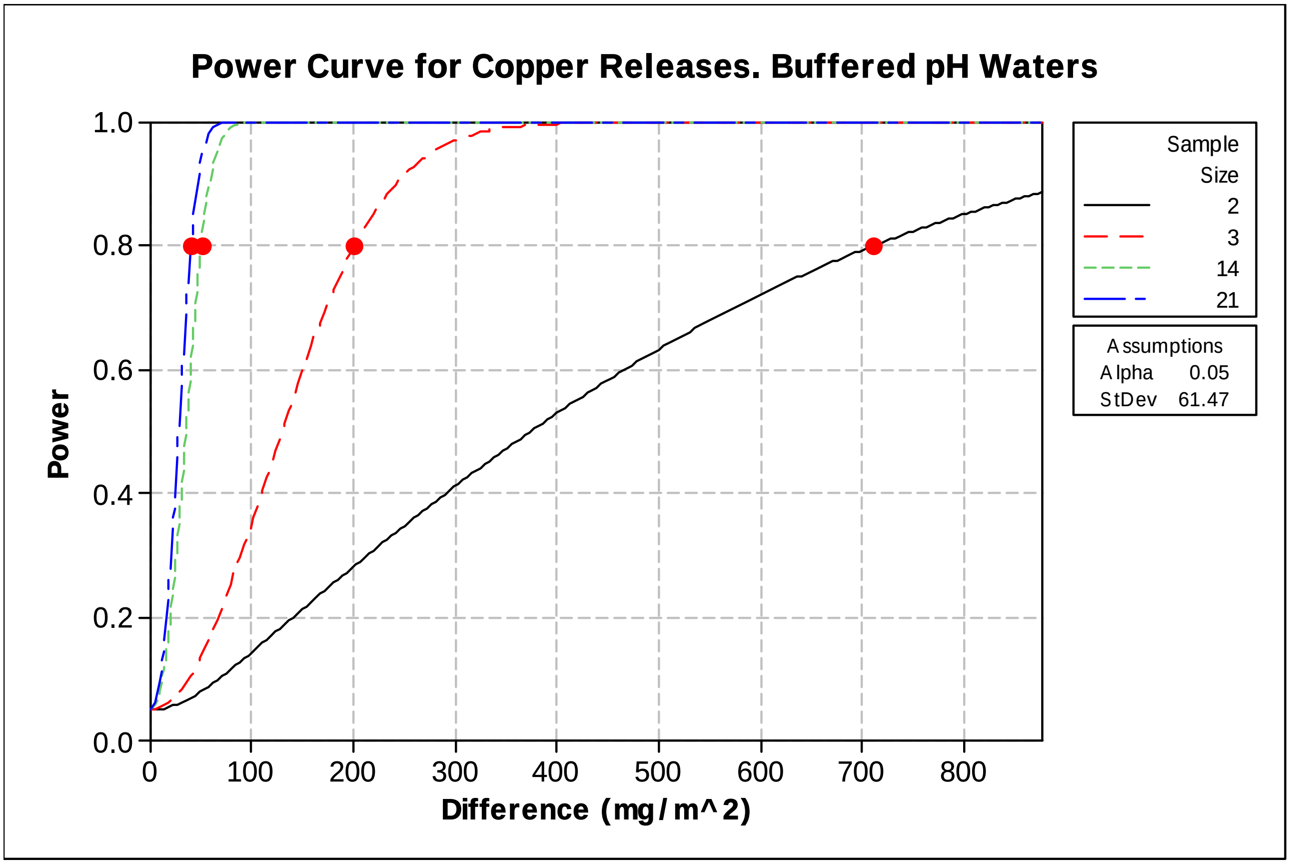


Figure 6.5.1. Power curve for copper releases. Buffered pH waters. (α = 0.05).

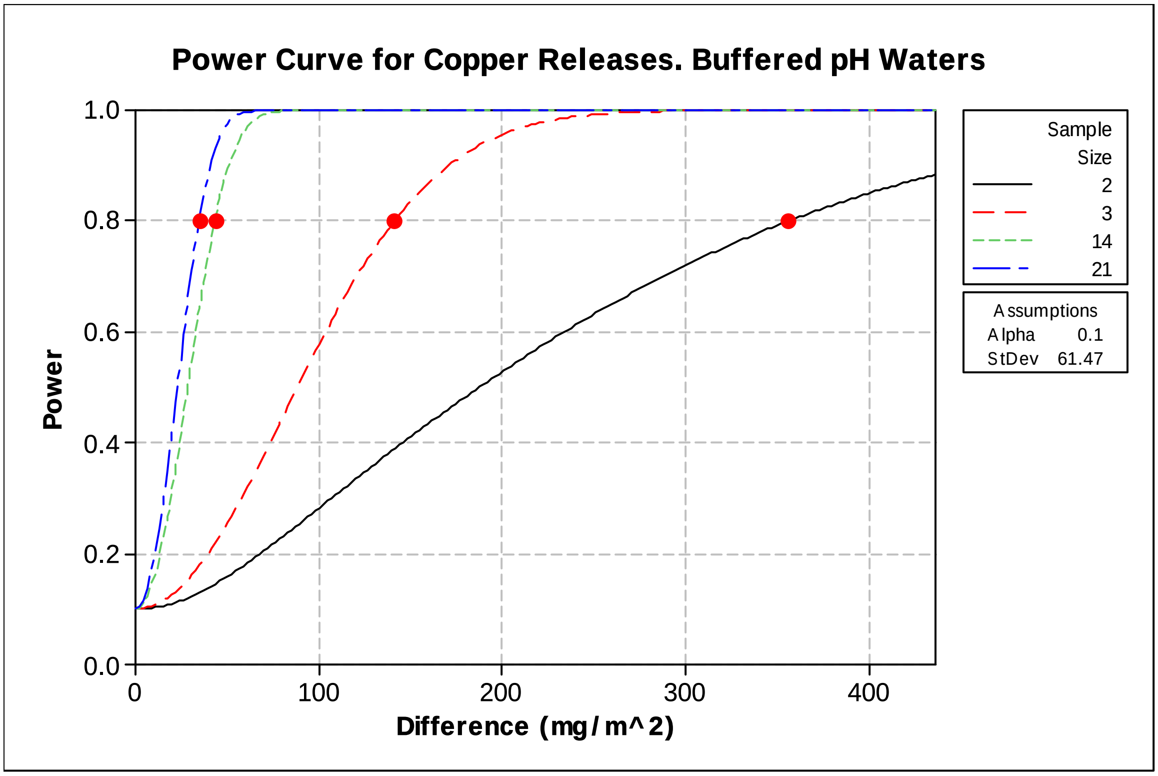


Figure 6.5.2. Power curve for copper releases. Buffered pH waters. (α = 0.1).

Significant factors and their interactions from the full 2^3 factorial analyses were used to combine the data for metal releases and toxicities into significant groups in order to identify critical combinations of materials, exposure times, and pH (during the first test series) and conductivity (during the second test series) and interaction of these factors. Retrospective sensitivity analyses for two full 2^3factorial experiments were conducted to determine how small of a difference could be detected with acceptable power and confidence levels given the existing sample sizes for the different sample groupings.

6.6 Combined Data Group Analyses

Figures 6.6.1 through 6.6.13 show metal releases and toxicities at 15 and 45 min for the combined data groups, based on the prior analyses. The significant factors and their interactions from 2^3factorial analyses were used for grouping the samples and conditions. The box plots were constructed only for the groups that were found to be significant. Group box plots were plotted for these constituents to illustrate the variations and differences between each group. Figure 6.6.1 is a group box plot of copper releases comparing the copper material samples with the all of the other samples for pH 5 and 8 conditions during both short and long exposure times. Full 2^3factorial analysis showed that the three-way interaction of pH x material x time was significant, therefore the main effects should not be interpreted (Navidi 2006).The data was combined into the groups according to the interaction of pH, material, and time. Copper materials were the most significant source of copper, as expected. Lower pH conditions increased the copper releases from the copper materials. The copper releases in the sample groups of all materials increased with exposure time. The combination of conditions, such as copper materials under pH 5 water conditions during short exposure time, significantly increased copper releases. Similarly, copper releases increased dramatically for copper materials immersed into pH 5 water for long exposure periods, as well as for copper materials immersed into pH 8 waters for long exposure periods. Figure 6.6.2 shows the groups combining the rest of the materials for pH 5 and pH 8 conditions during short exposure time into one group; also, the rest of the materials for pH 5 and pH 8 conditions during long exposure time into one group.

Copper Release. Controlled pH.

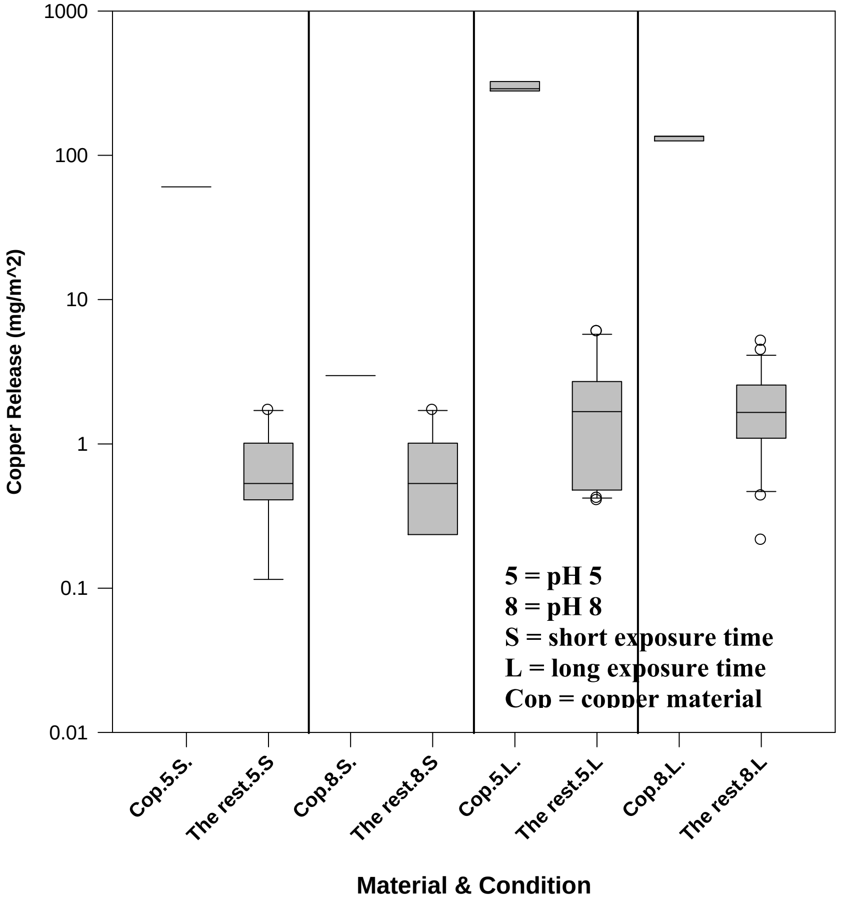


Figure 6.6.1. Group box plot for copper release in mg/m^2 for materials immersed in pH 5 and pH 8 waters.

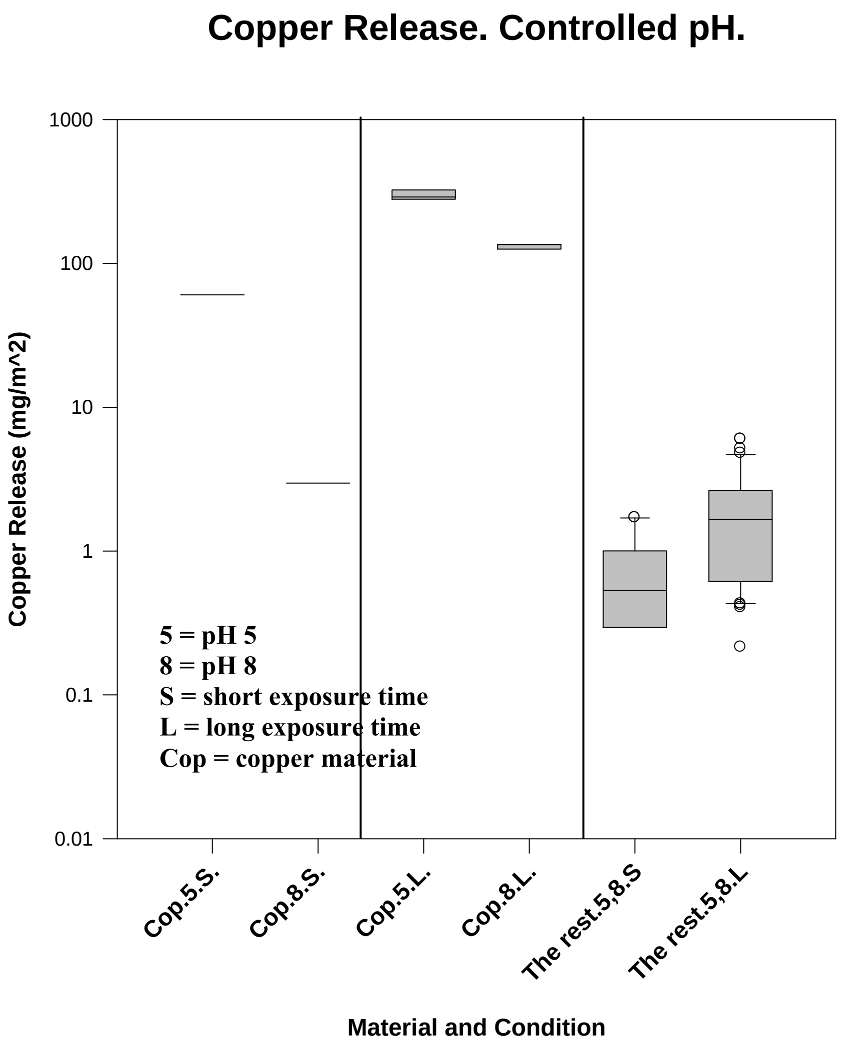


Figure 6.6.2. Group box plot for copper release in mg/m^2 for materials immersed in pH 5 and pH 8 waters.

Figure 6.6.3 shows copper releases in the pipe and gutter samples immersed in bay and river waters. Copper releases were detected during both short and long exposures for controlled pH conditions and for both the natural bay and river water tests. Copper concentrations were greater for bay water exposure tests compared to river water exposure tests. Exposure time also increased copper releases in the samples with copper gutter materials. The combination of copper materials, high conductivity, and long exposure periods, as well as copper materials, low conductivity, and long exposure periods, significantly increased copper releases.

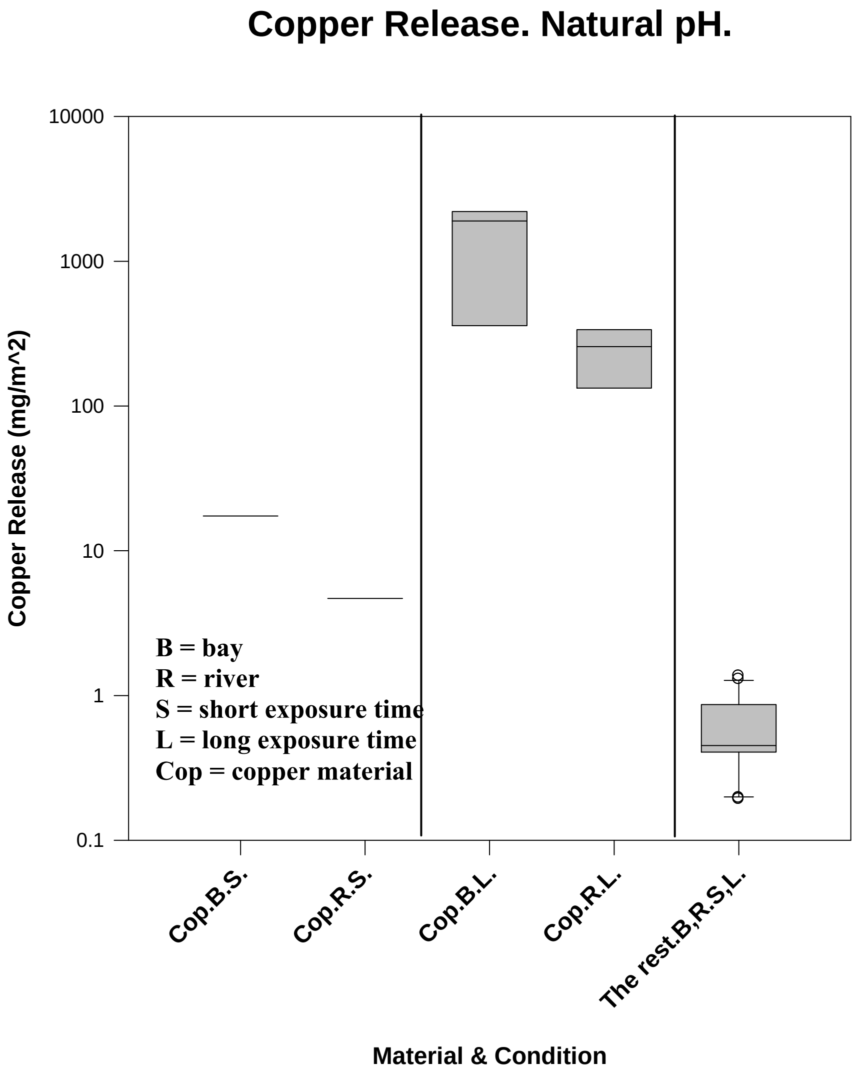


Figure 6.6.3. Group box plot for copper release in mg/m^2 for materials immersed in bay and river waters.

Figure 6.6.4 is a group box plot of zinc releases for the galvanized steel samples compared to the rest of the material samples for pH 5 and 8 conditions during short and long exposure periods. Galvanized steel materials were the greatest source of zinc. During short exposure times, low pH conditions increased zinc releases in the samples with galvanized materials, however during long exposure times, zinc releases were greater under controlled pH 8 conditions compared to controlled pH 5 conditions. Exposure time increased zinc releases in the samples with galvanized materials. The combination of such factors as galvanized materials, pH 5, and short exposure periods, resulted in significant increases in zinc releases. Similarly, zinc releases were much higher for galvanized materials immersed into pH 5 waters for long exposure periods, and for galvanized materials immersed into pH 8 waters for long exposure periods. Figure 6.6.5 shows "the rest" of the materials at pH 5 and pH 8 conditions during short and long exposure periods combined into one group.

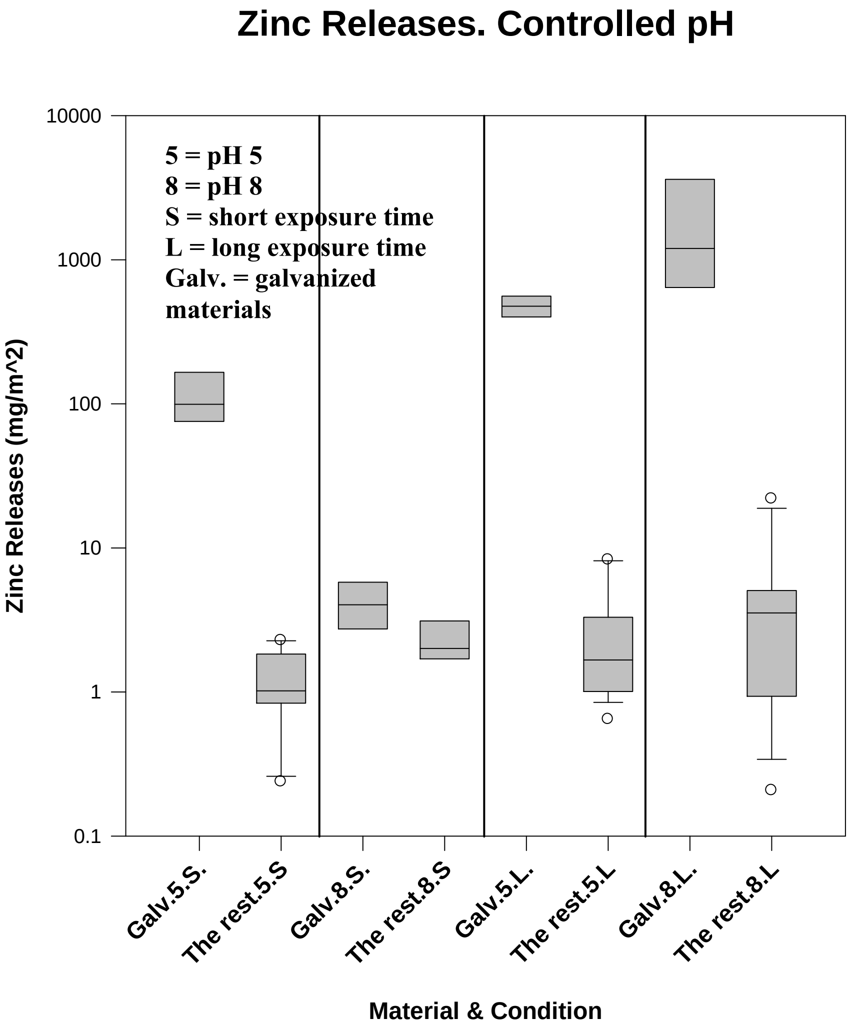


Figure 6.6.4. Group box plot for zinc release in mg/m^2 for materials immersed in pH 5 and pH 8 waters.

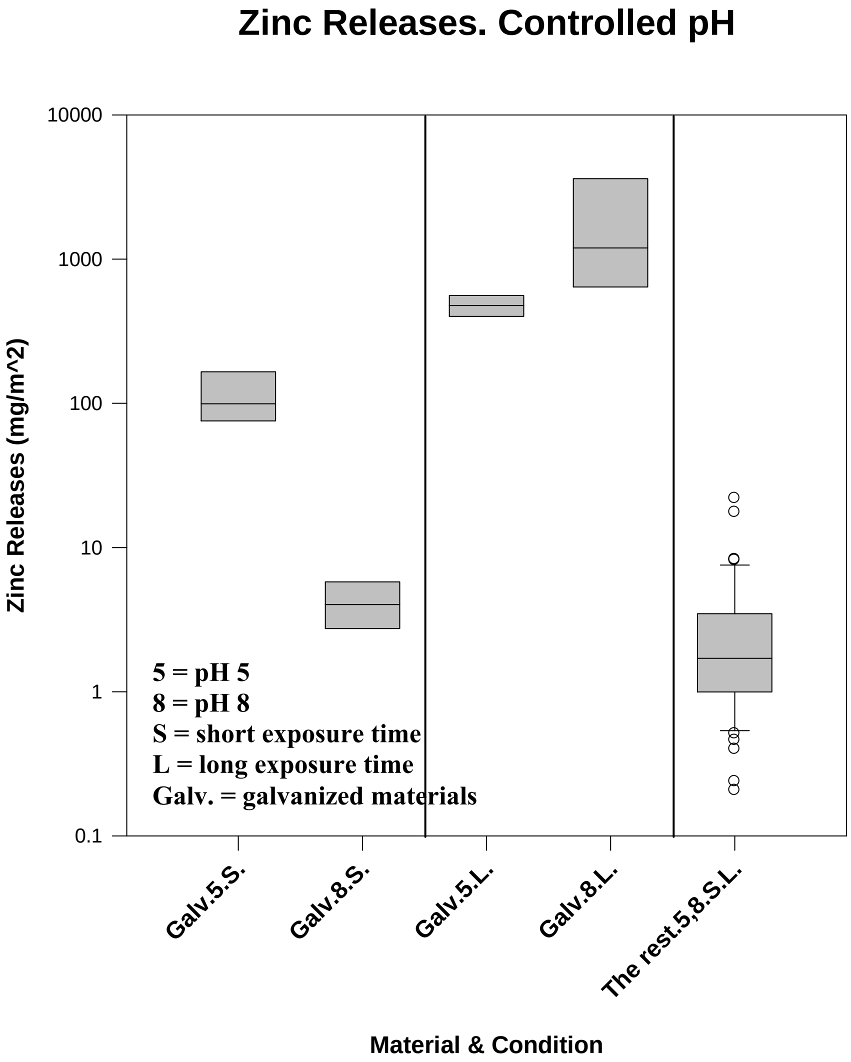


Figure 6.6.5. Group box plot for zinc release in mg/m^2 for materials immersed in pH 5 and pH 8 waters.

Zinc releases also increased with exposure time for galvanized steel pipes and gutters immersed in bay and river waters (Figure 6.6.6). In this example, the interaction of material and exposure time was significant. Galvanized materials exposed to natural pH waters during short periods resulted in elevated zinc releases. The combination of galvanized materials exposed to natural pH waters for long periods further increased zinc releases.

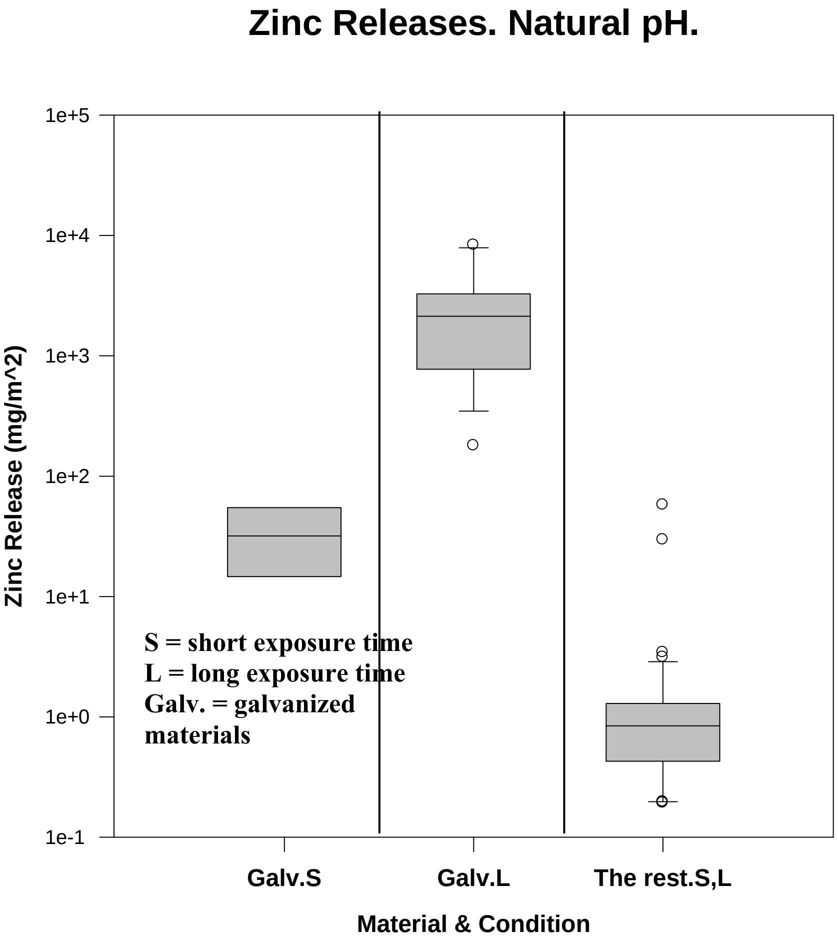


Figure 6.6.6. Group box plot for zinc release in mg/m^2 for materials immersed in bay and river waters.

Galvanized steel materials were the only source of lead releases. For lead releases under controlled pH conditions (Figure 6.6.7), there was a difference between the groups of galvanized materials during long exposure times and the group of galvanized materials during short exposure times and the rest of the materials during both short and long exposure times. Under controlled pH conditions, lead releases significantly increased for galvanized materials and long exposure periods.

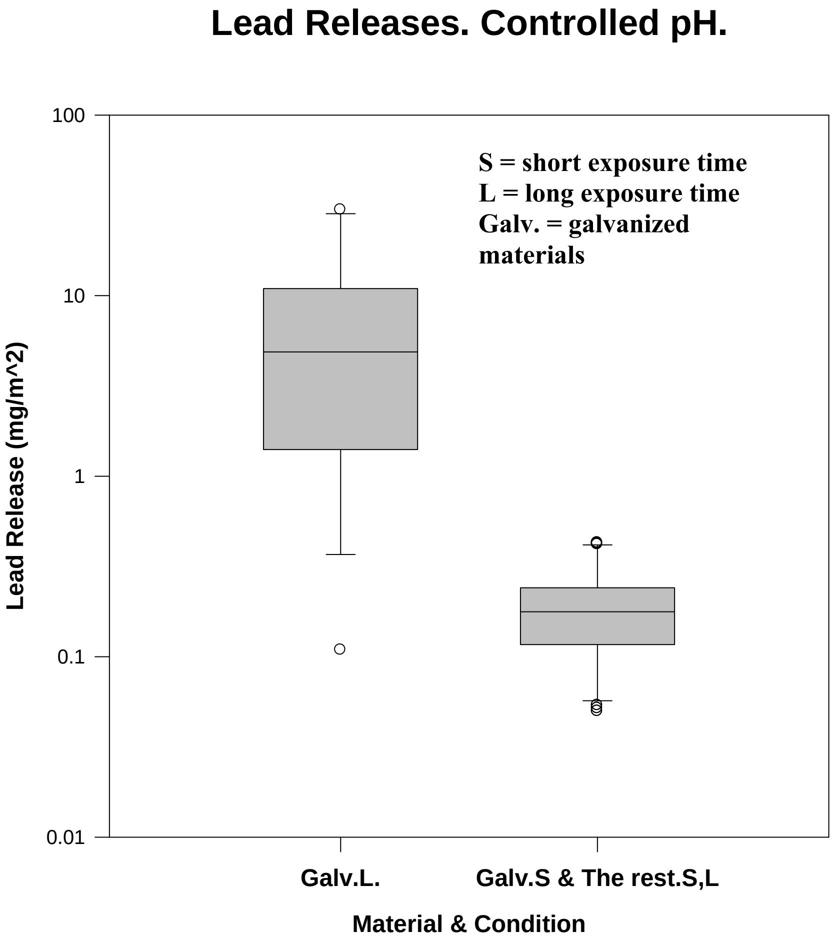


Figure 6.6.7. Group box plot for lead release in mg/m^2 for materials immersed in pH 5 and pH 8 waters.

Long exposure times increased lead releases in the samples with galvanized materials immersed into river water (Figure 6.6.8), however this tendency was not observed for galvanized steel materials immersed in bay water and can be explained by the metal releases being close to detection limit. Figure 6.6.9 shows that lead releases were combined in two groups.

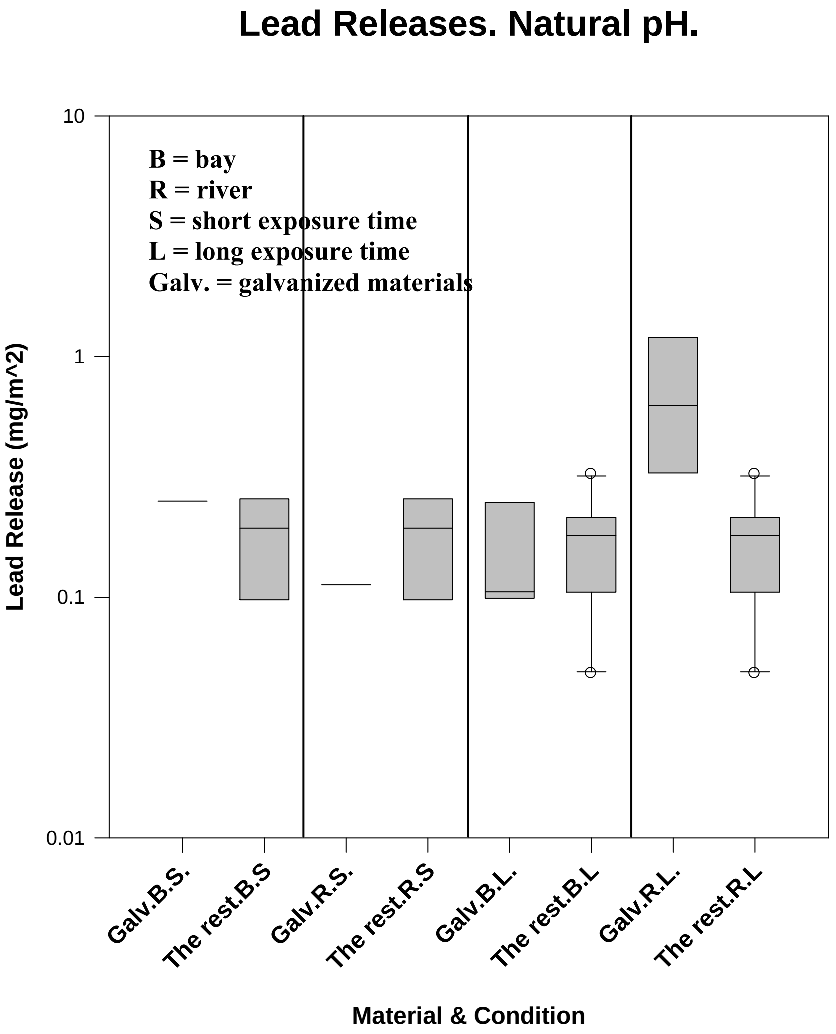


Figure 6.6.8. Group box plot for lead release in mg/m^2 for materials immersed in bay and river waters.

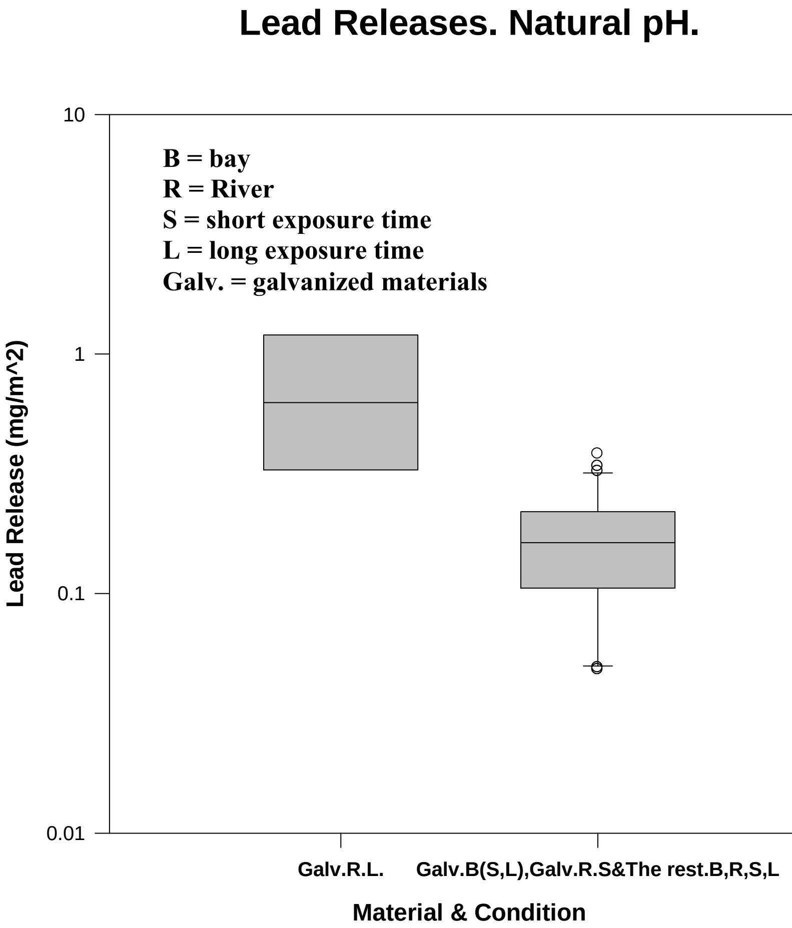
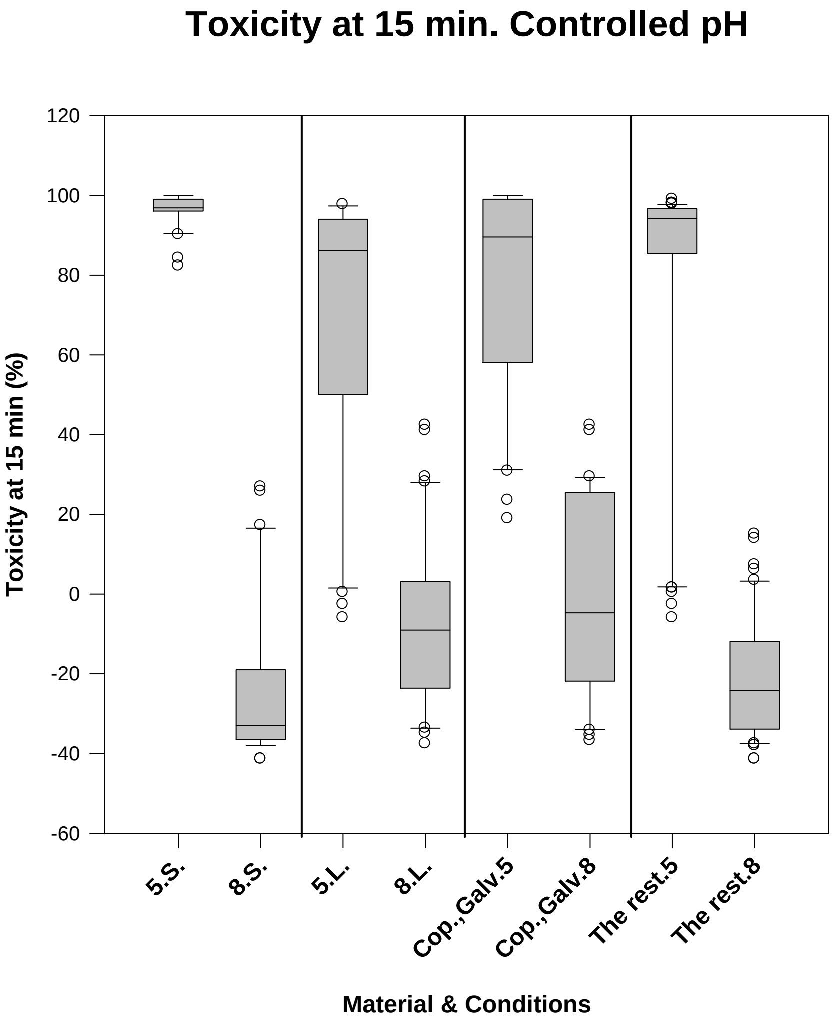


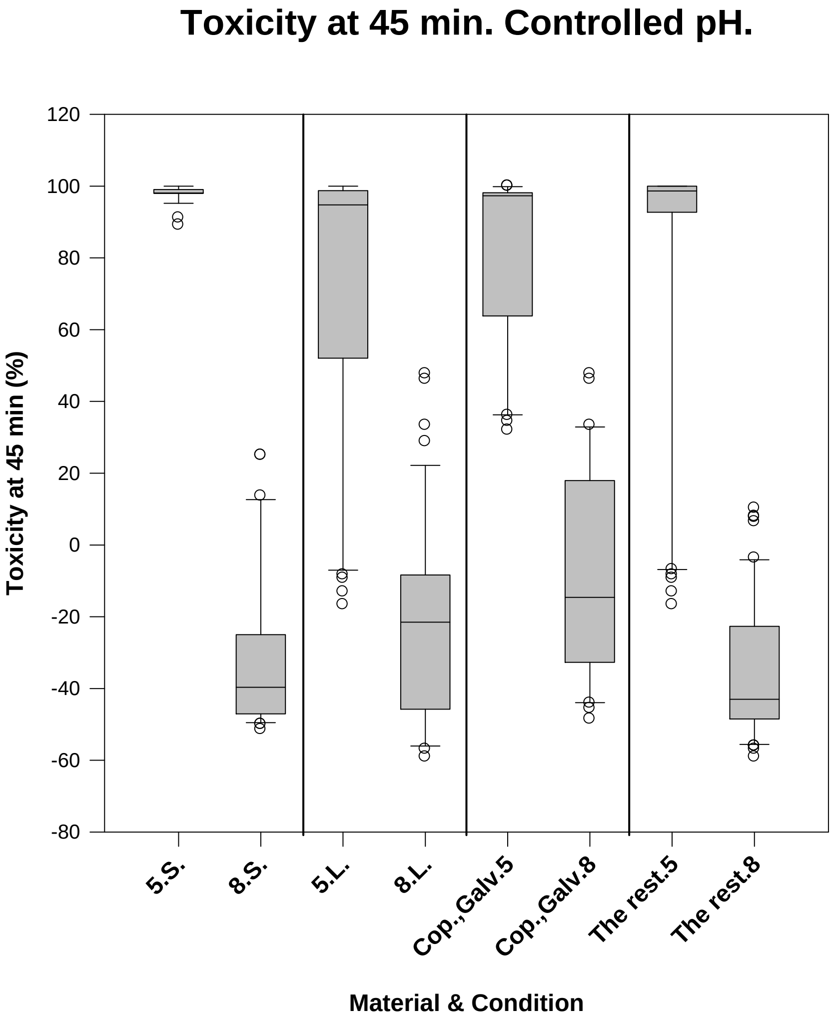
Figure 6.6.9 Group box plot for lead release in mg/m^2 for materials immersed in bay and river waters.

Figure 6.6.10 is a group box plot of toxicities at 15 min of bacteria exposure in the samples with galvanized steel, copper, and the rest of the materials under pH 5 and pH 8 conditions during both short and long exposure periods. Low pH conditions increased the toxicity effect for all pipe and gutter materials. The toxicity of the galvanized materials samples under low pH conditions decreased with material exposure time and was likely due to the increase in pH in the containers as the pH value approached the optimum pH range for the bacteria. The interactions of pH and material, and pH and exposure period, were significant. Low pH and short and long exposure periods resulted in toxicity values approaching 100%.The combination of concrete, plastic, and aluminum materials and controlled pH 8 water conditions produced conditions that were the least toxic for the Microtox test bacteria. Similar trends were observed for toxicity response at 45 min for the materials under controlled pH conditions (Figure 6.6.11).



Footnote: 5 = pH 5; 8 = pH 8; S = short exposure time; L = long exposure time; Cop. = copper material; Galv. = galvanized material.

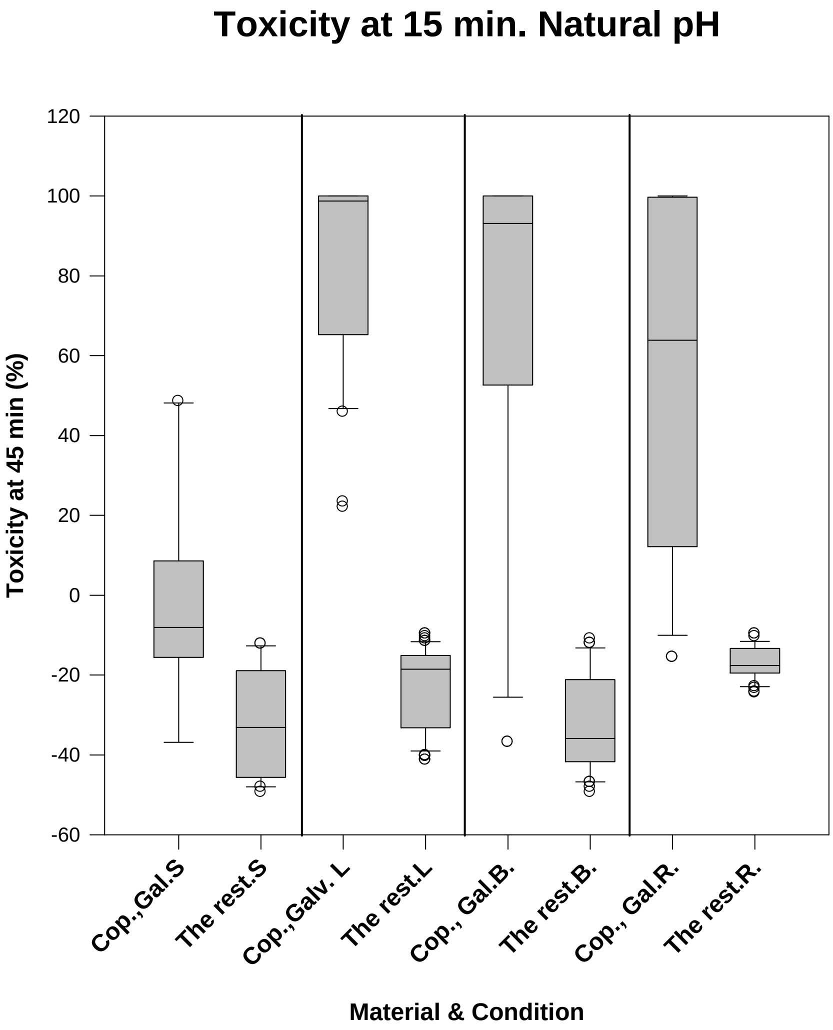
Figure 6.6.10. Group box plot for toxicity (%) at 15 min of bacteria exposure. Materials immersed in pH 5 and pH 8 waters.



Footnote: 5 = pH 5; 8 = pH 8; S = short exposure time; L = long exposure time; Cop. = copper material; Galv. = galvanized material.

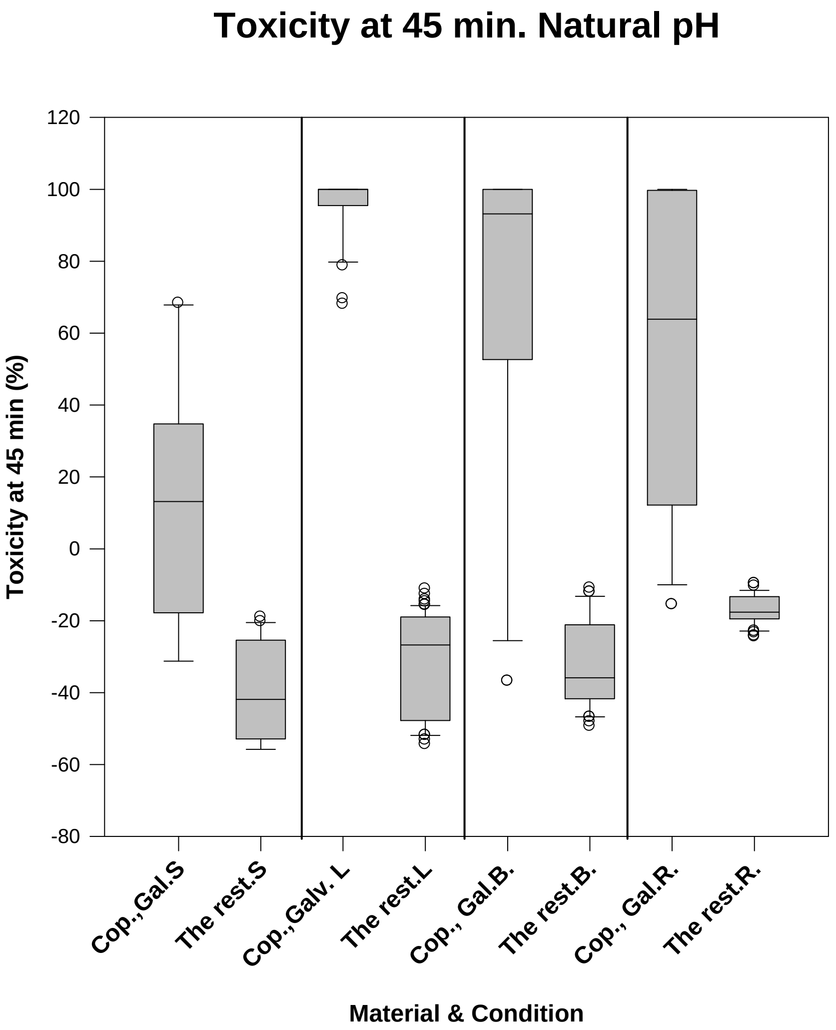
Figure 6.6.11. Group box plot for toxicity (%) at 45 min of bacteria exposure. Materials immersed in pH 5 and pH 8 waters.

Figure 6.6.12 is a group box plot of toxicities at 15 min of bacterial exposure in the samples with gutter and pipe materials immersed into bay and river water. There were no statistically significant differences between the toxicity effect in containers with copper and galvanized steel materials immersed in bay and river waters (P value of Mann-Whitney test = 0.38). The toxicity in the containers with galvanized steel and copper materials increased with time and can be explained by the increase in metal concentrations and the increase in pH values with time which exceeded the optimum pH range for the Microtox test bacteria. The interactions of conductivity and material, and material and exposure period were significant. The combination of copper and galvanized materials exposed during long exposure periods resulted in significant toxicity increases. Concrete, plastic, and aluminum materials and bay waters resulted in the least toxic conditions for all exposure periods. Similar trends were noted for toxicity at 45 min of Microtox test bacteria exposures (Figure 6.6.13).



Footnote: B = bay; R = River; S = short exposure time; L = long exposure time; Cop. = copper material; Galv. = galvanized material.

Figure 6.6.12. Group box plot for toxicity (%) at 15 min of bacteria exposure. Materials immersed in bay and river waters.



Footnote: B = bay; R = River; S = short exposure time; L = long exposure time; Cop. = copper material; Galv. = galvanized material.

Figure 6.6.13. Group box plot for toxicity (%) at 45 min of bacteria exposure. Materials immersed in bay and river waters.

Group box plots illustrated critical combinations of samples and conditions that resulted in elevated metal releases and resulting toxicities.

6.7 Predictive Model

The results from the full factorial experiments were used to build empirical models in order to determine which materials can safely be used for long term storage of water and for short term exposures such as for roof gutters and drainage pipes. Tables 6.7.1 and 6.7.2 show different levels of the factors and contrast coefficients used for 2^2 factorial analyses.

Table 6.7.1. Table of Contrast Coefficients (Controlled pH Conditions)

Mean	pH	Time	pH x Time
+	5 (-)	Short (-)	+
+	8 (+)	Short (-)	-
+	5 (-)	Long (+)	-
+	8 (+)	Long (+)	+

Table 6.7.2. Table of Contrast Coefficients (Natural pH Conditions)

Mean	Conductivity	Time	Cond. x Time
+	High (-)	Short (-)	+
+	Low (+)	Short (-)	-
+	High (-)	Long (+)	-
+	Low (+)	Long (+)	+

Tables 6.7.3 and 6.7.4 show an example of the ANOVA results for the factorial analyses for copper releases from PVC pipe under controlled pH conditions. Time was a significant factor in this example (indicated by the p-value of 0). pH and the interaction of pH and time were not significant at 0.05 alpha level. Constant term and time coefficients were significant at the 0.05 alpha level. Residual analyses (Figure 6.7.1) show that the residuals are approximately normally distributed with constant variance and have zero mean. ANOVA analyses indicated that only the effect of time was significant, therefore the reduced model was constructed that used only time as variable (Tables 6.7.5 and 6.7.6, and Figure 6.7.2).Figure 6.7.2 indicated that the model residuals approximately meet the assumptions of normality, constant variance, and zero mean. Since only the effect of time was significant, the regression analysis was performed for Cu releases per pipe surface area vs. exposure time (Tables 6.7.7 and 6.7.8). The p-values for the time coefficient and the regression were <0.001. Figures 6.7.3 and 6.7.4 show the regression equation and the residual analysis for the regression. ANOVA results and residual analysis for other materials and test conditions are shown in Appendix A.7.

Table 6.7.3. Example for Copper Releases from PVC Pipe Material for Controlled pH Conditions - Analysis of Variance.

Source	DF	Seq. SS	Adj. SS	Adj. MS	F	P
pH	1	2.157	2.157	2.157	3.31	0.106
Time	1	73.593	73.593	73.593	112.89	0.000
pH*Time	1	0.790	0.790	0.790	1.21	0.303
Error	8	5.215	5.215	0.652		
Total	11	81.755				

Table 6.7.4. Example for Copper Releases from PVC Pipe Material for Controlled pH Conditions - Coefficients.

Term	Coef.	SE Coef.	T	P
Constant	2.3200	0.2331	9.95	0.000
pH	0.4239	0.2331	1.82	0.106
Time	-2.4764	0.2331	-10.63	0.000
pH*Time	-0.2566	0.2331	-1.10	0.303

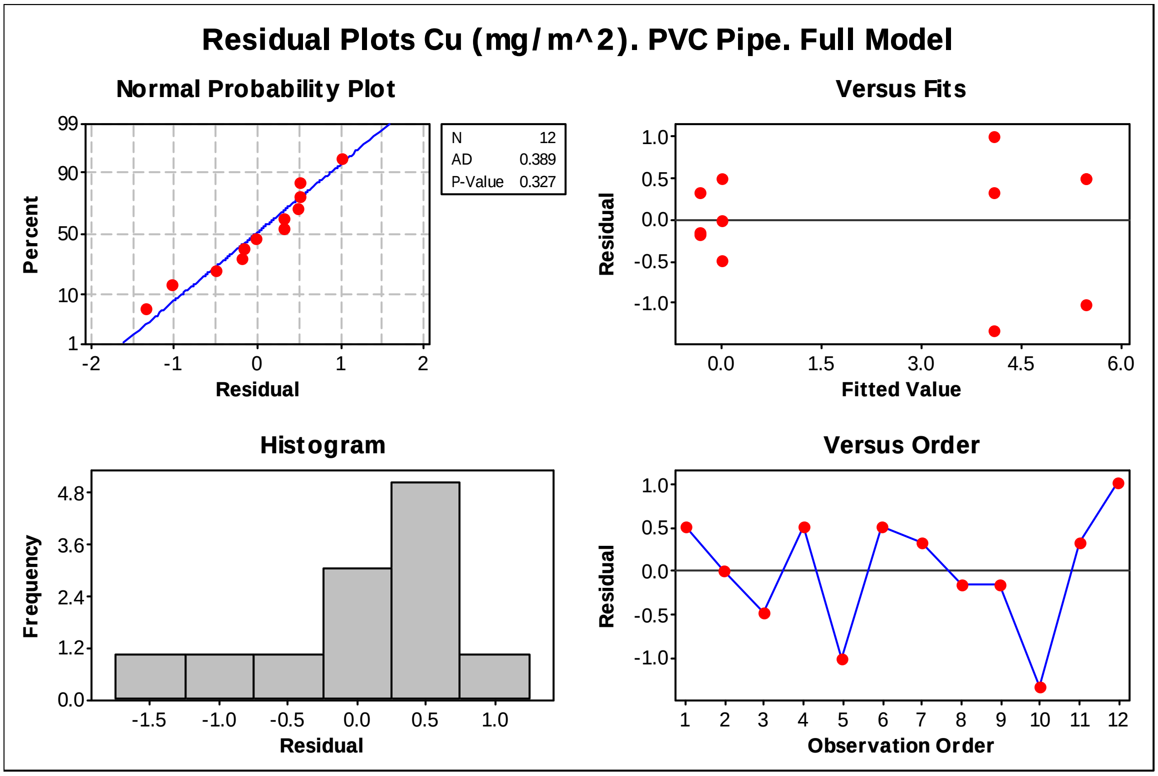


Figure 6.7.1. Residual plots for Cu releases from PVC pipe under controlled pH conditions. Full Model.

Table 6.7.5. Example - Analysis of Variance for Reduced Model.

Source	DF	Seq. SS	Adj. SS	Adj. MS	F	P
Time	1	73.593	73.593	73.593	90.17	0.000
Error	10	8.162	8.162	0.816		
Total	11	81.755				

Table 6.7.6. Example – Coefficients for Reduced Model.

Term	Coef.	SE Coef.	T	P
Constant	2.3200	0.2608	8.90	0.000
Time	-2.4764	0.2608	-9.50	0.000

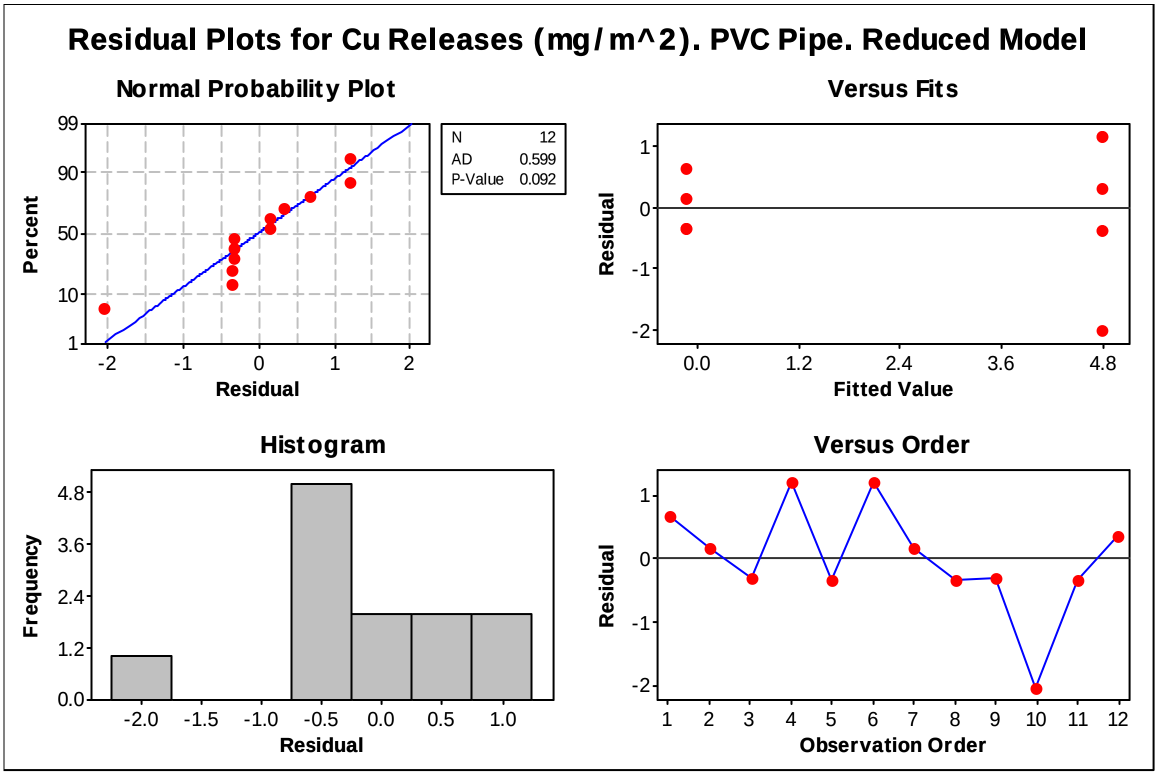


Figure 6.7.2. Residual plots for Cu releases from PVC pipe under controlled pH conditions. Reduced Model.

Table 6.7.7. Example - Coefficient for Final Model for Copper Releases as a Function of Time.

Predictor	Coef.	SE Coef.	T	P
Time	0.0028395	0.0003069	9.25	0.000

Table 6.7.8. Example - Analysis of Variance for Final Model.

Source	DF	SS	MS	F	P
Regression	1	129.68	129.68	85.62	0.000
Residual Error	11	16.66	1.51		
Total	12	146.34			

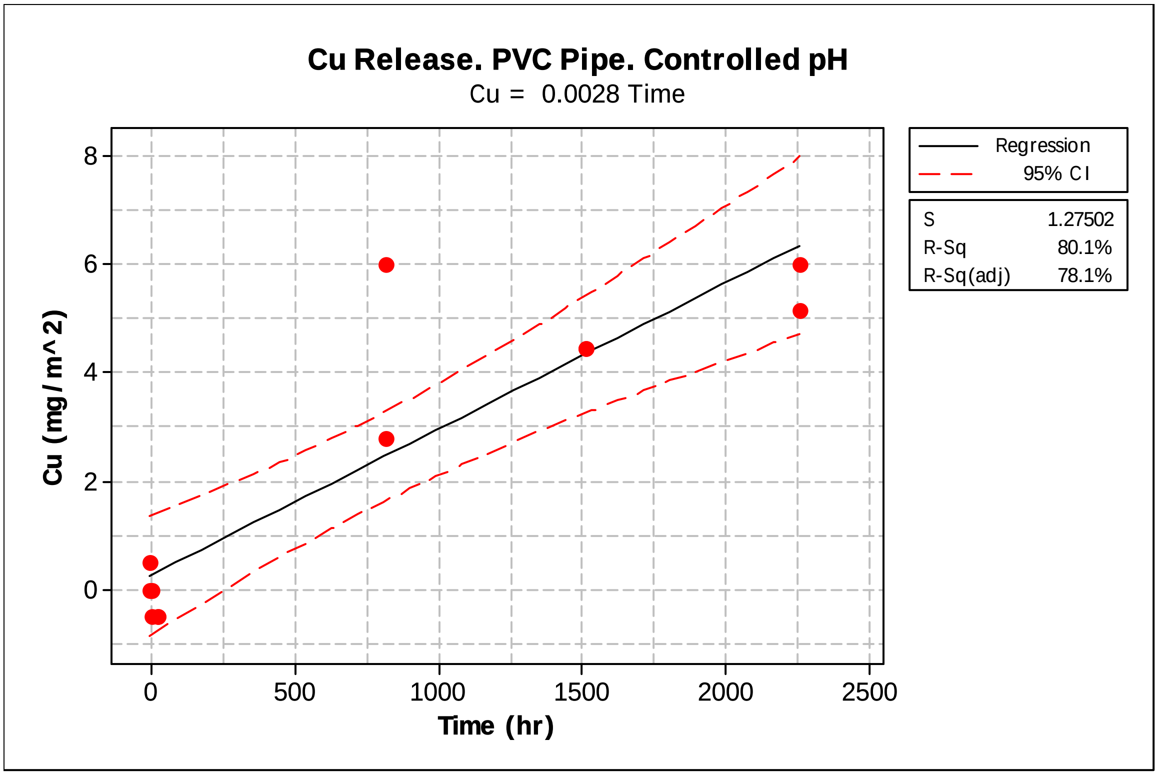


Figure 6.7.3. Linear regression for Cu releases. PVC pipe. Controlled pH.

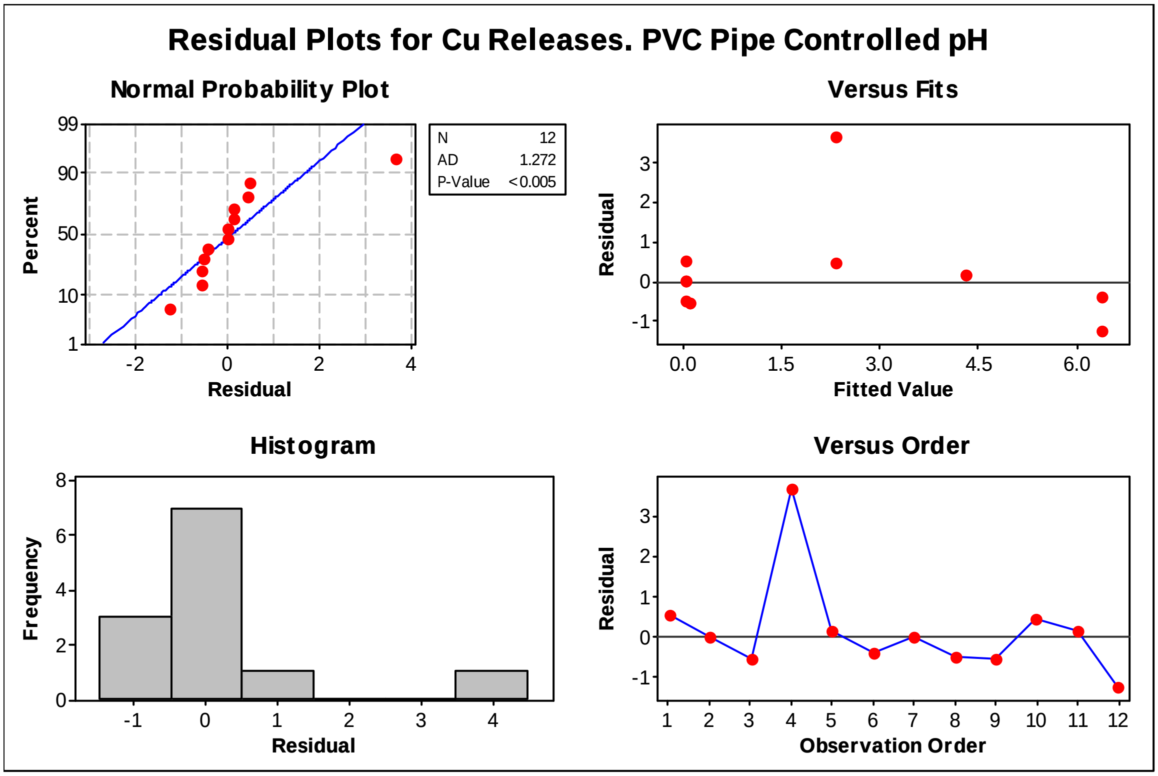


Figure 6.7.4. Residual plots for linear model for Cu releases from PVC pipe. Controlled pH. One residual value is seen to be much larger than the others. Cu release was slightly elevated after one month exposure period.

Scatter plots of modeled vs. observed values were constructed (shown in Appendix A.7) to evaluate the overall performance of the models. Figure 6.7.5 is an example of copper releases from PVC pipe under controlled pH conditions. It shows that the model predicts values for copper that are close to the observed values.

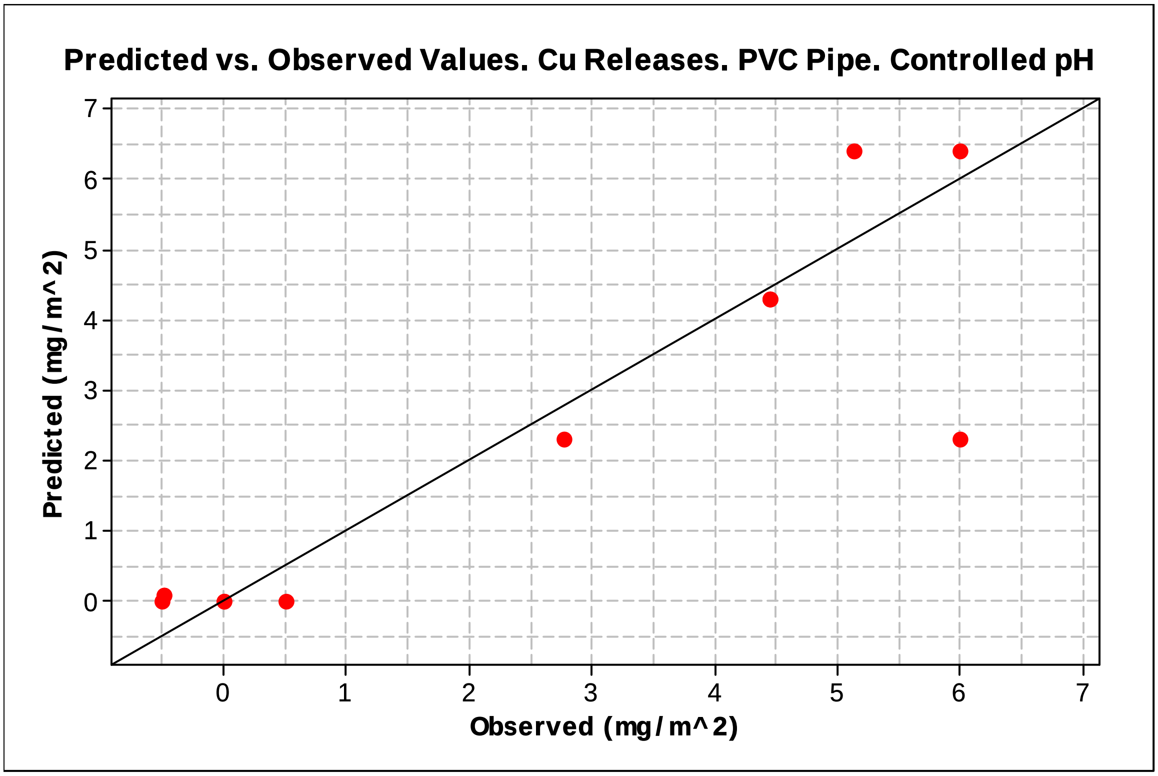


Figure 6.7.5. Predicted vs. observed values for linear model for Cu releases. PVC pipe. Controlled pH.

Tables 6.7.9 – 6.7.24 show significant conditions from the factorial analyses. Tables 6.7.25 and 6.7.40 represent simple models that quantify the expected contaminant releases for different material selections for different application uses (drainage system vs., storage tanks) and water types (low and high pHs and saline and non-saline waters).

It was found that copper materials are not advised for drainage system applications, especially when acidic rain conditions are expected, due to high copper releases and associated high toxicity. Galvanized materials should also be avoided as gutter and pipe materials as they release high zinc concentrations under all pH and exposure conditions. For stormwater drainage systems (gutters and pipes) exposed at pH 5 and pH 8 conditions, plastic and concrete materials can be used for most conditions. Galvanized steel and copper materials also should be avoided for storage tanks applications due to very high metal releases and toxicities. For stormwater storage applications, concrete, HDPE, and vinyl materials can be safely used due to their small, or non-detected, metal releases.

Table 6.7.9. Significant groups based on 2^2 Factorial analyses. Concrete pipe. Controlled pH tests

Constituent	**Concrete Pipe. Controlled pH Conditions**		**p-value**
Pb, mg/m^2	ND at pH 5 and 8		
Cu, mg/m^2	ND at pH 5 and 8		
Zn, mg/m^2	pH 5: Avg.= 1.68 (COV = 0.01)	pH 8: Avg.=3.07 (COV = 0.53)	0.062

Footnote: ND = non-detects

Table 6.7.10. Significant groups based on 2^2 Factorial analyses. Concrete pipe. Natural pH tests

Constituent	**Concrete Pipe. Natural pH Conditions**
Pb, mg/m^2	ND in bay and river waters
Cu, mg/m^2	ND in bay and river waters
Zn, mg/m^2	ND in bay and river waters

Footnote: ND = non-detects

Table 6.7.11. Significant groups based on 2^2 Factorial analyses. PVC pipe. Controlled pH tests

Constituent	**PVC Pipe. Controlled pH Conditions**		**p-value**
Pb, mg/m^2	ND at pH 5 and 8		
Cu, mg/m^2	S.: Avg.= -0.16* (COV= -2.58; St. Dev. = 0.40)	L.: Avg.= 4.8 (COV = 0.25)	0.000
Zn, mg/m^2	S.: Avg.= -0.65 (COV = -1.24; St. Dev. = 0.81)	L.: Avg.= 9.2 (COV = 0.69)	0.004

Footnote: S. = short exposure time; L. = long exposure time; ND = non-detects.
* the mg/m^2 releases are compared to initial time zero conditions without the material in the test water. If the observed concentrations decreased with time (such as from precipitation on the material), the observed release rate was negative. Obviously, zero should be used in predictions instead of negative values.

Table 6.7.12. Significant groups based on 2^2 Factorial analyses. PVC pipe. Natural pH tests

Constituent	**PVC Pipe. Natural pH Conditions**
Pb, mg/m^2	ND in bay and river waters
Cu, mg/m^2	ND in bay and river waters
Zn, mg/m^2	Avg.= 0.17-0.9; Median = 0-0.02; Min = 0.41; Max =1.24; # of Pts above DL: 2

Footnote: ND = non-detects

Table 6.7.13. Significant groups based on 2^2 Factorial analyses. HDPE pipe. Controlled pH tests

Constituent	HDPE Pipe. Controlled pH Conditions				p-value
Pb, mg/m^2	ND at pH 5 and 8				
Cu, mg/m^2	S.: Avg.= 0.23 (COV = 0.03)		L.: Avg.= 0.62 (COV = 0.56)		0.02
Zn, mg/m^2	pH5: Avg.= 1 (COV = 0.56)	pH8: -0.05* (COV = -6.1; St. Dev. = 0.32)	S.: 0.04 (COV = 10.6)	L.: 0.54 (COV = 0.8)	0.000 (for pH) 0.001 (for Time)

Footnote: S. = short exposure time; L. = long exposure time; ND = non-detects.
* the mg/m^2 releases are compared to initial time zero conditions without the material in the test water. If the observed concentrations decreased with time (such as from precipitation on the material), the observed release rate was negative. Obviously, zero should be used in predictions instead of negative values.

Table 6.7.14. Significant groups based on 2^2 Factorial analyses. HDPE pipe. Natural pH tests

Constituent	HDPE Pipe. Natural pH Conditions				p-value
Pb, mg/m^2	ND in bay and river waters				
Cu, mg/m^2	ND in bay and river waters				
Zn, mg/m^2	S.B.: Avg.= 0.21 (COV = 0.02)	S.R.: Avg.= -0.21* (COV = -0.02; St.Dev. = 0.0034)	L.B.: Avg.= 0.2 (COV = 0.02)	L.R.: Avg.= 0.2 (COV = 0.02)	0.000 (for Cond.) 0.000 (for Time) 0.000 (for Cond.*Time)

Footnote: S. = short exposure time; L. = long exposure time; B. = bay water; R. = river water; ND = non-detects.
* the mg/m^2 releases are compared to initial time zero conditions without the material in the test water. If the observed concentrations decreased with time (such as from precipitation on the material), the observed release rate was negative. Obviously, zero should be used in predictions instead of negative values.

Table 6.7.15. Significant groups based on 2^2 Factorial analyses. Steel pipe. Controlled pH tests

Constituent	Galvanized Steel Pipe. Controlled pH Conditions		p-value
Pb, mg/m^2	S.: Avg. =0.12 (COV = 0.03)	L. Avg.=14.1 (COV = 0.8)	0.012
Cu, mg/m^2	Avg.= 0.60 - 1.28; Median = 0- 0.02; Min= 0; Max= 4.785; # of Pts above DL: 3		
Zn, mg/m^2	S: Avg.=130; COV = 1.34	L: Avg.= 1088; COV = 1.07	0.073

Footnote: S. = short exposure time; L. = long exposure time.

Table 6.7.16. Significant groups based on 2^2 Factorial analyses. Steel pipe. Natural pH tests

Constituent	Galvanized Steel Pipe. Natural pH Conditions				p-value
Pb, mg/m^2	S.B.: Avg.= 0.4 (COV = 0.22)	S.R.: Avg.= 0.1 (COV = 0.02)	L.B.: Avg.= 0.1 (COV = 0.02)	L.R.: Avg.= 0.42 (COV = 0.79)	0.922 (for Cond.) 0.962 (for Time) 0.014 (for Cond.*Time)
Cu, mg/m^2	ND in bay and river waters				
Zn, mg/m^2	S.: Avg.= 208 (COV = 0.65)		L.: Avg.= 2230 (COV = 0.51)		p = 0.002

Footnote: S. = short exposure time; L. = long exposure time; B. = bay; R. = river; ND = non-detects.

Table 6.7.17. Significant groups based on 2^2 Factorial analyses. Vinyl gutter. Controlled pH tests

Constituent	Vinyl Gutter. Controlled pH Conditions				p-value
Pb, mg/m^2	ND at pH 5 and 8				
Cu, mg/m^2	S. pH 5: Avg.= 1.0 (COV = 0.03)	S. pH 8: Avg.= 1.0 (COV = 0.03)	L. pH 5: Avg.= 2.4 (COV = 0.19)	L. pH 8: Avg.= 1.5 (COV = 0.32)	0.047 (for pH) 0.001 (for Time) 0.047 (for pH*Time)
Zn, mg/m^2	pH5: Avg.=1 (COV = 0.57)		pH8: Avg.= 2.7 (COV = 0.38)		p =0.019

Footnote: S. = short exposure time; L. = long exposure time; ND = non-detects.

Table 6.7.18. Significant groups based on 2^2 Factorial analyses. Vinyl gutter. Natural pH tests

Constituent	Vinyl Gutter. Natural pH Conditions
Pb, mg/m^2	ND in bay and river waters
Cu, mg/m^2	ND in bay and river waters
Zn, mg/m^2	Avg.= 0.43 – 1.9; Median = 0-0.02; Min= 0; Max= 3.419; # of Pts above DL: 2

Footnote: ND = non-detects.

Table 6.7.19. Significant groups based on 2^2 Factorial analyses. Aluminum gutter. Controlled pH tests

Constituent	Aluminum Gutter. Controlled pH Conditions		p-value
Pb, mg/m^2	ND at pH 5 and 8		
Cu, mg/m^2	S.: Avg.= 0.96 (COV = 0.03)	L.: Avg.= 2.6 (COV = 0.03)	0.000
Zn, mg/m^2	Avg.= 2.97 – 3.60; Median = -0.88 – 0.02; Min= 0; Max = 17.53; # of Pts above DL: 8		

Footnote: S. = short exposure time; L. = long exposure time; ND = non-detects.

Table 6.7.20. Significant groups based on 2^2 Factorial analyses. Aluminum gutter. Natural pH tests

Constituent	Aluminum Gutter. Natural pH Conditions
Pb, mg/m^2	ND in bay and river waters
Cu, mg/m^2	ND in bay and river waters
Zn, mg/m^2	Avg.= 4.29 – 5.57; Median = 0 - 0.02; Min= -0.88*; Max= 57.55; # of Pts above DL: 3

Footnote: ND = non-detects.

* the mg/m^2 releases are compared to initial time zero conditions without the material in the test water. If the observed concentrations decreased with time (such as from precipitation on the material), the observed release rate was negative. Obviously, zero should be used in predictions instead of negative values.

Table 6.7.21. Significant groups based on 2^2 Factorial analyses. Steel gutter. Controlled pH tests

Constituent	Galvanized Steel Gutter. Controlled pH Conditions				p-value
Pb, mg/m^2	S. pH5: Avg.= 0.13 (COV = 0.03)	S. pH8: Avg.= 0.22 (COV = 0.7)	L. pH5: Avg.= 1.3 (COV = 0.26)	L. pH8: Avg.= 4.8 (COV = 0.05)	0.000 (for pH) 0.000 (for Time) 0.000 (for pH*Time)
Cu, mg/m^2	S. pH5: Avg.= 0.52 (COV = 0.03)	S. pH8: Avg.= 0.52 (COV = 0.03)	L. pH5: Avg.= 0.47 (COV = 0.04)	L. pH8: Avg.= 1.3 (COV = 0.19)	0.000 (for pH) 0.001 (for Time) 0.000 (for pH*Time)
Zn, mg/m^2	Avg.= 712.6 (COV = 1.64)				

Footnote: S. = short exposure time; L. = long exposure time.

Table 6.7.22. Significant groups based on 2^2 Factorial analyses. Steel gutter. Natural pH tests

Constituent	Galvanized Steel Gutter. Natural pH Conditions				p-value
Pb, mg/m^2	Avg. = 0.41 – 0.49; Median = 0.23 - 0.24; Min= 0; Max= 2.54; # of Pts above DL: 7				
Cu, mg/m^2	ND in bay and river waters				
Zn, mg/m^2	S. B.: Avg.= 151; COV = 0.74	S.R.: Avg.= 91; COV = 1.62	L. B.: Avg.= 841; COV = 0.85	L.R.: Avg.= 5387; COV = 0.73	0.089 (for Cond.) 0.032 (for Time) 0.082 (for Cond.*Time)

Footnote: S. = short exposure time; L. = long exposure time; B. = bay water; R. = river water; ND = non-detects.

Table 6.7.23. Significant groups based on 2^2 Factorial analyses. Copper gutter. Controlled pH tests

Constituent	Copper Gutter. Controlled pH Conditions		p-value
Pb, mg/m^2	ND at pH 5 and 8		
Cu, mg/m^2	pH5: Avg.= 250 (COV = 0.66)	pH 8: Avg.= 70.5 (COV = 0.96)	0.033
Zn, mg/m^2	pH5: Avg.= 3.2 (COV = 0.81)	pH 8: Avg.= 0.22 (COV = 1.55)	0.019

Footnote: ND = non-detects.

Table 6.7.24. Significant groups based on 2^2 Factorial analyses. Copper gutter. Natural pH tests

Constituent	Copper Gutter. Natural pH Conditions				p-value
Pb, mg/m^2	ND in bay and river waters				
Cu, mg/m^2	S.B: Avg.= 184 (COV = 1.04)	S.R: Avg.= 841 (COV = 0.91)	L.B.: Avg.= 1487 (COV = 0.67)	L.R.: Avg.= 242 (COV = 0.42)	0.045 (for Cond.) 0.033 (for Time) 0.096 (for Cond.*Time)
Zn, mg/m^2	Avg.= 3.46 - 3.79; Median = 1.27-1.62; Min= -0.67*; Max= 29.51; # of Pts above DL: 9				

Footnote: S. = short exposure time; L. = long exposure time; B. = bay water; R. = river water; ND = non-detects.
* the mg/m^2 releases are compared to initial time zero conditions without the material in the test water. If the observed concentrations decreased with time (such as from precipitation on the material), the observed release rate was negative. Obviously, zero should be used in predictions instead of negative values.

Table 6.7.25. Model based on 2^2 Factorial analyses. Concrete pipe. Controlled pH tests

Constituent	Concrete Pipe. Controlled pH Conditions	
Pb, mg/m^2	ND at pH 5 and 8	
Cu, mg/m^2	ND at pH 5 and 8	
Zn, mg/m^2	pH 5: Avg.= 1.68 (COV = 0.01)	pH 8: Avg.=3.07 (COV = 0.53)

Footnote: ND = non-detects

Table 6.7.26. Model based on 2^2 Factorial analyses. Concrete pipe. Natural pH tests

Constituent	Concrete Pipe. Natural pH Conditions
Pb, mg/m^2	ND in bay and river waters
Cu, mg/m^2	ND in bay and river waters
Zn, mg/m^2	ND in bay and river waters

Table 6.7.27. Model based on 2^2 Factorial analyses. PVC pipe. Controlled pH tests

Constituent	**PVC Pipe. Controlled pH Conditions**
Pb, mg/m^2	ND at pH 5 and 8
Cu, mg/m^2	Cu (mg/m^2) = 0.0028*Time (hr); R^2 = 78.1%; p-value for regression = 0.00
Zn, mg/m^2	Zn (mg/m^2) = 0.0061*Time (hr); R^2 = 76.8%; p -value for regression = 0.00

Footnote: ND = non-detects.

Table 6.7.28. Model based on 2^2 Factorial analyses. PVC pipe. Natural pH tests

Constituent	**PVC Pipe. Natural pH Conditions**
Pb, mg/m^2	ND in bay and river waters
Cu, mg/m^2	ND in bay and river waters
Zn, mg/m^2	Avg.= 0.17-0.9; Median = 0-0.02; Min = 0.41; Max =1.24; # of Pts above DL: 2

Footnote: ND = non-detects

Table 6.7.29. Model based on 2^2 Factorial analyses. HDPE pipe. Controlled pH tests

Constituent	**HDPE Pipe. Controlled pH Conditions**	
Pb, mg/m^2	ND at pH 5 and 8	
Cu, mg/m^2	Log Cu (mg/m^2) = -0.66+0.12*logTime(hr); R^2 = 48.1%; p=0.007	
Zn, mg/m^2	Zn (mg/m^2) @pH5 = 0.38 +0.00038*Time (hr); R^2 = 92.8%; p-value for regression = 0.001	Zn (mg/m^2) @pH8 = 0.0081*Time (hr); R^2 = 87.7%; p-value for regression = 0.00

Table 6.7.30. Model based on 2^2 Factorial analyses. HDPE pipe. Natural pH tests

Constituent	**HDPE Pipe. Natural pH Conditions**			
Pb, mg/m^2	ND in bay and river waters			
Cu, mg/m^2	ND in bay and river waters			
Zn, mg/m^2	S.B.: Avg.= 0.21 (COV = 0.02)	S.R.: Avg.= -0.21* (COV = -0.02; St. Dev. = 0.0034)	L.B.: Avg.= 0.2 (COV = 0.02)	L.R.: Avg.= 0.2 (COV = 0.02)

Footnote: S. = short exposure time; L. = long exposure time; B. = bay water; R. = river water; ND = non-detects.

* the mg/m^2 releases are compared to initial time zero conditions without the material in the test water. If the observed concentrations decreased with time (such as from precipitation on the material), the observed release rate was negative. Obviously, zero should be used in predictions instead of negative values.

Table 6.7.31. Model based on 2^2 Factorial analyses. Steel pipe. Controlled pH tests

Constituent	**Galvanized Steel Pipe. Controlled pH Conditions**
Pb, mg/m^2	Pb (mg/m^2) = 0.0092*Time (hr); R^2 = 59.2%; p-value for regression =0.00
Cu, mg/m^2	Avg.= 0.60 - 1.28; Median = 0- 0.02; Min= 0; Max= 4.785; # of Pts above DL: 3
Zn, mg/m^2	Log Zn (mg/m^2) = 1.38 +0.49*logTime (hr); R^2 = 59.8%; p -value for regression = 0.002

Table 6.7.32. Model groups based on 2^2 Factorial analyses. Steel pipe. Natural pH tests

Constituent	**Galvanized Steel Pipe. Natural pH Conditions**			
Pb, mg/m^2	S.B.: Avg.= 0.4 (COV = 0.22)	S.R.: Avg.= 0.1 (COV = 0.02)	L.B.: Avg.= 0.1 (COV = 0.02)	L.R.: Avg.= 0.42 (COV = 0.79)
Cu, mg/m^2	ND in bay and river waters			
Zn, mg/m^2	Log Zn (mg/m^2) = 1.63 +0.51*logTime (hr); R^2 = 81.2%; p-value for regression = 0.00			

Footnote: S. = short exposure time; L. = long exposure time; B. = bay; R. = river; ND = non-detects.

Table 6.7.33. Model based on 2^2 Factorial analyses. Vinyl gutter. Controlled pH tests

Constituent	**Vinyl Gutter. Controlled pH Conditions**	
Pb, mg/m^2	ND at pH 5 and 8	
Cu, mg/m^2	Cu (mg/m^2) @pH5 = 1.067 +0.00082*Time (hr); R^2 = 88.9%; p-value for regression = 0.003	Cu (mg/m^2) @pH8 = 0.96 +0.00038*Time (hr); R^2 = 70.1%; p-value for regression = 0.023
Zn, mg/m^2	pH5: Avg.=1 (COV = 0.57)	pH8: Avg.= 2.7 (COV = 0.38)

Footnote: ND = non-detects.

Table 6.7.34. Model based on 2^2 Factorial analyses. Vinyl gutter. Natural pH tests

Constituent	**Vinyl Gutter. Natural pH Conditions**
Pb, mg/m^2	ND in bay and river waters
Cu, mg/m^2	ND in bay and river waters
Zn, mg/m^2	Avg.= 0.43 – 1.9; Median = 0-0.02; Min= 0; Max= 3.419; # of Pts above DL: 2

Footnote: ND = non-detects.

Table 6.7.35. Model based on 2^2 Factorial analyses. Aluminum gutter. Controlled pH tests

Constituent	Aluminum Gutter. Controlled pH Conditions
Pb, mg/m^2	ND at pH 5 and 8
Cu, mg/m^2	Cu (mg/m^2) = 1.17 +0.0008*Time (hr); R^2 = 68.0%; p=0.001
Zn, mg/m^2	Avg.= 2.97 – 3.60; Median = -0.88 – 0.02; Min= 0; Max = 17.53; # of Pts above DL: 8

Footnote: ND = non-detects.

Table 6.7.36. Model based on 2^2 Factorial analyses. Aluminum gutter. Natural pH tests

Constituent	Aluminum Gutter. Natural pH Conditions
Pb, mg/m^2	ND in bay and river waters
Cu, mg/m^2	ND in bay and river waters
Zn, mg/m^2	Avg.= 4.29 – 5.57; Median = 0 - 0.02; Min= -0.88*; Max= 57.55; # of Pts above DL: 3

Footnote: ND = non-detects.

* the mg/m^2 releases are compared to initial time zero conditions without the material in the test water. If the observed concentrations decreased with time (such as from precipitation on the material), the observed release rate was negative. Obviously, zero should be used in predictions instead of negative values.

Table 6.7.37. Model based on 2^2 Factorial analyses. Steel gutter. Controlled pH tests

Constituent	Galvanized Steel Gutter. Controlled pH Conditions			
Pb, mg/m^2	S. pH5: Avg.= 0.13 (COV = 0.03)	S. pH8: Avg.= 0.22 (COV = 0.7)	L. pH5: Avg.= 1.3 (COV = 0.26)	L. pH8: Avg.= 4.8 (COV = 0.05)
Cu, mg/m^2	S. pH5: Avg.= 0.52 (COV = 0.03)	S. pH8: Avg.= 0.52 (COV = 0.03)	L. pH5: Avg.= 0.47 (COV = 0.04)	L. pH8: Avg.= 1.3 (COV = 0.19)
Zn, mg/m^2	Avg.= 712.6 (COV = 1.64)			

Footnote: S. = short exposure time; L. = long exposure time; ND = non-detects.

Table 6.7.38. Model based on 2^2 Factorial analyses. Steel gutter. Natural pH tests

Constituent	Galvanized Steel Gutter. Natural pH Conditions	
Pb, mg/m^2	(Avg. = 0.41 – 0.49; Median = 0.23 - 0.24; Min= 0; Max= 2.54; # of Pts above DL: 7	
Cu, mg/m^2	ND in bay and river waters	
Zn, mg/m^2	Bay Water: Log Zn (mg/m^2) = 1.44 +0.44*logTime (hr); R^2 = 74.5%; p-value for regression = 0.017	River Water: Log Zn (mg/m^2) = 0.8 +0.85*logTime (hr); R^2 = 90.1%; p-value for regression = 0.002

Table 6.7.39. Model based on 2^2 Factorial analyses. Copper gutter. Controlled pH tests

Constituent	**Copper Gutter. Controlled pH Conditions**	
Pb, mg/m^2	ND at pH 5 and 8	
Cu, mg/m^2	pH5: Avg.= 250 (COV = 0.66)	pH 8: Avg.= 70.5 (COV = 0.96)
Zn, mg/m^2	pH5: Avg.= 3.2 (COV = 0.81)	pH 8: Avg.= 0.22 (COV = 1.55)

Footnote: ND = non-detects.

Table 6.7.40. Model based on 2^2 Factorial analyses. Copper gutter. Natural pH tests

Constituent	**Copper Gutter. Natural pH Conditions**	
Pb, mg/m^2	ND in bay and river waters	
Cu, mg/m^2	Bay Water: Log Cu (mg/m^2) = 1.25 +0.59*logTime (hr); R^2 = 91.4%; p-value for regression = 0.002	River Water: Log Cu (mg/m^2) = 0.72 +0.52*logTime (hr); R^2 = 98.0%; p-value for regression = 0.00
Zn, mg/m^2	Avg.= 3.46 - 3.79; Median = 1.27-1.62; Min= -0.67**; Max= 29.51; # of Pts above DL: 9	

Footnote: ND = non-detects.

** the mg/m^2 releases are compared to initial time zero conditions without the material in the test water. If the observed concentrations decreased with time (such as from precipitation on the material), the observed release rate was negative. Obviously, zero should be used in predictions instead of negative values.

The models showed that copper materials had elevated copper releases in pH 5 waters (250 mg/m^2) and in bay and river waters during short exposure times (180 and 840 mg/m^2 respectively). Long term exposure periods of copper materials under both high and low salinity conditions also resulted in high copper releases (1490 and 240 mg/m^2 respectively). Zinc concentrations released from galvanized steel materials were very high under both low and high pH conditions and during both short and long exposure times for controlled pH experiments (the average of 130 and 1088 mg/m^2 for steel pipe during short and long exposure time respectively; and 710 mg/m^2 for steel gutter). For natural pH tests, long exposure periods resulted in high zinc concentrations released from galvanized pipes for waters with both high and low salinities (2,230 mg/m^2). Galvanized steel gutters immersed in bay and river waters had very high zinc releases during long term exposures (840 and 5,387 mg/m^2 for bay and river waters respectively). Elevated lead releases from galvanized steel materials were observed for pH 5 and 8 waters during long exposure periods, and for bay waters during short exposure periods and river waters during long exposure periods for steel pipe and for steel gutter during natural pH tests.

The residual analyses of the models indicated that the residuals were approximately normally distributed with constant variance and have zero mean (shown in Appendix A.7). The slight deviation from the residual requirements could be explained by small data samples available. Table 6.7.41 shows unusual conditions for the final models.

Scatter plots of observed vs. modeled values were used (Figures A.7.20 through A.7.30, Appendix A.7) to evaluate performance of the models. Scatter plots for copper releases from copper materials and for lead releases from steel pipe under controlled pH conditions, for zinc releases from galvanized steel materials under natural pH conditions, and for metal releases from aluminum gutter under controlled and natural pH conditions showed that the models predicted values that are both higher and lower than observed for the large releases. The plots showed that models for galvanized steel gutter and PVC materials under controlled pH conditions represent metal releases reasonably well. Also, metal releases from HDPE materials under both controlled and natural pH conditions and copper releases from copper materials under natural pH conditions were modeled reasonably well.

Table 6.7.41. Unusual Conditions. Final Models

Constituent	Material and Conditions	Unusual Conditions
Cu	PVC Pipe. Controlled pH	at pH5 after 1 mo. of exposure
Pb	Steel Pipe. Controlled pH	at pH 5 after 3mo of exposure and at pH 8 after 1 and 2 mo. of exposure
Cu	Steel Pipe. Controlled pH	at pH 5 after 2 mo of exposure
Pb	Steel Pipe. Natural pH	river water after 2 and 3 mo. of exposure; bay water after 27 h and 1 week of exposure
Zn	Aluminum Gutter. Controlled pH	pH 8 after 3 mo. of exposure
Zn	Aluminum Gutter. Natural pH	bay after 2 mo of exposure
Zn	Steel Gutter. Controlled pH	at pH 8 after 2 mo. of exposure
Pb	Steel Gutter. Natural pH	river after 3 mo. of exposure
Zn	Copper Gutter. Controlled pH	at pH5 after 3 mo. of exposure
Cu	Copper Gutter. Bay water	bay after 1 mo. of exposure
Zn	Copper Gutter. Natural pH	river water after 3 mo. of exposure

6.8 Chapter Summary

The Spearman Correlation Analyses indicated that pH values and metal releases influence the water toxicity during these tests. Under natural pH conditions, the toxicity in the samples with galvanized steel materials was strongly associated with zinc losses, and the toxicity in the samples with copper materials was strongly associated with copper releases. Cluster analyses also confirmed that toxicities were affected by both metal releases and pH values, and the metal losses were influenced by pH, conductivity, and time of exposure.

Principal Component Analyses showed that the first four principal components explained about 78% of total variance. Toxicity and pH have high loadings on the first principal component. The second principal component has high loadings of time, Pb, and Zn. Copper has a large loading on the third principal component. Conductivity, pH, and material type were the highest loadings on the fourth principal component. Principal component analysis showed groupings of samples with similar characteristic. Samples with concrete, plastic, and aluminum materials immersed in controlled pH 8 waters had low lead and zinc releases and low toxicities. The samples with controlled pH 5 waters were associated with high toxicities.

Full 2^3 Factorial Analyses showed that for the controlled pH conditions, three-way interactions of pH, material, and time of exposure had a significant effect on copper and zinc releases; the two-way interactions of material and time were important for lead releases. The two-way interactions of pH and material and pH and time had significant effects on toxicity. During the natural pH tests, the three-way interaction of conductivity, material, and time had a significant effect on copper and lead releases. For zinc releases, the two-way interaction of material and exposure period was significant. The two-way interactions of conductivity and material, and material and time, both had significant effects of toxicity during the natural pH test series.

Full 2^2 Factorial Analyses that examined the type of material indicated that for copper materials under controlled pH conditions, pH had a significant effect on copper releases; under natural pH condition, time and conductivity had significant effects on copper concentrations. For zinc releases from galvanized materials under natural pH conditions, time had a significant effect on zinc releases. For lead releases from galvanized steel pipe, exposure time was significant, and for galvanized steel gutter materials, the interaction of pH and time was significant. The interaction of exposure time and conductivity had an effect of lead releases from steel pipe under during natural pH tests.

The results from the factorial analyses were used to build an empirical model to identify the significant factors, materials, exposure times, and their combinations that influence pollutant releases. Copper and galvanized steel roof gutters and pipes should not be used when acidic water conditions are expected due to high copper (for copper materials) and high zinc (for galvanized steel materials) releases and high toxicity. For stormwater drainage systems (gutters and pipes) exposed to pH 5 and 8 conditions, concrete and plastic materials can be employed. Galvanized steel and copper materials are not advised for use in storage tanks applications due to very high metal releases and associated toxicity. For stormwater storage applications, concrete, HDPE, and vinyl materials can be used due to their little or non-detected metal losses.

7. NUTRIENT RELEASES ASSOCIATED WITH MATERIAL DEGRADATION

This chapter describes nutrient releases from different pipe and gutter materials subjected to different water conditions. Ammonia nitrogen, total nitrogen, nitrate nitrogen, and Chemical Oxygen Demand analyses were performed on the samples collected during controlled pH tests. The nutrient tests were conducted using HACH methods listed in Table 1.16.

7.1 Results and Discussion

There were low periodic releases of nitrogen compounds from the roofing and piping materials under controlled pH conditions. Figure 7.2.1 shows nitrate releases from different pipe and gutter materials immersed in pH 5 water. There were no increases in nitrate concentrations detected in many containers with pH 5 water; for pH 8 waters, there were very small increases in nitrate concentrations (on the order of 0.1-0.3 mg/L as N).

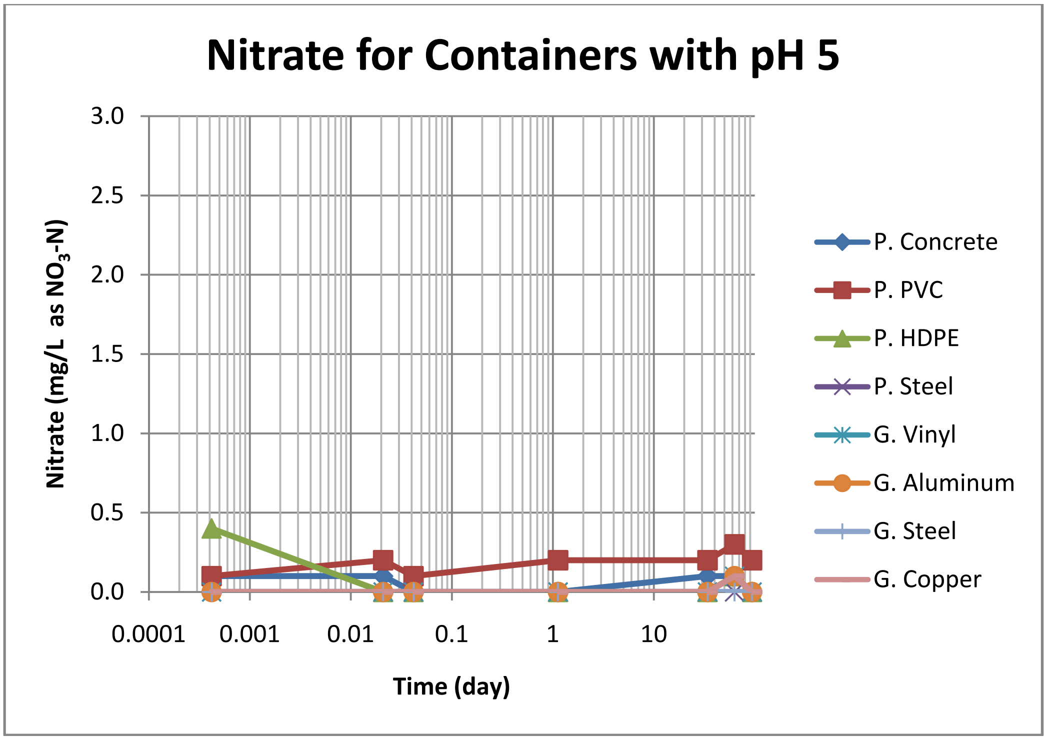


Figure 7.2.1. Nitrate concentrations in the containers with pH 5 water.

Releases of other nutrients from gutter and pipe materials under different water conditions are shown in Appendix H. At pH 5, for the time interval between time zero and one months, zero ammonia nitrogen concentrations were observed. Only after two to three months of exposure were very low ammonia nitrogen concentrations (below 1 mg/L as N) were detected. At pH 8, very small spikes of concentrations were seen. Concentrations of 0.21 mg/L ammonia as N were reached for PVC and concrete pipes after three months of exposure time.

After two to three months of exposure, there was a very small amount of total nitrogen detected. The increase of total nitrogen concentrations in the test containers was about1 mg/L as N. In the container with PVC pipe immersed in pH 8 water, there was an increase of total nitrogen concentration that reached 5 mg/L as N before dropping back down.

There were also periodic elevated COD concentrations. For the concrete sample under controlled pH 5 conditions, a spike of 27mg/L as COD was noted after 0.5 hr exposure. Clark et al. (2007, 2008 a, b) also observed nutrient releases (ammonia, nitrates, total nitrogen, and phosphate) from uncoated galvanized steel and vinyl roofing materials that were close to background levels, but with intermittent elevated concentrations. For example, for new uncoated galvanized steel roof samples, nitrate concentrations were less than 1 mg/L; for galvanized aluminum, there was a nitrate spike of 35 mg/L at day 50. Clark et al. (2007, 2008 a, b) also found that plastic/vinyl materials didn’t release any noticeable concentrations of COD, compared to periodic COD releases that ranged up to 13 mg/L under controlled pH 5 and 8 conditions during this research.

Phosphorus releases could not be analyzed during the first series of experiments due to the high phosphorus content of the buffer chemicals. During the second test series, phosphorus releases were analyzed by Stillbrook lab and were all below detection limits (0.02 mg/L).

7.2. Chapter Summary

There were low periodic releases of nitrogen compounds observed from the drainage and pipe materials under controlled pH conditions, but were inconsistent and low in concentrations. Phosphorus releases were only monitored during the natural pH tests, but were not detected.

8. CONCLUSIONS

8.1 Introduction

The goal of this dissertation research was to determine how different drainage and storage system (pipe, gutter, and storage tank) materials and water quality characteristics can affect water quality. This research was conducted to examine heavy metals (cadmium, chromium, lead, copper, zinc, aluminum, and iron), toxicity, and nutrients (nitrogen compounds and COD) leaching from these various materials and to answer the question which stormwater drainage materials are more beneficial to use under expected environmental conditions. A wide range of construction materials under various environmental conditions were evaluated. Factors (such as pH, salinity, and major water ions, and their interactions) causing degradation of the materials with time of exposure were examined.

The hypothesis was tested through a series of long-term static leaching controlled laboratory experiments by immersing sections of the eight different construction materials in large quantities of pH buffered solutions made using locally collected roof and parking lot runoff. Additional tests were conducted using local un-buffered waters, but having different conductivity values (bay vs. river water). The gutter materials tested were vinyl, aluminum, copper, and galvanized steel. The pipe materials tested were concrete, PVC (polyvinyl chloride), HDPE (high density polyethylene), and galvanized steel.

During this research, water samples from each leaching container were periodically analyzed over a three month period for heavy metals (cadmium, chromium, lead, copper, zinc, aluminum, and iron), and for nutrients (ammonia nitrogen, total nitrogen, nitrate and nitrite, and chemical oxygen demand), and toxicity (using Microtox screening methods); pH, conductivity, and Eh.

The experiments were performed in two stages. Each section of pipe and gutter material was immersed in containers with pH 5 and 8 values during the first series of tests; the gutter materials were immersed in buffered roof runoff (at pH 5 and 8) and the pipe materials were immersed in the buffered parking lot runoff (at pH5 and 8). During the second series of experiments, new sections of the same materials were immersed in containers having un-buffered bay and river waters having different conductivities.

Metal releases were assessed using spearman correlations, cluster analyses, principal component analyses, and factorial analyses. Also, the Medusa water chemistry program was used to predict the chemical forms of the released metals. Eh-pH and log Concentration-pH diagrams were constructed (using guidance from Medusa) and metal forms were determined that influence metal fate and toxicity. A simple model was finally prepared that quantified the expected pollutant releases for different materials for different uses (drainage system vs., storage tanks) and water types (low and high pHs, and saline and non-saline waters,).

8.2 Dissertation Research Hypothesis

The hypothesis of this dissertation research was:

The type of pipe and storage tank material, environmental parameters causing degradation of the material, and time of contact, all affect water quality.

Spearman correlation analyses were conducted to identify the associations between constituents and the degree of those associations for each type of material. Cluster analyses were conducted to further examine how pH, conductivity, material, and time of exposure affected the metal releases and toxicity of the samples. The Spearman correlation matrices showed that toxicity is influenced by pH values and metal releases. During natural pH tests, the toxicity in the samples with galvanized steel pipes and gutters was strongly associated with zinc releases, and the toxicity in the samples with copper materials was strongly associated with copper losses. Cluster analyses also confirmed that toxicities are influenced by metal releases and pH values, and metal releases are affected by pH, conductivity, and time of exposure.

Principal Component Analyses (PCA) were conducted to determine whether the number of measured parameters can be reduced to a smaller number of variables and to identify groupings of parameters with similar characteristics. It was found that the first four principal components account for about 78% of the total variance and can reasonably represent the data set. Toxicity values have high loadings on the first principal component. The second principal component has high loadings of time, Pb, and Zn (also high loading for PC3). Copper and Zn have large loading on the third principal component. Conductivity, pH and material type have high loadings on the fourth principal component.

Full 2^3 Factorial analyses were conducted on Cu, Zn, Pb constituents (expressed in mg per m^2 surface area of exposed material units) and toxicities for 15 and 45 min of bacteria exposure time to determine the effect of the factors. Time, pH, and material and their interactions were examined during the first testing series, and the effects of time, conductivity, and material and their interactions were examined during the second testing stage. It was found that for the controlled pH conditions, the interaction of pH, material, and time affected the copper and zinc releases, and the interaction of material and time were important for the lead releases. The interactions of pH and material, and pH and time, had significant effects on toxicity.

During the natural pH tests, the interaction of conductivity, material, and time had a significant effect on copper and lead releases. For zinc releases, the interaction of material and time was significant. The two-way interactions of conductivity and material, and material and time, had significant effects on toxicity during the second test series.

8.3 Suggestions for Future Research

The metal releases from naturally aged materials have been previously investigated (Clark et al. 2007, Lasheen et al. 2008, Good 1993, Zobrist 2000, Davis and Burns, 1999). These other studies indicated that aged materials and their coatings continue to leach significant amounts of metals into the environment during the material's service life. Further research could be conducted with aged materials in order to investigate metal releases and toxicity under different water conditions for comparison with the results with the new drainage and piping materials. For the factorial analysis, midpoints could be used to determine the shape of the resulting response surface. Many other building materials also need similar testing to identify the role of material selection on stormwater quality (such as asphalt, along with building siding and fencing materials, for example). The benefits of coatings on the materials to reduce pollutant degradation and material damage should also be investigated.

8.4 Summary of Dissertation Research Findings

This research found that:

- Some stormwater drainage system and tank materials can release large amounts of zinc, copper, and lead under controlled and natural pH and different salinity conditions during both short and long exposure periods.

- Galvanized steel pipes and gutters were the most significant source of lead and zinc, while copper materials were the greatest source of copper.
- During short exposure times, only copper materials were a source of copper under both high and low buffered pH conditions. Under natural pH conditions, copper concentrations were detected only for copper materials during both short and long exposure times and exceeded 35 mg/L in bay samples after 3 months of exposure.
- During the controlled pH experiments, copper losses from copper gutters increased as pH decreased.
- During the natural pH experiments, copper releases were greater in containers with saline bay water compared to releases in containers with river water.
- Concrete pipes were not a source of copper under either controlled or natural pH conditions. Besides the copper material tests, low copper concentrations were found for the HDPE, vinyl, galvanized steel, and aluminum sample exposure tests during the controlled pH conditions.
- The greatest sources of zinc were galvanized steel materials. Zinc releases from galvanized steel materials were detected during both short (0.5 to 27 h) and long exposure (after 1 to 3 months) for all water conditions. Under controlled pH conditions, zinc releases in the samples with galvanized steel materials were greater and more rapidly released at higher pH values during long exposure times. The least sources of zinc were concrete and plastic materials.
- During short exposure times, zinc releases from galvanized materials were lower in river water samples compared to the bay water samples; however, during long

exposures, zinc concentrations in the river water samples exceeded those in the bay water samples.

- Galvanized steel materials were found to be the only source of lead releases, with lead concentrations detected during both short and long exposure times, for both controlled and uncontrolled pH tests, and for both high and low salinity conditions.
- The valence of zinc and copper species varied from zero to two and will have a great effect on toxicity and treatability of the stormwater.
- The highest aluminum concentrations were observed from the aluminum materials.
- For controlled pH conditions, the largest concentrations of iron (>20 mg/L at pH 5) were found to be leaching from galvanized steel materials. During natural pH conditions, concrete and galvanized steel materials were the greatest sources of iron.
- During controlled pH tests, there were low periodic releases of nitrogen compounds from the drainage and pipe materials.
- For controlled pH tests, the toxicities of the roof and pipe materials were much greater under lower pH conditions than under higher pH conditions. The concrete pipes were found to be least toxic under the lower pH conditions. Under higher pH conditions during the controlled pH tests, concrete pipes and vinyl roofing materials were found to be the least toxic, while copper and galvanized materials were the most toxic. For bay and river waters, copper materials had the highest toxicity, followed by galvanized steel materials.
- Concrete, HDPE, and vinyl materials had little or non-detected metal releases during both short and long-term exposure times and therefore can be safely used as drainage system components or storage tanks materials. The use of copper materials for gutter

systems is not advised due to high copper releases under a wide range of pH values, especially in the presence of chloride ions in coastal areas. The use of galvanized materials is not advised for drainage systems, and especially for storage tank materials, due to substantial zinc releases under all water conditions.

- Concrete pipes can be used under a wide range of water pH values with minimal heavy metal releases and non detected toxicities. In natural water environments with pH values from 7 to 8 and with low and high salinity values, PVC, HDPE, vinyl, aluminum materials also can be safely used.
- Heavy metals were released from drainage system materials into the water quickly after the water came in contact with the materials. This releases continued during long periods of exposure corresponding to storage facilities. Metallic gutter, pipe, and storage tank materials have the potential to release high concentrations of zinc, copper, and lead under acidic and alkali conditions and at various conductivity values.
- Awareness of the amount of the pollutants coming from the gutter and piping materials will facilitate the development of management and planning procedures, specifically stressing the benefits of pollution prevention as a stormwater management option (especially compared to advanced metal removal controls).
- The information on gutter and pipe stormwater quality runoff degradation will enable government officials to make better regulatory policies concerning pollution prevention and to enable safer choice of stormwater tank and piping materials. Manufactures of these materials can also offer coatings or alternative materials having reduced metal releases. The information of pollutant releases can also be included into stormwater quality models.

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APPENDIX A: HEAVY METAL DATA

During the natural pH tests, the samples were analyzed at time zero (natural bay or river water without pipes), 1 hour, 27 hours, 1week, 1 month, 2 months, and 3 months for the total metal concentrations of lead, copper, and zinc. The samples were also analyzed for the total aluminum and iron concentrations at time zero and for the total aluminum, iron, and the filterable iron concentrations after 3 months.

A.1. Lead Data

The concentration values that were above the detection limits are highlighted in green.

Table A.1.1 Total lead (mg/L). Containers with pH 5

Time, hr	P. Concrete	P. PVC	P. HDPE	P. Steel	G. Vinyl	G. Aluminum	G. Steel	G. Copper
0.01	< 0.005	< 0.005	< 0.005	< 0.005	< 0.005	< 0.005	< 0.005	< 0.005
0.5	< 0.005	< 0.005	< 0.005	< 0.005	< 0.005	< 0.005	< 0.005	< 0.005
1	< 0.005	< 0.005	< 0.005	< 0.005	< 0.005	< 0.005	< 0.005	< 0.005
27	< 0.005	< 0.005	< 0.005	< 0.005	< 0.005	< 0.005	< 0.005	< 0.005
816	< 0.005	< 0.005	< 0.005	0.183	< 0.005	< 0.005	0.02	< 0.005
1512	< 0.005	< 0.005	< 0.005	0.268	< 0.005	< 0.005	0.028	< 0.005
2256	< 0.005	< 0.005	< 0.005	0.247	< 0.005	< 0.005	0.037	< 0.005

Table A.1.2 Total lead (mg/L). Containers with pH 8

Time, hr	P. Concrete	P. PVC	P. HDPE	P. Steel	G. Vinyl	G. Aluminum	G. Steel	G. Copper
0.01	< 0.005	< 0.005	< 0.005	< 0.005	< 0.005	< 0.005	< 0.005	< 0.005
0.5	< 0.005	< 0.005	< 0.005	< 0.005	< 0.005	< 0.005	< 0.005	< 0.005
1	< 0.005	< 0.005	< 0.005	< 0.005	< 0.005	< 0.005	< 0.005	< 0.005
27	< 0.005	< 0.005	< 0.005	< 0.005	< 0.005	< 0.005	0.008	< 0.005
816	< 0.005	< 0.005	< 0.005	< 0.005	< 0.005	< 0.005	0.097	< 0.005
1512	< 0.005	< 0.005	< 0.005	0.710	< 0.005	< 0.005	0.107	< 0.005
2256	< 0.005	< 0.005	< 0.005	0.628	< 0.005	< 0.005	0.100	< 0.005

Table A.1.3 Total lead (mg/L). Containers with bay water

Time, hr	P. Concrete	P. PVC	P. HDPE	P. Steel	G. Vinyl	G. Aluminum	G. Steel	G. Copper
0.01	< 0.005	< 0.005	< 0.005	< 0.005	< 0.005	< 0.005	< 0.005	< 0.005
1	< 0.005	< 0.005	< 0.005	0.009	< 0.005	< 0.005	< 0.005	< 0.005
27	< 0.005	< 0.005	< 0.005	0.012	< 0.005	< 0.005	0.005	< 0.005
168	< 0.005	< 0.005	< 0.005	0.008	< 0.005	< 0.005	< 0.005	< 0.005
816	< 0.005	< 0.005	< 0.005	< 0.005	< 0.005	< 0.005	0.005	< 0.005
1512	< 0.005	< 0.005	< 0.005	< 0.005	< 0.005	< 0.005	0.007	< 0.005
2256	< 0.005	< 0.005	< 0.005	< 0.005	< 0.005	< 0.005	< 0.005	< 0.005

Table A.1.4 Total lead (mg/L). Containers with river water

Time, hr	P. Concrete	P. PVC	P. HDPE	P. Steel	G. Vinyl	G. Aluminum	G. Steel	G. Copper
0.01	< 0.005	< 0.005	< 0.005	< 0.005	< 0.005	< 0.005	< 0.005	< 0.005
1	< 0.005	< 0.005	< 0.005	< 0.005	< 0.005	< 0.005	< 0.005	< 0.005
27	< 0.005	< 0.005	< 0.005	< 0.005	< 0.005	< 0.005	< 0.005	< 0.005
168	< 0.005	< 0.005	< 0.005	< 0.005	< 0.005	< 0.005	0.006	< 0.005
816	< 0.005	< 0.005	< 0.005	0.001	< 0.005	< 0.005	0.011	< 0.005
1512	< 0.005	< 0.005	< 0.005	0.019	< 0.005	< 0.005	0.017	< 0.005
2256	< 0.005	< 0.005	< 0.005	< 0.005	< 0.005	< 0.005	0.058	< 0.005

For non-detected metal concentrations, mg/m^2 values were based on the half of detection limit.

Table A.1.5 Total lead (mg/m^2). Containers with pH 5

Time, hr	P. Concrete	P. PVC	P. HDPE	P. Steel	G. Vinyl	G. Aluminum	G. Steel	G. Copper
0.01	0.43	0.13	0.061	0.12	0.27	0.26	0.14	0.20
0.5	0.43	0.13	0.059	0.12	0.26	0.25	0.13	0.19
1	0.42	0.12	0.057	0.12	0.25	0.24	0.13	0.18
27	0.42	0.12	0.056	0.11	0.24	0.23	0.13	0.18
816	0.42	0.12	0.054	7.96	0.23	0.22	0.97	0.17
1512	0.42	0.11	0.052	11.24	0.23	0.22	1.31	0.16
2256	0.41	0.11	0.050	9.98	0.22	0.21	1.67	0.16

Table A.1.6 Total lead (mg/m^2). Containers with pH 8

Time, hr	P. Concrete	P. PVC	P. HDPE	P. Steel	G. Vinyl	G. Aluminum	G. Steel	G. Copper
0.01	0.43	0.13	0.061	0.12	0.27	0.26	0.14	0.20
0.5	0.43	0.13	0.059	0.12	0.26	0.25	0.13	0.19
1	0.42	0.12	0.057	0.12	0.25	0.24	0.13	0.18
27	0.42	0.12	0.056	0.11	0.24	0.23	4.72	0.18
816	0.42	0.12	0.054	0.11	0.23	0.22	5.02	0.17
1512	0.42	0.11	0.052	29.78	0.23	0.22	4.52	0.16
2256	0.41	0.11	0.050	25.37	0.22	0.21	4.72	0.16

Table A.1.7 Total lead (mg/m^2). Containers with bay water

Time, hr	P. Concrete	P. PVC	P. HDPE	P. Steel	G. Vinyl	G. Aluminum	G. Steel	G. Copper
0.01	0.35	0.12	0.054	0.11	0.23	0.22	0.12	0.17
1	0.34	0.11	0.052	0.38	0.23	0.22	0.12	0.17
27	0.33	0.11	0.052	0.50	0.22	0.22	0.23	0.16
168	0.33	0.11	0.051	0.33	0.22	0.21	0.12	0.16
816	0.32	0.11	0.050	0.10	0.22	0.21	0.23	0.16
1512	0.32	0.11	0.049	0.10	0.21	0.21	0.31	0.16
2256	0.31	0.10	0.048	0.10	0.21	0.20	0.11	0.15

Table A.1.8 Total lead (mg/m^2). Containers with river water

Time, hr	P. Concrete	P. PVC	P. HDPE	P. Steel	G. Vinyl	G. Aluminum	G. Steel	G. Copper
0.01	0.35	0.12	0.054	0.11	0.23	0.22	0.12	0.17
1	0.34	0.11	0.052	0.38	0.23	0.22	0.12	0.17
27	0.33	0.11	0.052	0.50	0.22	0.22	0.12	0.16
168	0.33	0.11	0.051	0.33	0.22	0.21	0.28	0.16
816	0.32	0.11	0.050	0.10	0.22	0.21	0.50	0.16
1512	0.32	0.11	0.049	0.10	0.21	0.21	0.76	0.16
2256	0.31	0.10	0.048	0.10	0.21	0.20	2.54	0.15

Table A.1.9 Filterable fraction of lead after three months of exposure

Water	Material	Total, mg/L	Filtered, mg/L	% Filterable
pH 5	Concrete Pipe	< 0.005	< 0.005	n/a
	PVC Pipe	< 0.005	< 0.005	n/a
	HDPE Pipe	< 0.005	< 0.005	n/a
	Steel Pipe	0.247	< 0.005	<2.02
	Vinyl Gutter	< 0.005	< 0.005	n/a
	Aluminum Gutter	< 0.005	< 0.005	n/a
	Steel Gutter	0.037	< 0.005	<13.51
	Copper Gutter	< 0.005	< 0.005	n/a
pH 8	Concrete Pipe	< 0.005	< 0.005	n/a
	PVC Pipe	< 0.005	< 0.005	n/a
	HDPE Pipe	< 0.005	< 0.005	n/a
	Steel Pipe	0.628	0.479	76
	Vinyl Gutter	< 0.005	< 0.005	n/a
	Aluminum Gutter	< 0.005	< 0.005	n/a
	Steel Gutter	0.100	0.096	96
	Copper Gutter	< 0.005	< 0.005	n/a

A.2. Copper Data

Table A.2.1 Total copper (mg/L). Containers with pH 5

Time, hr	P. Concrete	P. PVC	P. HDPE	P. Steel	G. Vinyl	G. Aluminum	G. Steel	G. Copper
0.01	< 0.02	0.09	< 0.02	< 0.02	< 0.02	< 0.02	< 0.02	< 0.02
0.5	< 0.02	0.10	< 0.02	< 0.02	< 0.02	< 0.02	< 0.02	0.58
1	< 0.02	0.09	< 0.02	< 0.02	< 0.02	< 0.02	< 0.02	1.05
27	< 0.02	0.08	< 0.02	< 0.02	< 0.02	< 0.02	< 0.02	6.82
816	< 0.02	0.22	0.02	0.11	0.02	0.03	< 0.02	4.08
1512	< 0.02	0.19	0.03	< 0.02	0.03	0.03	< 0.02	4.39
2256	< 0.02	0.23	0.03	< 0.02	0.03	0.03	< 0.02	5.10

Table A.2.2 Total copper (mg/L). Containers with pH 8

Time, hr	P. Concrete	P. PVC	P. HDPE	P. Steel	G. Vinyl	G. Aluminum	G. Steel	G. Copper
0.01	< 0.02	0.09	< 0.02	< 0.02	< 0.02	< 0.02	< 0.02	< 0.02
0.5	< 0.02	0.09	< 0.02	< 0.02	< 0.02	< 0.02	< 0.02	0.03
1	< 0.02	0.08	< 0.02	< 0.02	< 0.02	< 0.02	< 0.02	0.05
27	< 0.02	0.08	< 0.02	< 0.02	< 0.02	< 0.02	< 0.02	0.29
816	< 0.02	0.15	< 0.02	< 0.02	< 0.02	0.03	0.02	1.84
1512	< 0.02	0.19	0.06	0.03	0.02	0.03	0.03	2.05
2256	< 0.02	0.21	0.03	0.03	0.02	0.03	0.03	2.13

Table A.2.3 Total copper (mg/L). Containers with bay water

Time, hr	P. Concrete	P. PVC	P. HDPE	P. Steel	G. Vinyl	G. Aluminum	G. Steel	G. Copper
0.01	< 0.02	< 0.02	< 0.02	< 0.02	< 0.02	< 0.02	< 0.02	< 0.02
1	< 0.02	< 0.02	< 0.02	< 0.02	< 0.02	< 0.02	< 0.02	0.26
27	< 0.02	< 0.02	< 0.02	< 0.02	< 0.02	< 0.02	< 0.02	2.11
168	< 0.02	< 0.02	< 0.02	< 0.02	< 0.02	< 0.02	< 0.02	6.11
816	< 0.02	< 0.02	< 0.02	< 0.02	< 0.02	< 0.02	< 0.02	5.64
1512	< 0.02	< 0.02	< 0.02	< 0.02	< 0.02	< 0.02	< 0.02	30.30
2256	< 0.02	< 0.02	< 0.02	< 0.02	< 0.02	< 0.02	< 0.02	35.90

Table A.2.4 Total copper (mg/L). Containers with river water

Time, hr	P. Concrete	P. PVC	P. HDPE	P. Steel	G. Vinyl	G. Aluminum	G. Steel	G. Copper
0.01	< 0.02	< 0.02	< 0.02	< 0.02	< 0.02	< 0.02	< 0.02	< 0.02
1	< 0.02	< 0.02	< 0.02	< 0.02	< 0.02	< 0.02	< 0.02	0.07
27	< 0.02	< 0.02	< 0.02	< 0.02	< 0.02	< 0.02	< 0.02	0.60
168	< 0.02	< 0.02	< 0.02	< 0.02	< 0.02	< 0.02	< 0.02	1.22
816	< 0.02	< 0.02	< 0.02	< 0.02	< 0.02	< 0.02	< 0.02	2.09
1512	< 0.02	< 0.02	< 0.02	< 0.02	< 0.02	< 0.02	< 0.02	4.10
2256	< 0.02	< 0.02	< 0.02	< 0.02	< 0.02	< 0.02	< 0.02	5.47

Table A.2.5 Total copper (mg/m^2). Containers with pH 5

Time, hr	P. Concrete	P. PVC	P. HDPE	P. Steel	G. Vinyl	G. Aluminum	G. Steel	G. Copper
0.01	1.72	0.00	0.24	0.50	1.07	1.03	0.56	0.78
0.5	1.71	0.51	0.24	0.48	1.04	1.00	0.54	43.93
1	1.69	0.00	0.23	0.47	1.00	0.96	0.52	76.96
27	1.68	-0.48	0.22	0.45	0.97	0.93	0.50	483.24
816	1.67	5.99	0.43	4.79	1.87	2.70	0.49	279.12
1512	1.66	4.45	0.62	0.42	2.70	2.60	0.47	289.60
2256	1.65	5.99	0.60	0.40	2.60	2.50	0.45	323.98

Table A.2.6 Total copper (mg/m^2). Containers with pH 8

Time, hr	P. Concrete	P. PVC	P. HDPE	P. Steel	G. Vinyl	G. Aluminum	G. Steel	G. Copper
0.01	1.72	0.00	0.24	0.50	1.07	1.03	0.56	0.78
0.5	1.71	0.00	0.24	0.48	1.04	1.00	0.54	2.27
1	1.69	-0.49	0.23	0.47	1.00	0.96	0.52	3.66
27	1.68	-0.48	0.22	0.45	0.97	0.93	0.50	20.55
816	1.67	2.77	0.21	0.44	0.93	2.70	0.97	125.88
1512	1.66	4.45	1.24	1.258	1.80	2.60	1.41	135.24
2256	1.65	5.14	0.60	1.212	1.74	2.50	1.36	135.31

Table A.2.7 Total copper (mg/m^2). Containers with bay water

Time, hr	P. Concrete	P. PVC	P. HDPE	P. Steel	G. Vinyl	G. Aluminum	G. Steel	G. Copper
0.01	1.39	0.46	0.21	0.44	0.93	0.90	0.49	0.68
1	1.36	0.45	0.21	0.43	0.91	0.88	0.48	17.38
27	1.34	0.44	0.21	0.42	0.90	0.86	0.47	138.78
168	1.32	0.44	0.20	0.41	0.88	0.85	0.46	395.31
816	1.29	0.43	0.20	0.40	0.87	0.84	0.45	358.84
1512	1.27	0.42	0.20	0.40	0.85	0.82	0.45	1895.22
2256	1.25	0.41	0.19	0.39	0.84	0.81	0.44	2206.89

Table A.2.8 Total copper (mg/m^2). Containers with river water

Time, hr	P. Concrete	P. PVC	P. HDPE	P. Steel	G. Vinyl	G. Aluminum	G. Steel	G. Copper
0.01	1.39	0.46	0.21	0.44	0.93	0.90	0.49	0.68
1	1.36	0.45	0.21	0.43	0.91	0.88	0.48	4.68
27	1.34	0.44	0.21	0.42	0.90	0.86	0.47	39.46
168	1.32	0.44	0.20	0.41	0.88	0.85	0.46	78.93
816	1.29	0.43	0.20	0.40	0.87	0.84	0.45	132.97
1512	1.27	0.42	0.20	0.40	0.85	0.82	0.45	256.45
2256	1.25	0.41	0.19	0.39	0.84	0.81	0.44	336.26

Table A.2.9 Filterable fraction of copper after three months of exposure

Water	Material	Total, mg/L	Filtered, mg/L	% Filterable
pH 5	Concrete Pipe	< 0.02	< 0.02	n/a
	PVC Pipe	0.23	0.22	96
	HDPE Pipe	0.03	0.03	100
	Steel Pipe	< 0.02	< 0.02	n/a
	Vinyl Gutter	0.03	0.03	100
	Aluminum Gutter	0.03	0.04	133
	Steel Gutter	< 0.02	< 0.02	n/a
	Copper Gutter	5.10	5.10	100
pH 8	Concrete Pipe	< 0.02	< 0.02	n/a
	PVC Pipe	0.21	0.15	71
	HDPE Pipe	0.03	0.03	100
	Steel Pipe	0.03	0.02	67
	Vinyl Gutter	0.02	0.02	100
	Aluminum Gutter	0.03	0.03	100
	Steel Gutter	0.03	0.03	100
	Copper Gutter	2.13	0.36	17

A.3. Zinc Data

Table A.3.1 Total zinc (mg/L). Containers with pH 5

Time, hr	P. Concrete	P. PVC	P. HDPE	P. Steel	G. Vinyl	G. Aluminum	G. Steel	G. Copper
0.01	< 0.02	0.25	< 0.02	< 0.02	< 0.02	< 0.02	< 0.02	< 0.02
0.5	< 0.02	0.22	< 0.02	1.80	< 0.02	< 0.02	1.33	0.03
1	< 0.02	0.23	0.02	3.93	< 0.02	< 0.02	2.14	0.03
27	< 0.02	0.22	0.02	10.20	< 0.02	< 0.02	14.20	0.04
816	< 0.02	0.36	0.03	8.45	< 0.02	< 0.02	8.46	< 0.02
1512	< 0.02	0.42	0.05	12.70	0.03	0.03	10.20	0.03
2256	< 0.02	0.44	0.06	11.70	< 0.02	0.02	14.10	0.13

Table A.3.2 Total zinc (mg/L). Containers with pH 8

Time, hr	P. Concrete	P. PVC	P. HDPE	P. Steel	G. Vinyl	G. Aluminum	G. Steel	G. Copper
0.01	< 0.02	0.17	0.03	0.02	< 0.02	< 0.02	0.02	0.02
0.5	0.02	0.18	0.02	0.07	0.03	0.03	0.10	0.02
1	< 0.02	0.17	< 0.02	0.10	0.02	0.02	0.14	0.02
27	< 0.02	0.16	0.02	1.01	< 0.02	0.02	2.09	0.02
816	< 0.02	0.28	0.03	16.30	0.03	0.04	27.80	0.03
1512	0.03	0.34	0.04	24.80	0.04	0.04	89.90	0.03
2256	0.03	0.68	0.05	84.30	0.04	0.21	9.69	0.02

Table A.3.3 Total zinc (mg/L). Containers with bay water

Time, hr	P. Concrete	P. PVC	P. HDPE	P. Steel	G. Vinyl	G. Aluminum	G. Steel	G. Copper
0.01	< 0.02	< 0.02	< 0.02	< 0.02	< 0.02	< 0.02	< 0.02	< 0.02
1	< 0.02	< 0.02	< 0.02	1.40	< 0.02	< 0.02	0.48	< 0.02
27	< 0.02	< 0.02	< 0.02	8.40	< 0.02	< 0.02	4.84	0.05
168	< 0.02	< 0.02	< 0.02	8.28	< 0.02	< 0.02	4.43	0.03
816	< 0.02	< 0.02	< 0.02	18.9	< 0.02	< 0.02	3.95	0.03
1512	< 0.02	< 0.02	< 0.02	69.5	0.04	0.70	16.6	0.05
2256	< 0.02	< 0.02	< 0.02	78.6	< 0.02	< 0.02	36.7	< 0.02

Table A.3.4 Total zinc (mg/L). Containers with river water

Time, hr	P. Concrete	P. PVC	P. HDPE	P. Steel	G. Vinyl	G. Aluminum	G. Steel	G. Copper
0.01	< 0.02	< 0.02	0.02	< 0.02	< 0.02	0.02	0.02	0.02
1	< 0.02	< 0.02	< 0.02	0.96	< 0.02	< 0.02	0.27	< 0.02
27	< 0.02	< 0.02	< 0.02	6.06	< 0.02	< 0.02	1.2	0.02
168	< 0.02	< 0.02	< 0.02	4.93	< 0.02	< 0.02	5.73	0.02
816	< 0.02	< 0.02	0.03	19.9	< 0.02	< 0.02	20.06	0.03
1512	< 0.02	0.02	0.03	84.100	0.02	0.02	156	0.06
2256	< 0.02	0.03	0.03	67.800	< 0.02	0.03	190	0.50

Table A.3.5 Total zinc (mg/m^2). Containers with pH 5

Time, hr	P. Concrete	P. PVC	P. HDPE	P. Steel	G. Vinyl	G. Aluminum	G. Steel	G. Copper
0.01	1.72	0.00	0.24	0.50	1.07	1.03	0.56	0.78
0.5	1.71	-1.53	0.24	86.70	1.04	1.00	71.69	2.27
1	1.69	-0.99	0.46	183.18	1.00	0.96	111.62	2.20
27	1.68	-1.43	0.44	459.58	0.97	0.93	715.99	2.83
816	1.67	5.07	0.64	367.60	0.93	0.90	411.86	1.37
1512	1.66	7.56	1.03	532.76	2.70	2.60	478.84	1.98
2256	1.65	8.13	1.19	472.63	0.87	1.67	637.41	8.26

Table A.3.6 Total zinc (mg/m^2). Containers with pH 8

Time, hr	P. Concrete	P. PVC	P. HDPE	P. Steel	G. Vinyl	G. Aluminum	G. Steel	G. Copper
0.01	1.72	0.00	0.00	0.01	1.07	1.03	0.01	0.00
0.5	3.41	0.51	-0.24	2.41	3.11	2.99	4.31	0.00
1	1.69	0.00	-0.46	3.73	2.00	1.93	6.26	0.00
27	1.68	-0.48	-0.22	44.61	0.97	1.86	104.37	0.00
816	1.67	5.07	0.00	708.23	2.80	3.60	1352.43	0.68
1512	4.99	7.56	0.21	1039.51	3.61	3.47	4219.40	0.66
2256	4.96	21.83	0.40	3404.55	3.47	17.53	437.14	0.00

Table A.3.7 Total zinc (mg/m^2). Containers with bay water

Time, hr	P. Concrete	P. PVC	P. HDPE	P. Steel	G. Vinyl	G. Aluminum	G. Steel	G. Copper
0.01	1.39	0.46	0.21	0.44	0.93	0.90	0.49	0.68
1	1.36	0.45	0.21	59.51	0.91	0.88	22.83	0.67
27	1.34	0.44	0.21	351.33	0.90	0.86	226.54	3.29
168	1.32	0.44	0.20	340.65	0.88	0.85	203.96	1.94
816	1.29	0.43	0.20	764.65	0.87	0.84	178.84	1.91
1512	1.27	0.42	0.20	2764.31	3.42	57.55	738.88	3.13
2256	1.25	0.41	0.19	3072.52	0.84	0.81	1605.46	0.61

Table A.3.8 Total zinc (mg/m^2). Containers with river water

Time, hr	P. Concrete	P. PVC	P. HDPE	P. Steel	G. Vinyl	G. Aluminum	G. Steel	G. Copper
0.01	1.39	0.46	0.00	0.44	0.93	0.00	0.01	0.00
1	1.36	0.45	-0.21	40.81	0.91	-0.88	11.89	-0.67
27	1.34	0.44	-0.21	253.46	0.90	-0.86	55.23	0.00
168	1.32	0.44	-0.20	202.83	0.88	-0.85	262.89	0.00
816	1.29	0.43	0.20	805.11	0.87	-0.84	907.32	0.64
1512	1.27	0.84	0.20	3345.01	1.71	0.00	6942.76	2.50
2256	1.25	1.24	0.19	2650.34	0.84	0.81	8310.78	29.51

Table A.3.9 Filterable fraction of zinc after three months of exposure

Water	Material	Total, mg/L	Filtered, mg/L	% Filterable
pH 5	Concrete Pipe	< 0.02	< 0.02	n/a
	PVC Pipe	0.44	0.39	89
	HDPE Pipe	0.06	0.05	83
	Steel Pipe	11.70	2.77	24
	Vinyl Gutter	< 0.02	< 0.02	n/a
	Aluminum Gutter	0.02	0.04	200
	Steel Gutter	14.10	7.23	51
	Copper Gutter	0.13	< 0.02	< 15.38
pH 8	Concrete Pipe	0.03	< 0.02	< 66.67
	PVC Pipe	0.68	0.12	18
	HDPE Pipe	0.05	0.05	100
	Steel Pipe	84.30	0.29	0.34
	Vinyl Gutter	0.04	0.04	100
	Aluminum Gutter	0.21	0.05	24
	Steel Gutter	9.69	0.16	1.7
	Copper Gutter	0.02	0.02	100

A.4 Aluminum Data

Table A.4.1 Total aluminum (mg/L). Containers with pH 5

Time, hr	P. Concrete	P. PVC	P. HDPE	P. Steel	G. Vinyl	G. Aluminum	G. Steel	G. Copper
0.01	n/a	n/a	n/a	n/a	n/a	n/a	n/a	n/a
0.5	n/a	n/a	n/a	n/a	n/a	n/a	n/a	n/a
1	n/a	n/a	n/a	n/a	n/a	n/a	n/a	n/a
27	n/a	n/a	n/a	n/a	n/a	n/a	n/a	n/a
816	n/a	n/a	n/a	n/a	n/a	n/a	n/a	n/a
1512	n/a	n/a	n/a	n/a	n/a	n/a	n/a	n/a
2256	< 0.1	0.1	< 0.1	< 0.1	< 0.1	0.3	< 0.1	< 0.1

Table A.4.2 Total aluminum (mg/L). Containers with pH 8

Time, hr	P. Concrete	P. PVC	P. HDPE	P. Steel	G. Vinyl	G. Aluminum	G. Steel	G. Copper
0.01	n/a	n/a	n/a	n/a	n/a	n/a	n/a	n/a
0.5	n/a	n/a	n/a	n/a	n/a	n/a	n/a	n/a
1	n/a	n/a	n/a	n/a	n/a	n/a	n/a	n/a
27	n/a	n/a	n/a	n/a	n/a	n/a	n/a	n/a
816	n/a	n/a	n/a	n/a	n/a	n/a	n/a	n/a
1512	n/a	n/a	n/a	n/a	n/a	n/a	n/a	n/a
2256	< 0.1	0.1	0.2	< 0.1	0.2	0.4	0.2	< 0.1

Table A.4.3 Total aluminum (mg/L). Containers with bay water

Time, hr	P. Concrete	P. PVC	P. HDPE	P. Steel	G. Vinyl	G. Aluminum	G. Steel	G. Copper
0.01	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1
1	n/a	n/a	n/a	n/a	n/a	n/a	n/a	n/a
27	n/a	n/a	n/a	n/a	n/a	n/a	n/a	n/a
168	n/a	n/a	n/a	n/a	n/a	n/a	n/a	n/a
816	n/a	n/a	n/a	n/a	n/a	n/a	n/a	n/a
1512	n/a	n/a	n/a	n/a	n/a	n/a	n/a	n/a
2256	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1	0.30	< 0.1	< 0.1

Table A.4.4 Total aluminum (mg/L). Containers with river water

Time, hr	P. Concrete	P. PVC	P. HDPE	P. Steel	G. Vinyl	G. Aluminum	G. Steel	G. Copper
0.01	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1
1	n/a	n/a	n/a	n/a	n/a	n/a	n/a	n/a
27	n/a	n/a	n/a	n/a	n/a	n/a	n/a	n/a
168	n/a	n/a	n/a	n/a	n/a	n/a	n/a	n/a
816	n/a	n/a	n/a	n/a	n/a	n/a	n/a	n/a
1512	n/a	n/a	n/a	n/a	n/a	n/a	n/a	n/a
2256	0.10	0.20	0.30	< 0.1	< 0.1	1.00	0.100	< 0.1

Table A.4.5 Filterable fraction of aluminum after three months of exposure

Water	Material	Total, mg/L	Filtered, mg/L	% Filterable
pH 5	Concrete Pipe	< 0.1	< 0.1	n/a
	PVC Pipe	0.10	0.10	100
	HDPE Pipe	< 0.1	< 0.1	n/a
	Steel Pipe	< 0.1	< 0.1	n/a
	Vinyl Gutter	< 0.1	< 0.1	n/a
	Aluminum Gutter	0.30	0.30	100
	Steel Gutter	< 0.1	< 0.1	n/a
	Copper Gutter	< 0.1	< 0.1	n/a
pH 8	Concrete Pipe	< 0.1	< 0.1	n/a
	PVC Pipe	0.10	< 0.1	< 100
	HDPE Pipe	0.20	0.20	100
	Steel Pipe	< 0.1	< 0.1	n/a
	Vinyl Gutter	0.20	0.10	50
	Aluminum Gutter	0.40	0.40	100
	Steel Gutter	0.20	0.10	50
	Copper Gutter	< 0.1	< 0.1	n/a

A.5 Iron Data

Table A.5.1 Total iron (mg/L). Containers with pH 5

Time, hr	P. Concrete	P. PVC	P. HDPE	P. Steel	G. Vinyl	G. Aluminum	G. Steel	G. Copper
0.01	n/a	n/a	n/a	n/a	n/a	n/a	n/a	n/a
0.5	n/a	n/a	n/a	n/a	n/a	n/a	n/a	n/a
1	n/a	n/a	n/a	n/a	n/a	n/a	n/a	n/a
27	n/a	n/a	n/a	n/a	n/a	n/a	n/a	n/a
816	n/a	n/a	n/a	n/a	n/a	n/a	n/a	n/a
1512	n/a	n/a	n/a	n/a	n/a	n/a	n/a	n/a
2256	n/a	n/a	n/a	n/a	n/a	n/a	n/a	n/a
3144	0.10	0.12	0.15	21.90	0.12	0.12	5.89	0.15

Table A.5.2 Total iron (mg/L). Containers with pH 8

Time, hr	P. Concrete	P. PVC	P. HDPE	P. Steel	G. Vinyl	G. Aluminum	G. Steel	G. Copper
0.01	n/a	n/a	n/a	n/a	n/a	n/a	n/a	n/a
0.5	n/a	n/a	n/a	n/a	n/a	n/a	n/a	n/a
1	n/a	n/a	n/a	n/a	n/a	n/a	n/a	n/a
27	n/a	n/a	n/a	n/a	n/a	n/a	n/a	n/a
816	n/a	n/a	n/a	n/a	n/a	n/a	n/a	n/a
1512	n/a	n/a	n/a	n/a	n/a	n/a	n/a	n/a
2256	n/a	n/a	n/a	n/a	n/a	n/a	n/a	n/a
2712	< 0.02	0.13	0.13	1.18	0.15	0.13	0.34	0.15

Table A.5.3 Total iron (mg/L). Containers with bay water

Time, hr	P. Concrete	P. PVC	P. HDPE	P. Steel	G. Vinyl	G. Aluminum	G. Steel	G. Copper
0.01	0.06	0.63	0.63	0.65	0.75	0.78	0.78	0.74
1	n/a	n/a	n/a	n/a	n/a	n/a	n/a	n/a
27	n/a	n/a	n/a	n/a	n/a	n/a	n/a	n/a
168	n/a	n/a	n/a	n/a	n/a	n/a	n/a	n/a
816	n/a	n/a	n/a	n/a	n/a	n/a	n/a	n/a
1512	n/a	n/a	n/a	n/a	n/a	n/a	n/a	n/a
2256	2.59	0.93	1.10	1.95	1.08	1.25	2.30	2.10

Table A.5.4 Total iron (mg/L). Containers with river water

Time, hr	P. Concrete	P. PVC	P. HDPE	P. Steel	G. Vinyl	G. Aluminum	G. Steel	G. Copper
0.01	0.21	0.24	0.21	0.19	0.17	0.22	0.19	0.20
1	n/a	n/a	n/a	n/a	n/a	n/a	n/a	n/a
27	n/a	n/a	n/a	n/a	n/a	n/a	n/a	n/a
168	n/a	n/a	n/a	n/a	n/a	n/a	n/a	n/a
816	n/a	n/a	n/a	n/a	n/a	n/a	n/a	n/a
1512	n/a	n/a	n/a	n/a	n/a	n/a	n/a	n/a
2256	1.14	0.62	0.43	1.42	0.45	0.46	1.44	1.78

Table A.5.5 Filterable fraction of iron after three months of exposure

		After Three Months of Exposure		
Water	**Material**	**Total, mg/L**	**Filtered, mg/L**	**% Filterable**
Bay	Concrete Pipe	2.59	0.76	29
	PVC Pipe	0.93	0.84	90
	HDPE Pipe	1.10	0.92	84
	Steel Pipe	1.95	0.96	49
	Vinyl Gutter	1.08	0.99	92
	Aluminum Gutter	1.25	1.10	88
	Steel Gutter	2.30	0.95	41
	Copper Gutter	2.10	0.90	43
River	Concrete Pipe	1.14	0.21	18
	PVC Pipe	0.62	0.45	73
	HDPE Pipe	0.43	0.33	77
	Steel Pipe	1.42	0.08	6
	Vinyl Gutter	0.45	0.31	69
	Aluminum Gutter	0.46	0.32	70
	Steel Gutter	1.44	0.27	19
	Copper Gutter	1.78	0.29	16

A.6 Pipe and Gutter Material Composition Data

Table A.6.1 Pipe and gutter material composition (mg/kg).

	Material Composition, mg/kg				
Material	**Lead, Pb**	**Copper, Cu**	**Zinc, Zn**	**Aluminum, Al**	**Iron, Fe**
Concrete Pipe	14.9	72	45	6500	150000
PVC Pipe	< 0.5	< 2	< 2	34	89
HDPE Pipe	< 0.5	3	< 2	690	51
Steel Pipe	46.5	275	28000	452	971000
Vinyl Gutter	< 0.5	< 2	< 2	93	48
Aluminum Gutter	13.4	1210	943	943000	3100
Steel Gutter	12.2	520	18100	685	980000
Copper Gutter	7.0	998000	7	1020	102
Detection Limit, mg/kg	0.5	2	2	10	2

Table A.6.2 Metal Detection Limits. Shavings

Constituent	Detection Limit, mg/kg
Lead, Pb	0.5
Copper, Cu	2
Zinc, Zn	2
Aluminum, Al	10
Iron, Fe	2

A.7. 2^2 Factorial and Regression Analysis Results

Concrete Pipe. Controlled pH

Zn Releases, Concrete Pipe, Controlled pH

Factorial Analysis:

```
Analysis of Variance for Y, using Adjusted SS for Tests

Source  DF  Seq SS  Adj SS  Adj MS     F      P
pH       1   5.788   5.788   5.788  4.41  0.062
Error   10  13.114  13.114   1.311
Total   11  18.902


S = 1.14515   R-Sq = 30.62%   R-Sq(adj) = 23.68%


Term          Coef  SE Coef      T      P
Constant    2.3732   0.3306   7.18  0.000
pH
5          -0.6945   0.3306  -2.10  0.062
```

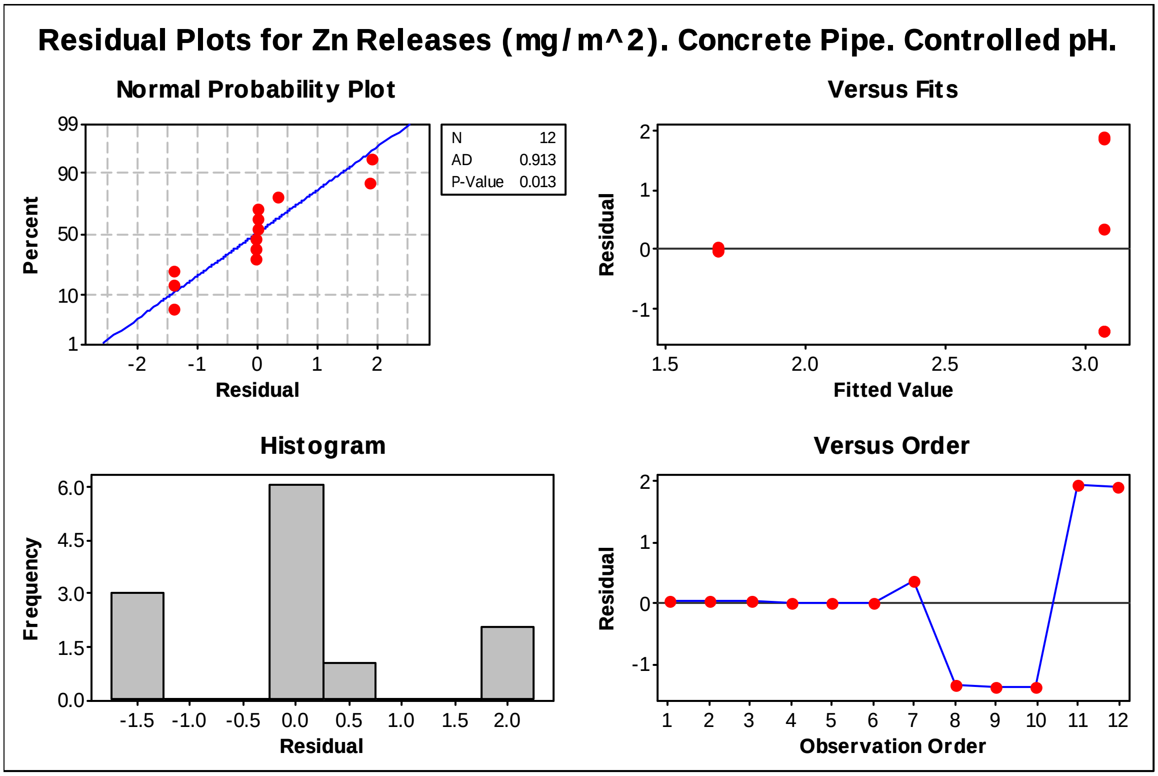


Figure A.7.1. Residual plots for Zn releases from Concrete pipe under controlled pH conditions.

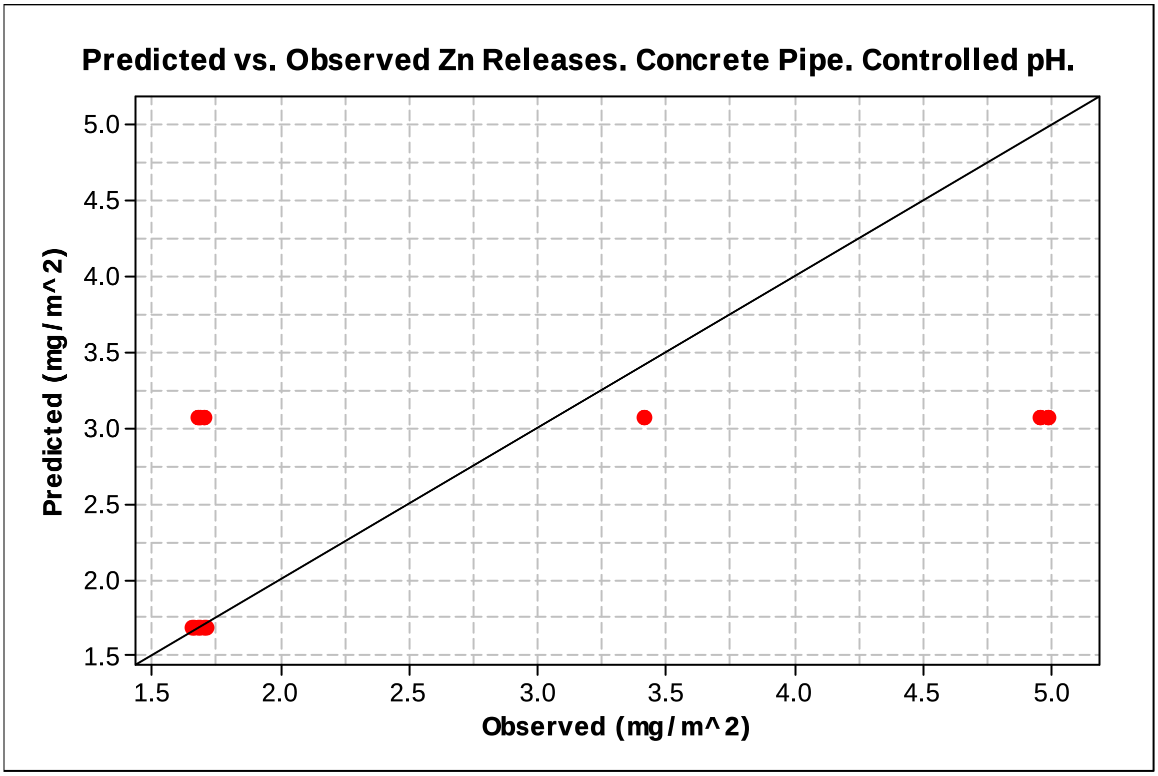


Figure A.7.2. Predicted vs. observed values for Zn releases. Concrete pipe. Controlled pH.

PVC Pipe. Controlled pH

Cu Releases, PVC Pipe, Controlled pH

Factorial Analysis:

```
Analysis of Variance for Y, using Adjusted SS for Tests

Source  DF  Seq SS  Adj SS  Adj MS      F      P
Time     1  73.593  73.593  73.593  90.17  0.000
Error   10   8.162   8.162   0.816
Total   11  81.755

S = 0.903426   R-Sq = 90.02%   R-Sq(adj) = 89.02%

Term          Coef  SE Coef      T      P
Constant    2.3200   0.2608   8.90  0.000
Time       -2.4764   0.2608  -9.50  0.000
```

Regression Analysis:

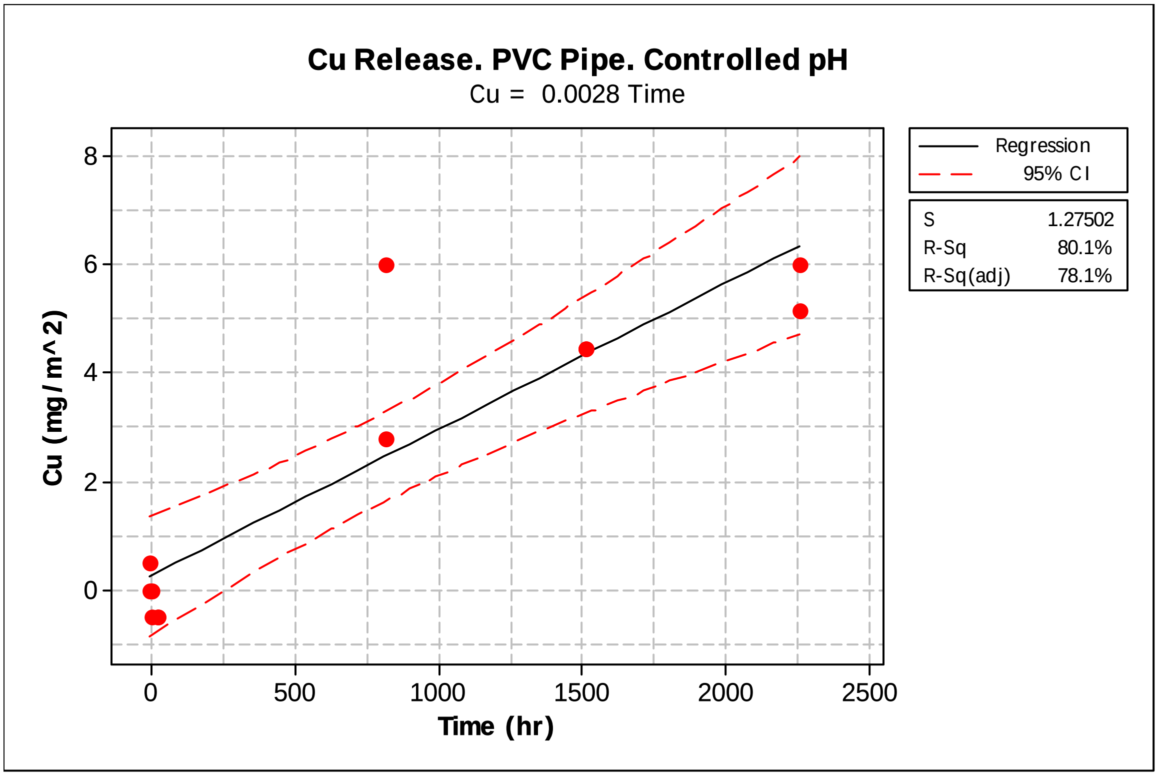


Figure A.7.3. Linear regression for Cu releases. PVC pipe. Controlled pH.

```
The regression equation is
Cu = 0.00284 Time


Predictor        Coef     SE Coef      T      P
Noconstant
Time        0.0028395  0.0003069   9.25  0.000


S = 1.23069

PRESS = 19.9181


Analysis of Variance

Source          DF      SS      MS      F      P
Regression       1  129.68  129.68  85.62  0.000
Residual Error  11   16.66    1.51
Total           12  146.34
```

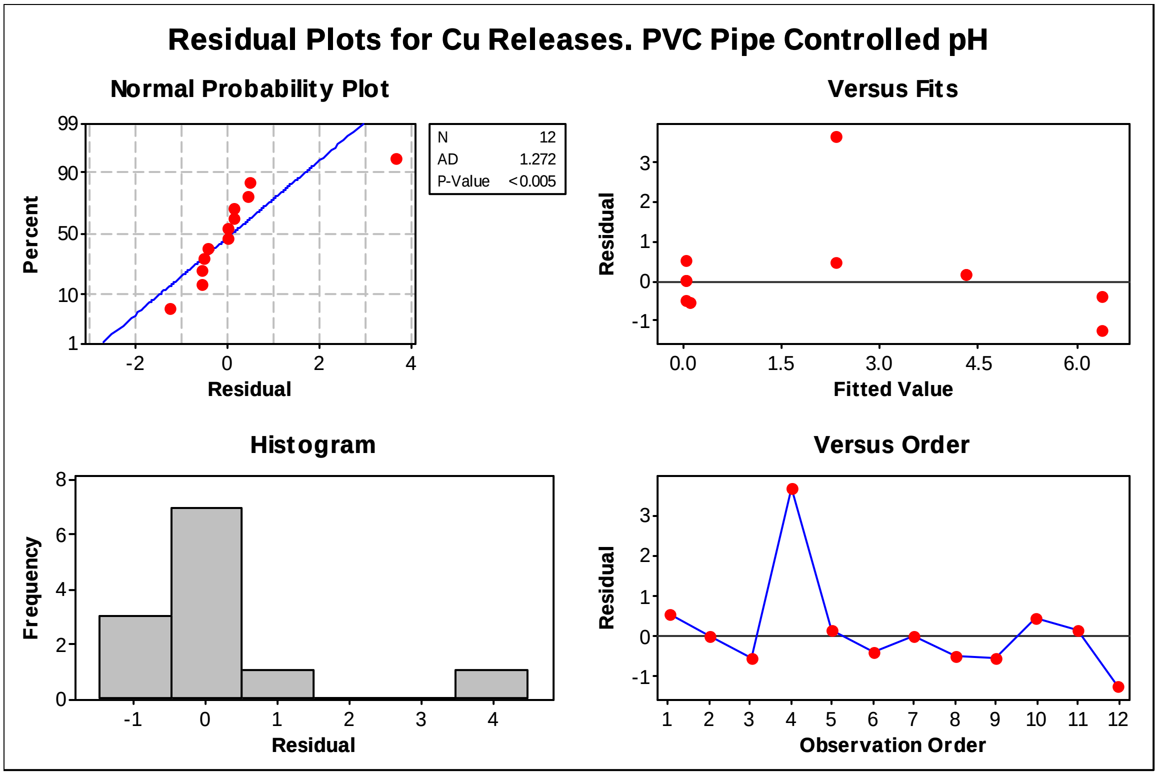


Figure A.7.4. Residual plots for Cu releases from PVC pipe under controlled pH conditions.

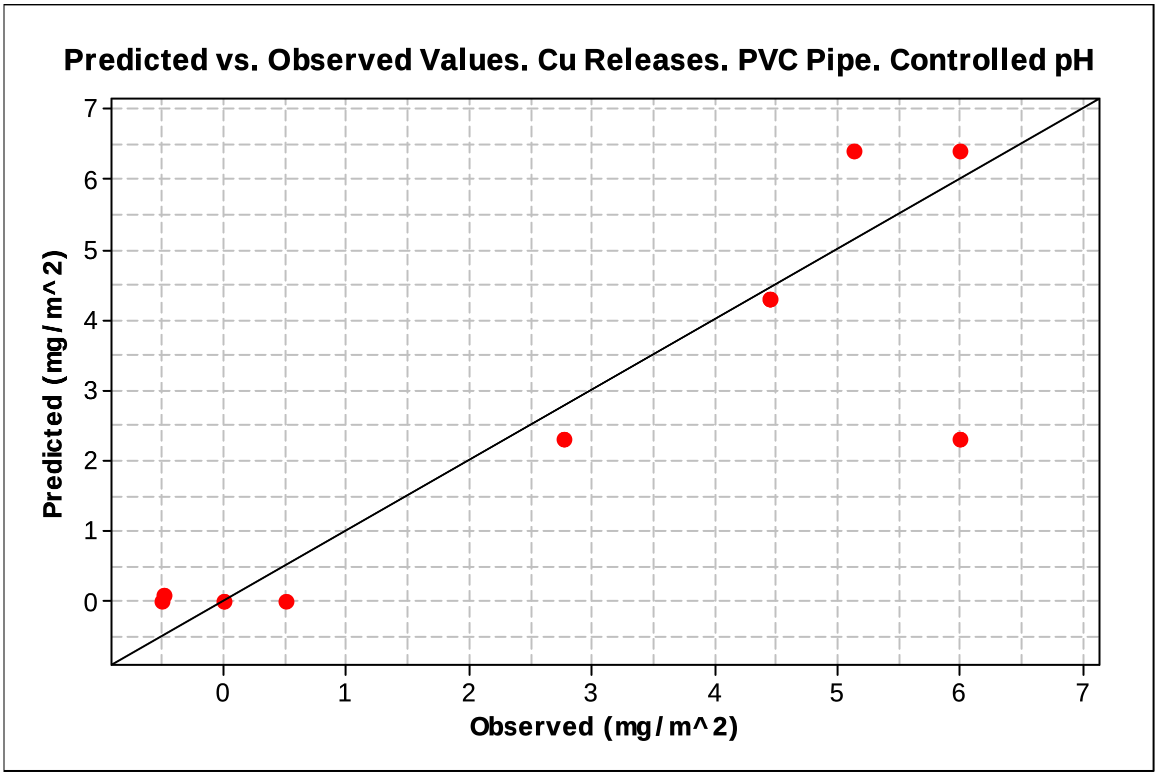


Figure A.7.5. Predicted vs. observed values for Cu releases. PVC pipe. Controlled pH.

Zn Releases, PVC Pipe, Controlled pH

Factorial Analysis:

```
Analysis of Variance for Y, using Adjusted SS for Tests

Source  DF  Seq SS  Adj SS  Adj MS      F      P
Time     1  291.44  291.44  291.44  14.32  0.004
Error   10  203.48  203.48   20.35
Total   11  494.92

S = 4.51090   R-Sq = 58.89%   R-Sq(adj) = 54.77%

Term         Coef  SE Coef      T      P
Constant    4.275    1.302   3.28  0.008
Time       -4.928    1.302  -3.78  0.004
```

Regression Analysis:

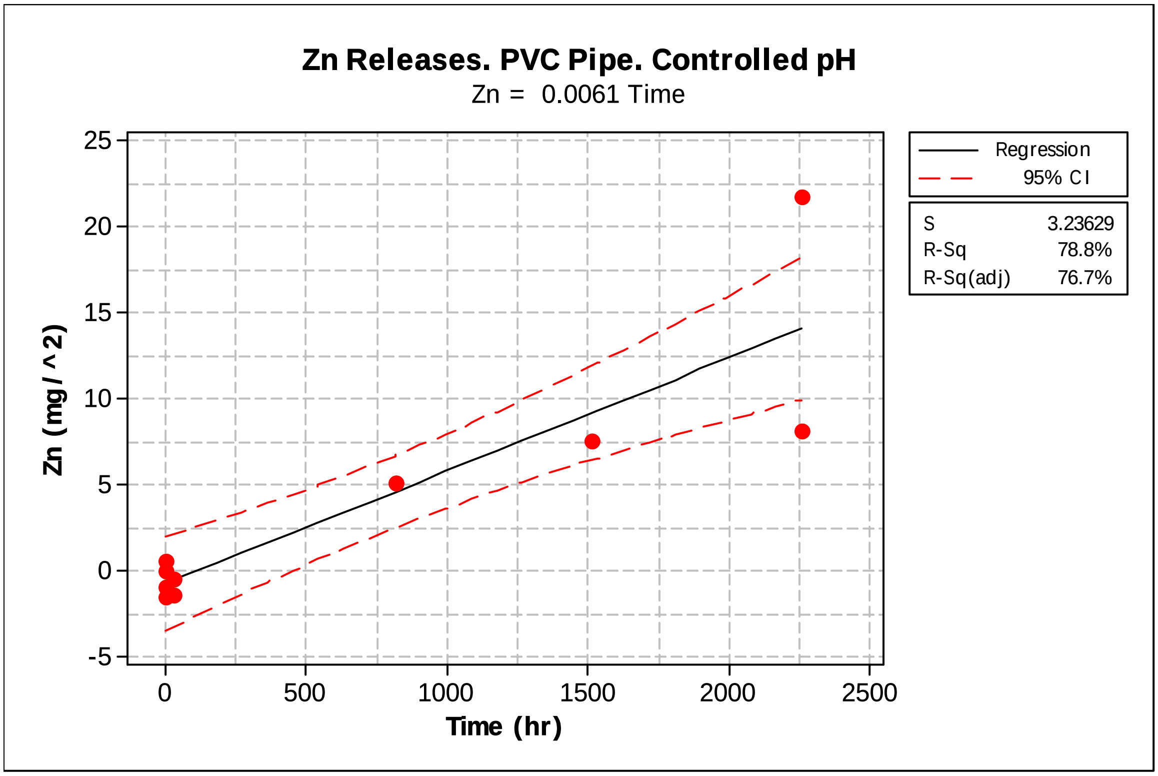


Figure A.7.6. Linear regression for Zn releases. PVC pipe. Controlled pH.

```
The regression equation is
Zn = 0.00613 Time


Predictor        Coef     SE Coef     T      P
Noconstant
Time        0.0061347  0.0007846  7.82  0.000


S = 3.14655

PRESS = 220.961


Analysis of Variance

Source          DF      SS      MS      F      P
Regression       1  605.33  605.33  61.14  0.000
Residual Error  11  108.91    9.90
Total           12  714.24
```

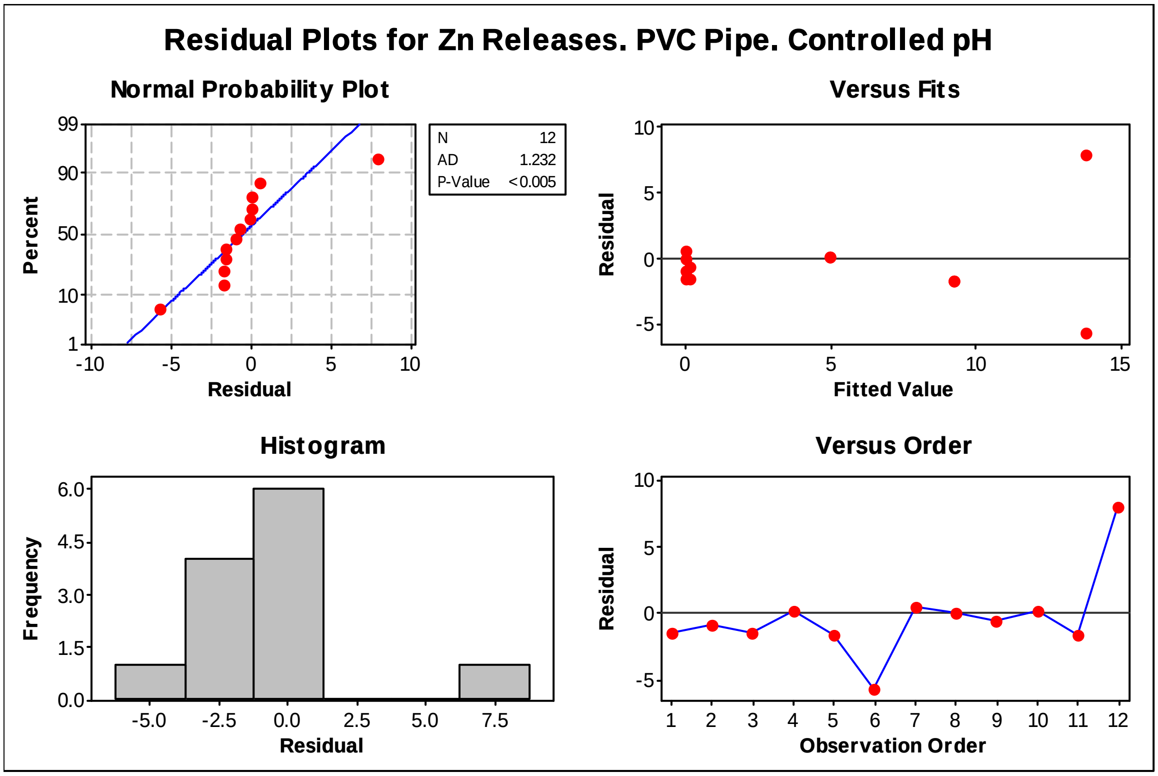


Figure A.7.7. Residual plots for Zn releases from PVC pipe under controlled pH conditions.

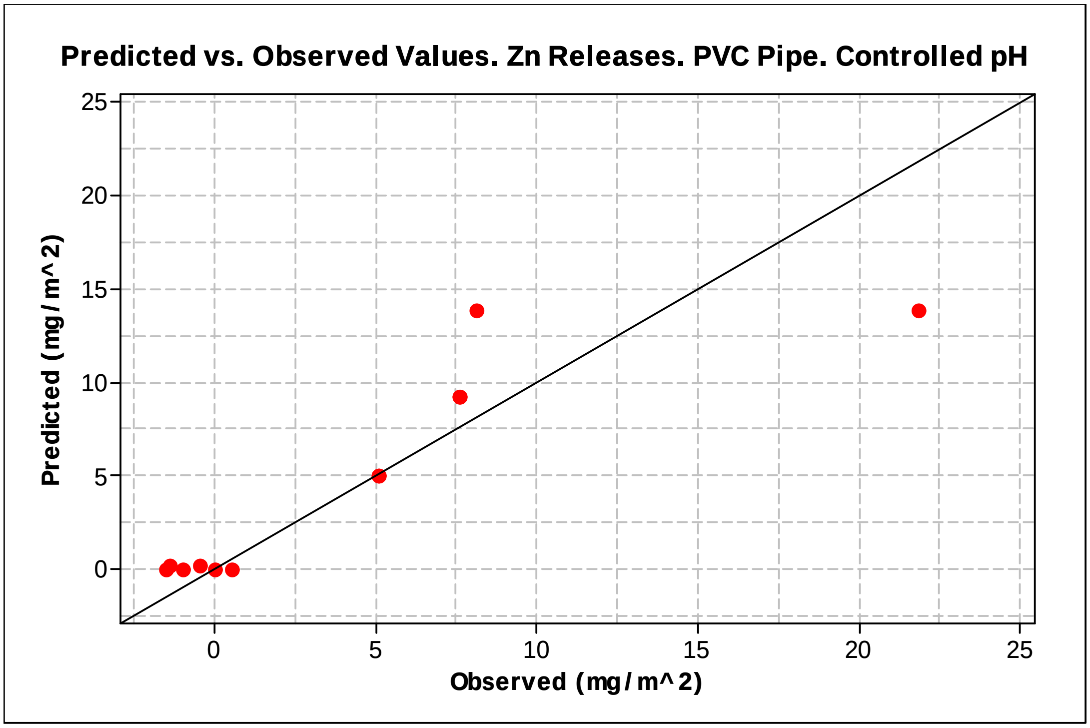


Figure A.7.8. Predicte vs. observed values for Zn releases. PVC pipe. Controlled pH.

PVC Pipe. Natural pH

Zn Releases, PVC Pipe, Natural pH

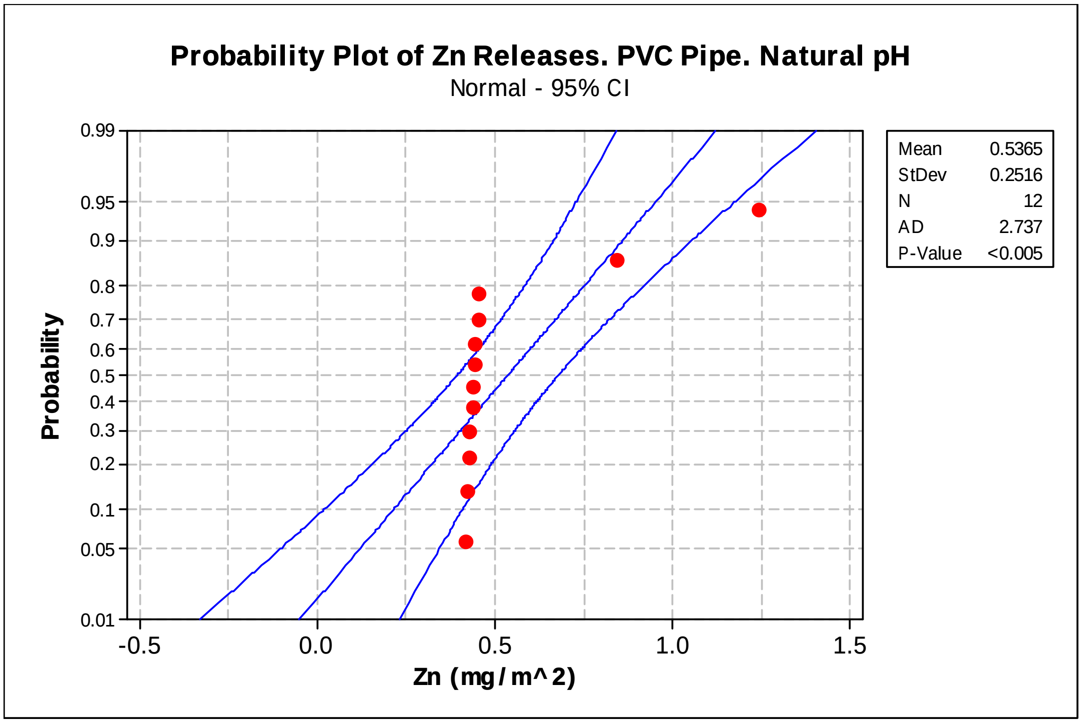


Figure A.7.9. Probability for Zn releases. PVC pipe. Natural pH.

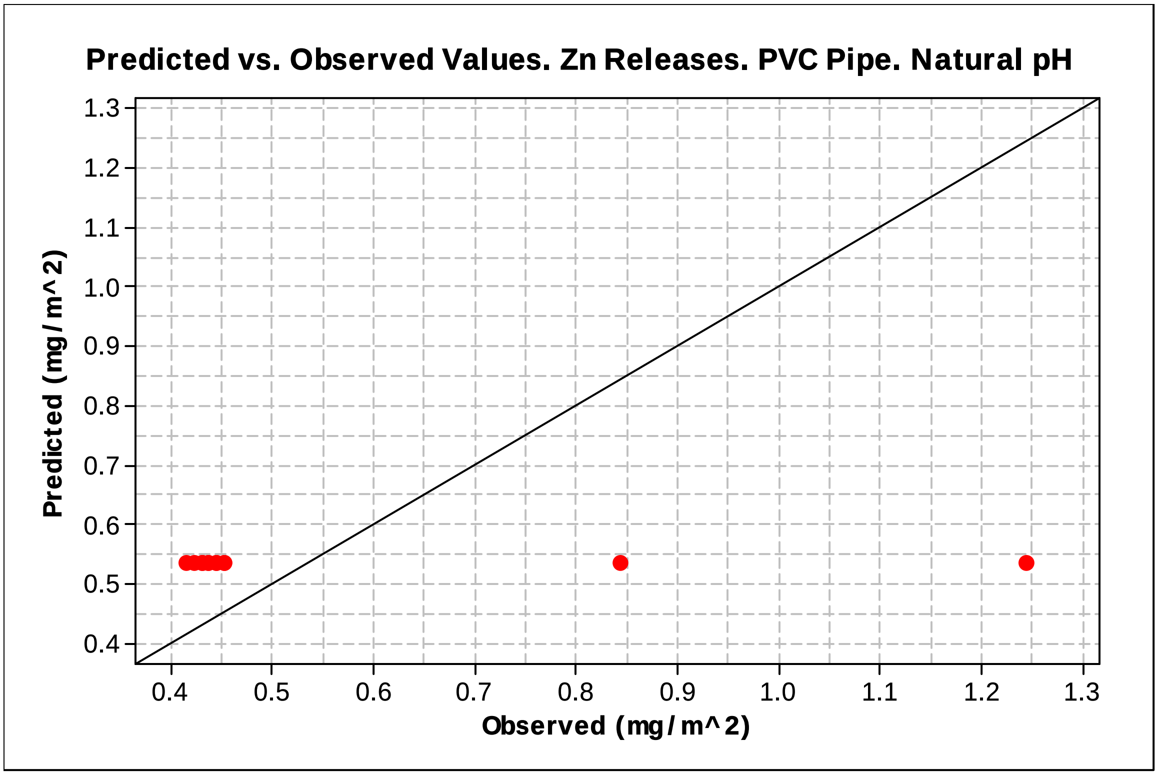


Figure A.7.10. Predicted vs. observed values for Zn releases. PVC pipe. Natural pH.

HDPE Pipe. Controlled pH

Cu Releases, HDPE Pipe, Controlled pH

Factorial Analysis:

```
Analysis of Variance for Y, using Adjusted SS for Tests

Source  DF   Seq SS   Adj SS   Adj MS     F      P
Time     1  0.44846  0.44846  0.44846  7.64  0.020
Error   10  0.58707  0.58707  0.05871
Total   11  1.03553

S = 0.242295   R-Sq = 43.31%   R-Sq(adj) = 37.64%

Term          Coef  SE Coef      T      P
Constant   0.42300  0.06994   6.05  0.000
Time      -0.19332  0.06994  -2.76  0.020
```

Regression Analysis:

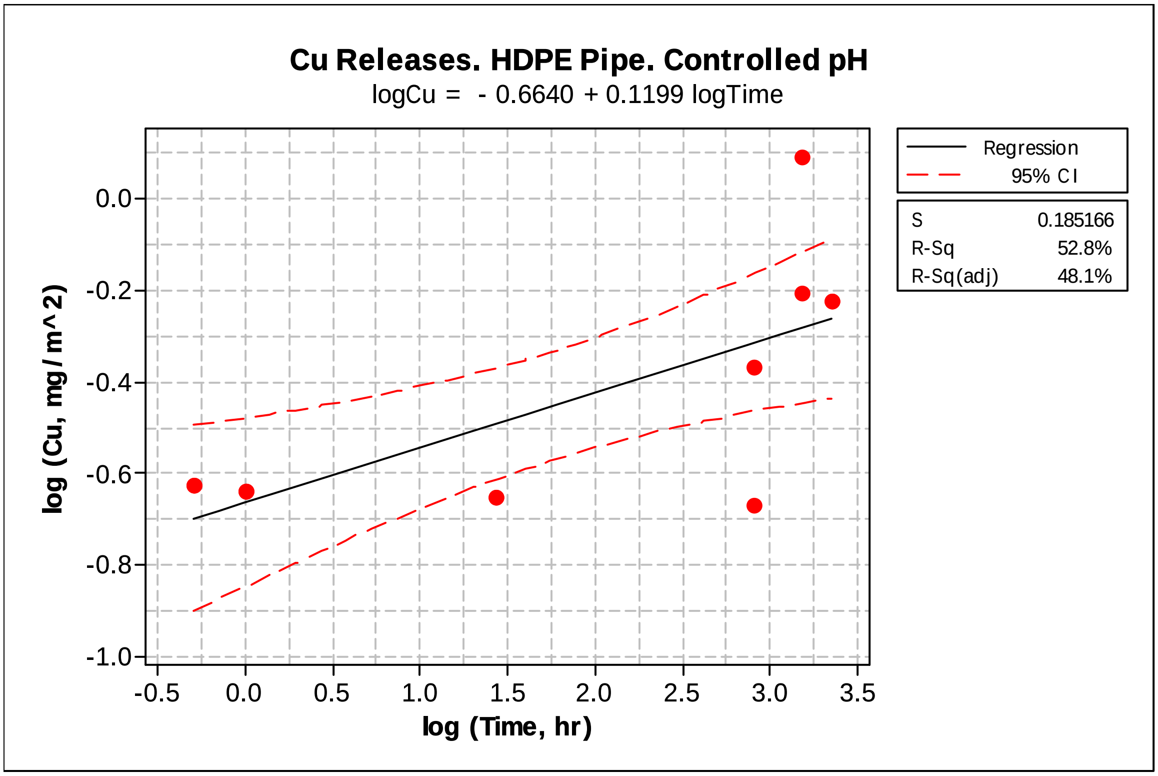


Figure A.7.11. Linear regression for Cu releases. HDPE pipe. Controlled pH.

```
The regression equation is
logCu = - 0.664 + 0.120 logTime


Predictor      Coef  SE Coef      T      P
Constant   -0.66404  0.08277  -8.02  0.000
logTime     0.11990  0.03586   3.34  0.007


S = 0.185166   R-Sq = 52.8%   R-Sq(adj) = 48.1%

PRESS = 0.466925   R-Sq(pred) = 35.71%


Analysis of Variance

Source          DF       SS       MS      F      P
Regression       1  0.38339  0.38339  11.18  0.007
Residual Error  10  0.34287  0.03429
Total           11  0.72626

Durbin-Watson statistic = 2.30492
```

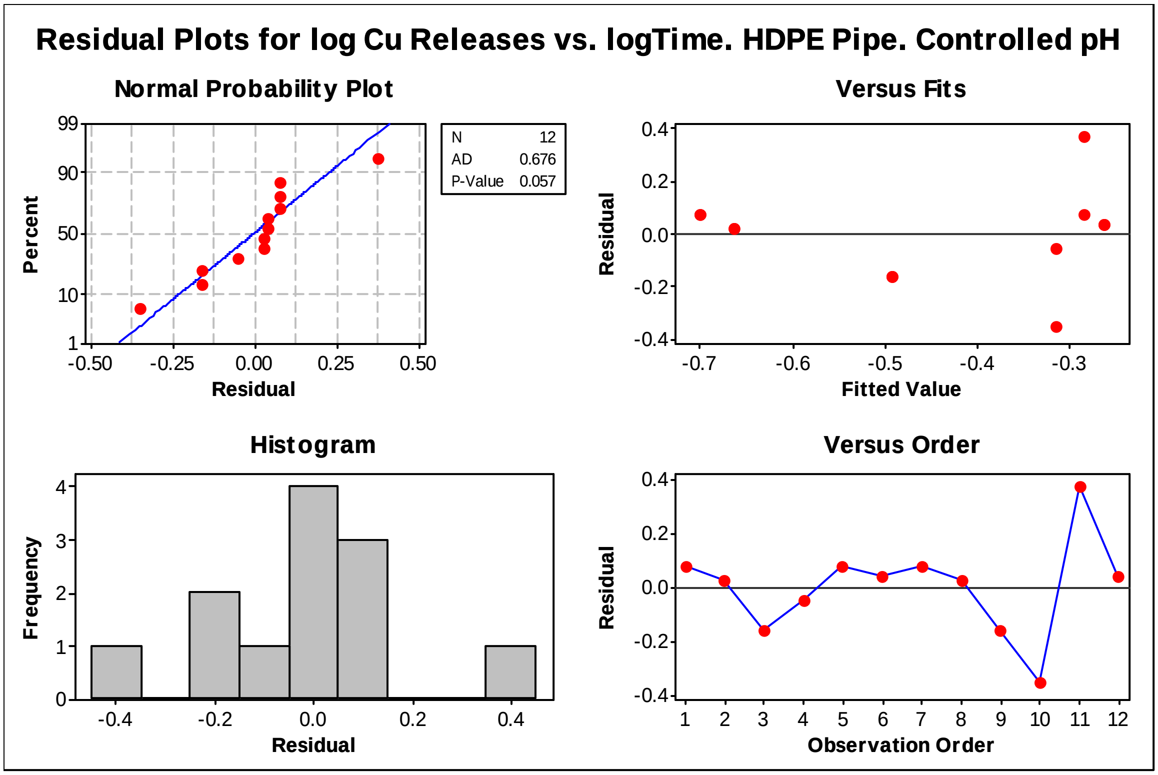


Figure A.7.12. Residual plots for Cu releases from HDPE pipe under controlled pH conditions.

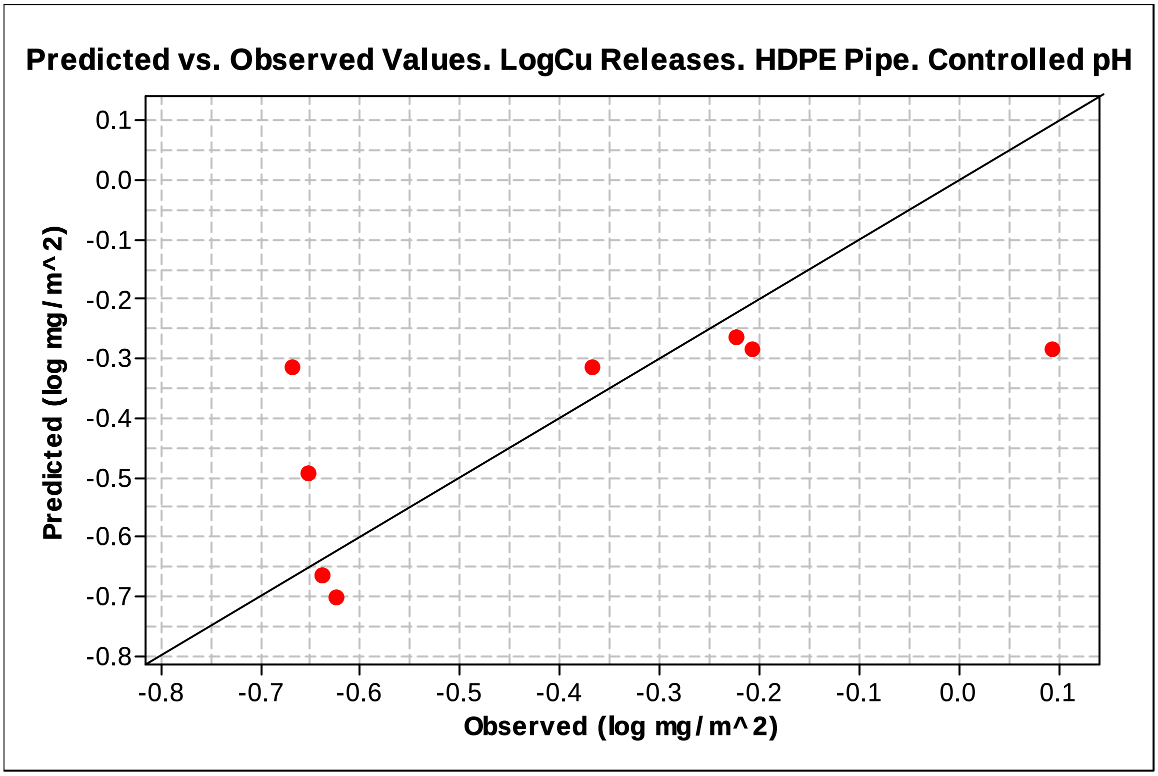


Figure A.7.13. Predicted vs. observed values for Cu releases. HDPE pipe. Controlled pH.

Zn Releases, HDPE Pipe, Controlled pH

Factorial Analysis:

```
Analysis of Variance for Y, using Adjusted SS for Tests

Source  DF  Seq SS  Adj SS  Adj MS      F      P
pH       1  1.5593  1.5593  1.5593  45.33  0.000
Time     1  0.8823  0.8823  0.8823  25.65  0.001
Error    9  0.3096  0.3096  0.0344
Total   11  2.7512

S = 0.185477   R-Sq = 88.75%   R-Sq(adj) = 86.25%


Term          Coef  SE Coef      T      P
Constant   0.30816  0.05354   5.76  0.000
pH         0.36048  0.05354   6.73  0.000
Time      -0.27115  0.05354  -5.06  0.001
```

Regression Analysis:

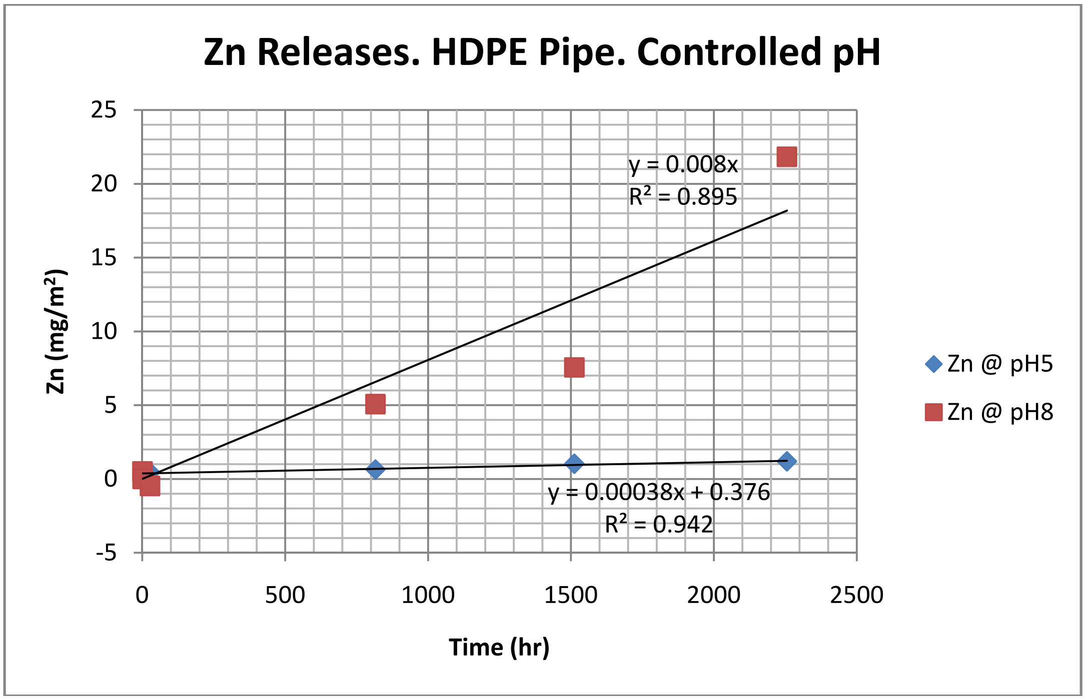


Figure A.7.14. Linear regression for Zn releases. HDPE pipe. Controlled pH.

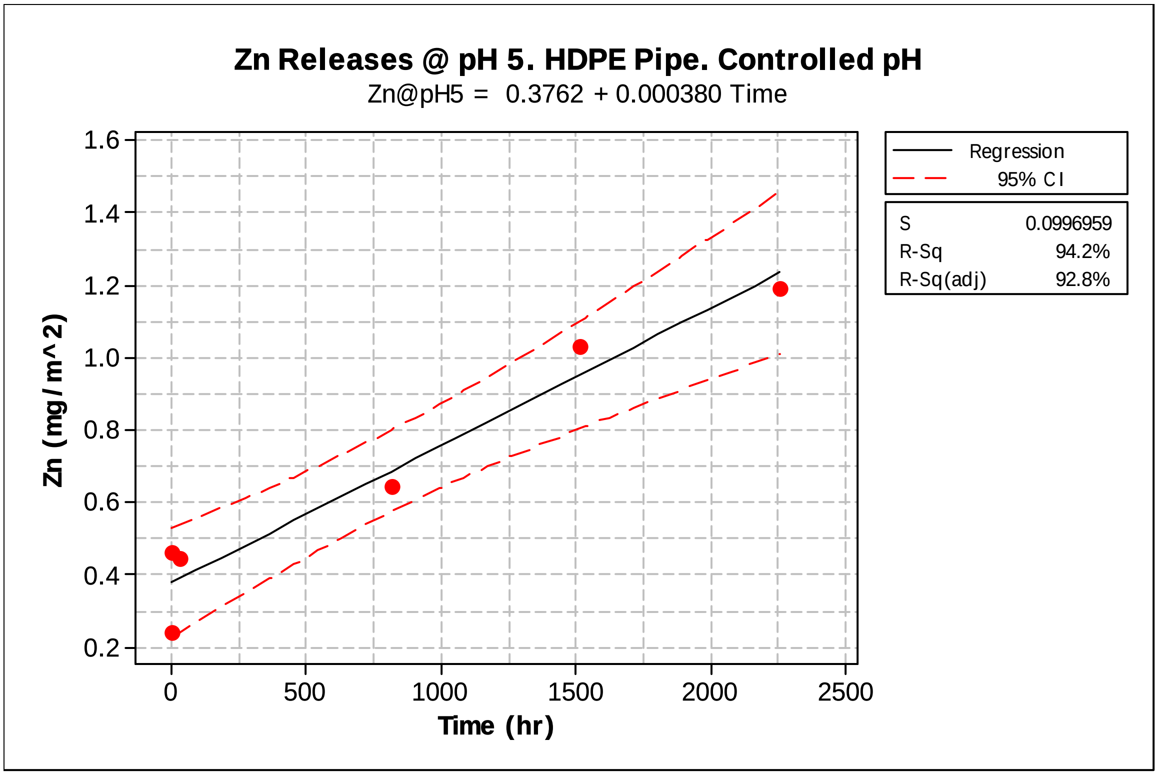


Figure A.7.15. Linear regression for Zn releases. HDPE pipe. Controlled pH 5.

```
The regression equation is
Zn@pH5 = 0.376 + 0.000380 Time


Predictor        Coef      SE Coef     T      P
Constant      0.37619      0.05443  6.91  0.002
Time       0.00038042   0.00004702  8.09  0.001


S = 0.0996959   R-Sq = 94.2%   R-Sq(adj) = 92.8%

PRESS = 0.0895606   R-Sq(pred) = 87.03%


Analysis of Variance

Source          DF       SS       MS      F      P
Regression       1  0.65070  0.65070  65.47  0.001
Residual Error   4  0.03976  0.00994
Total            5  0.69046

Durbin-Watson statistic = 2.28411
```

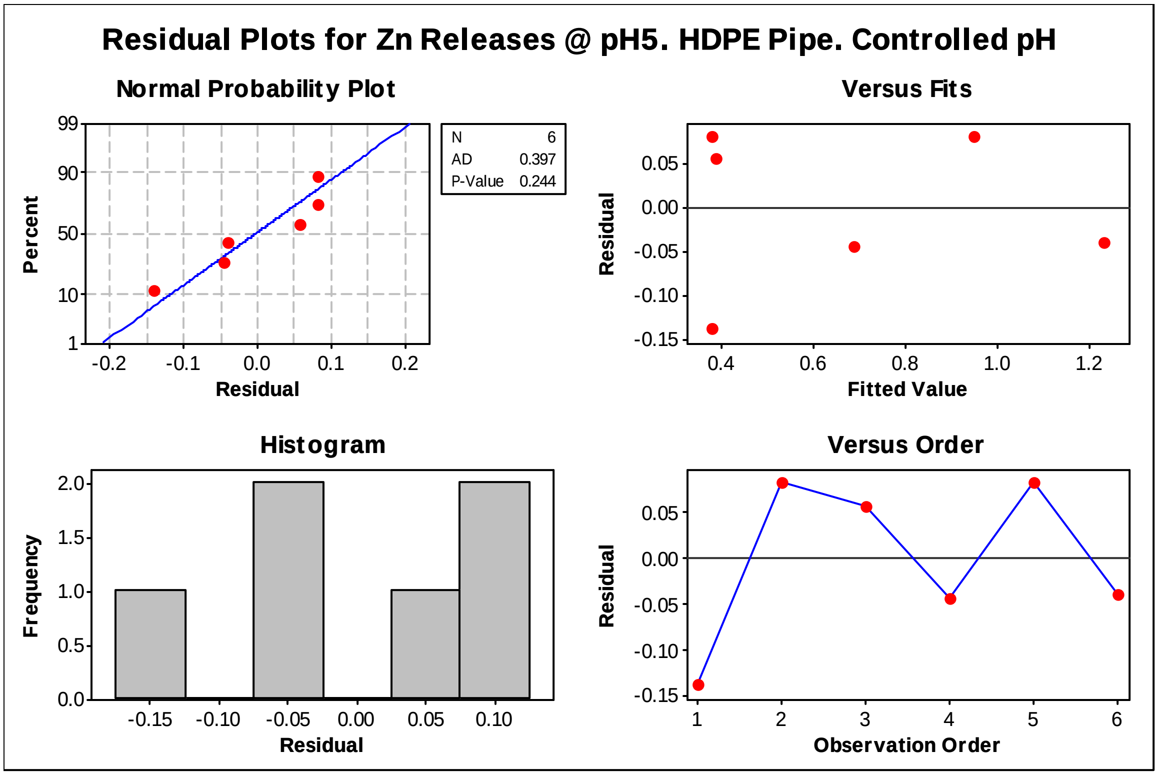


Figure A.7.16. Residual plots for Zn releases from HDPE pipe under controlled pH5 conditions.

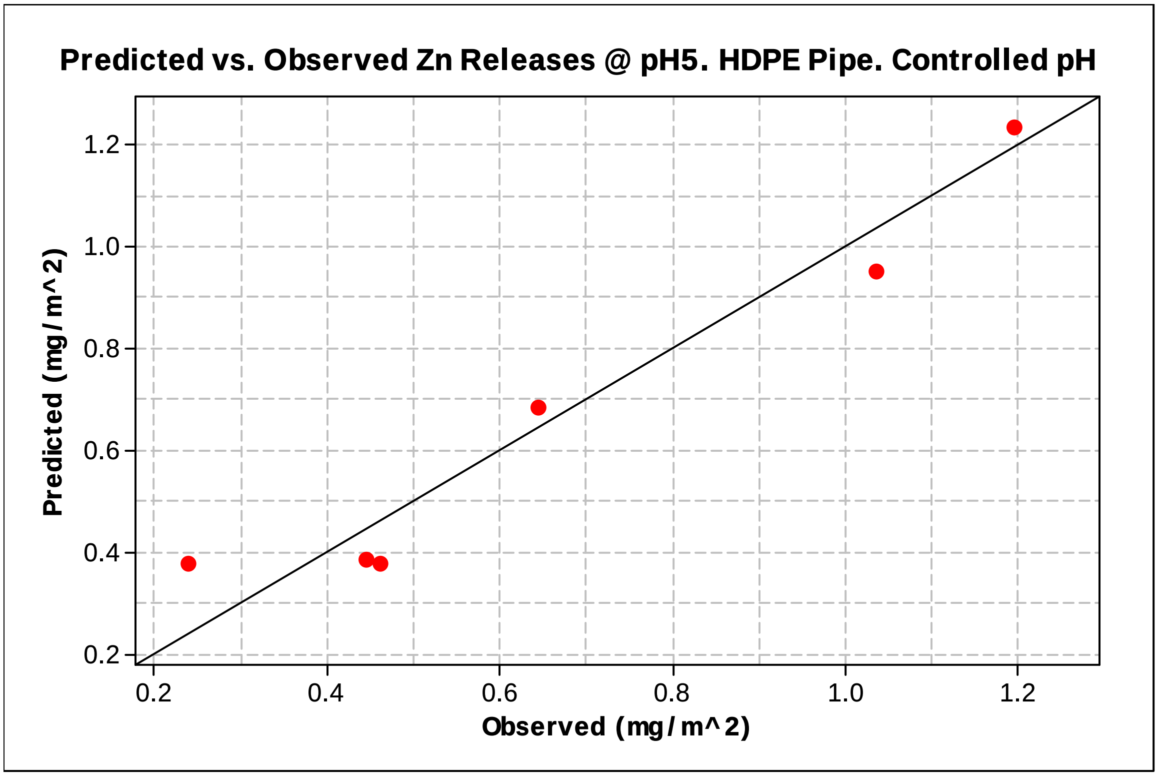


Figure A.7.17. Predicted vs. observed values for Zn releases. HDPE pipe. Controlled pH5.

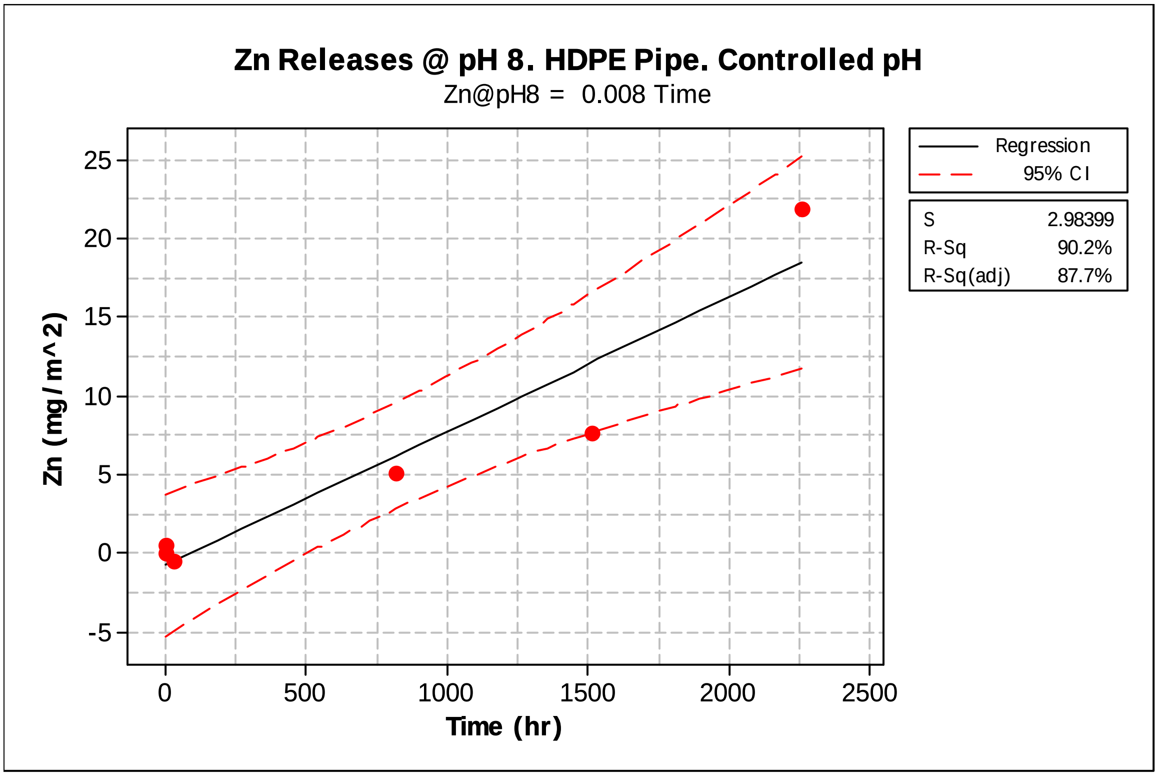


Figure A.7.18. Linear regression for Zn releases. HDPE pipe. Controlled pH 8.

```
The regression equation is
Zn@pH8 = 0.00806 Time


Predictor         Coef     SE Coef      T      P
Noconstant
Time         0.0080577  0.0009689  8.32  0.000


S = 2.74768

PRESS = 144.198


Analysis of Variance

Source          DF      SS      MS      F      P
Regression       1  522.15  522.15  69.16  0.000
Residual Error   5   37.75    7.55
Total            6  559.90

Durbin-Watson statistic = 2.11092
```

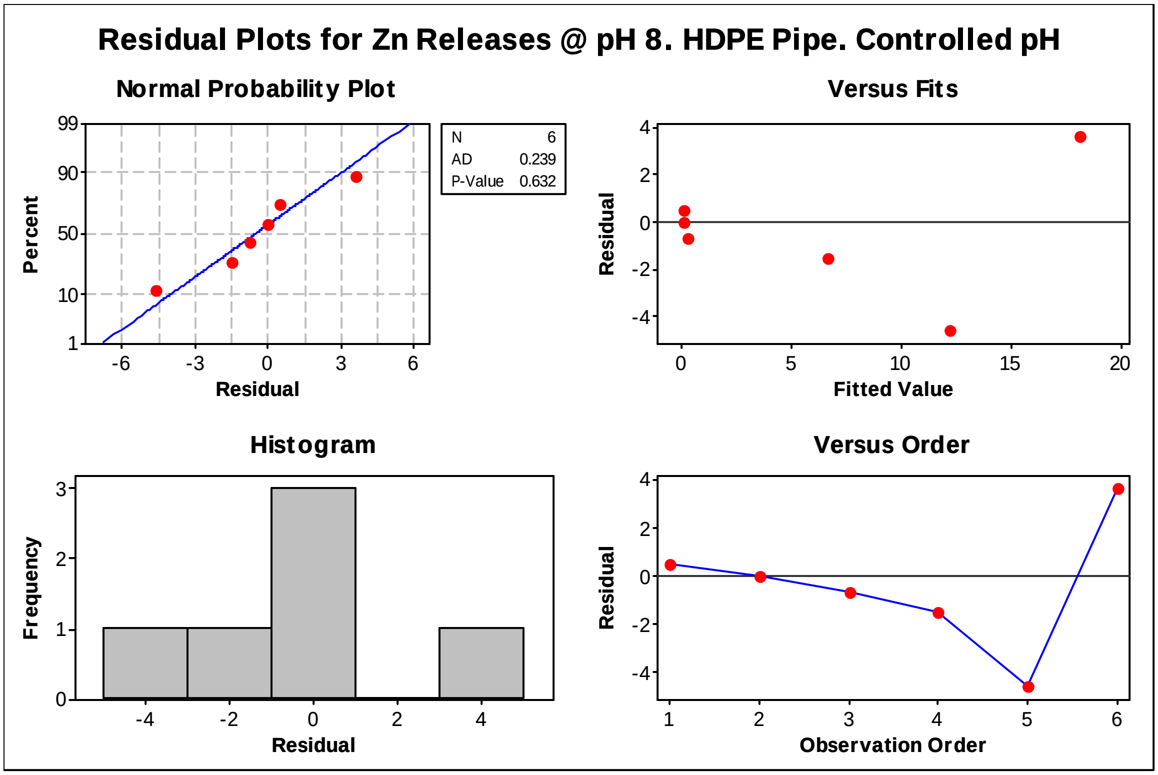


Figure A.7.19. Residual plots for Zn releases from HDPE pipe under controlled pH8 conditions.

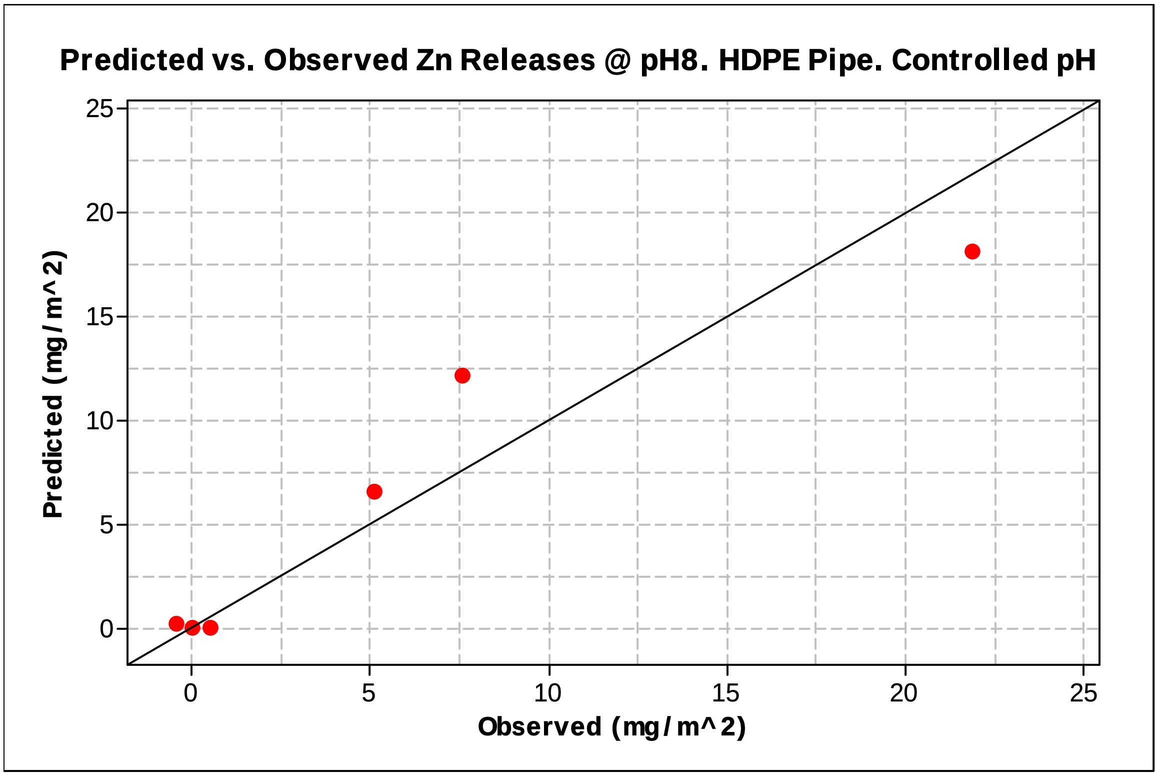


Figure A.7.20. Predicted vs. observed values for Zn releases. HDPE pipe. Controlled pH8.

HDPE Pipe. Natural pH

Zn Releases, HDPE Pipe, Natural pH

Factorial Analysis:

```
Analysis of Variance for Y, using Adjusted SS for Tests

Source      DF    Seq SS    Adj SS    Adj MS         F      P
Cond         1   0.12743   0.12743   0.12743  11229.64  0.000
Time         1   0.11524   0.11524   0.11524  10155.37  0.000
Cond*Time    1   0.12743   0.12743   0.12743  11229.64  0.000
Error        8   0.00009   0.00009   0.00001
Total       11   0.37020

S = 0.00336869   R-Sq = 99.98%   R-Sq(adj) = 99.97%

Term             Coef   SE Coef        T      P
Constant     0.097998  0.000972   100.77  0.000
Cond         0.103051  0.000972   105.97  0.000
Time        -0.097998  0.000972  -100.77  0.000
Cond*Time    0.103051  0.000972   105.97  0.000
```

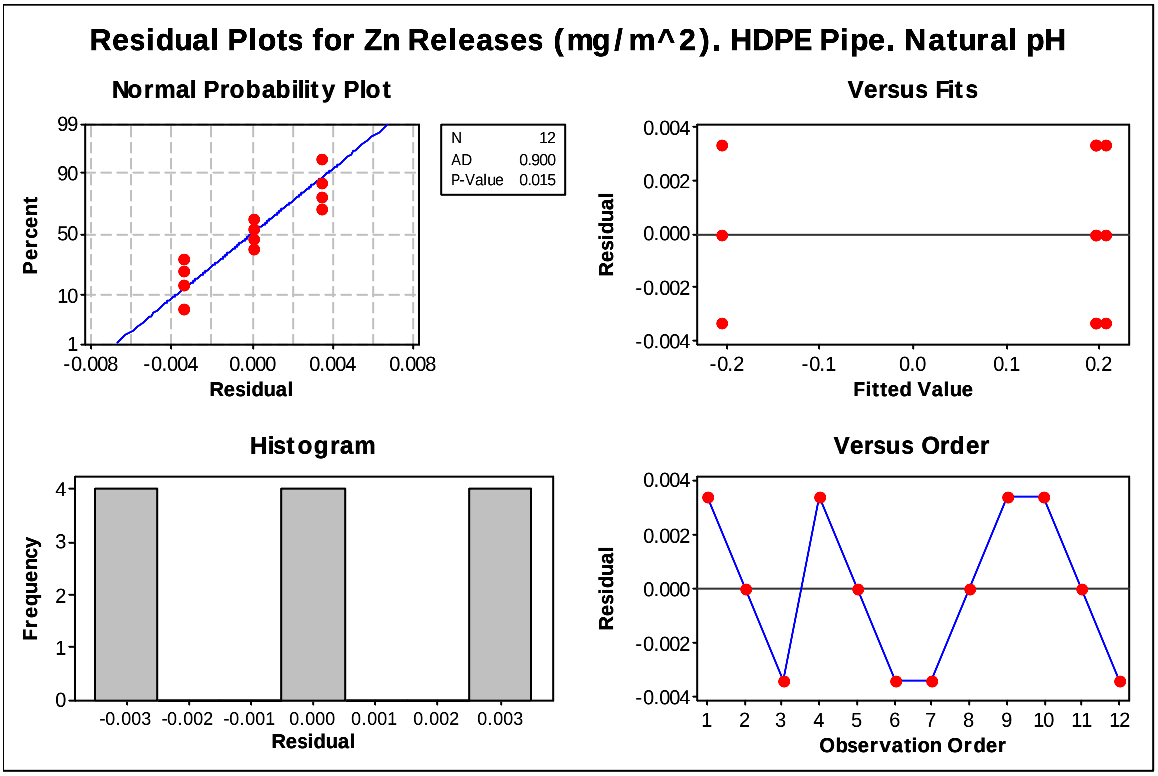


Figure A.7.21. Residual plots for Zn releases from HDPE pipe under natural pH conditions.

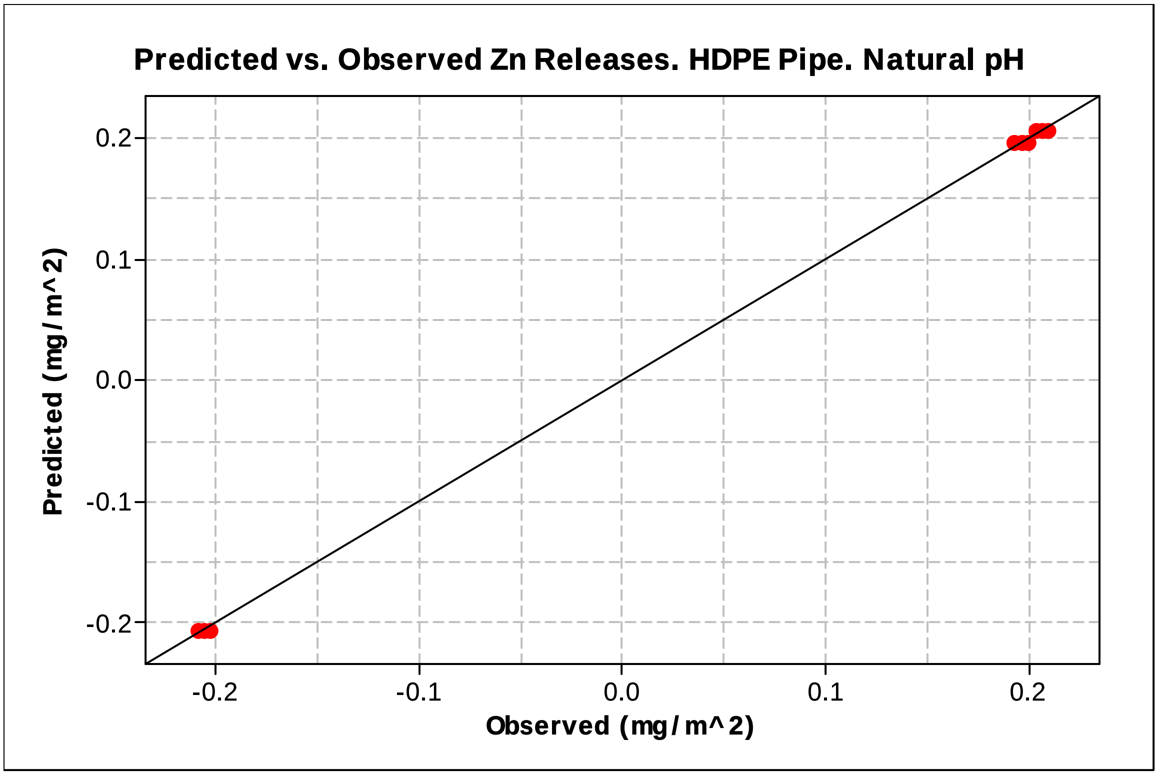


Figure A.7.22. Predicted vs. observed values for Zn releases. HDPE pipe. Natural pH conditions.

Steel Pipe. Controlled pH

Zn Releases, Steel Pipe, Controlled pH

Factorial Analysis:

```
Analysis of Variance for Y, using Adjusted SS for Tests

Source  DF   Seq SS   Adj SS   Adj MS     F      P
Time     1  2750495  2750495  2750495  4.00  0.073
Error   10  6871777  6871777   687178
Total   11  9622271


S = 828.962   R-Sq = 28.58%   R-Sq(adj) = 21.44%


Term         Coef  SE Coef      T      P
Constant    608.8    239.3   2.54  0.029
Time
S.         -478.8    239.3  -2.00  0.073
```

Regression Analysis:

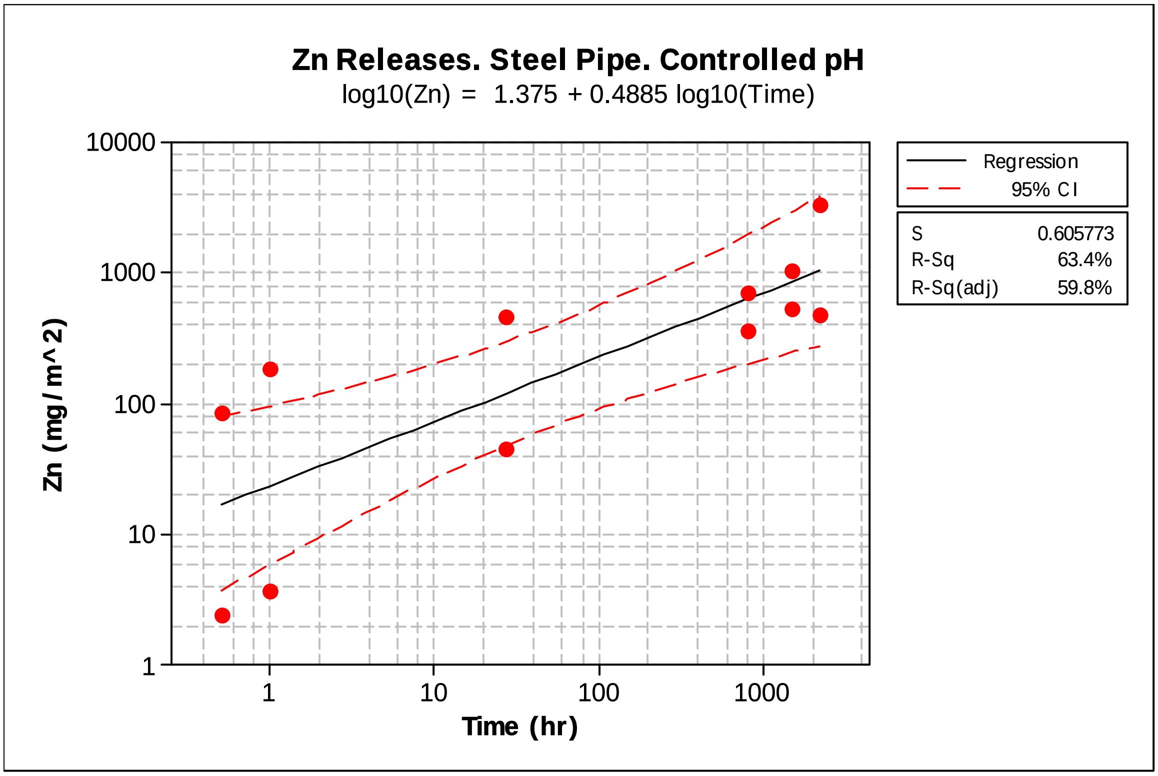


Figure A.7.23. Linear regression for Zn releases. Steel pipe. Controlled pH.

```
The regression equation is
logZn = 1.38 + 0.488 logTime


Predictor     Coef  SE Coef     T      P
Constant    1.3750   0.2708  5.08  0.000
logTime     0.4885   0.1173  4.16  0.002


S = 0.605773   R-Sq = 63.4%   R-Sq(adj) = 59.8%

PRESS = 5.71339   R-Sq(pred) = 43.05%


Analysis of Variance

Source          DF       SS      MS      F      P
Regression       1   6.3627  6.3627  17.34  0.002
Residual Error  10   3.6696  0.3670
Total           11  10.0323

Durbin-Watson statistic = 0.444561
```

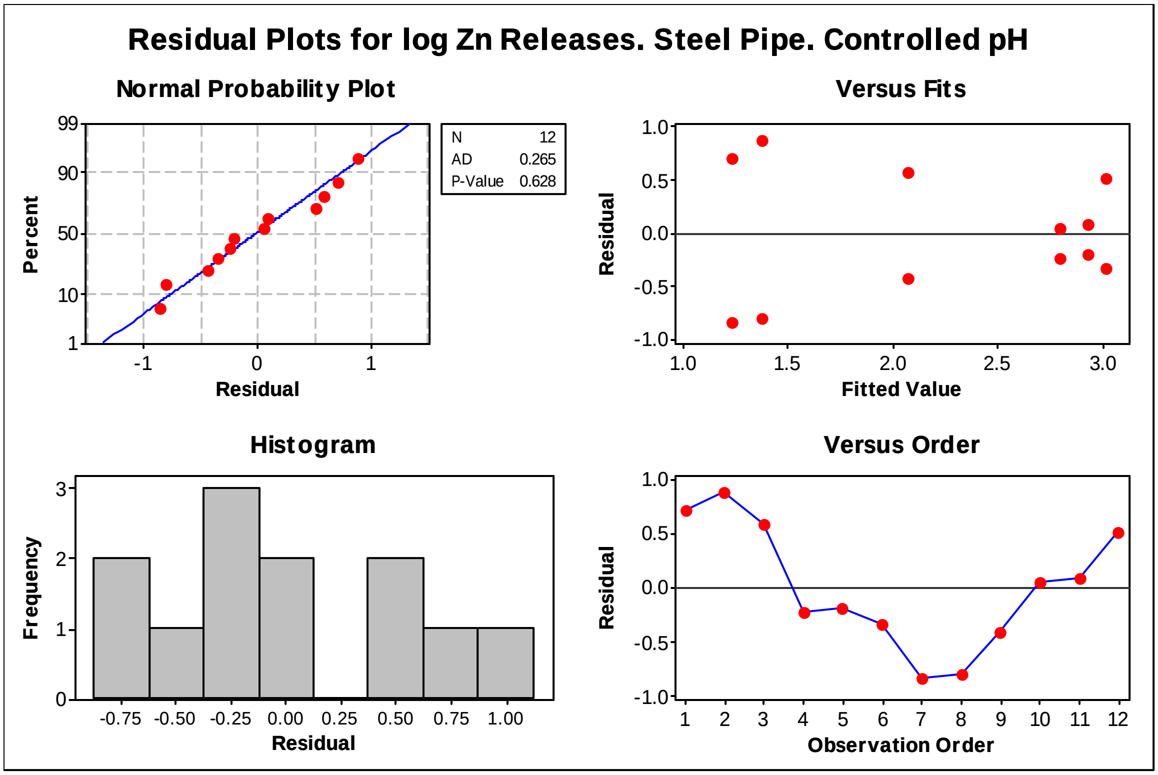


Figure A.7.24. Residual plots for Zn releases from steel pipe under controlled pH conditions.

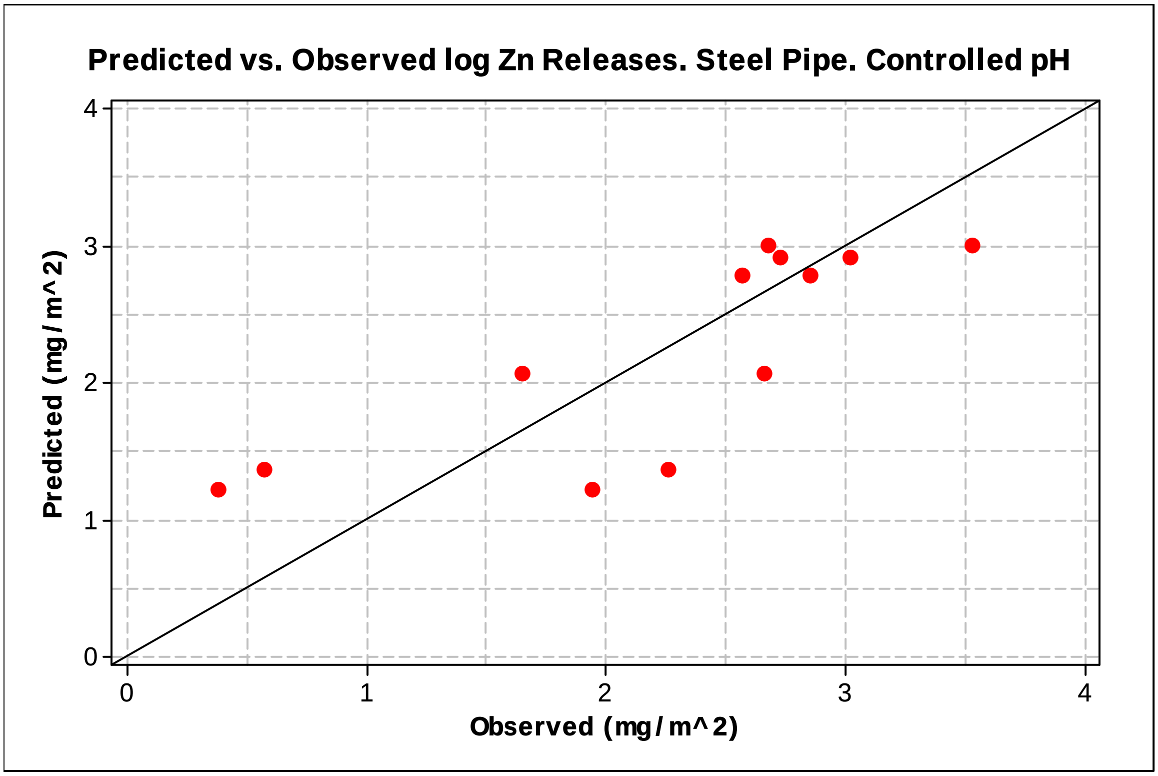


Figure A.7.25. Predicted vs. observed values for Zn releases. Steel pipe. Controlled pH.

Pb Releases, Steel Pipe, Controlled pH

Factorial Analysis:

```
Analysis of Variance for Y, using Adjusted SS for Tests

Source  DF    Seq SS  Adj SS  Adj MS     F      P
Time     1    584.41  584.41  584.41  9.25  0.012
Error   10    631.57  631.57   63.16
Total   11  1215.98

S = 7.94711   R-Sq = 48.06%   R-Sq(adj) = 42.87%

Term         Coef  SE Coef      T      P
Constant    7.095    2.294   3.09  0.011
Time       -6.979    2.294  -3.04  0.012
```

Regression Analysis:

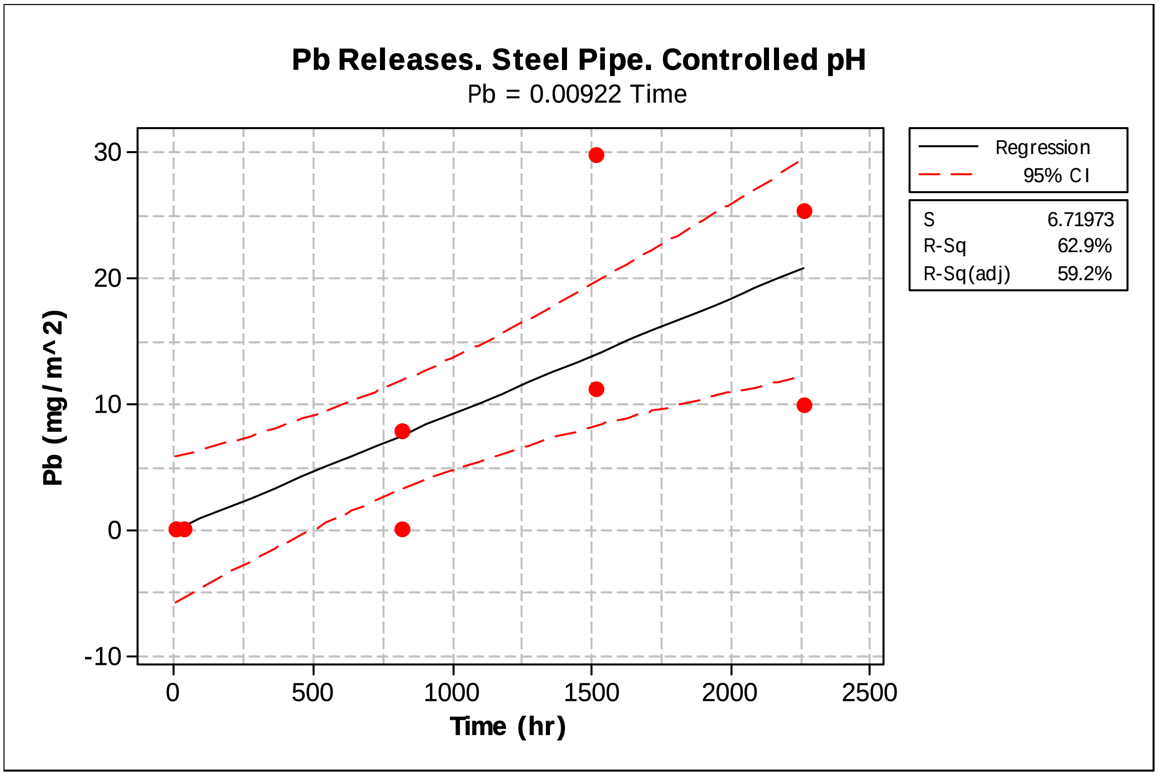


Figure A.7.26. Linear regression for Pb releases. Steel pipe. Controlled pH.

```
The regression equation is
Pb = 0.00922 Time


Predictor        Coef    SE Coef      T      P
Noconstant
Time         0.009224   0.001598   5.77   0.000


S = 6.40701

PRESS = 706.498


Analysis of Variance

Source          DF      SS      MS      F      P
Regression       1  1368.5  1368.5  33.34  0.000
Residual Error  11   451.5    41.0
Total           12  1820.1

Durbin-Watson statistic = 2.03131
```

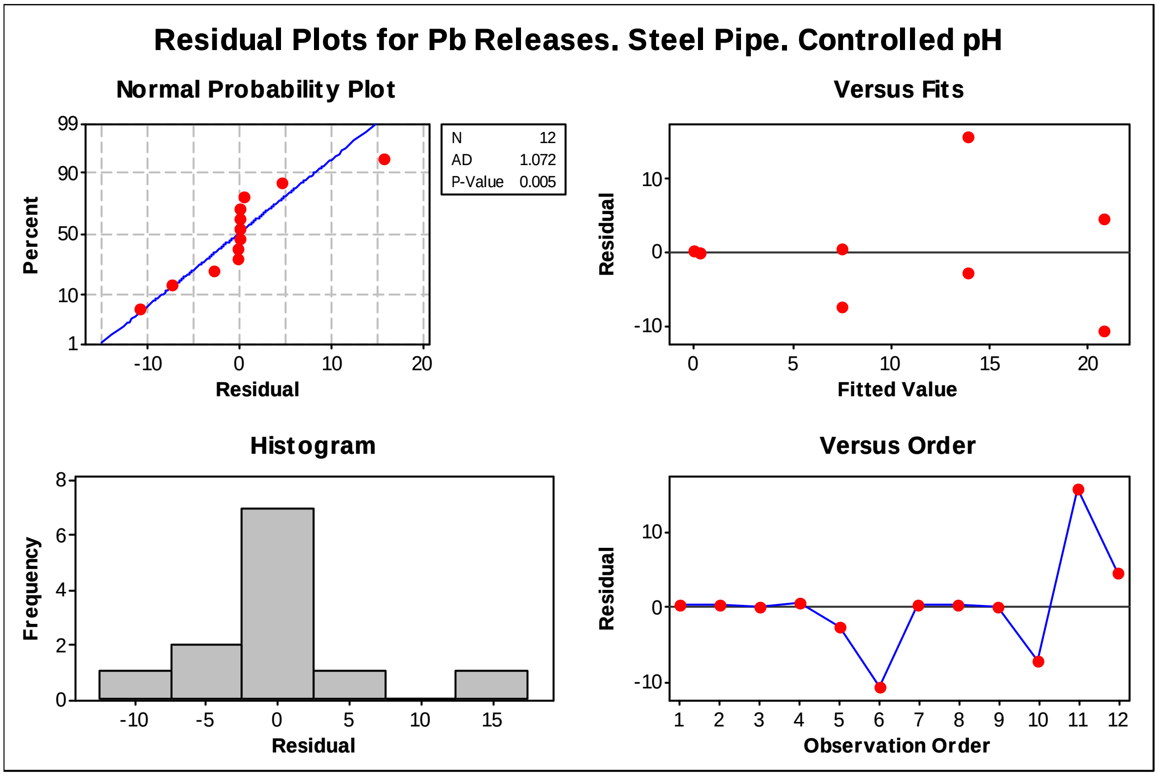


Figure A.7.27. Residual plots for Pb releases from steel pipe under controlled pH conditions.

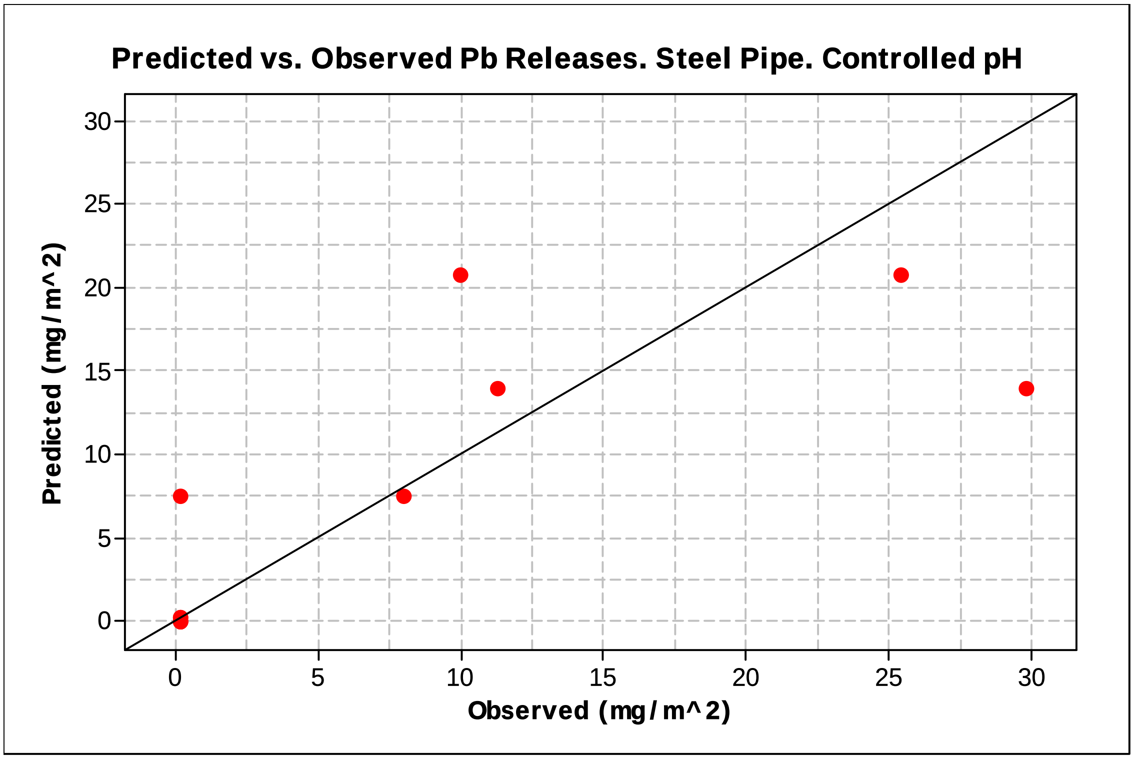


Figure A.7.28. Predicted vs. observed values for Pb releases. Steel pipe. Controlled pH.

Cu Releases, Steel Pipe, Controlled pH

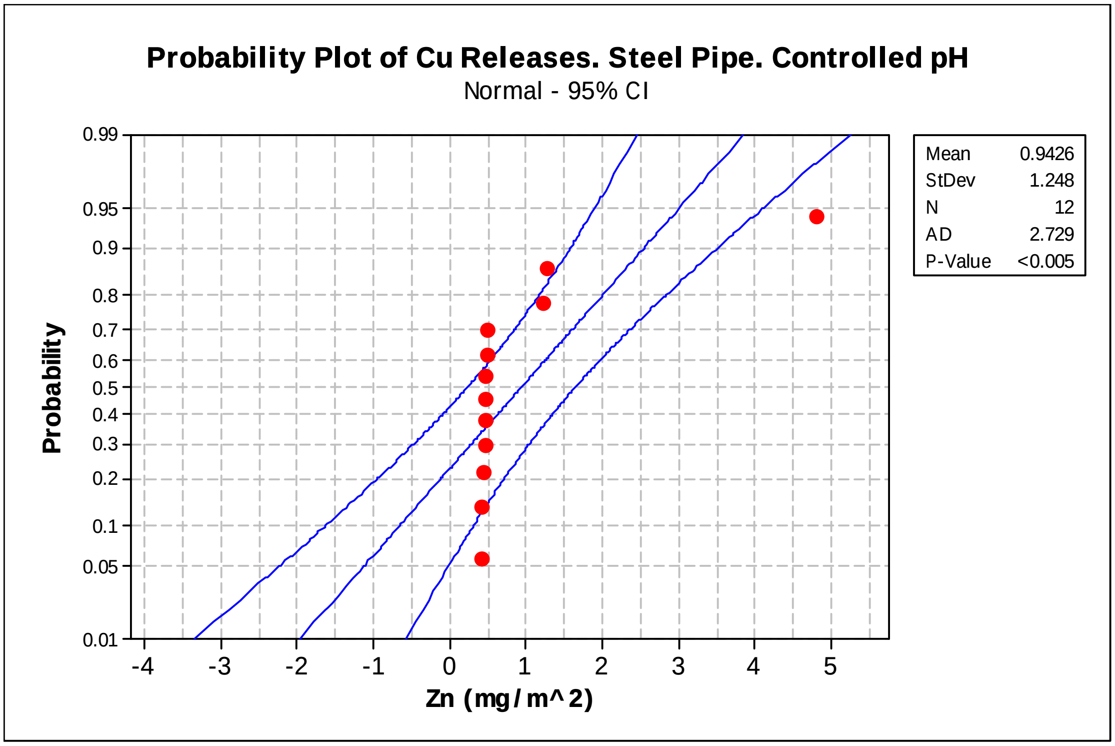


Figure A.7.29. Probability for Cu releases. Steel pipe. Controlled pH.

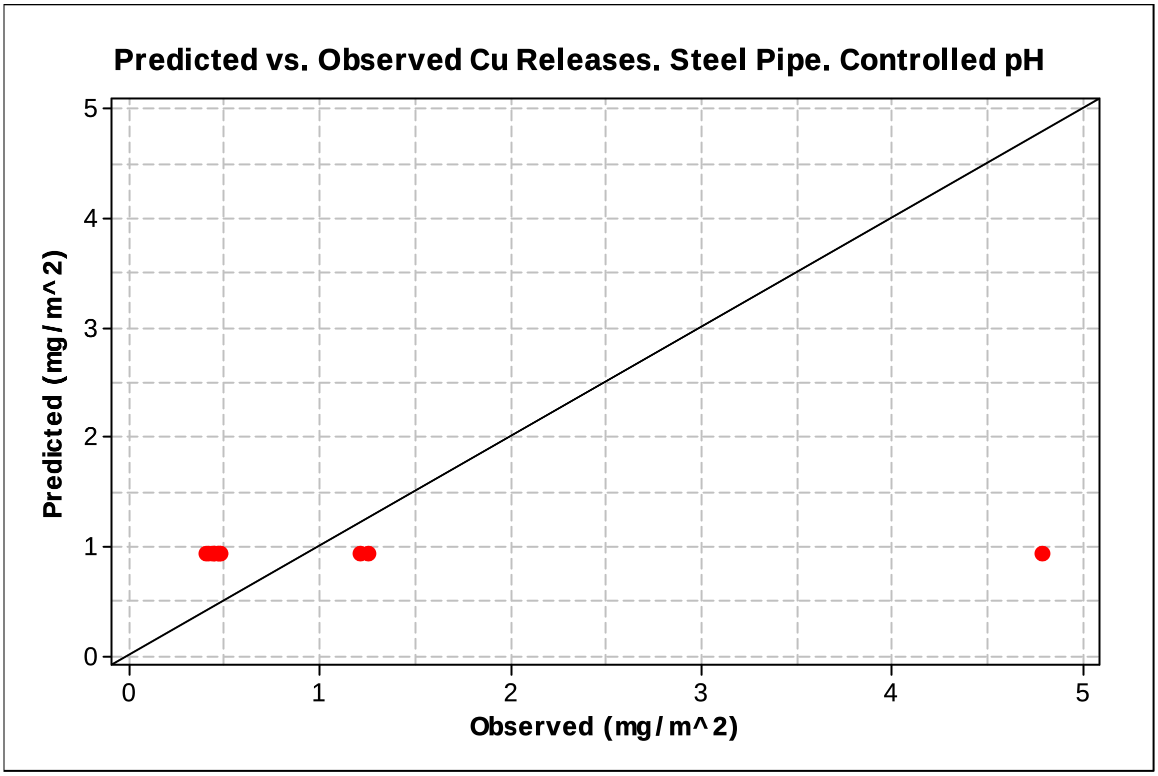


Figure A.7.30. Predicted vs. observed values for Cu releases. Steel pipe. Controlled pH.

Steel Pipe. Natural pH.

Pb Releases, Steel Pipe, Natural pH

Factorial Analysis:

```
Analysis of Variance for Y, using Adjusted SS for Tests

Source      DF    Seq SS    Adj SS    Adj MS     F       P
Cond         1  0.00030   0.00030   0.00030   0.01  0.922
Time         1  0.00007   0.00007   0.00007   0.00  0.962
Cond*Time    1  0.28819   0.28819   0.28819   9.92  0.014
Error        8  0.23246   0.23246   0.02906
Total       11  0.52101

S = 0.170462   R-Sq = 55.38%   R-Sq(adj) = 38.65%

Term            Coef  SE Coef       T      P
Constant     0.25697  0.04921    5.22  0.001
Cond        -0.00498  0.04921   -0.10  0.922
Time        -0.00242  0.04921   -0.05  0.962
Cond*Time    0.15497  0.04921    3.15  0.014
```

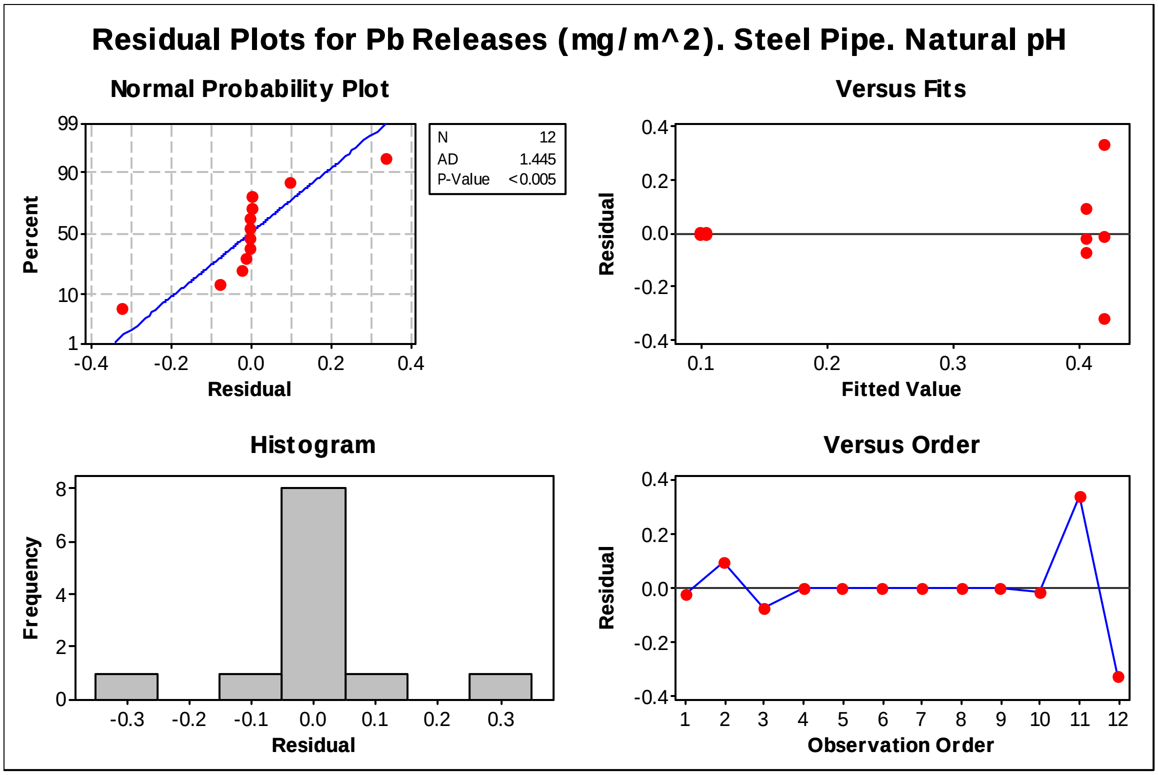


Figure A.7.31. Residual plots for Pb releases from steel pipe under natural pH conditions.

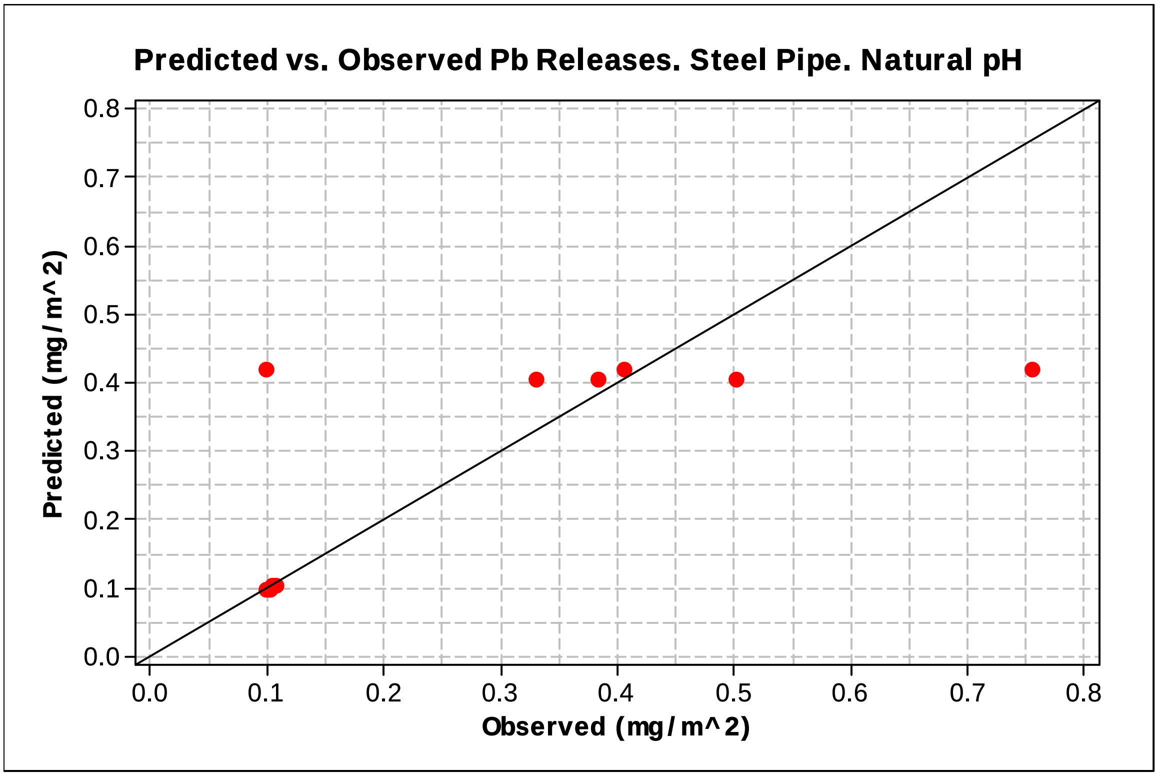


Figure A.7.32. Predicted vs. observed values for Pb releases. Steel pipe. Natural pH.

Zn Releases, Steel Pipe, Natural pH

Factorial Analysis:

```
Analysis of Variance for Y, using Adjusted SS for Tests

Source   DF     Seq SS    Adj SS    Adj MS      F      P
Time      1  12308694  12308694  12308694  18.42  0.002
Error    10   6682981   6682981    668298
Total    11  18991675

S = 817.495   R-Sq = 64.81%   R-Sq(adj) = 61.29%

Term          Coef  SE Coef      T      P
Constant    1220.9    236.0   5.17  0.000
Time       -1012.8    236.0  -4.29  0.002
```

Regression Analysis:

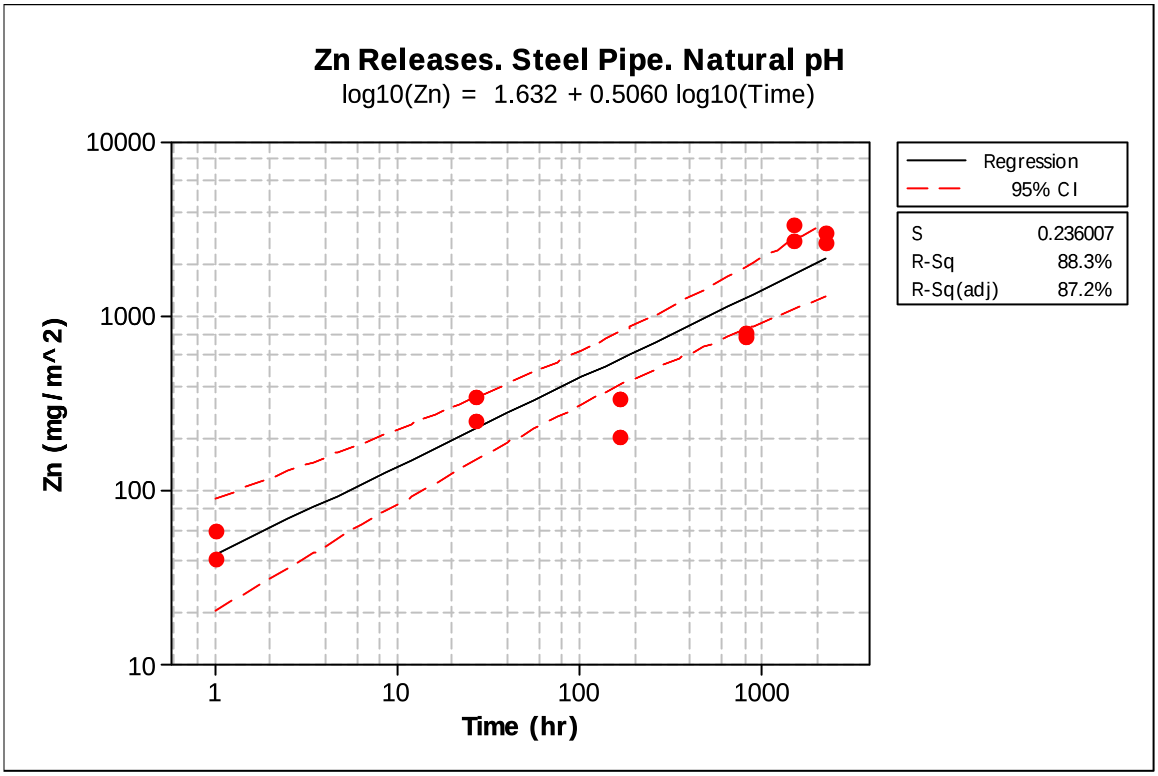


Figure A.7.33. Linear regression for Zn releases. Steel pipe. Natural pH.

```
The regression equation is
logZn. = 1.63 + 0.506 logTime


Predictor      Coef  SE Coef      T      P
Constant     1.6318   0.1442  11.32  0.000
logTime     0.50601  0.05819   8.70  0.000


S = 0.236007   R-Sq = 88.3%   R-Sq(adj) = 87.2%

PRESS = 0.732117   R-Sq(pred) = 84.65%


Analysis of Variance

Source          DF      SS      MS      F      P
Regression       1  4.2125  4.2125  75.63  0.000
Residual Error  10  0.5570  0.0557
Total           11  4.7695

Durbin-Watson statistic = 1.74648
```

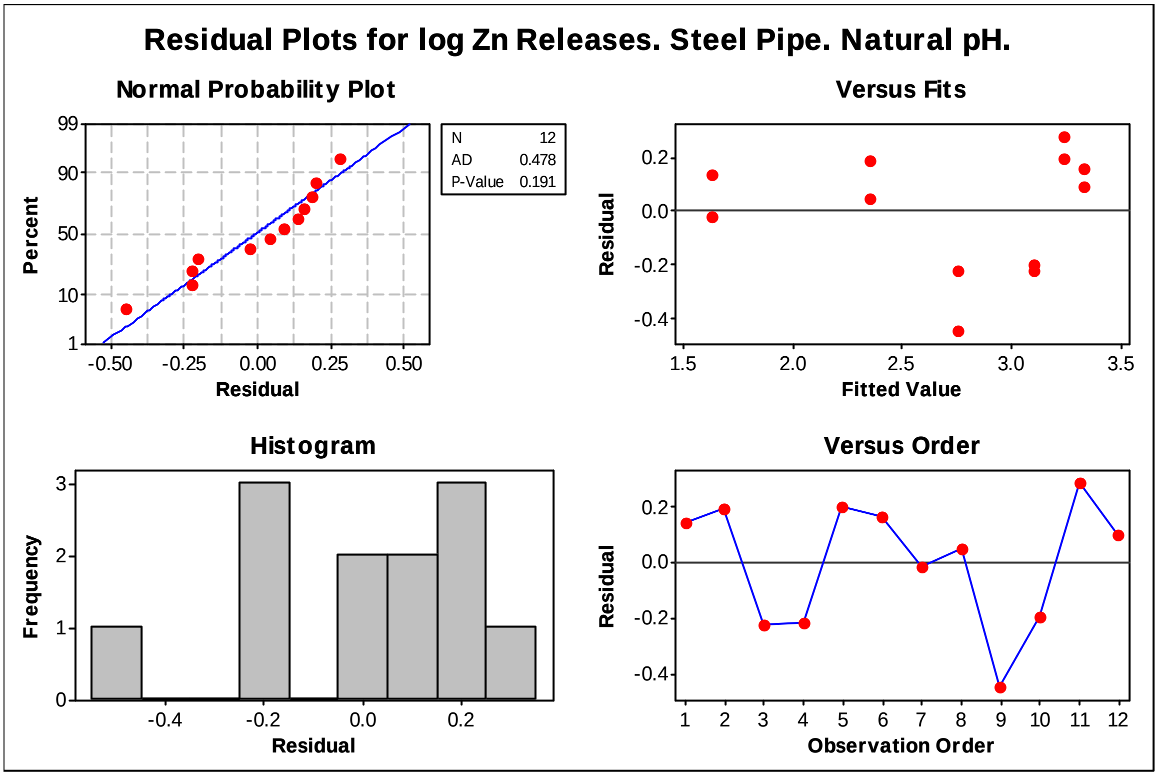


Figure A.7.34. Residual plots for Zn releases from steel pipe under natural pH conditions.

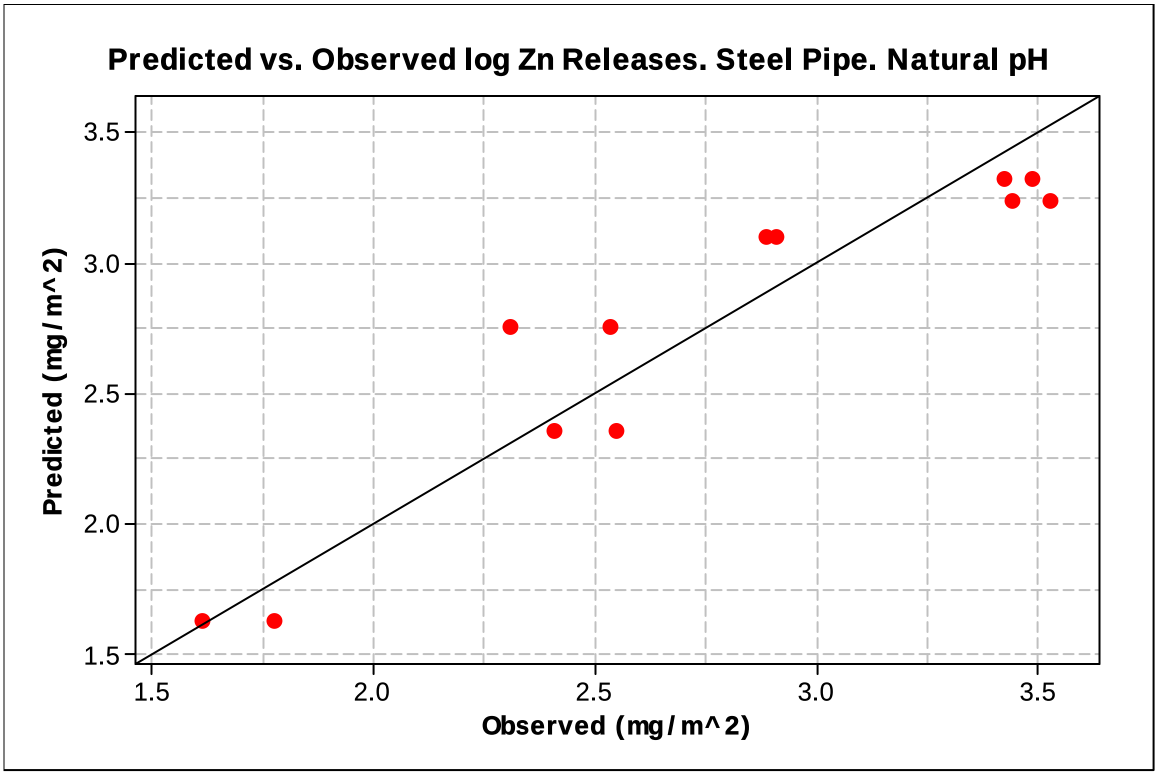


Figure A.7.35. Predicted vs. observed values for Zn releases. Steel pipe. Natural pH.

Vinyl Gutter. Controlled pH

Cu Releases, Vinyl Gutter, Controlled pH

Factorial Analysis:

```
Analysis of Variance for Y, using Adjusted SS for Tests

Source    DF  Seq SS  Adj SS  Adj MS      F      P
pH         1  0.6096  0.6096  0.6096   5.50  0.047
Time       1  2.6538  2.6538  2.6538  23.94  0.001
pH*Time    1  0.6096  0.6096  0.6096   5.50  0.047
Error      8  0.8868  0.8868  0.1108
Total     11  4.7598

S = 0.332939   R-Sq = 81.37%   R-Sq(adj) = 74.38%

Term          Coef  SE Coef      T      P
Constant   1.47201  0.09611  15.32  0.000
pH         0.22539  0.09611   2.35  0.047
Time      -0.47026  0.09611  -4.89  0.001
pH*Time   -0.22539  0.09611  -2.35  0.047
```

Regression Analysis:

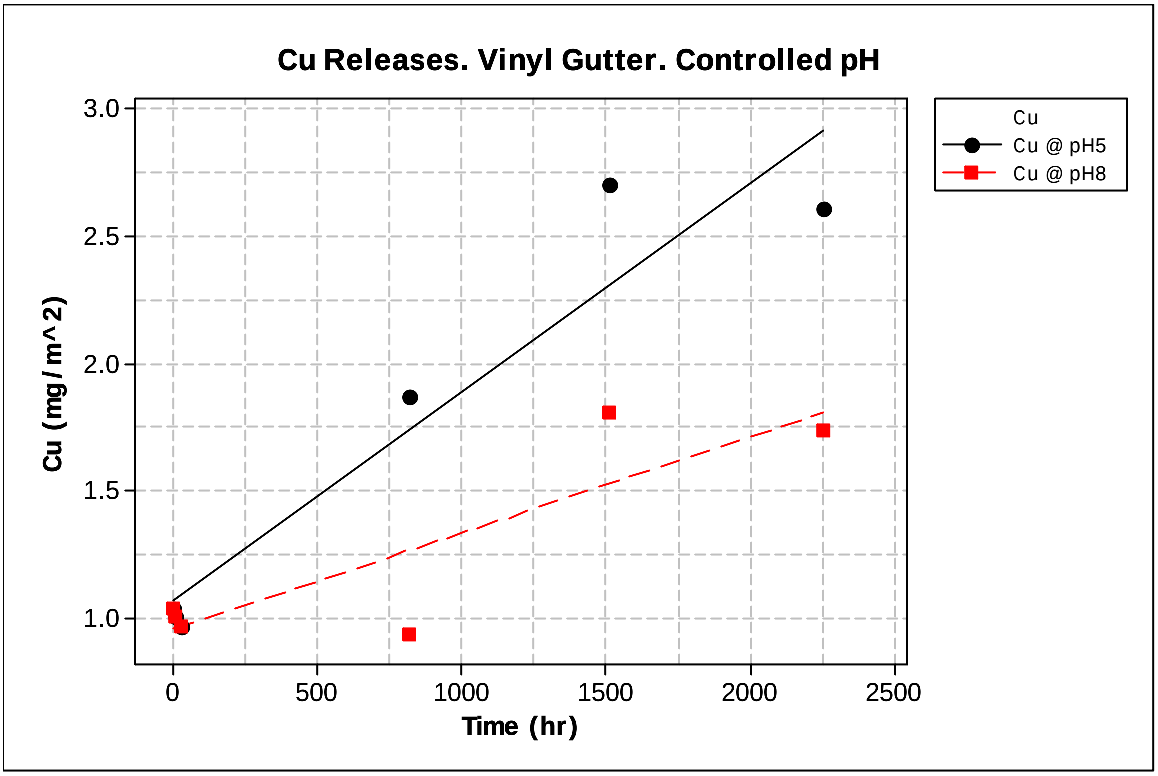


Figure A.7.36. Linear regression for Cu releases. Vinyl gutter. Controlled pH.

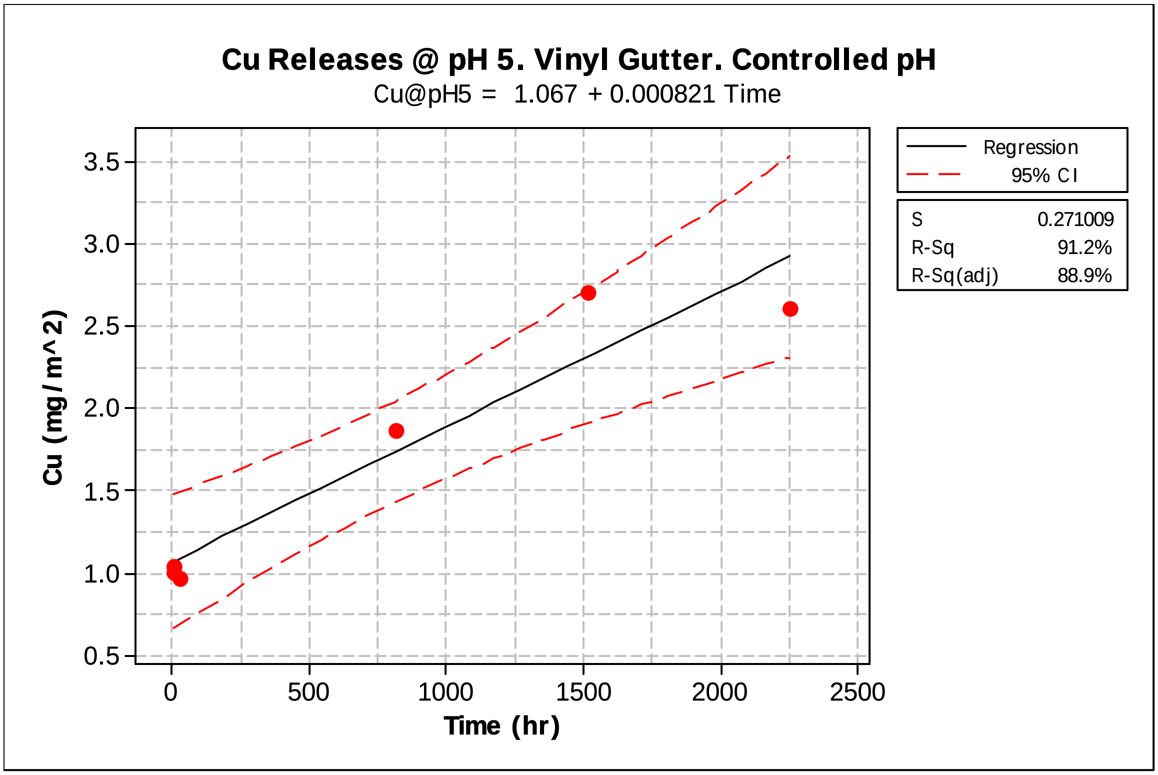


Figure A.7.37. Linear regression for Cu releases. Vinyl gutter. Controlled pH 5.

```
The regression equation is
Cu@pH5 = 1.07 + 0.000821 Time


Predictor        Coef     SE Coef     T      P
Constant       1.0666      0.1480  7.21  0.002
Time        0.0008206   0.0001278  6.42  0.003


S = 0.271009   R-Sq = 91.2%   R-Sq(adj) = 88.9%


Analysis of Variance

Source          DF      SS      MS      F      P
Regression       1  3.0276  3.0276  41.22  0.003
Residual Error   4  0.2938  0.0734
Total            5  3.3214

Durbin-Watson statistic = 2.18974
```

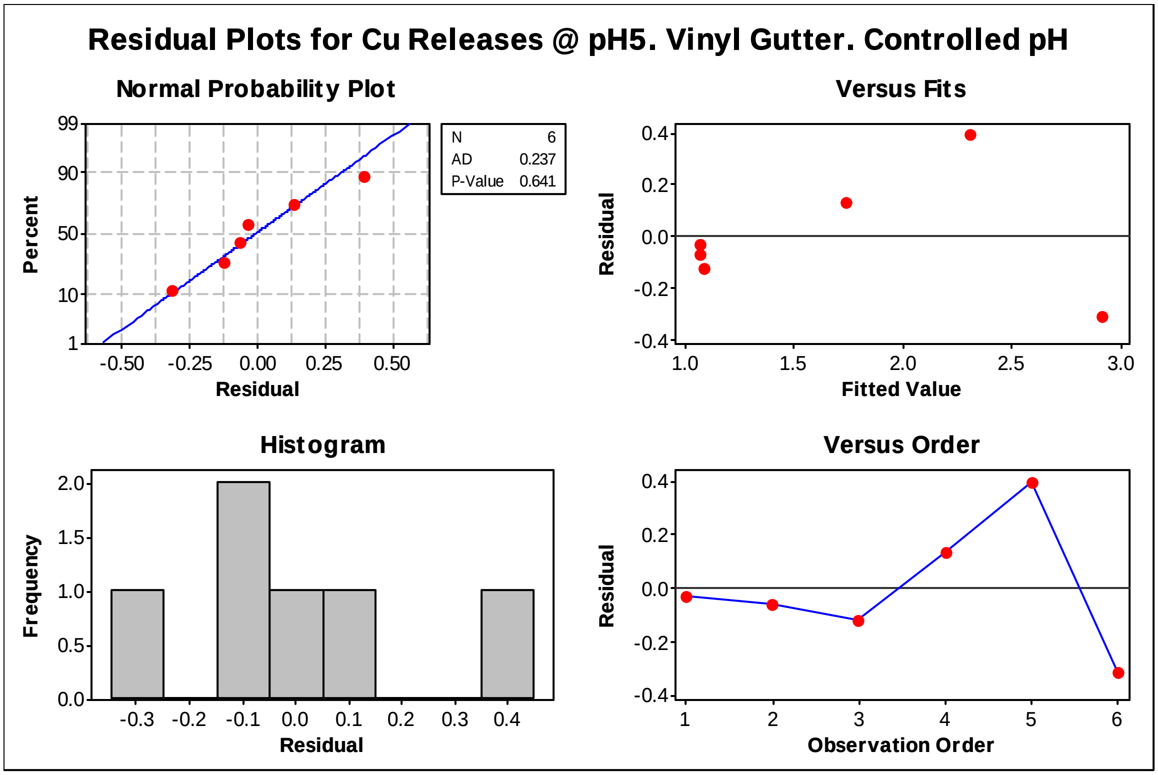


Figure A.7.38. Residual plots for Cu releases from vinyl gutter under controlled pH 5 conditions.

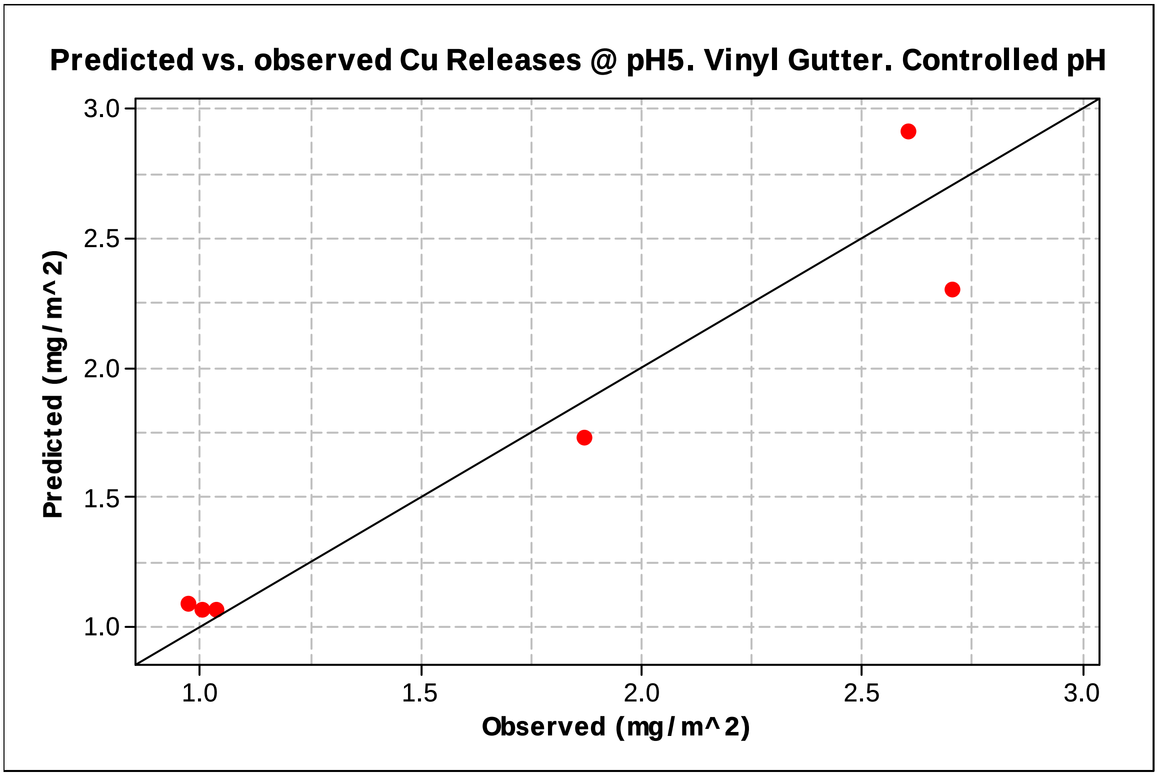


Figure A.7.39. Predicted vs. observed values for Cu releases. Vinyl Gutter. Controlled pH 5.

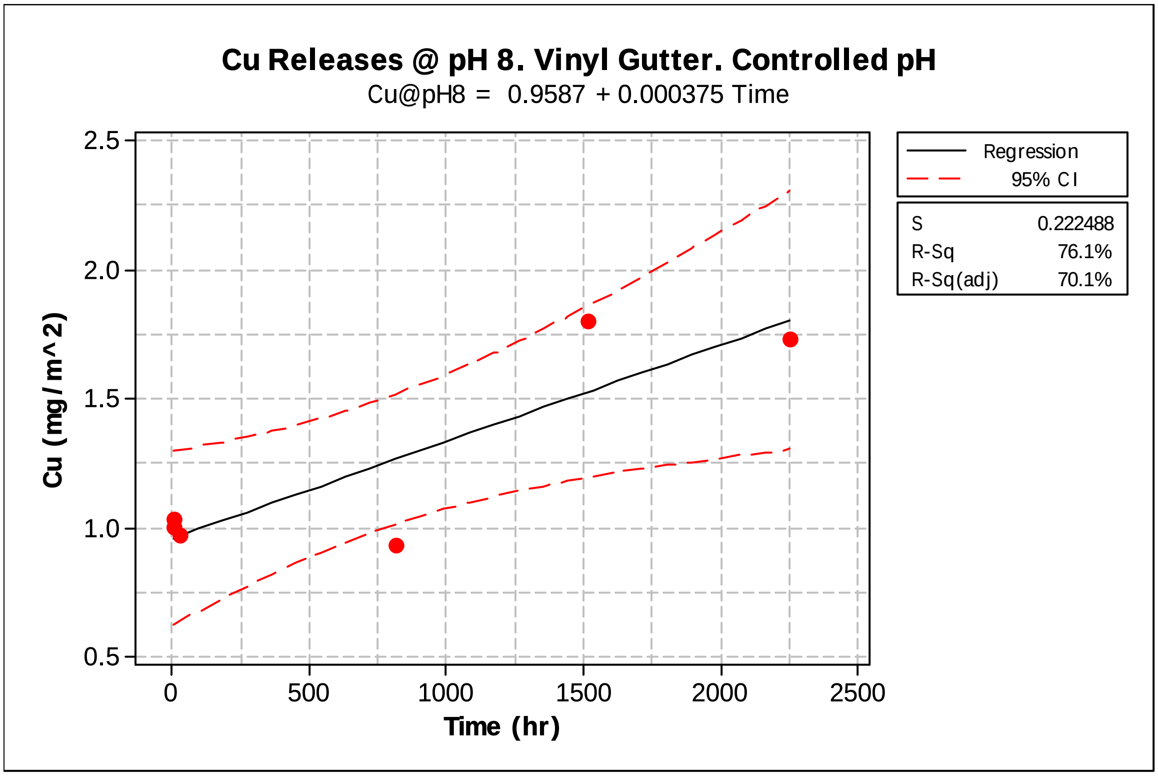


Figure A.7.40. Linear regression for Cu releases. Vinyl gutter. Controlled pH 8.

```
The regression equation is
Cu@pH8 = 0.959 + 0.000375 Time


Predictor        Coef     SE Coef     T      P
Constant       0.9587      0.1215  7.89  0.001
Time        0.0003746   0.0001049  3.57  0.023


S = 0.222488   R-Sq = 76.1%   R-Sq(adj) = 70.1%


Analysis of Variance

Source          DF       SS       MS      F      P
Regression       1  0.63080  0.63080  12.74  0.023
Residual Error   4  0.19800  0.04950
Total            5  0.82881
```

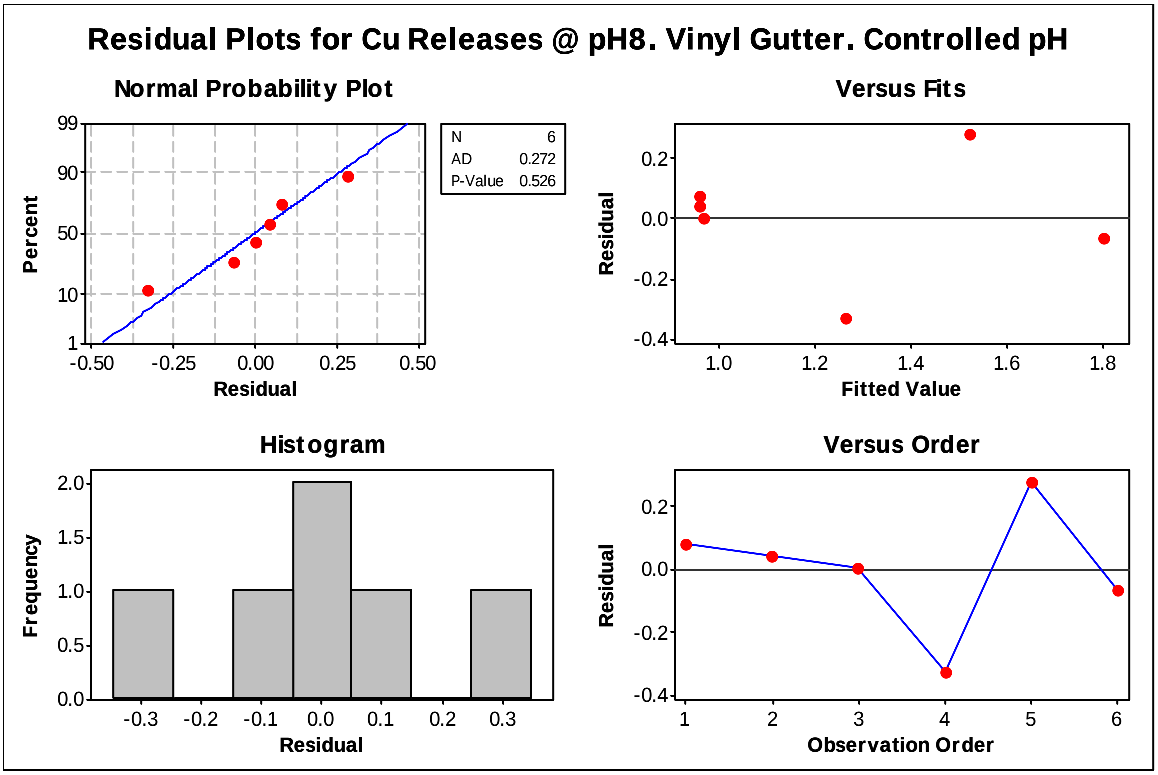


Figure A.7.41. Residual plots for Cu releases from vinyl gutter under controlled pH 8 conditions.

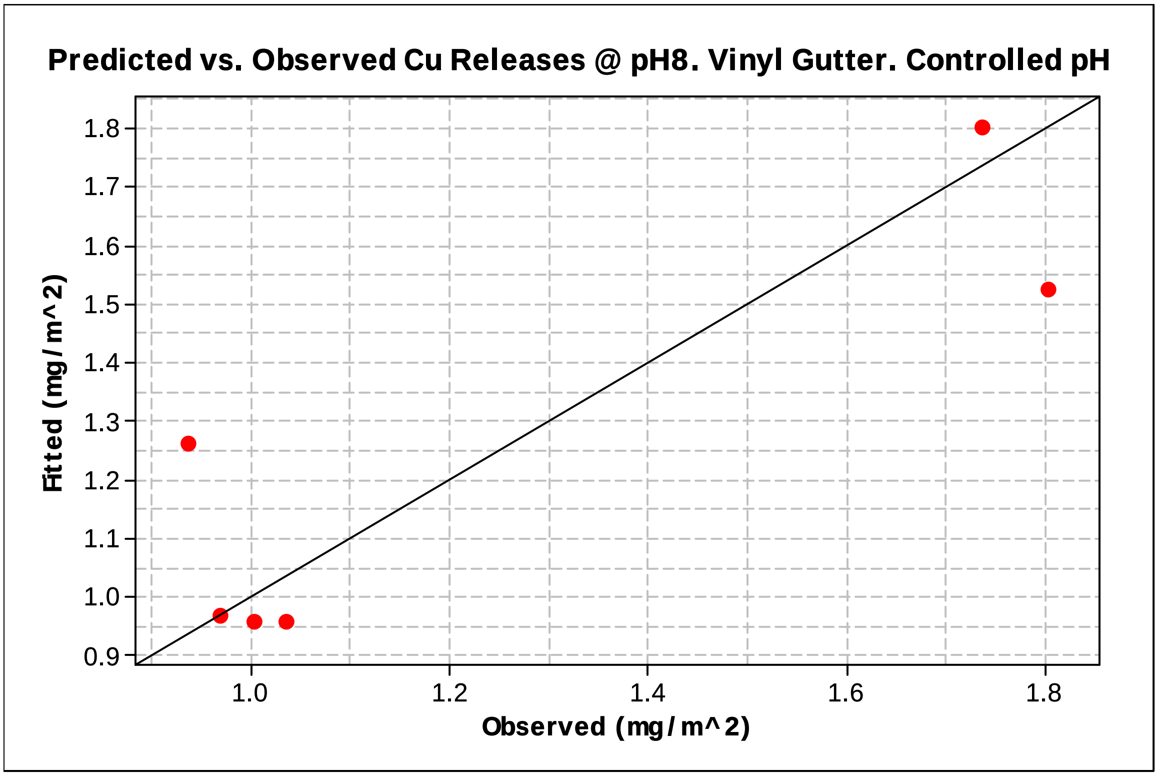


Figure A.7.42. Predicted vs. observed values for Cu releases. Vinyl gutter. Controlled pH8.

Zn Releases, Vinyl Gutter, Controlled pH

Factorial Analysis:

```
Analysis of Variance for Y, using Adjusted SS for Tests

Source  DF   Seq SS  Adj SS  Adj MS     F      P
pH       1   5.9474  5.9474  5.9474  7.81  0.019
Error   10   7.6163  7.6163  0.7616
Total   11  13.5637

S = 0.872714   R-Sq = 43.85%   R-Sq(adj) = 38.23%

Term          Coef  SE Coef      T      P
Constant    1.9562   0.2519   7.76  0.000
pH         -0.7040   0.2519  -2.79  0.019
```

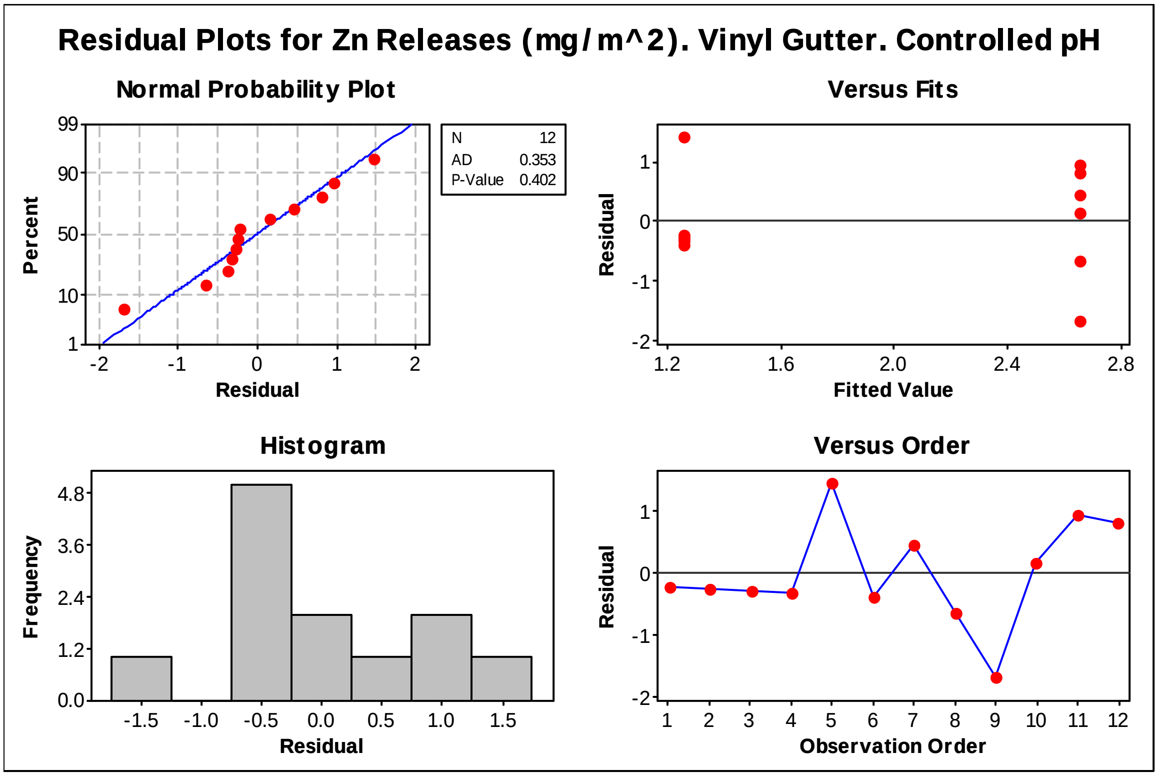


Figure A.7.43. Residual plots for Zn releases from vinyl gutter under controlled pH conditions.

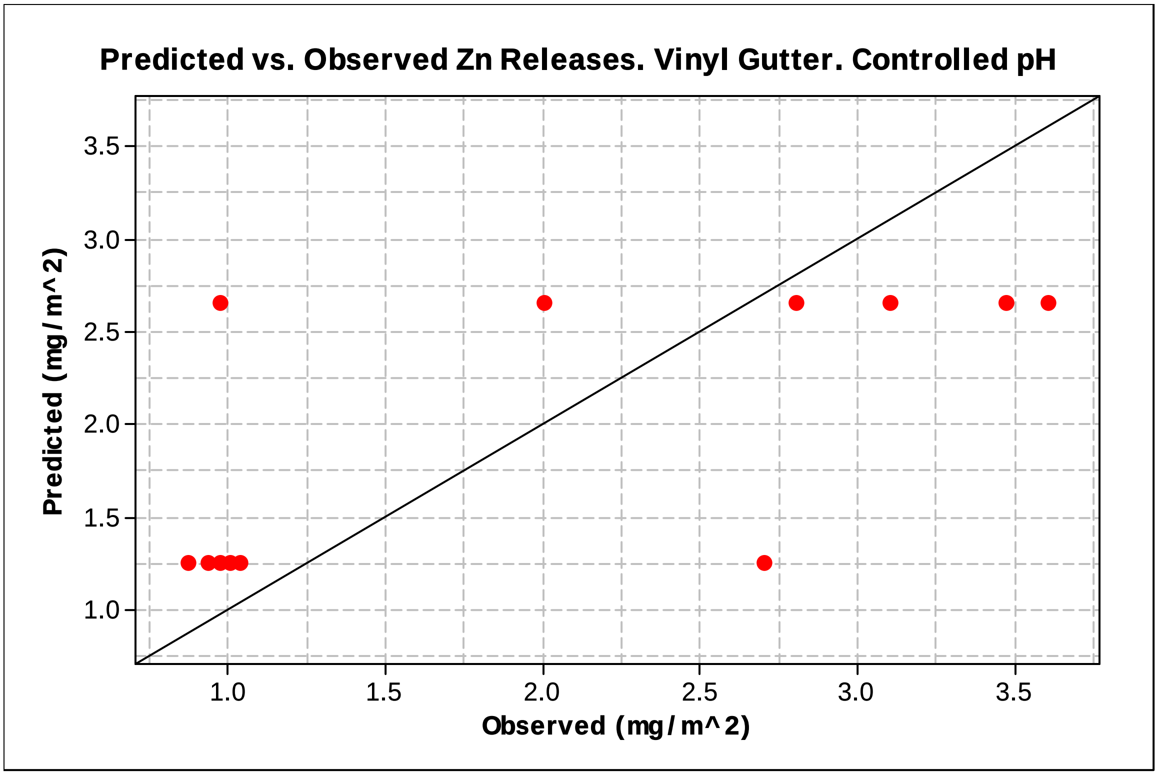


Figure A.7.44. Predicted vs. observed values for Zn releases. Vinyl gutter. Controlled pH.

Vinyl Gutter. Natural pH

Zn Releases, Vinyl Gutter, Natural pH

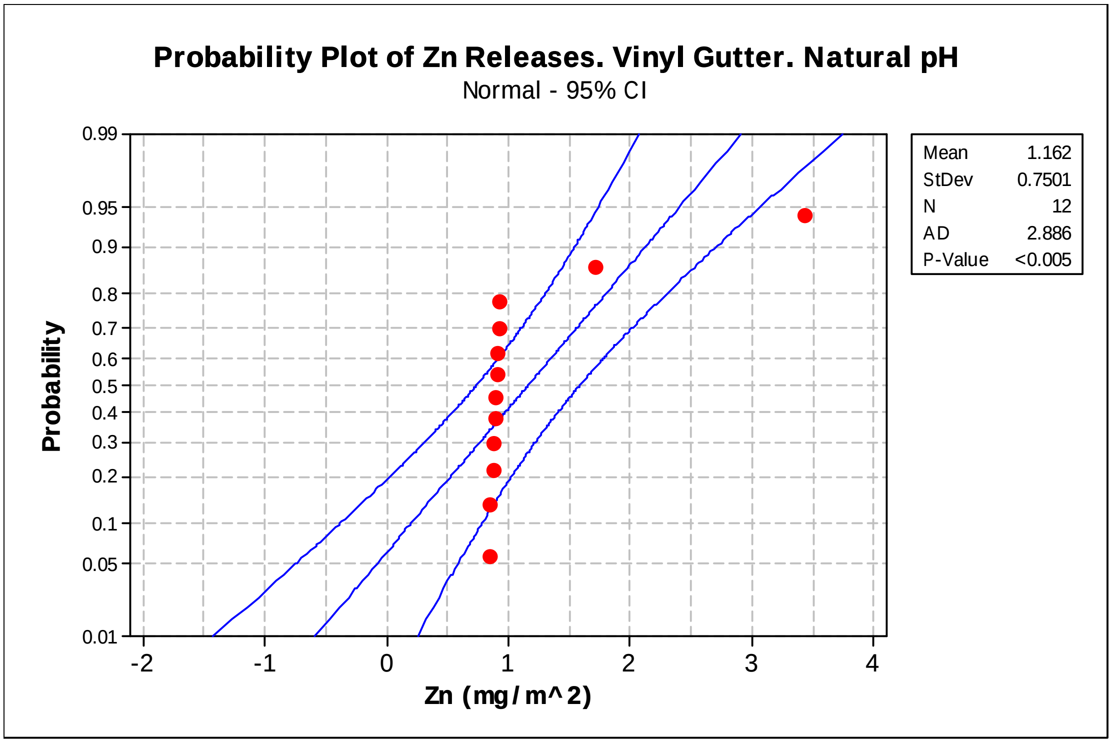


Figure A.7.45. Probability for Zn releases. Vinyl gutter. Natural pH.

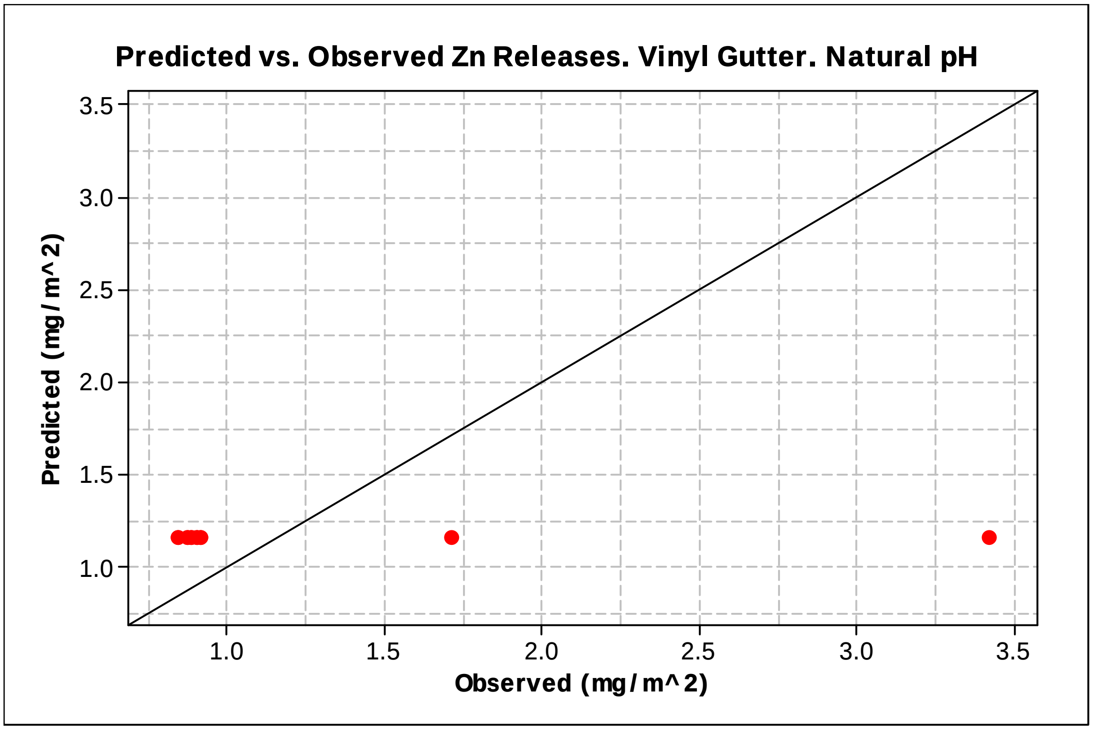


Figure A.7.46. Predicted vs. observed values for Zn releases. Vinyl gutter. Natural pH.

Aluminum Gutter. Controlled pH

Cu Releases, Aluminum Gutter, Controlled pH

Factorial Analysis:

```
Analysis of Variance for Y, using Adjusted SS for Tests

Source  DF  Seq SS  Adj SS  Adj MS        F      P
Time     1  8.0480  8.0480  8.0480  1950.75  0.000
Error   10  0.0413  0.0413  0.0041
Total   11  8.0892

S = 0.0642307   R-Sq = 99.49%   R-Sq(adj) = 99.44%

Term          Coef  SE Coef        T      P
Constant   1.78240  0.01854    96.13  0.000
Time      -0.81894  0.01854   -44.17  0.000
```

Regression Analysis:

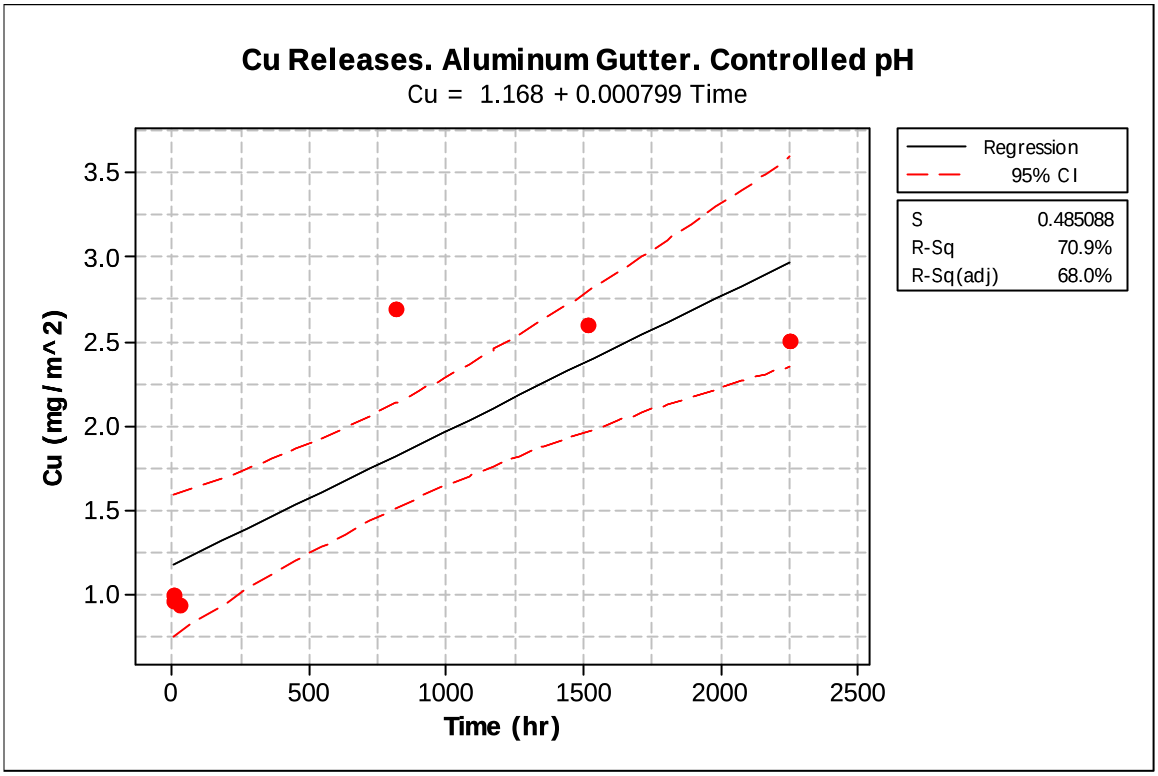


Figure A.7.47. Linear regression for Cu releases. Aluminum gutter. Controlled pH.

```
The regression equation is
Cu = 1.17 + 0.000799 Time
```

```
Predictor         Coef    SE Coef     T      P
Constant        1.1684     0.1873  6.24  0.000
Time         0.0007987  0.0001618  4.94  0.001


S = 0.485088   R-Sq = 70.9%   R-Sq(adj) = 68.0%

PRESS = 3.31761   R-Sq(pred) = 58.99%


Analysis of Variance

Source          DF      SS      MS      F      P
Regression       1  5.7361  5.7361  24.38  0.001
Residual Error  10  2.3531  0.2353
Total           11  8.0892

Durbin-Watson statistic = 1.90358
```

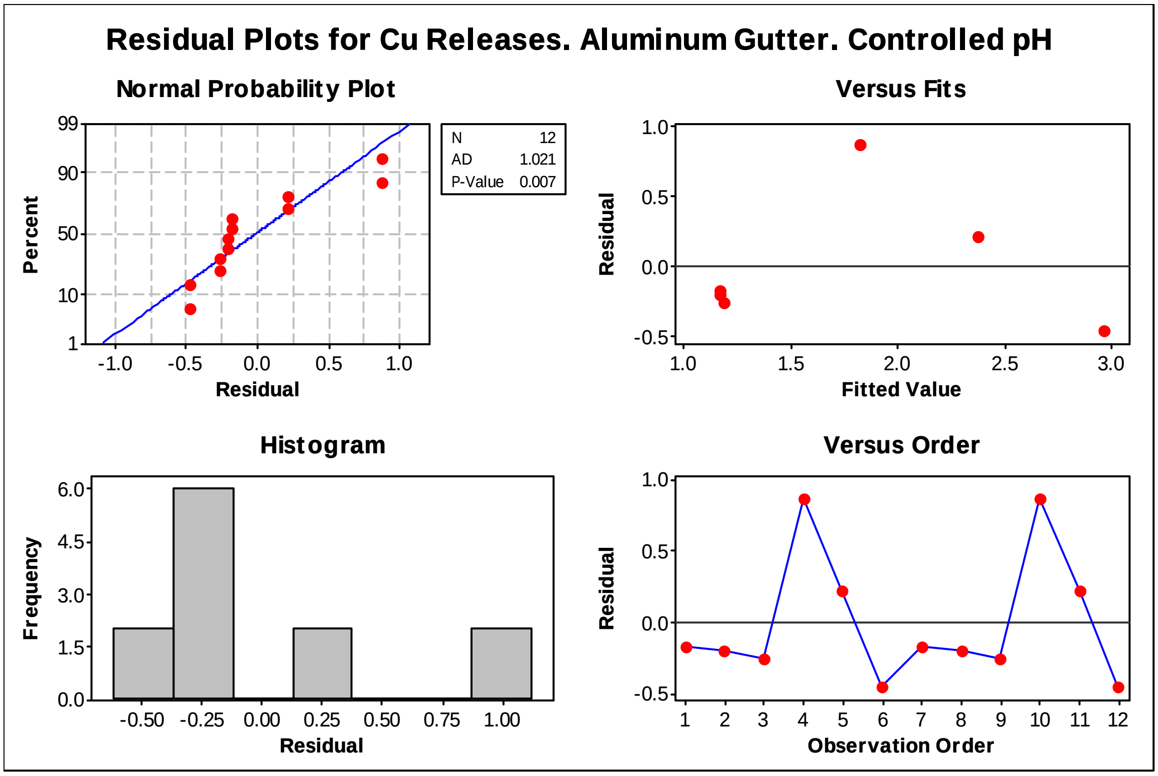


Figure A.7.48. Residual plots for Cu releases from aluminum gutter. Controlled pH.

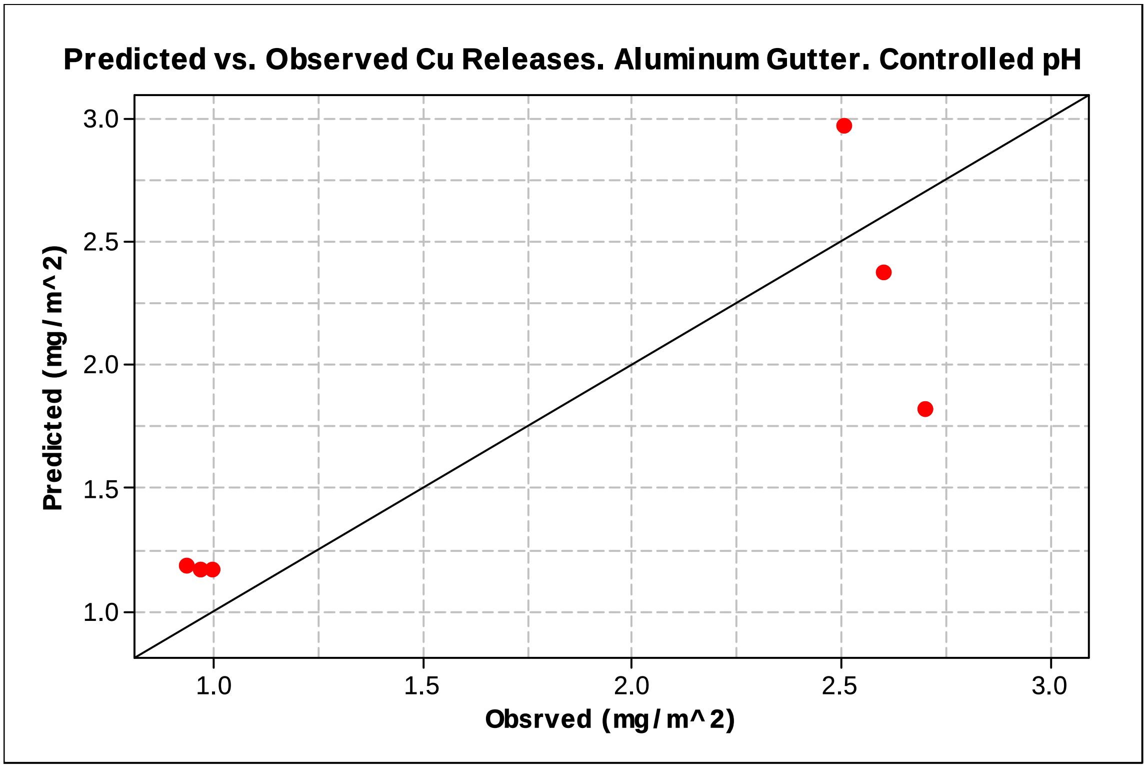


Figure A.7.49. Predicted vs. observed values for Cu releases. Aluminum gutter. Controlled pH.

Zn Releases, Aluminum Gutter, Controlled pH

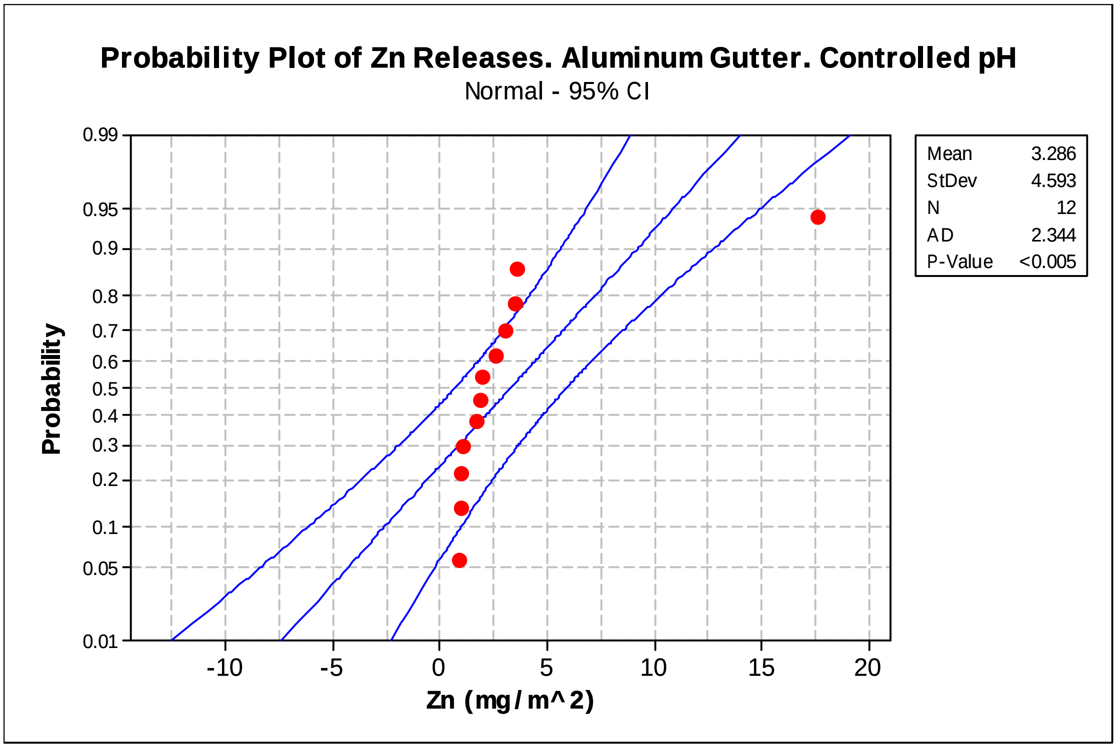


Figure A.7.50. Probability for Zn releases. Aluminum gutter. Controlled pH.

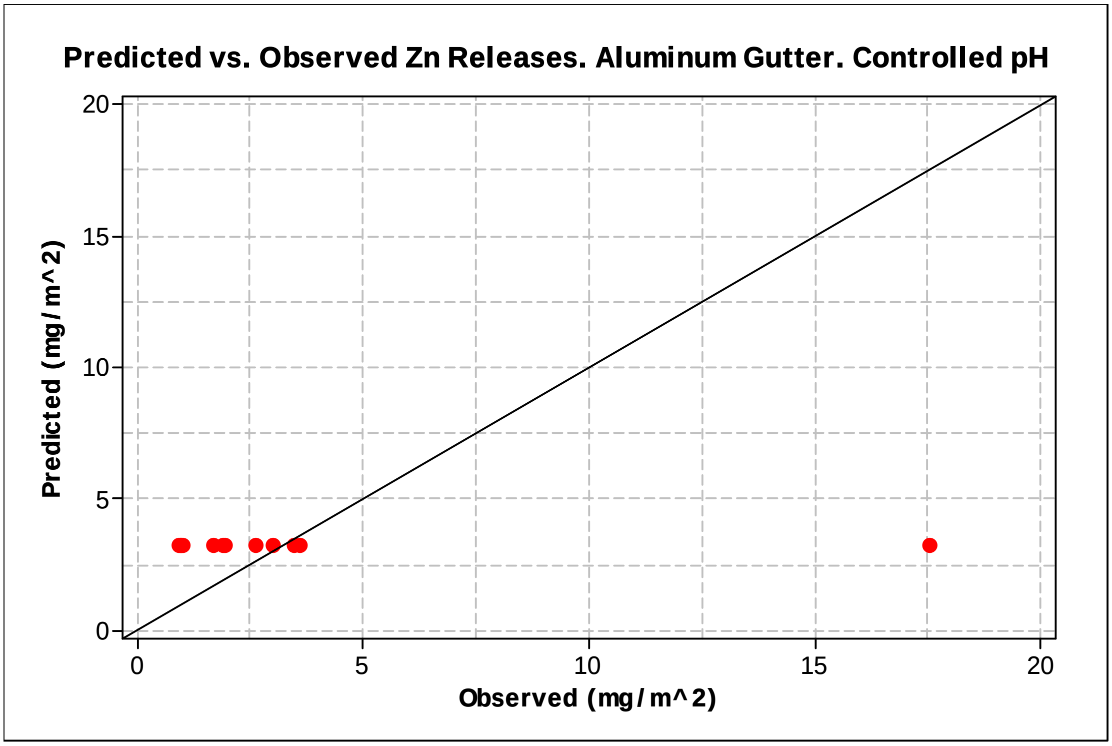


Figure A.7.51. Predicted vs. observed values for Zn releases. Aluminum gutter. Controlled pH.

Aluminum Gutter. Natural pH

Zn Releases, Aluminum Gutter, Natural pH

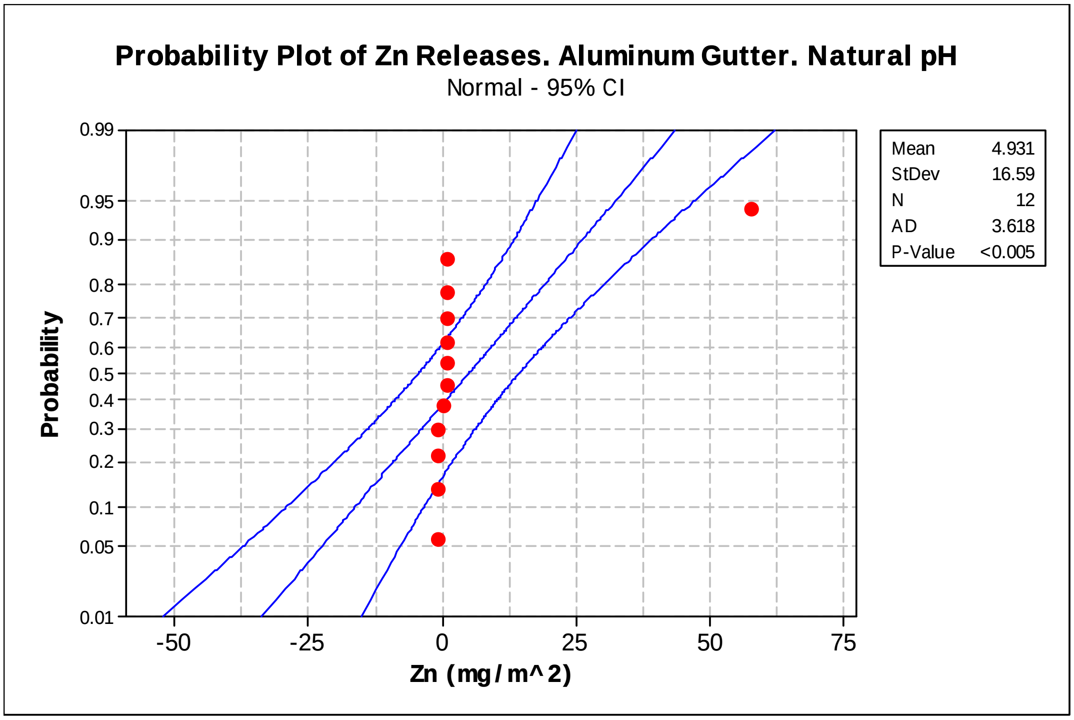


Figure A.7.52. Probability for Zn releases. Aluminum gutter. Natural pH.

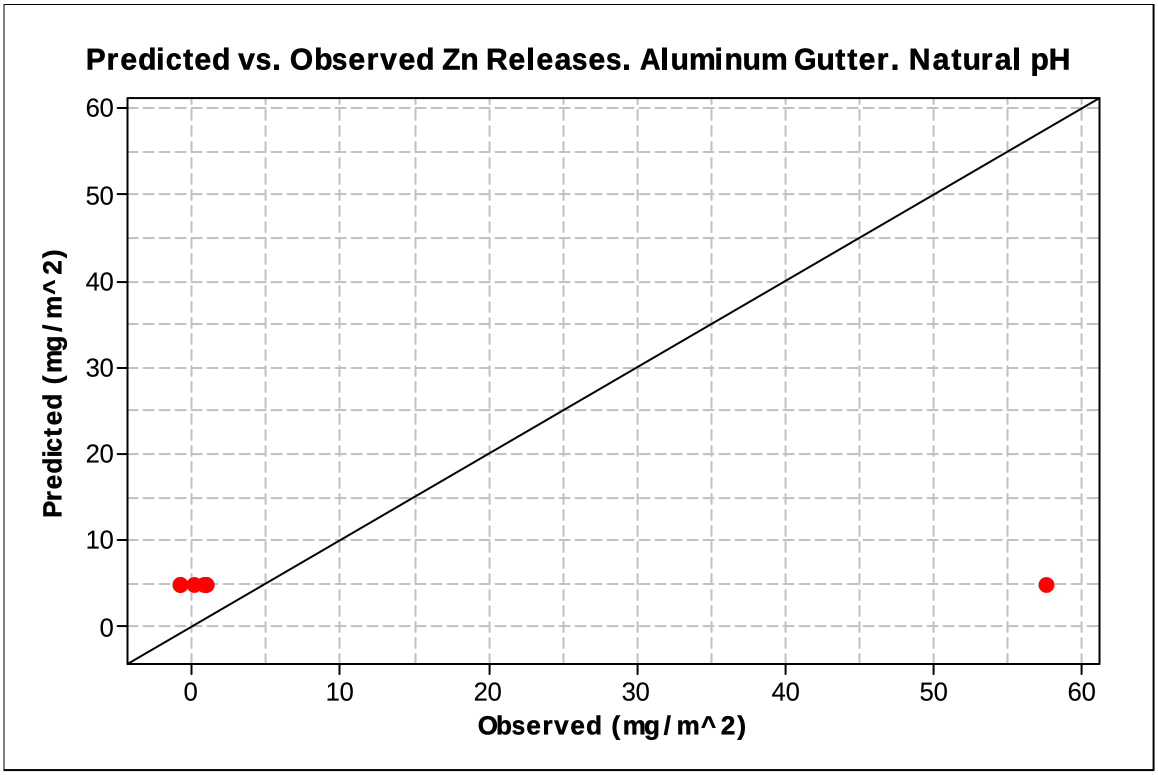


Figure A.7.53. Predicted vs. observed values for Zn releases. Aluminum gutter. Natural pH.

Steel Gutter. Controlled pH

Pb Releases, Steel Gutter, Controlled pH

Factorial Analysis:

```
Analysis of Variance for Y, using Adjusted SS for Tests

Source    DF   Seq SS   Adj SS   Adj MS       F      P
pH         1    9.333    9.333    9.333  177.28  0.000
Time       1   24.559   24.559   24.559  466.52  0.000
pH*Time    1    8.380    8.380    8.380  159.19  0.000
Error      8    0.421    0.421    0.053
Total     11   42.692

S = 0.229439   R-Sq = 99.01%   R-Sq(adj) = 98.64%

Term          Coef  SE Coef       T      P
Constant   1.60721  0.06623   24.27  0.000
pH        -0.88188  0.06623  -13.31  0.000
Time      -1.43058  0.06623  -21.60  0.000
pH*Time    0.83566  0.06623   12.62  0.000
```

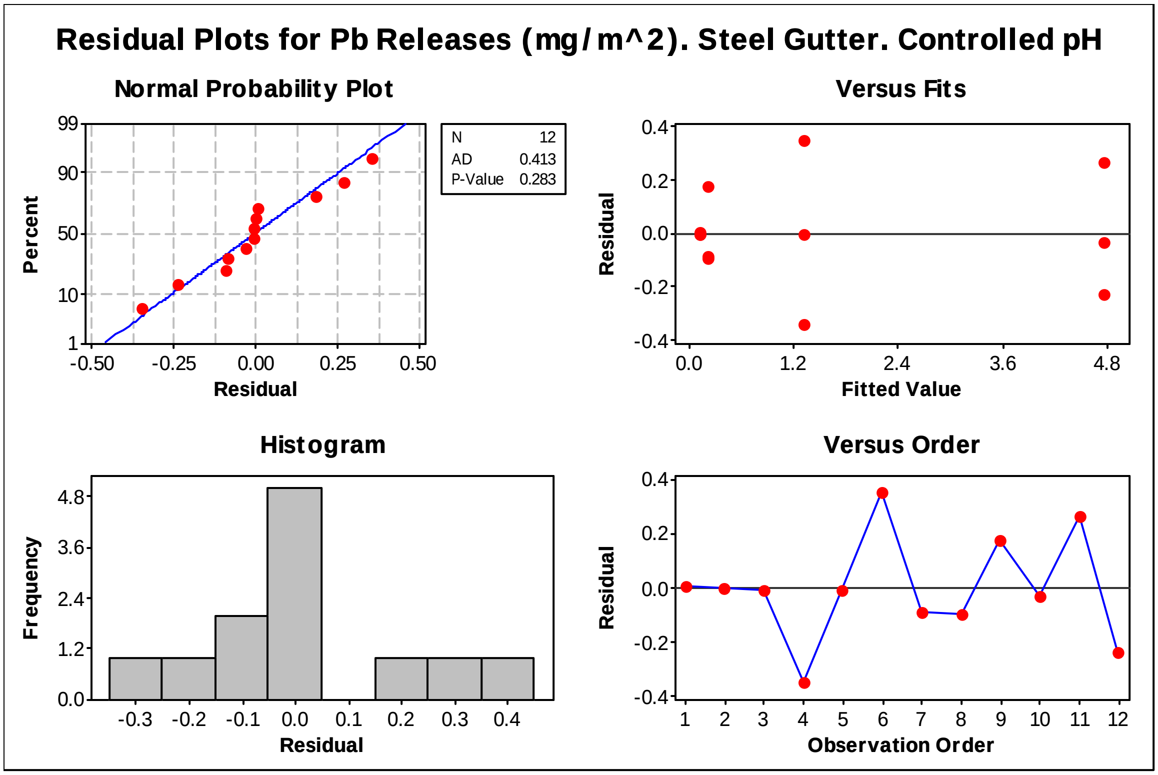


Figure A.7.54. Residual plots for Pb releases from steel gutter under controlled pH conditions.

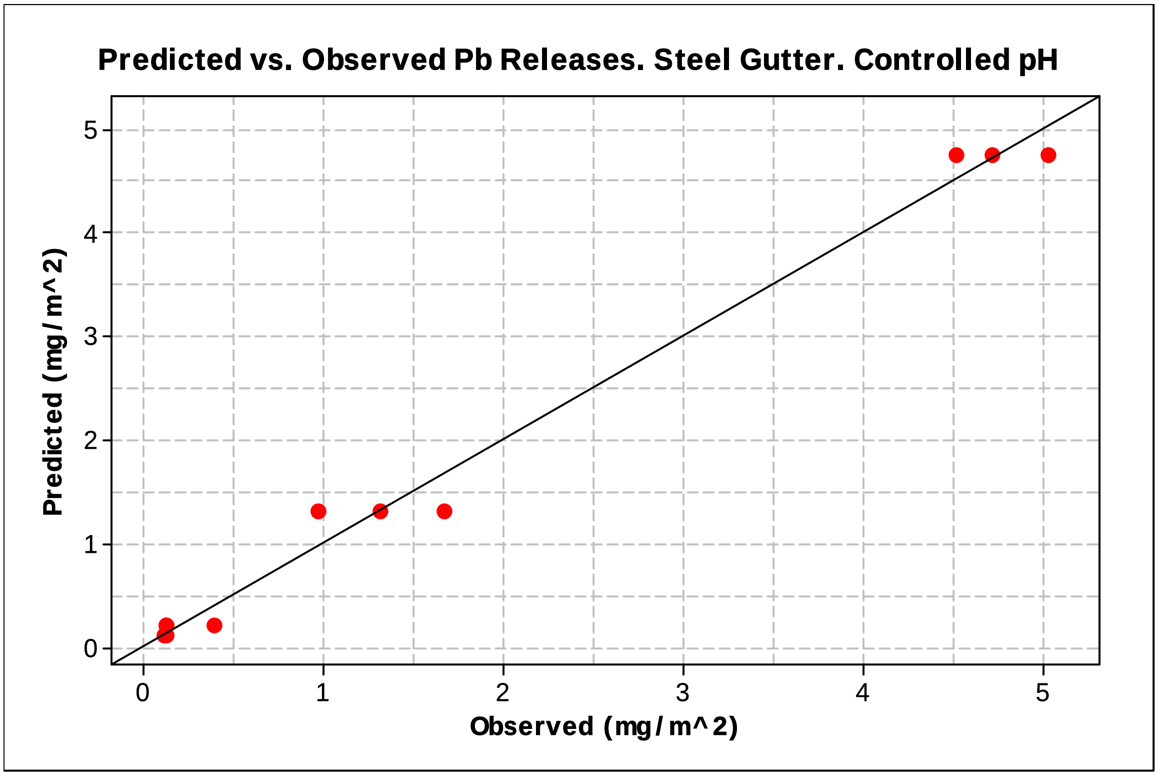


Figure A.7.55. Predicted vs. observed values for Pb releases. Steel gutter. Controlled pH.

Cu Releases, Steel Gutter, Controlled pH

Factorial Analysis:

```
Analysis of Variance for Y, using Adjusted SS for Tests

Source    DF   Seq SS   Adj SS   Adj MS      F      P
pH         1  0.45235  0.45235  0.45235  31.61  0.000
Time       1  0.33899  0.33899  0.33899  23.69  0.001
pH*Time    1  0.45235  0.45235  0.45235  31.61  0.000
Error      8  0.11447  0.11447  0.01431
Total     11  1.35816

S = 0.119621   R-Sq = 91.57%   R-Sq(adj) = 88.41%

Term          Coef  SE Coef      T      P
Constant   0.68968  0.03453  19.97  0.000
pH        -0.19415  0.03453  -5.62  0.000
Time      -0.16807  0.03453  -4.87  0.001
pH*Time    0.19415  0.03453   5.62  0.000
```

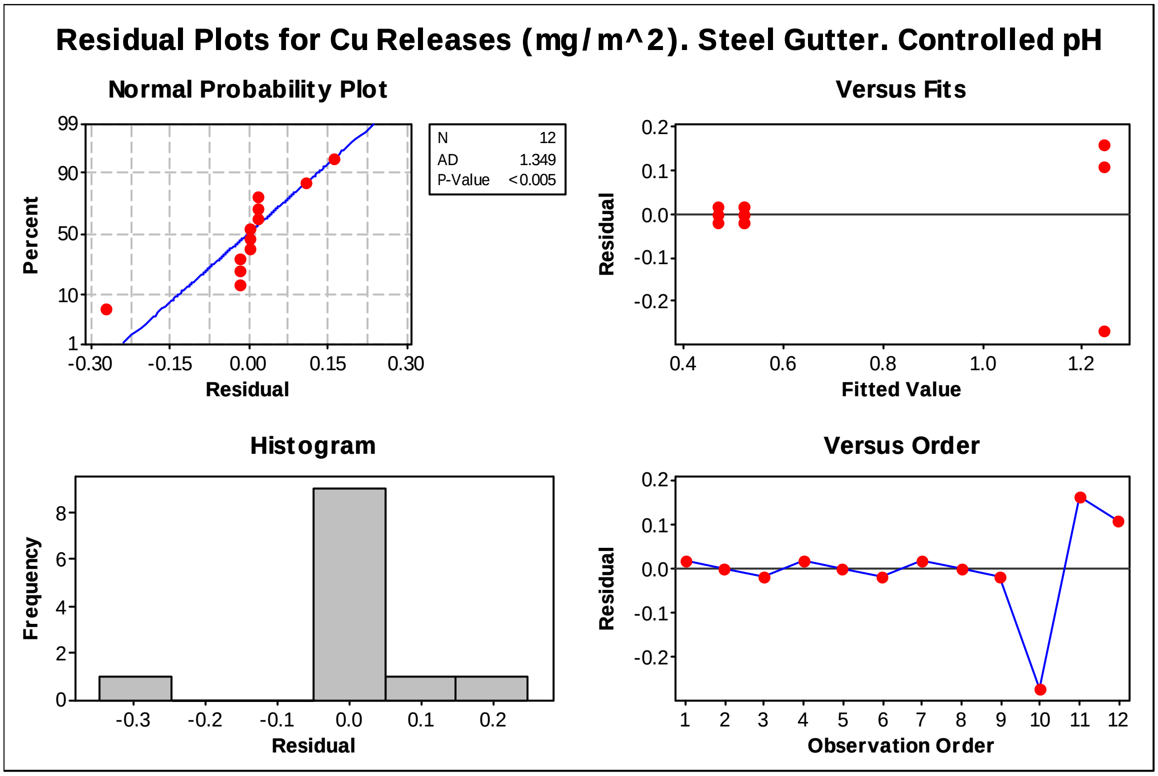


Figure A.7.56. Residual plots for Cu releases from steel gutter under controlled pH conditions.

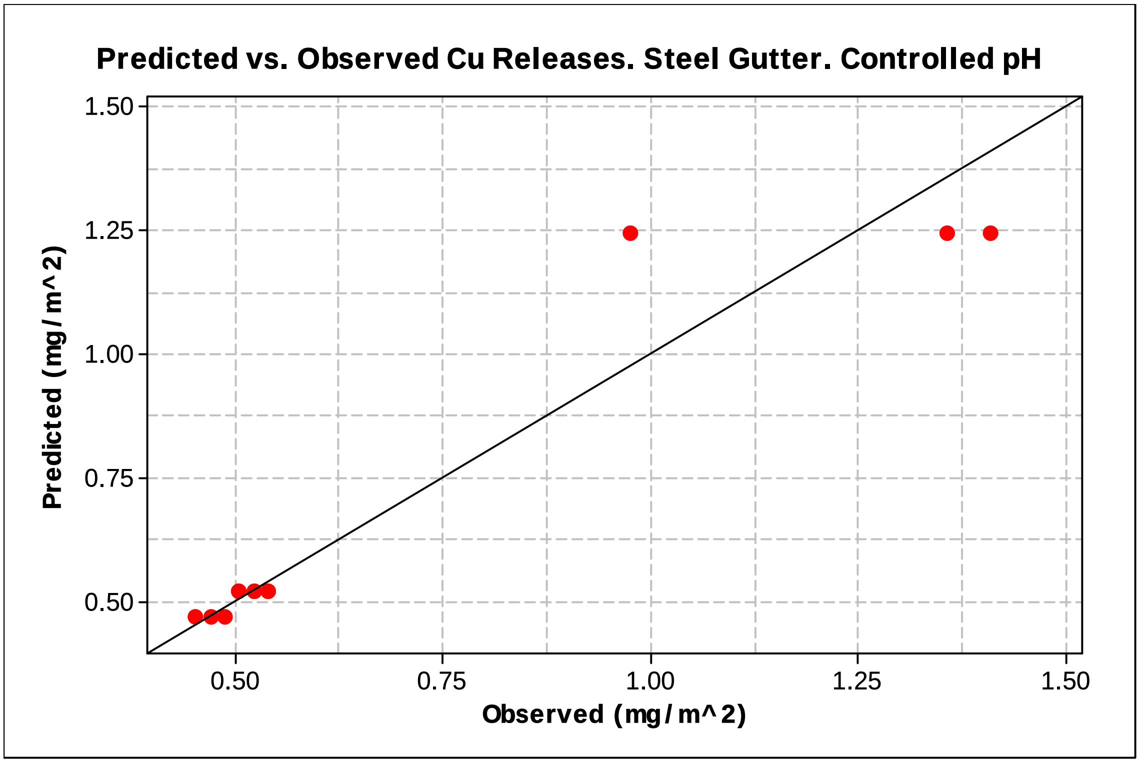


Figure A.7.57. Predicted vs. observed values for Cu releases. Steel gutter. Controlled pH.

Zn Releases, Steel Gutter, Controlled pH

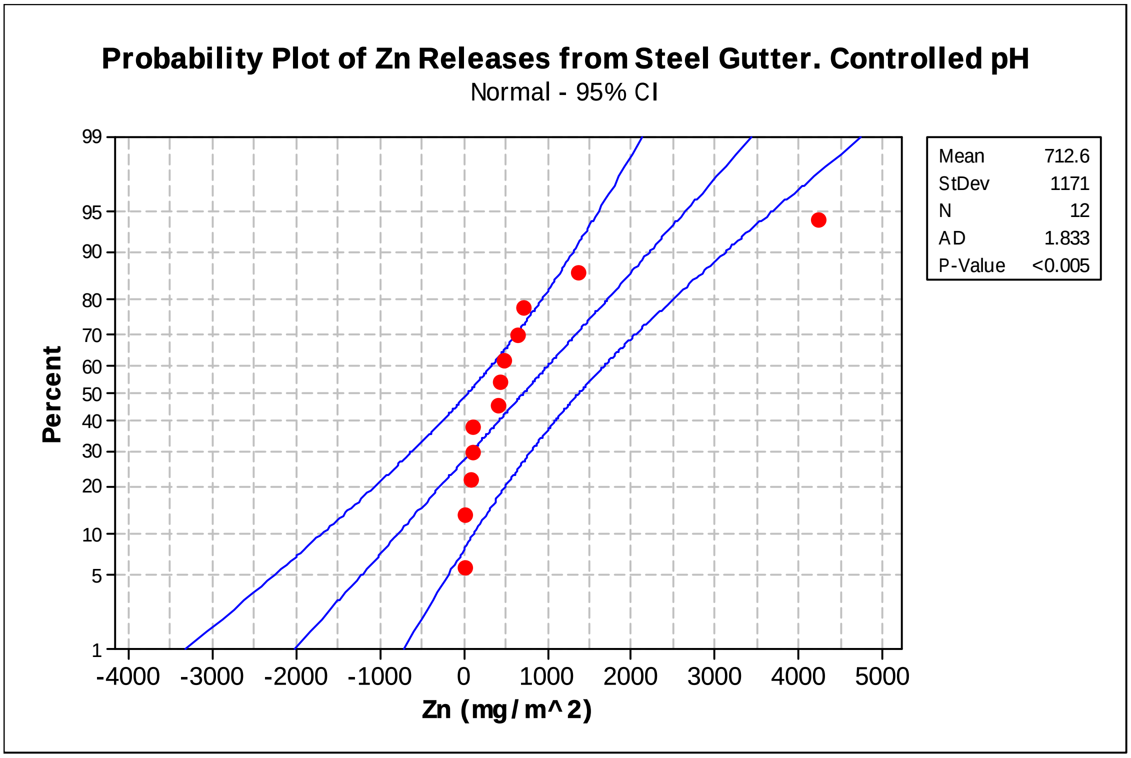


Figure A.7.58. Probability for Zn releases. Steel gutter. Controlled pH.

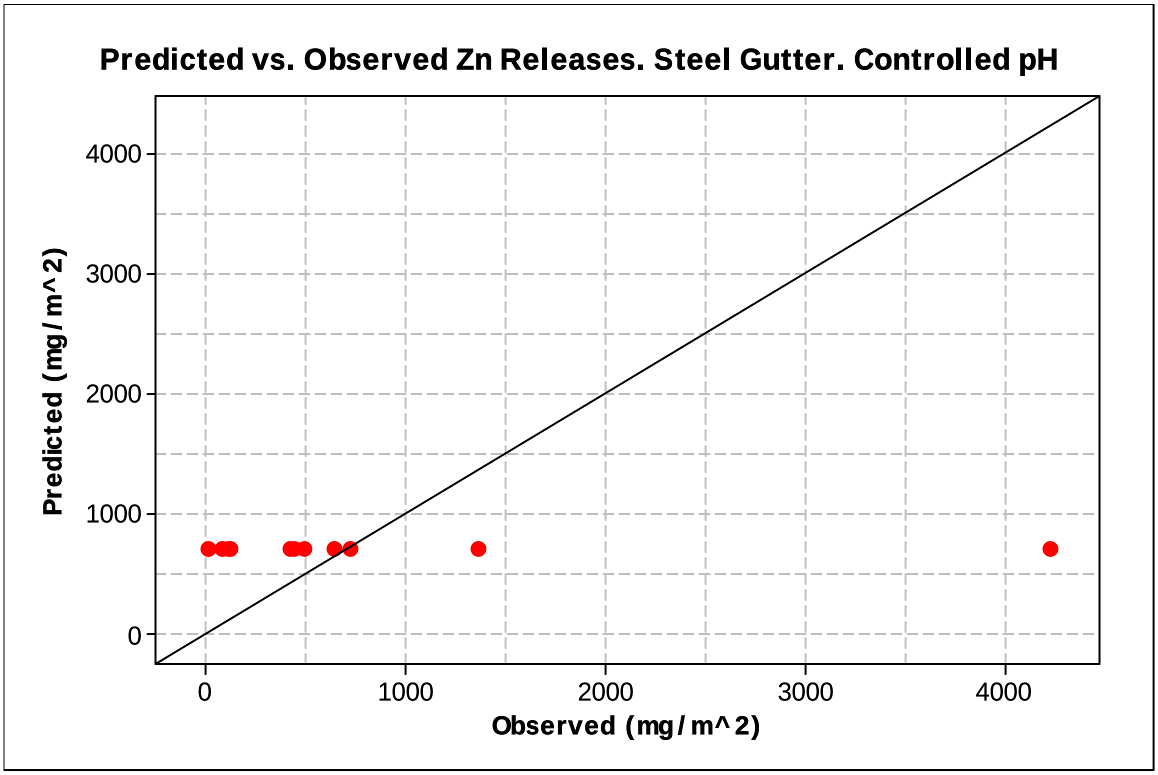


Figure A.7.59. Predicted vs. observed values for Zn releases. Steel gutter. Controlled pH.

Steel Gutter. Natural pH

Zn Releases, Steel Gutter, Natural pH

Factorial Analysis:

```
Analysis of Variance for Y, using Adjusted SS for Tests

Source      DF    Seq SS    Adj SS    Adj MS     F      P
Cond         1  15094657  15094657  15094657  3.76  0.089
Time         1  26869337  26869337  26869337  6.69  0.032
Cond*Time    1  15908449  15908449  15908449  3.96  0.082
Error        8  32138794  32138794   4017349
Total       11  90011237


S = 2004.33   R-Sq = 64.29%   R-Sq(adj) = 50.91%

Term          Coef  SE Coef      T      P
Constant    1617.6    578.6   2.80  0.023
Cond       -1121.6    578.6  -1.94  0.089
Time       -1496.4    578.6  -2.59  0.032
Cond*Time   1151.4    578.6   1.99  0.082
```

Regression Analysis:

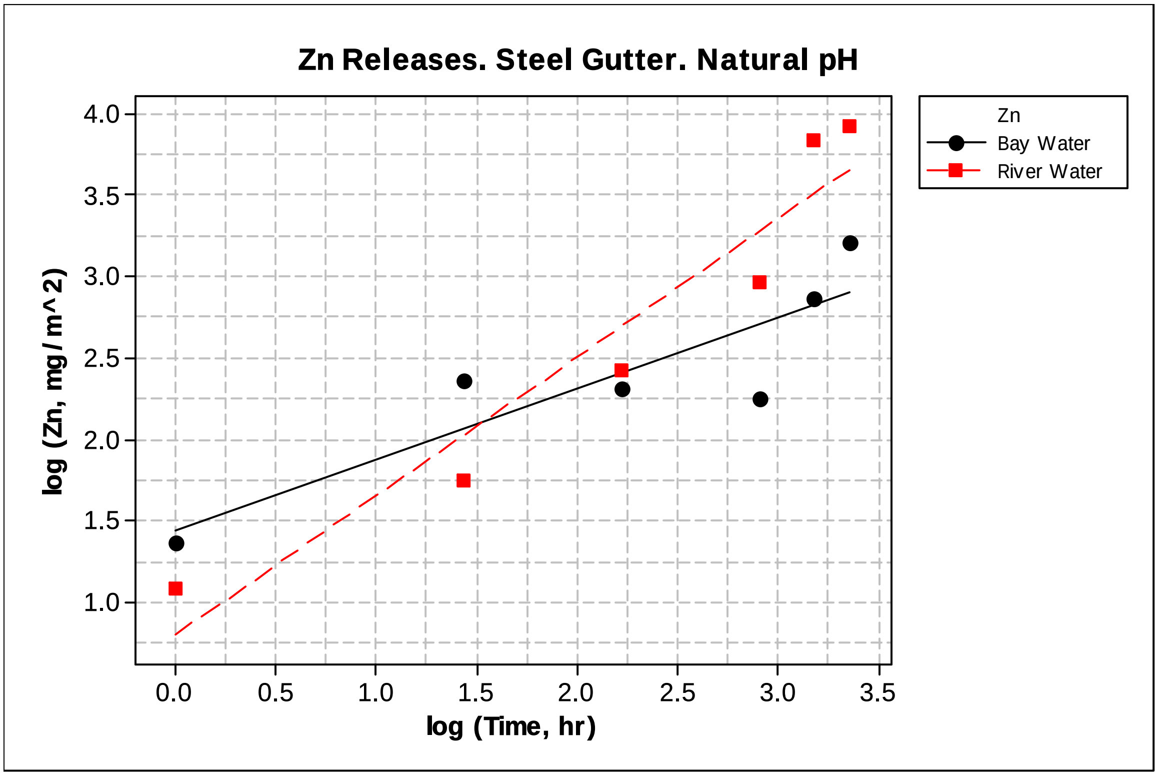


Figure A.7.60. Linear regression for Zn releases. Steel gutter. Natural pH.

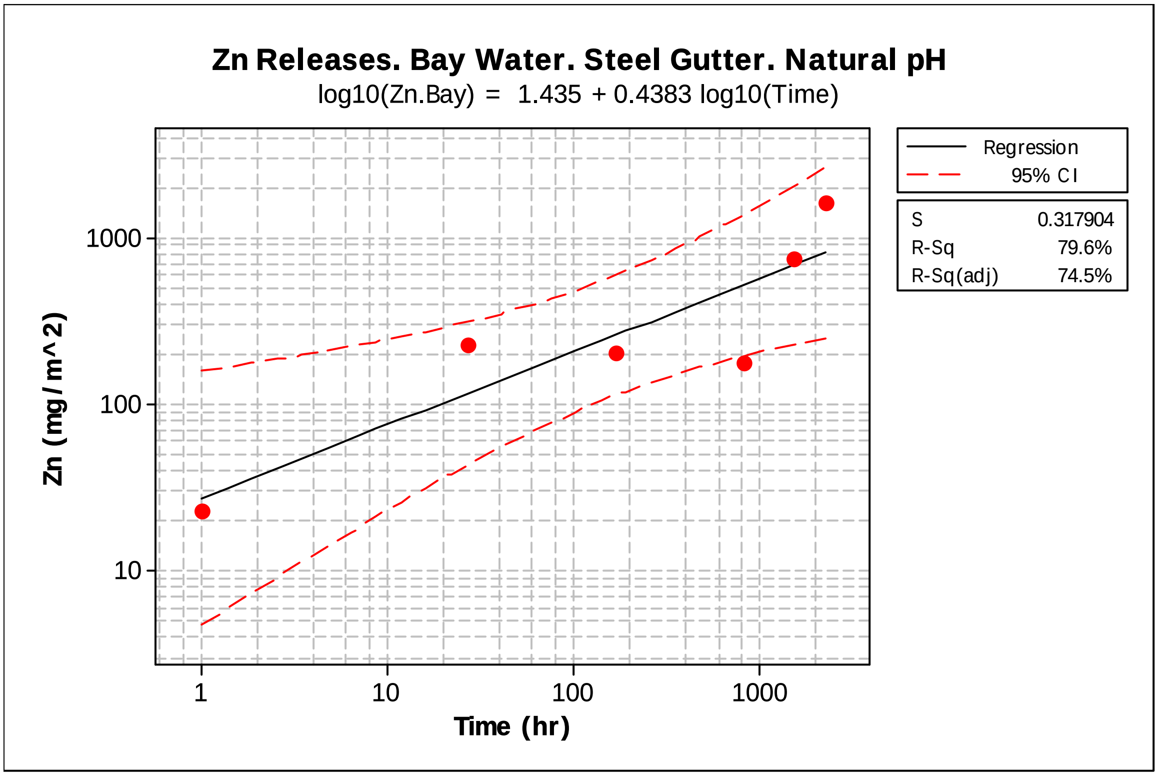


Figure A.7.61. Linear regression for Zn releases. Steel gutter. Bay water.

```
The regression equation is
logZn B = 1.43 + 0.438 logTime


Predictor     Coef  SE Coef     T      P
Constant    1.4346   0.2746  5.22  0.006
logTime     0.4383   0.1108  3.95  0.017


S = 0.317904   R-Sq = 79.6%   R-Sq(adj) = 74.5%


Analysis of Variance

Source          DF      SS      MS      F      P
Regression       1  1.5804  1.5804  15.64  0.017
Residual Error   4  0.4043  0.1011
Total            5  1.9846

Durbin-Watson statistic = 1.82083
```

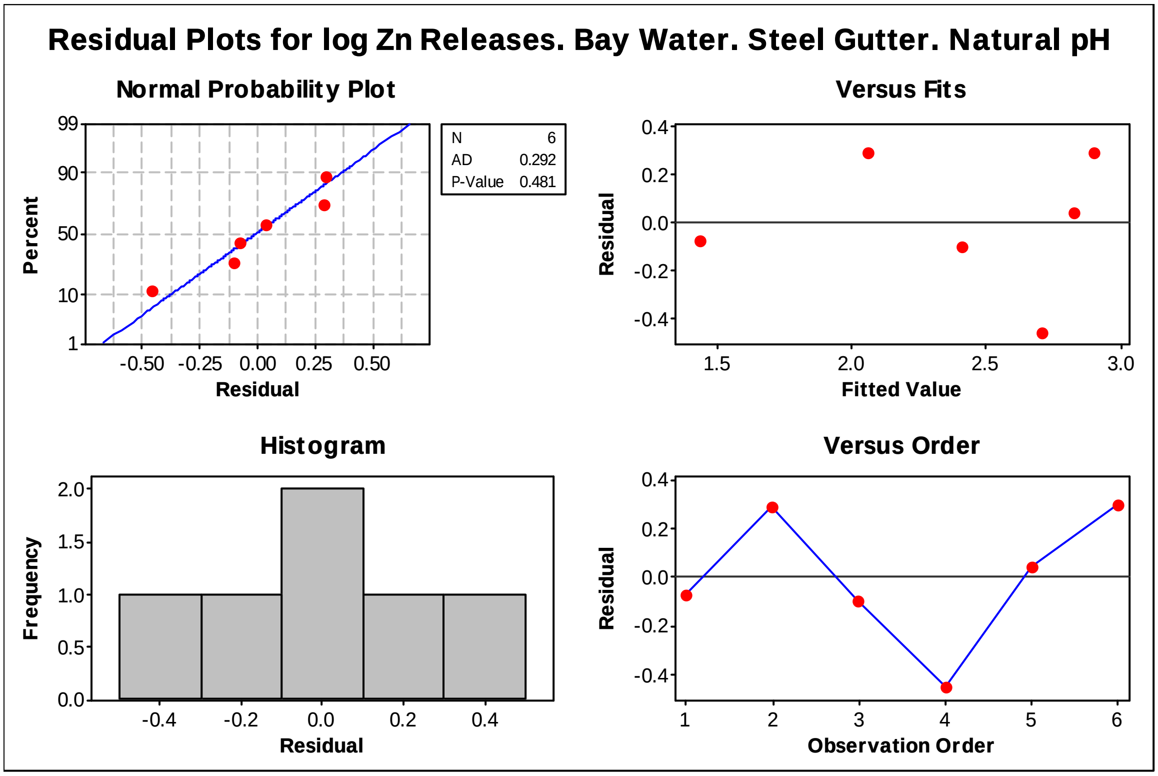


Figure A.7.62. Residual plots for Zn releases from steel gutter. Bay water.

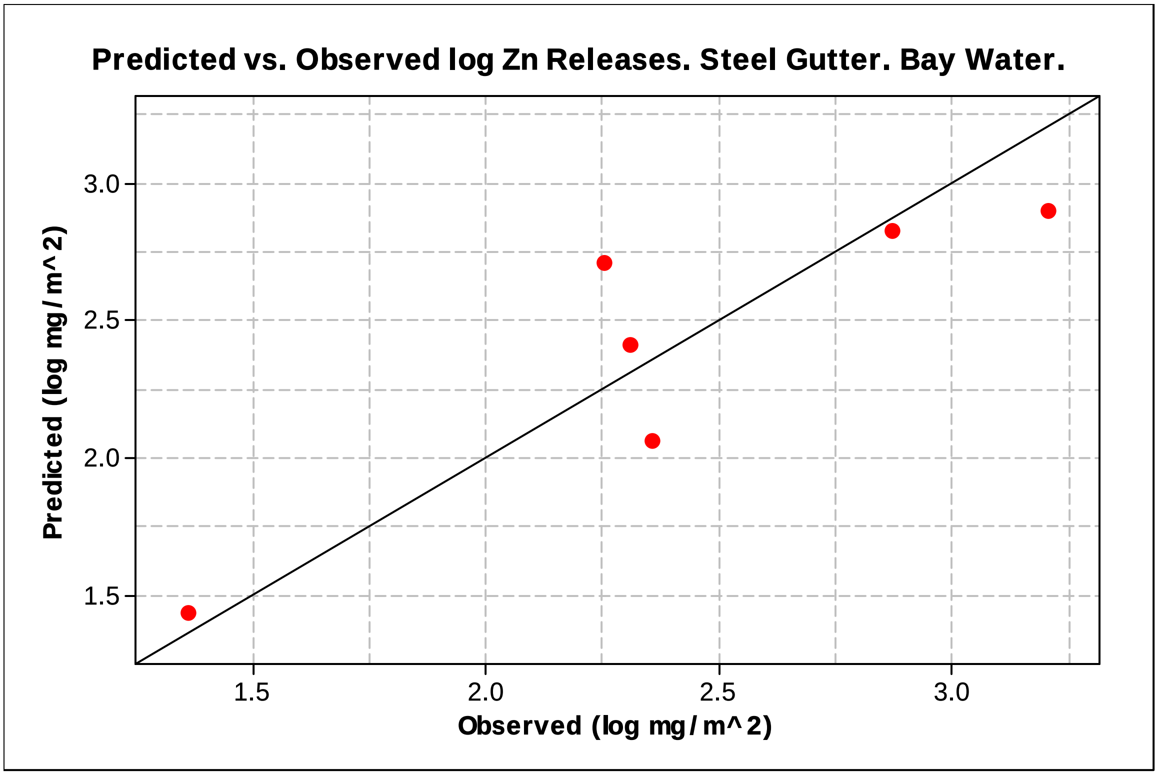


Figure A.7.63. Predicted vs. observed values for Zn releases. Steel gutter. Bay water.

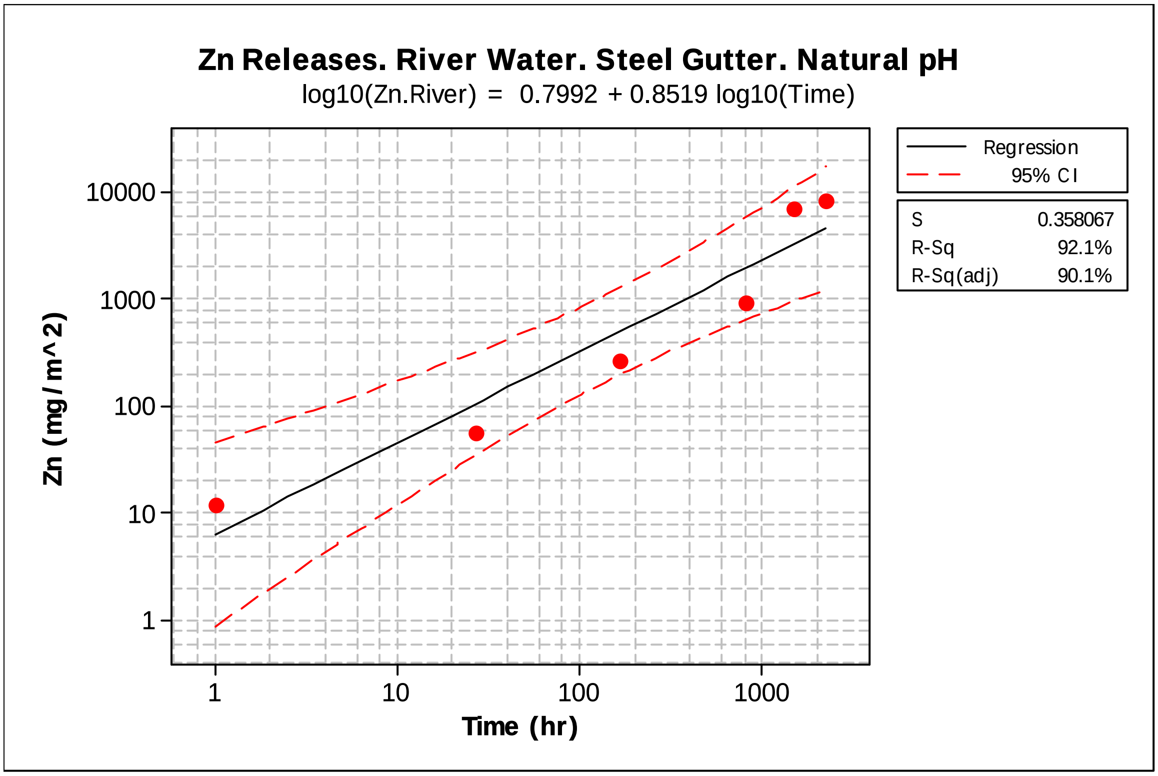


Figure A.7.64. Linear regression for Zn releases. Steel gutter. River water.

```
The regression equation is
logZn R = 0.799 + 0.852 logTime


Predictor     Coef  SE Coef     T      P
Constant    0.7992   0.3093  2.58  0.061
logTime     0.8519   0.1248  6.82  0.002


S = 0.358067   R-Sq = 92.1%   R-Sq(adj) = 90.1%


Analysis of Variance

Source          DF      SS      MS      F      P
Regression       1  5.9700  5.9700  46.56  0.002
Residual Error   4  0.5128  0.1282
Total            5  6.4828

Durbin-Watson statistic = 1.44702
```

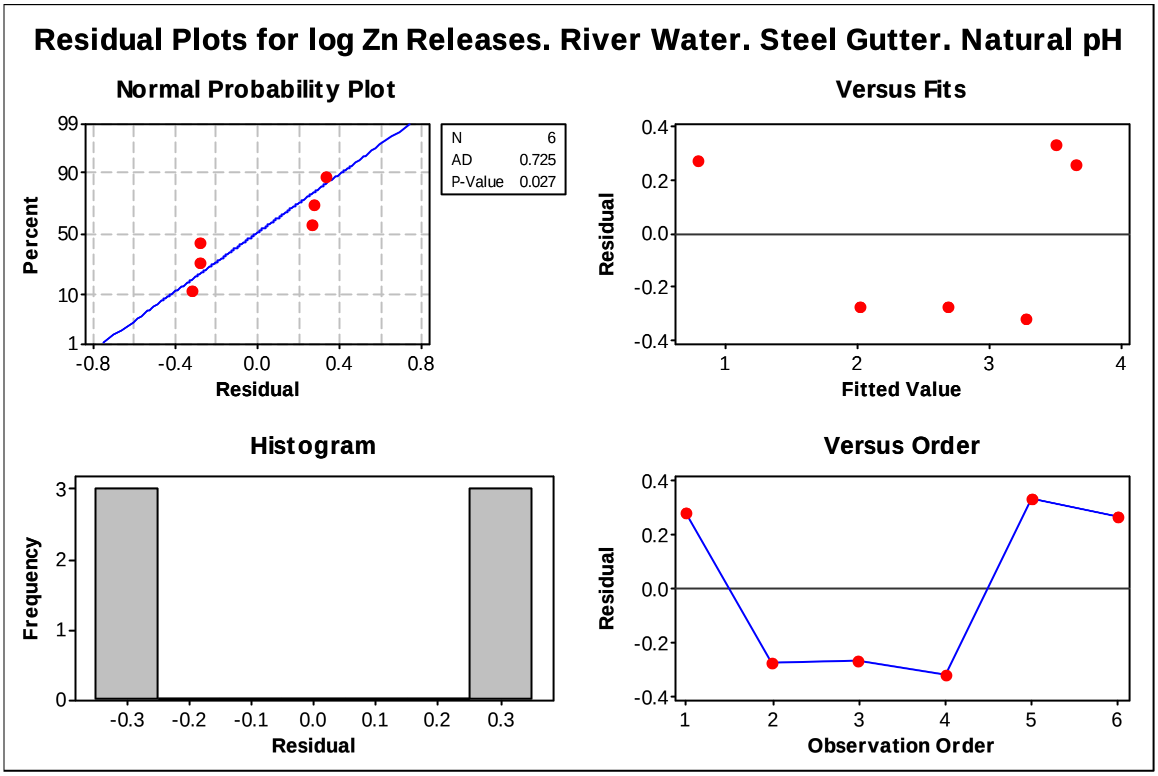


Figure A.7.65. Residual plots for Zn releases from steel gutter. River water.

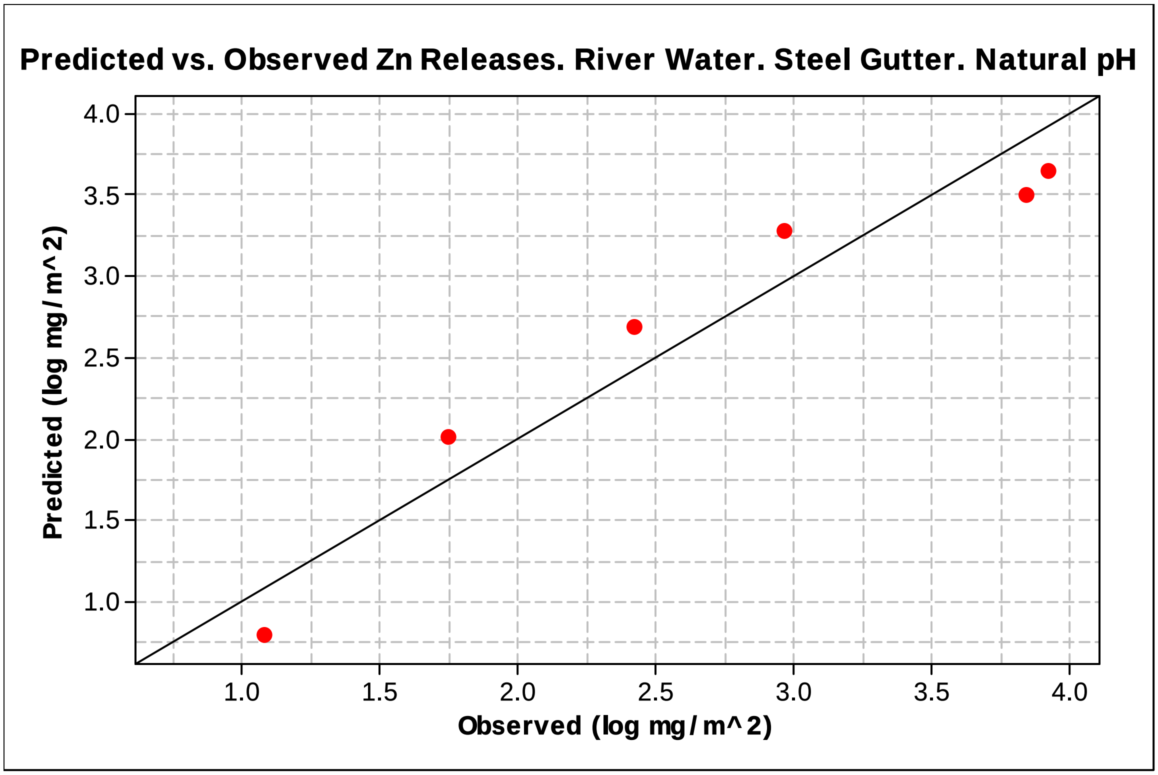


Figure A.7.66. Predicted vs. observed values for Zn releases. Steel gutter. Natural pH.

Pb Releases, Steel Gutter, Natural pH

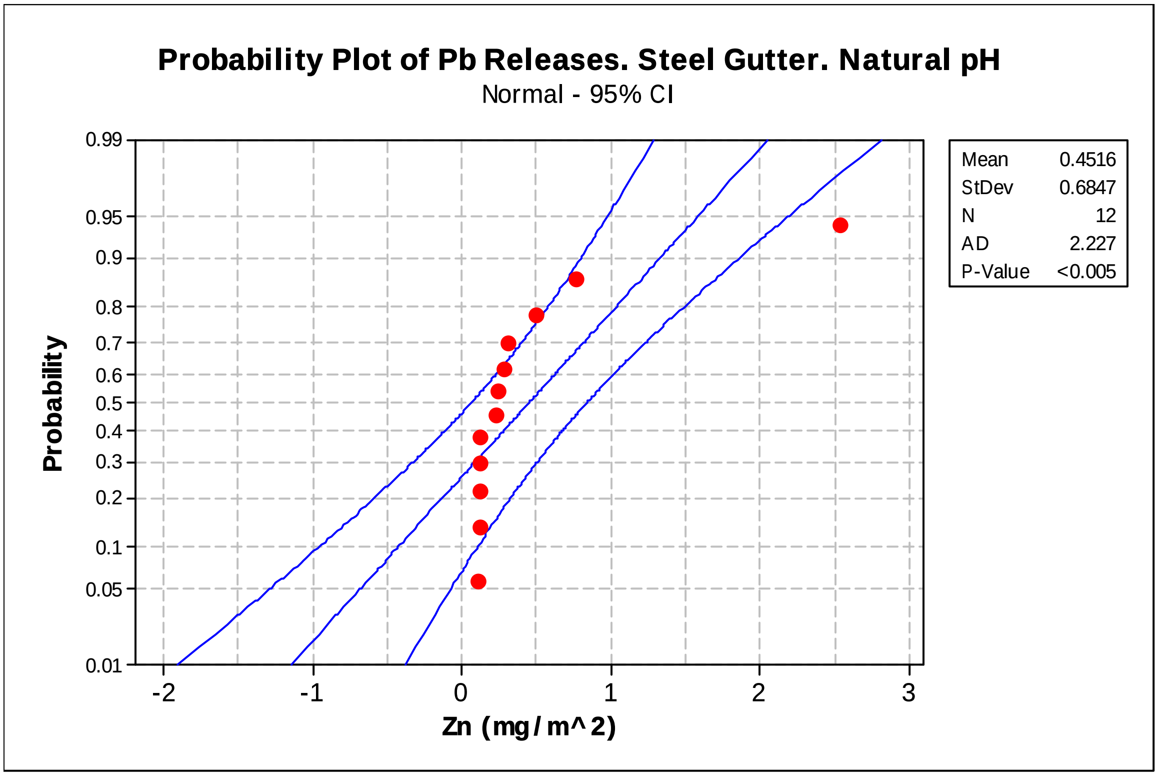


Figure A.7.67. Probability for Pb releases. Steel gutter. Natural pH.

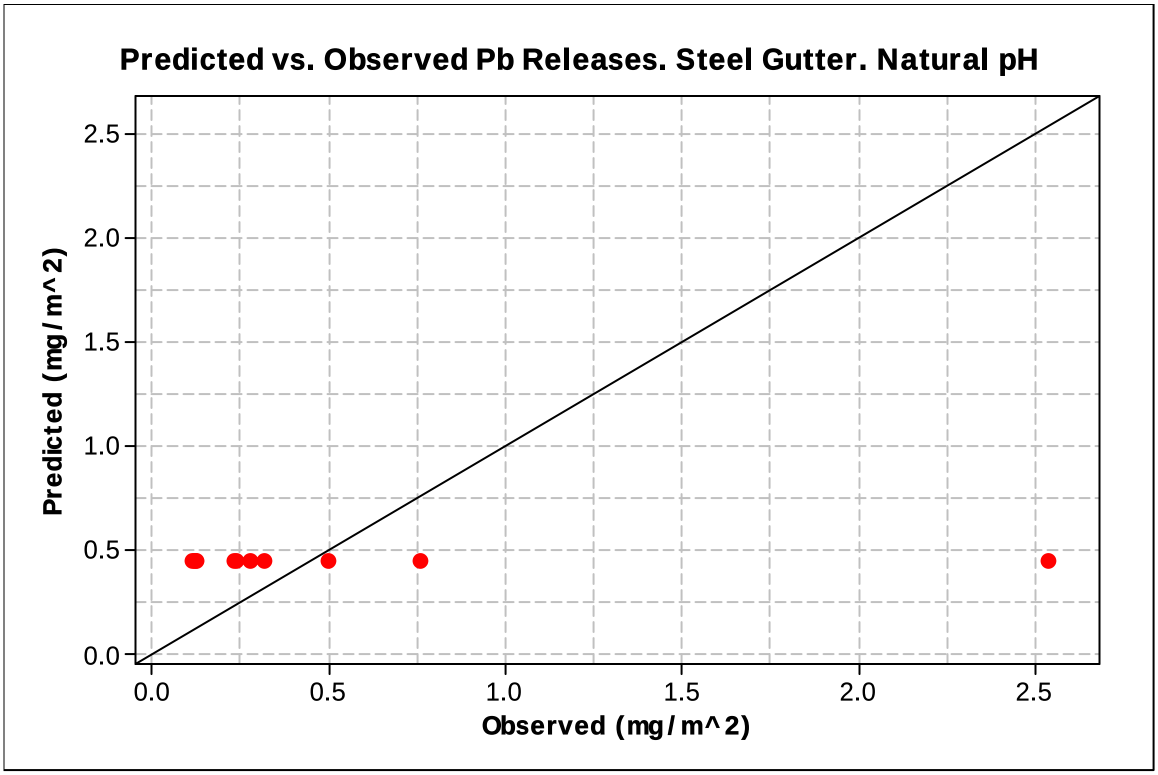


Figure A.7.68. Predicted vs. observed values for Pb releases. Steel gutter. Natural pH.

Copper Gutter. Controlled pH.

Cu Releases, Copper Gutter, Controlled pH

Factorial Analysis:

```
Source   DF  Seq SS  Adj SS  Adj MS     F      P
pH        1   96110   96110   96110  6.09  0.033
Error    10  157768  157768   15777
Total    11  253878

S = 125.606   R-Sq = 37.86%   R-Sq(adj) = 31.64%

Term        Coef  SE Coef     T      P
Constant  159.98    36.26  4.41  0.001
pH         89.49    36.26  2.47  0.033
```

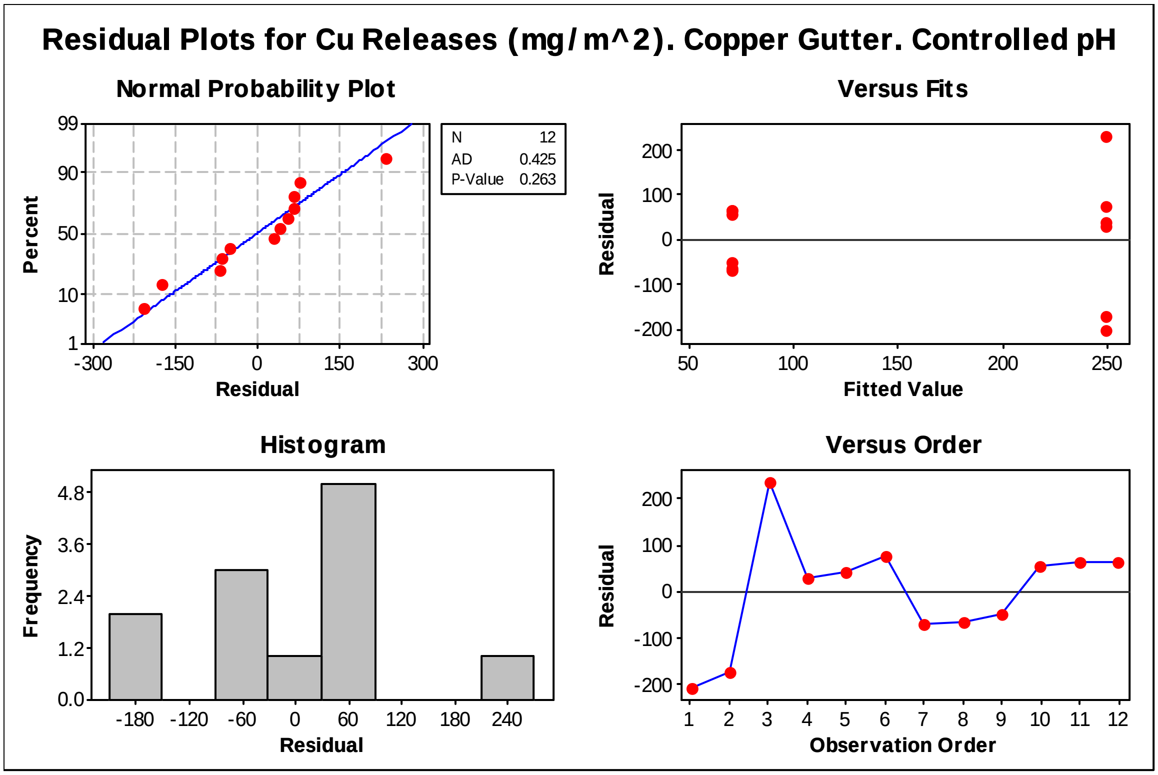


Figure A.7.69. Residual plots for Cu releases from copper gutter under controlled pH conditions.

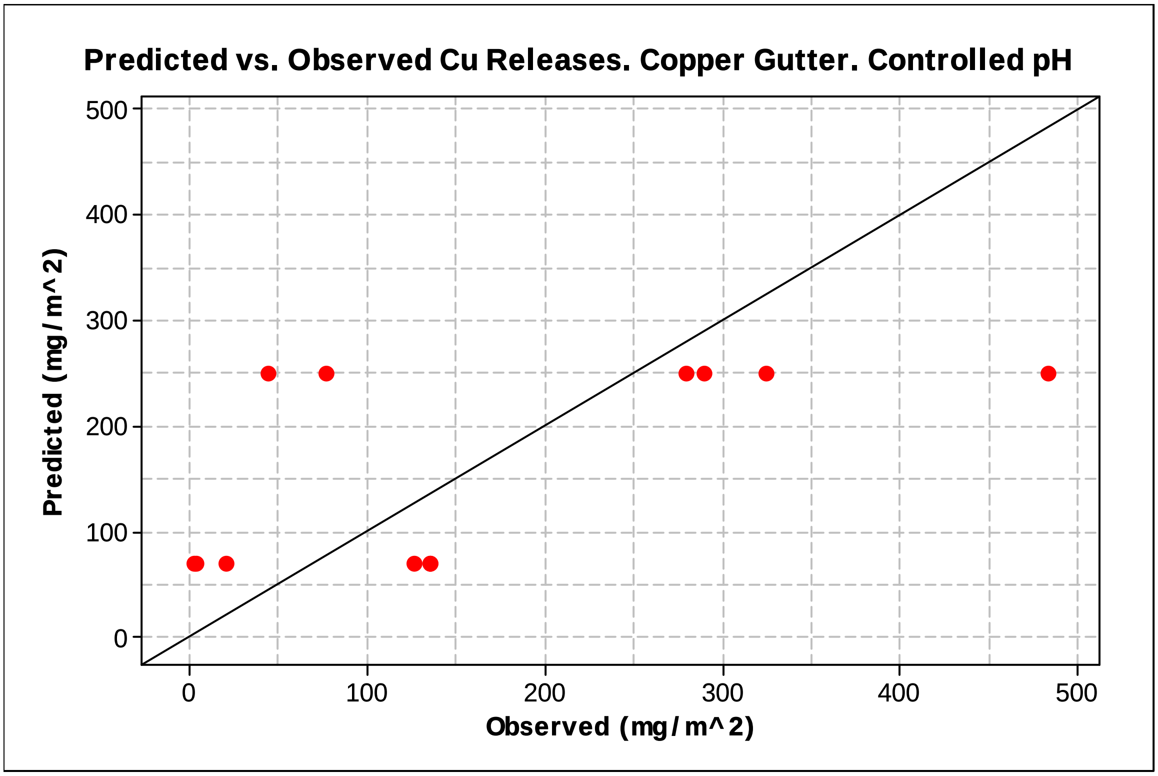


Figure A.7.70. Predicted vs. observed values for Cu releases. Copper gutter. Controlled pH.

Zn Releases, Copper Gutter, Controlled pH

Factorial Analysis:

```
Analysis of Variance for Y, using Adjusted SS for Tests

Source  DF  Seq SS  Adj SS  Adj MS     F      P
pH       1  25.718  25.718  25.718  7.79  0.019
Error   10  33.018  33.018   3.302
Total   11  58.735

S = 1.81708   R-Sq = 43.79%   R-Sq(adj) = 38.16%

Term        Coef  SE Coef     T      P
Constant  1.6879   0.5245  3.22  0.009
pH        1.4639   0.5245  2.79  0.019
```

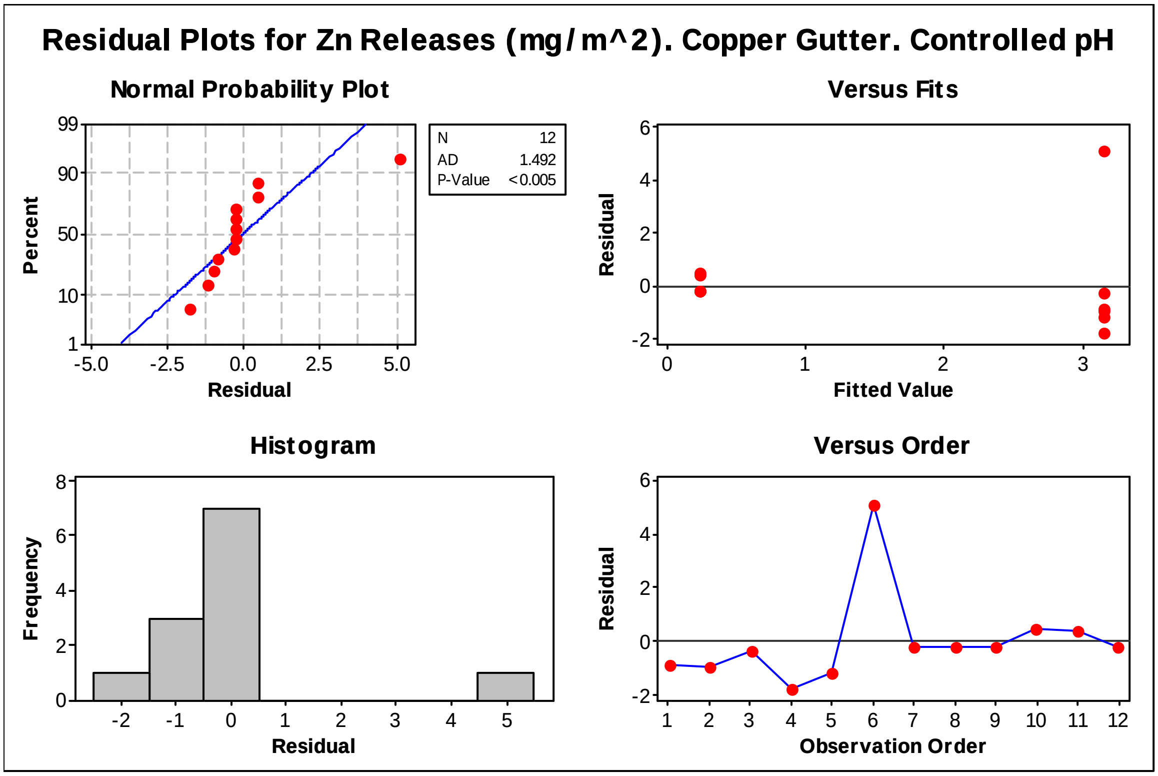


Figure A.7.71. Residual plots for Zn releases from copper gutter under controlled pH conditions.

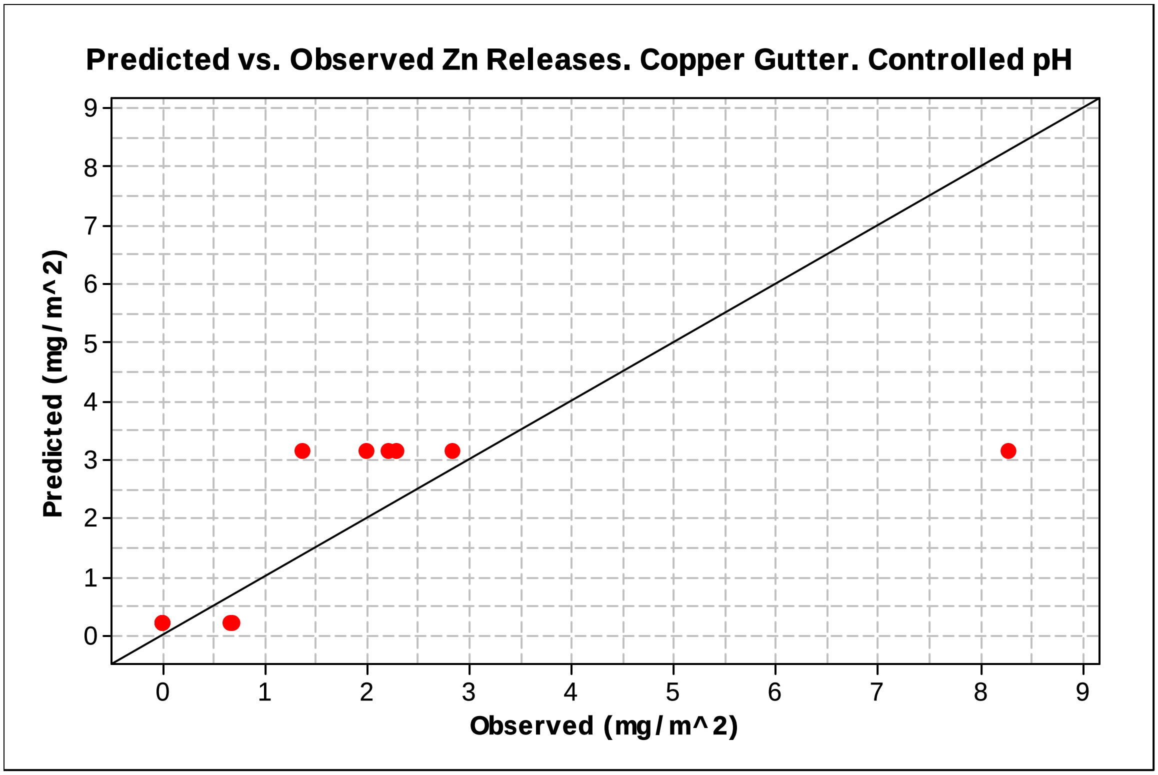


Figure A.7.72. Predicted vs. observed values for Zn releases. Copper gutter. Controlled pH.

Copper Gutter. Natural pH

Cu Releases, Copper Gutter, Natural pH

Factorial Analysis:

```
Analysis of Variance for Y, using Adjusted SS for Tests

Source      DF   Seq SS   Adj SS   Adj MS     F      P
Cond         1  1444672  1444672  1444672  5.62  0.045
Time         1  1696573  1696573  1696573  6.60  0.033
Cond*Time    1   911283   911283   911283  3.55  0.096
Error        8  2055839  2055839   256980
Total       11  6108367


S = 506.932   R-Sq = 66.34%   R-Sq(adj) = 53.72%

Term          Coef  SE Coef      T      P
Constant     488.4    146.3   3.34  0.010
Cond         347.0    146.3   2.37  0.045
Time        -376.0    146.3  -2.57  0.033
Cond*Time   -275.6    146.3  -1.88  0.096
```

Regression Analysis:

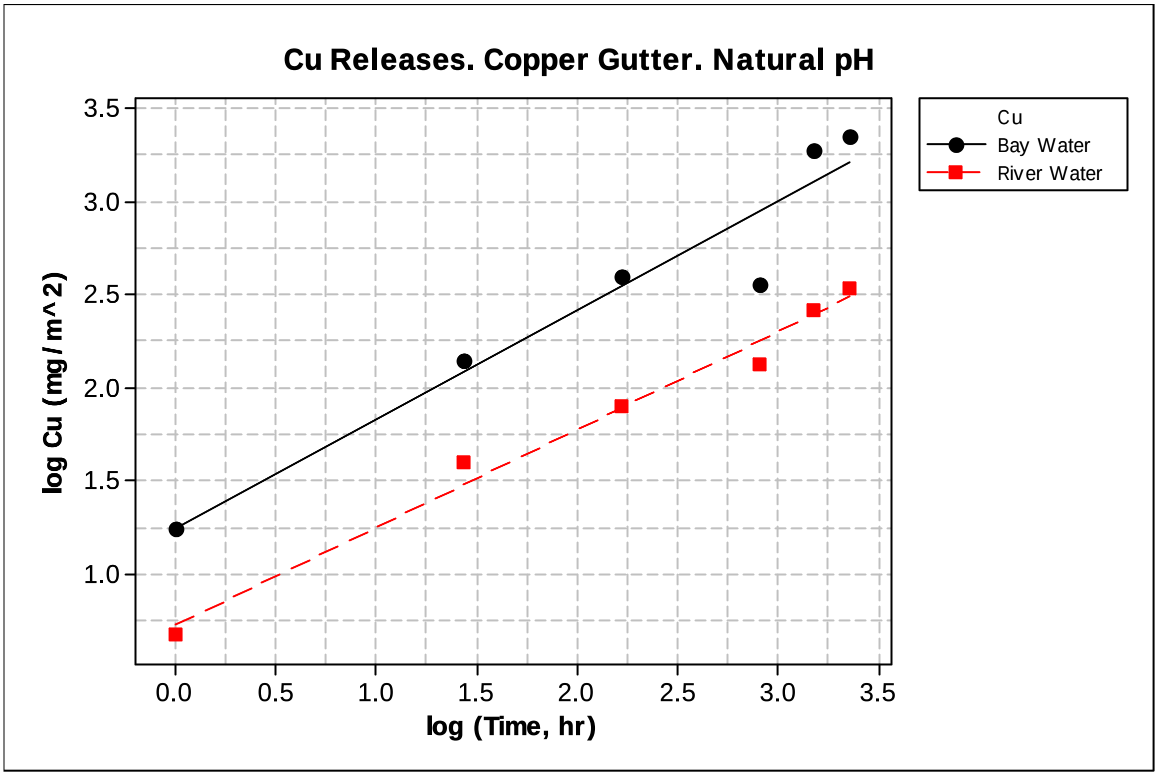


Figure A.7.73. Linear regression for Cu releases. Copper gutter. Natural pH.

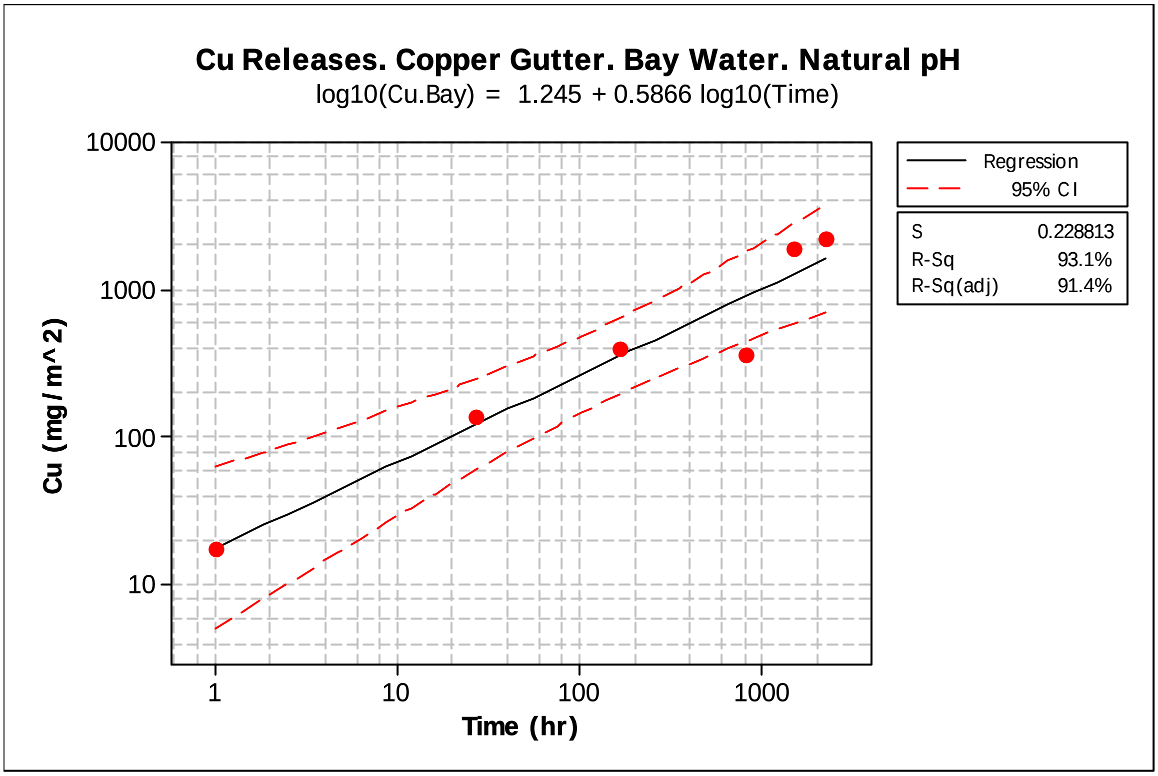


Figure A.7.74. Linear regression for Cu releases. Copper gutter. Bay water.

```
The regression equation is
logCu.Bay = 1.24 + 0.587 logTime


Predictor      Coef  SE Coef     T      P
Constant     1.2450   0.1977  6.30  0.003
logTime     0.58665  0.07978  7.35  0.002


S = 0.228813   R-Sq = 93.1%   R-Sq(adj) = 91.4%


Analysis of Variance

Source          DF      SS      MS      F      P
Regression       1  2.8310  2.8310  54.07  0.002
Residual Error   4  0.2094  0.0524
Total            5  3.0405
```

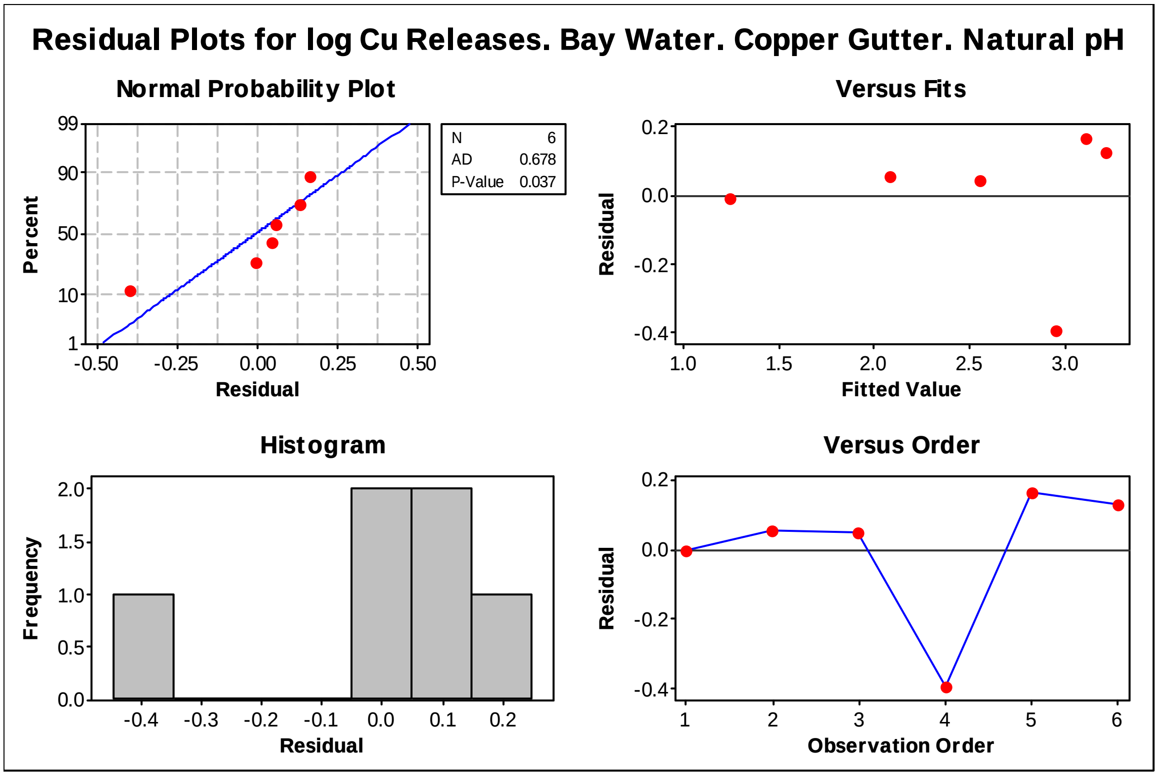


Figure A.7.75. Residual plots for Cu releases from copper gutter. Bay water.

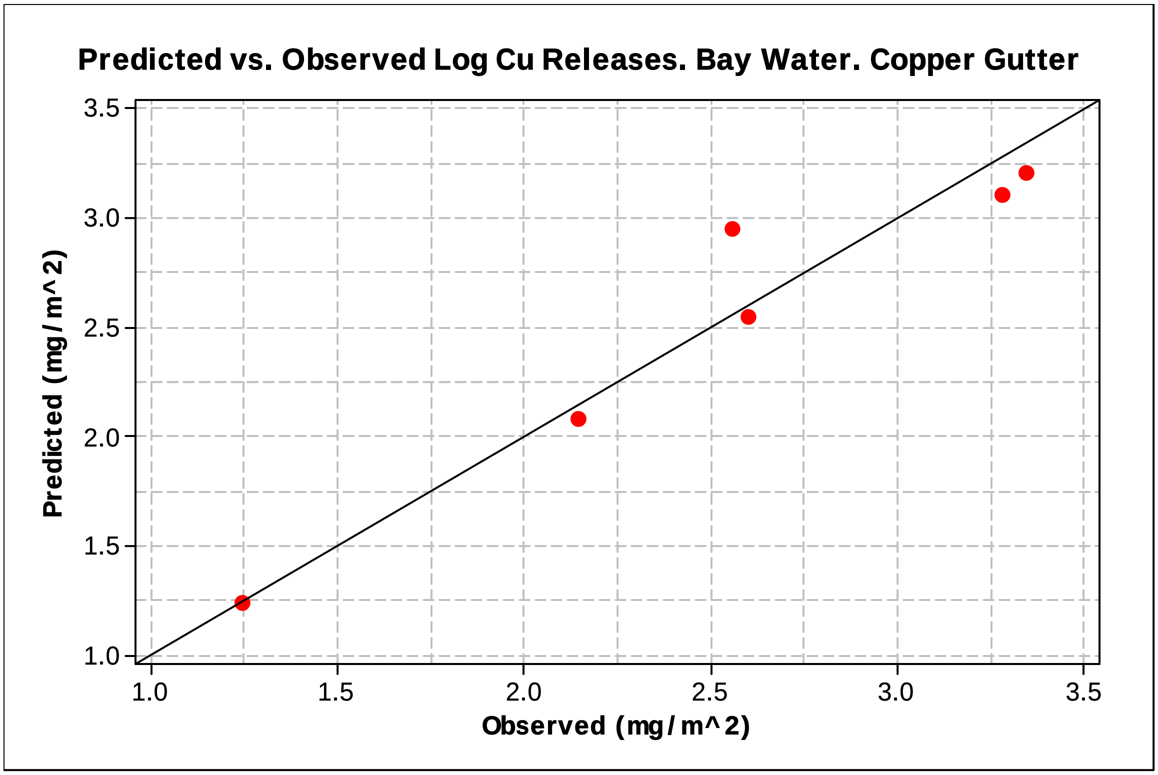


Figure A.7.76. Predicted vs. observed values for Cu releases. Copper gutter. Bay water.

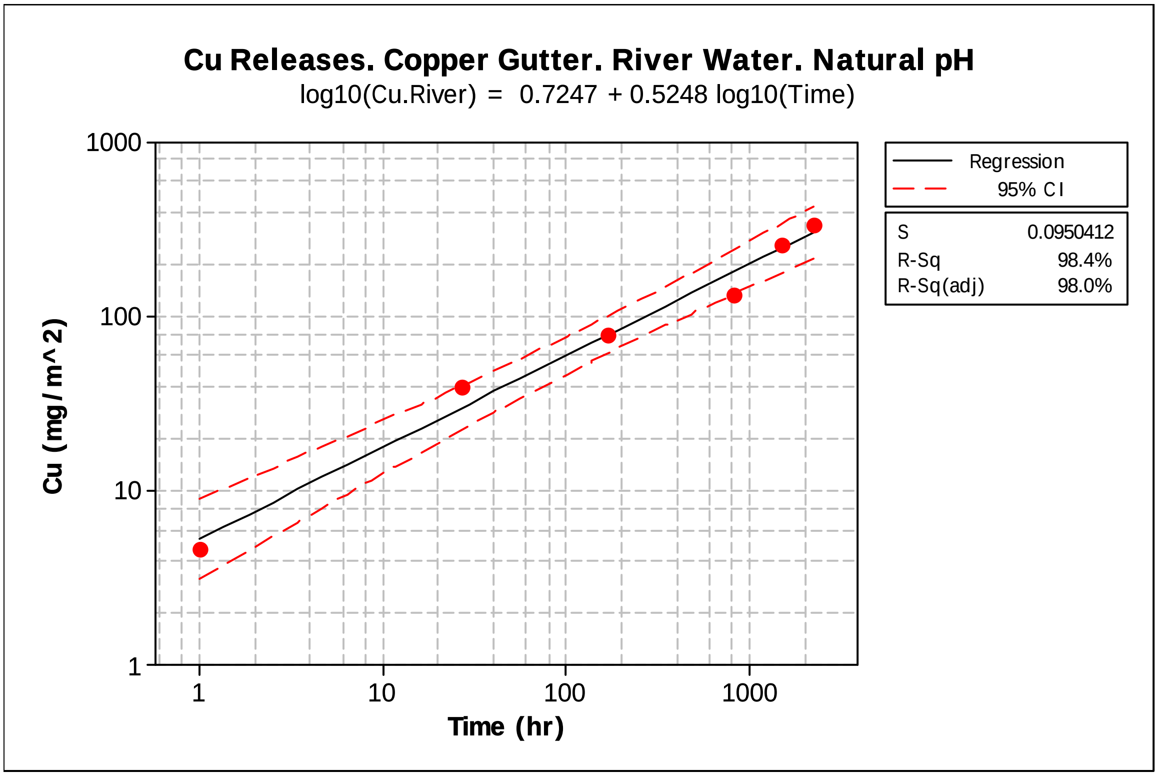


Figure A.7.77. Linear regression for Cu releases. Copper gutter. River water.

```
The regression equation is
logCu.Riv = 0.725 + 0.525 logTime


Predictor      Coef  SE Coef      T      P
Constant    0.72467  0.08210   8.83  0.001
logTime     0.52476  0.03314  15.84  0.000


S = 0.0950412   R-Sq = 98.4%   R-Sq(adj) = 98.0%


Analysis of Variance

Source          DF      SS      MS       F      P
Regression       1  2.2653  2.2653  250.78  0.000
Residual Error   4  0.0361  0.0090
Total            5  2.3014

Durbin-Watson statistic = 2.30949
```

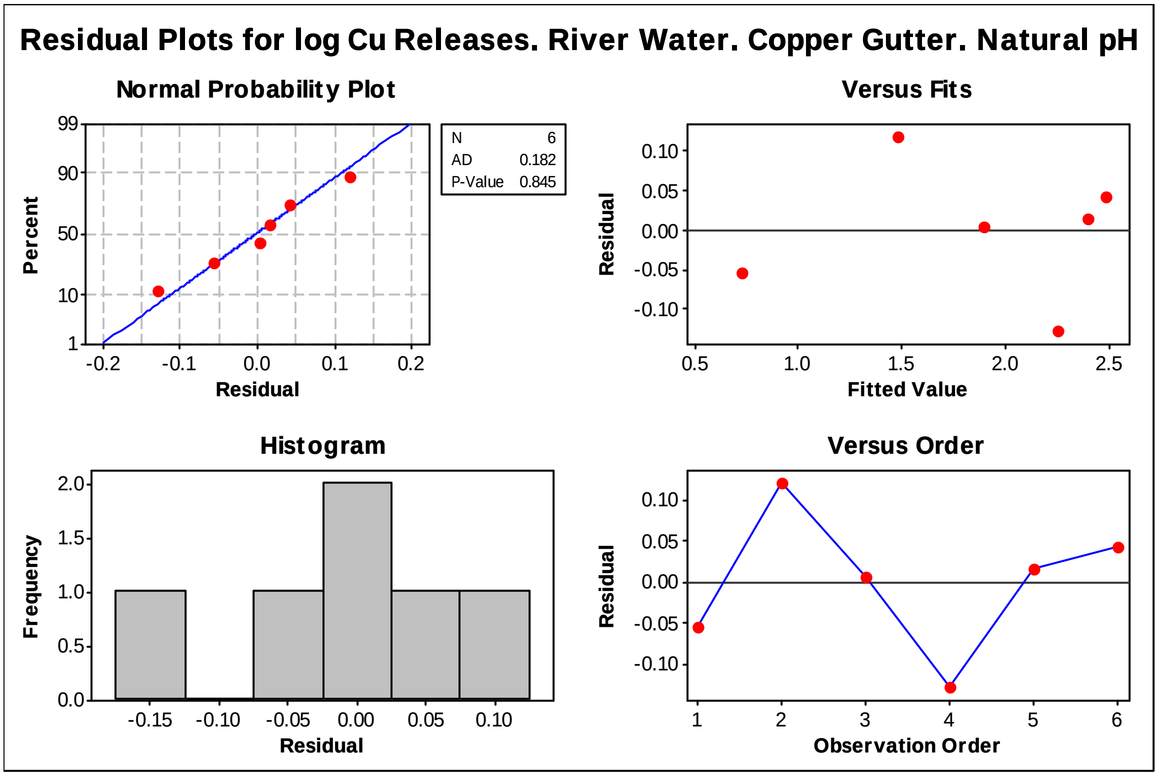


Figure A.7.78. Residual plots for Cu releases from copper gutter. River water.

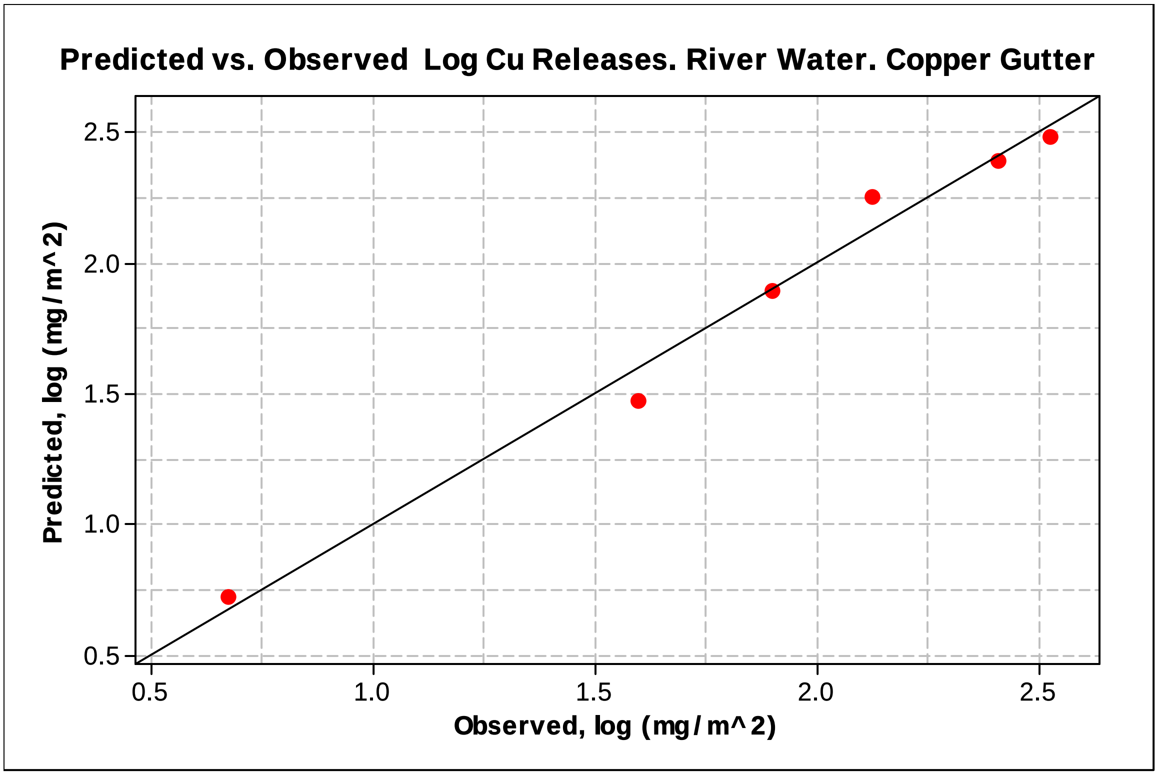


Figure A.7.79. Predicted vs. observed values for Cu releases. Copper gutter. River water.

Zn Releases, Copper Gutter, Natural pH

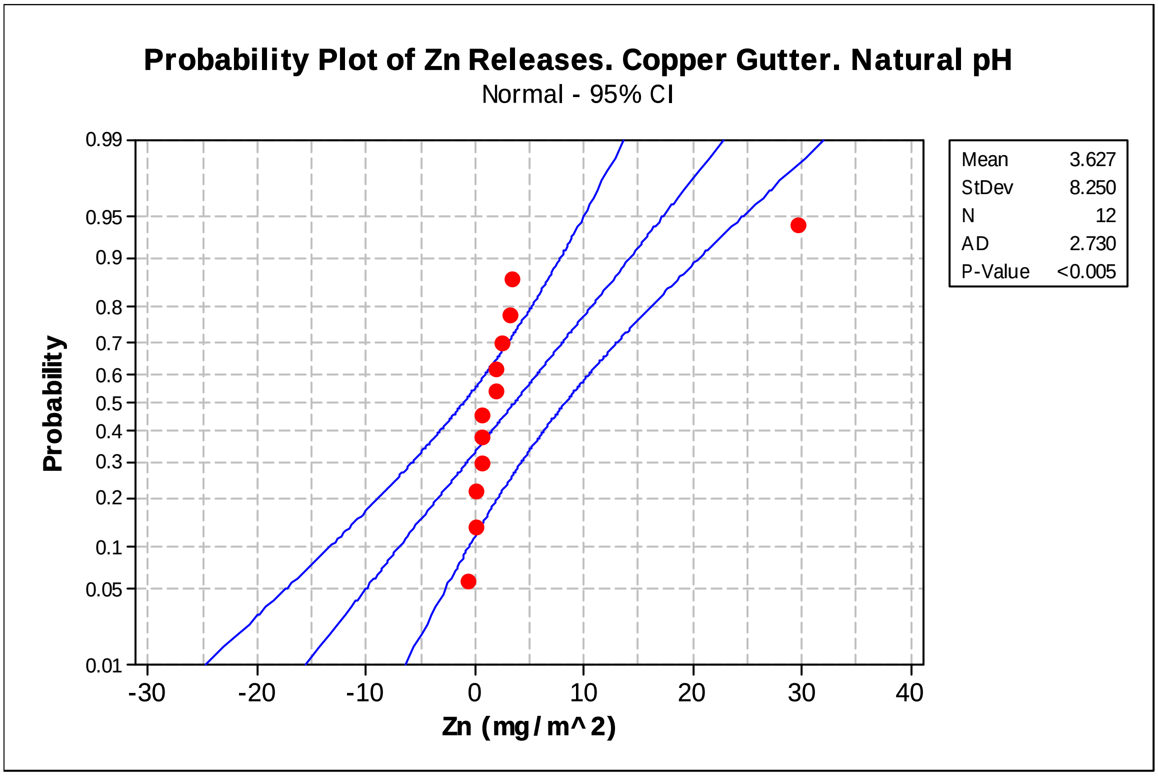


Figure A.7.80. Probability for Zn releases. Copper gutter. Natural pH.

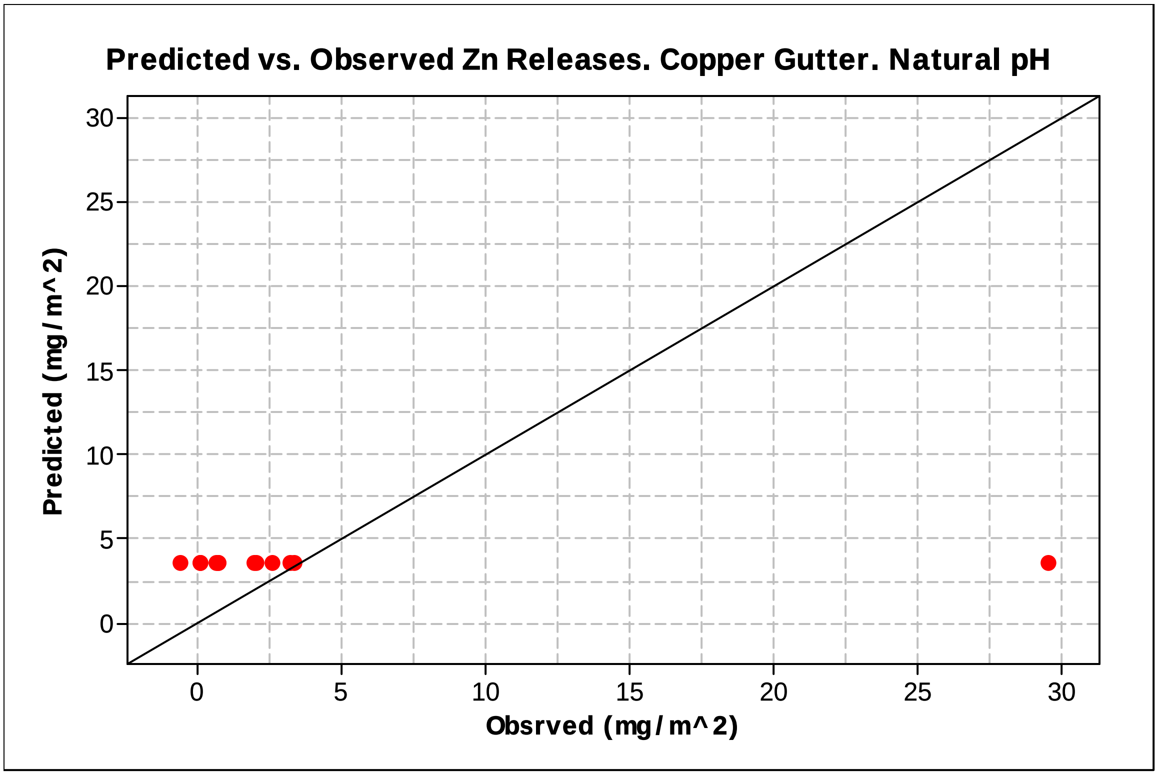


Figure A.7.81. Predicted vs. observed values for Zn releases. Copper Gutter. Natural pH.

Table A.7.1. 2^2 Factorial Analyses. Buffered Tests

Material	Constituent	Estimate of Variance, S^2	Variance of an Effect, V(eff.)	Standard Error of Main Effects and Interactions, SE (eff.)	Average Effect and Standard Error of Average Effect	pH Effect	Time Effect	(pH x Time) Interaction	Avg.	COV
Concrete Pipe	Pb	ND								
	Cu	ND								
	Zn	1.15	0.38	0.62	2.37 ± 0.30	1.39	0.79	0.82	2.37	0.55
PVC Pipe	Pb	ND								
	Cu	0.65	0.22	0.47	2.32 ± 0.84	-0.85	4.95	-0.51		
	Zn	21.20	7.07	2.66	4.28 ± 1.74	2.95	9.86	1.62		
HDPE Pipe	Pb	ND								
	Cu	0.07	0.02	0.15	0.42 ± 0.07	0.07	0.39	0.07		
	Zn	0.04	0.013	0.11	0.31 ± 0.15	-0.72	0.54	-0.03		
Steel Pipe	Pb	64.78	21.59	4.65	7.10 ± 2.54	4.35	13.96	4.35		
	Cu	1.65	0.55	0.74	0.94 ± 0.19	-0.45	0.95	-0.45	0.94	1.32
	Zn	551811	183937	428.88	608.79 ± 219.59	516.76	957.51	743.00	608.79	1.54
Vinyl Gutter	Pb	ND								
	Cu	0.11	0.04	0.19	1.47 ± 0.19	-0.45	0.94	-0.45		
	Zn	0.60	0.20	0.45	1.96 ± 0.28	1.41	0.88	0.38		
Aluminum Gutter	Pb	ND								
	Cu	0.01	0.0017	0.04	1.78 ± 0.27	0.00	1.64	0.00		
	Zn	16.62	5.54	2.35	3.29 ± 0.96	3.89	3.35	2.59	3.29	1.40
Steel Gutter	Pb	0.05	0.02	0.13	1.61 ± 0.63	1.76	2.86	1.67		
	Cu	0.01	4.77E-03	0.07	0.69 ± 0.11	0.39	0.34	0.39		
	Zn	1010201	336734	580	712.61 ± 254.49	616.08	1087.14	877.54	712.61	1.64
Copper Gutter	Pb	ND								
	Cu	15135	5045	71.03	159.98 ± 35.07	-178.99	109.75	13.56		
	Zn	3.70	1.23	1.11	1.69 ± 0.52	-2.93	0.94	-0.49		

Footnote: Statistically significant effects and their interactions are highlighted in red.

Table A.7.2. 2^2 Factorial Analyses. Natural pH Tests

Material	**Constituent**	**Estimate of Variance, S^2**	**Variance of an Effect, V(eff.)**	**Standard Error of Main Effects and Interactions, SE (eff.)**	**Average Effect and Standard Error of Average Effect**	**pH Effect**	**Time Effect**	**(pH x Time) Interaction**	**Avg.**	**COV**
Concrete Pipe	Pb	ND								
	Cu	ND								
	Zn	ND								
PVC Pipe	Pb	ND								
	Cu	ND								
	Zn	0.04	0.014	0.12	0.54 ± 0.06	0.21	0.19	0.21	0.54	0.47
HDPE Pipe	Pb	ND								
	Cu	ND								
	Zn	1.13E-05	3.78E-06	1.94E-03	0.10 ± 0.06	-0.21	0.20	0.21		
Steel Pipe	Pb	0.03	0.01	0.10	0.26 ± 0.05	0.01	4.84E-03	0.31		
	Cu	ND								
	Zn	833199	277733	527	1220.88 ± 337.83	-9.24	2025.56	75.56		
Vinyl Gutter	Pb	ND								
	Cu	ND								
	Zn	0.61	0.20	0.45	1.16 ± 0.11	-0.28	0.53	-0.28	1.16	0.65
Aluminum Gutter	Pb	ND								
	Cu	ND								
	Zn	268.35	89.45	9.46	4.93 ± 2.86	-10.74	9.86	-9.01	4.93	3.36
Steel Gutter	Pb	0.31	0.10	0.32	0.45 ± 0.16	0.53	0.58	0.52	0.45	1.20
	Cu	ND								
	Zn	4017349	1339116	1157	11617.64 ± 732.02	2243.11	2992.73	2302.78		
Copper Gutter	Pb	ND								
	Cu	256980	85660	293	488.43 ± 193.71	-693.94	752.01	-551.15		
	Zn	66.12	22.04	4.69	3.63 ± 1.43	3.40	5.51	5.59	3.63	2.27

Footnote: Statistically significant effects and their interactions are highlighted in red.

The significant p-values and the 2^2 Factorial Effect/Pooled Standard Error of the Effect Ratio are highlighted in red.

Table A.7.3. 2^2 Factorial Effect/Pooled Standard Error of the Effect Ratio. Buffered Tests

		Effect/Standard Error of the Effect		
Material	**Constituent**	**pH Effect/SE(eff.)**	**Time Effect/SE(eff.)**	**(pH x Time) Effect/SE(eff.)**
P. Concrete	Pb	ND at pH 5 and 8		
	Cu	ND at pH 5 and 8		
	Zn	2.24	1.27	1.32
P. PVC	Pb	ND at pH 5 and 8		
	Cu	-1.82	10.63	-1.10
	Zn	1.11	3.71	0.61
P. HDPE	Pb	ND at pH 5 and 8		
	Cu	0.44	2.53	0.44
	Zn	-6.38	4.80	-0.31
P. Steel	Pb	0.94	3.00	0.94
	Cu	-0.61	1.29	-0.61
	Zn	1.20	2.23	1.73
G. Vinyl	Pb	ND at pH 5 and 8		
	Cu	-2.35	4.89	-2.35
	Zn	3.14	1.97	0.86
G. Aluminum	Pb	ND at pH 5 and 8		
	Cu	0.00	39.50	0.00
	Zn	1.65	1.42	1.10
G. Steel	Pb	13.31	21.60	12.62
	Cu	5.62	4.87	5.62
	Zn	1.06	1.87	1.51
G. Copper	Pb	ND at pH 5 and 8		
	Cu	-2.52	1.55	0.19
	Zn	-2.63	0.85	-0.44

Footnote: Statistically significant effect/pooled standard error of the effect ratios are highlighted in red.

Table A.7.4. P-Value of the 2^2 Factorial Effect. Buffered Tests

		P-value		
Material	**Constituent**	**pH Effect P-value**	**Time Effect P-value**	**(pH x Time) Effect P-value**
P. Concrete	Pb	ND at pH 5 and 8		
	Cu	ND at pH 5 and 8		
	Zn	0.055	0.239	0.222
P. PVC	Pb	ND at pH 5 and 8		
	Cu	0.106	0.000	0.303
	Zn	0.300	0.006	0.559
P. HDPE	Pb	ND at pH 5 and 8		
	Cu	0.670	0.035	0.670
	Zn	0.0002	0.001	0.768
P. Steel	Pb	0.377	0.017	0.377
	Cu	0.560	0.234	0.560
	Zn	0.263	0.056	0.121
G. Vinyl	Pb	ND at pH 5 and 8		
	Cu	0.047	0.001	0.047
	Zn	0.014	0.084	0.417
G. Aluminum	Pb	ND at pH 5 and 8		
	Cu	1.000	1.85E-10	1.000
	Zn	0.137	0.192	0.303
G. Steel	Pb	9.67E-07	2.22E-08	1.46E-06
	Cu	0.0005	0.001	0.0005
	Zn	0.319	0.098	0.169
G. Copper	Pb	ND at pH 5 and 8		
	Cu	0.036	0.161	0.853
	Zn	0.030	0.422	0.669

Footnote: Statistically significant effect/pooled standard error of the effect ratios are highlighted in red.

Figure A.7.82. Shows the relationship between factorial effect/pooled standard error ratio and p-value. 0.05 p-value corresponds to 2.3 Factorial Effect/Pooled standard error ratio.

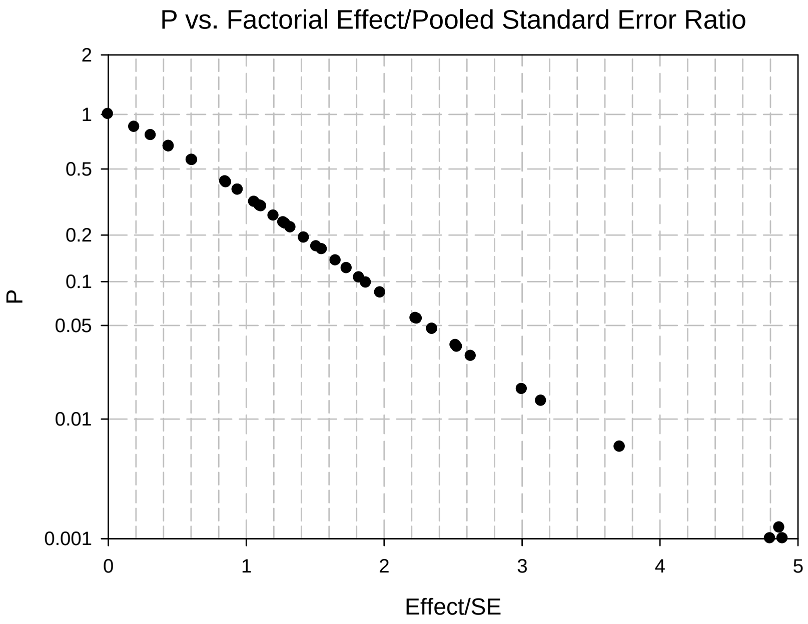


Figure A.7.82. P-value vs. 2^2 Factorial effect/pooled standard error ratio. Buffered Tests

Table A.7.5. 2^2 Factorial Effect/Pooled Standard Error of the Effect Ratio. Natural pH Tests.

		Effect/Standard Error of the Effect		
Material	**Constituent**	**Conductivity Effect/SE(eff.)**	**Time Effect/SE(eff.)**	**(Cond. x Time) Effect/SE(eff.)**
P. Concrete	Pb	ND		
	Cu	ND		
	Zn	ND		
P. PVC	Pb	ND		
	Cu	ND		
	Zn	1.77	1.59	1.77
P. HDPE	Pb	ND		
	Cu	ND		
	Zn	-105.97	100.77	105.97
P. Steel	Pb	0.10	0.05	3.15
	Cu	ND		
	Zn	-0.02	3.84	0.14
G. Vinyl	Pb	ND		
	Cu	ND		
	Zn	-0.63	1.17	-0.63
G. Aluminum	Pb	ND		
	Cu	ND		
	Zn	-1.14	1.04	-0.95
G. Steel	Pb	1.64	1.78	1.60
	Cu	ND		
	Zn	1.94	2.59	1.99
G. Copper	Pb	ND		
	Cu	-2.37	2.57	-1.88
	Zn	0.73	1.17	1.19

Footnote: Statistically significant effect/pooled standard error of the effect ratios are highlighted in red.

Table A.7.6. P-Value of the 2^2 Factorial Effects. Natural pH Tests.

		P-value		
Material	**Constituent**	**pH Effect P-value**	**Time Effect P-value**	**(pH x Time) Effect P-value**
P. Concrete	Pb	ND		
	Cu	ND		
	Zn	ND		
P. PVC	Pb	ND		
	Cu	ND		
	Zn	0.114	0.151	0.114
P. HDPE	Pb	ND		
	Cu	ND		
	Zn	0.000	0.000	0.000
P. Steel	Pb	0.922	0.962	0.014
	Cu	ND		
	Zn	0.986	0.005	0.890
G. Vinyl	Pb	ND		
	Cu	ND		
	Zn	0.545	0.277	0.545
G. Aluminum	Pb	ND		
	Cu	ND		
	Zn	0.289	0.328	0.369
G. Steel	Pb	0.139	0.113	0.149
	Cu	ND		
	Zn	0.089	0.032	0.082
G. Copper	Pb	ND		
	Cu	0.045	0.033	0.096
	Zn	0.489	0.274	0.268

Footnote: Statistically significant effect/pooled standard error of the effect ratios are highlighted in red.

Figure A.7.83. Shows the relationship between factorial effect/pooled standard error ratio and p-value. The ratio must be at least 2.3 to correspond to a p value of 0.05, or less, for these conditions.

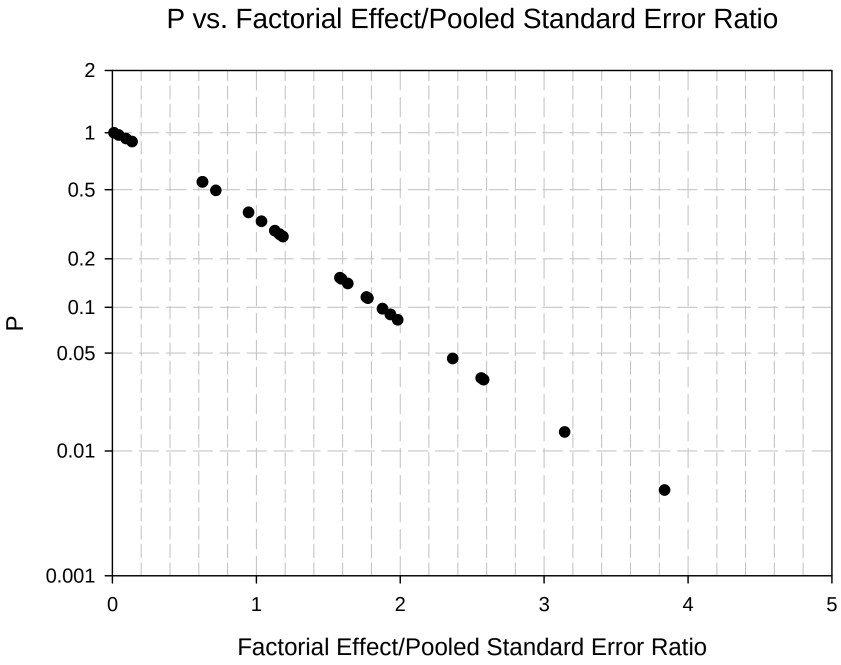


Figure A.7.83. P-value vs. 2^2 Factorial effect/pooled standard error ratio. Natural pH Tests.

A.8 Mann-Whitney Test Results

This section shows Mann-Whitney test results. Statistically significant p-values (α = 0.05) are highlighted in red.

Table A.8.1 Mann-Whitney test P-values for zinc releases under controlled pH conditions.

	Con	**PVC S.**	**PVC L.**	**HDPE 5**	**HDPE 8**	**HDPE S.**	**HDPE L**	**P. St**	**Vinyl 5**	**Vinyl 8**	**Alum**	**G.St**	**Cop. 5**	**Cop.8**
Con		<0.001	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001	0.013	0.325	0.931	<0.001	0.281	<0.001
PVC S.			0.002	0.015	0.18	0.18	0.015	<0.001	0.002	0.002	<0.001	<0.001	0.002	0.065
PVC L.				0.002	0.002	0.002	0.002	0.028	0.003	0.003	0.004	0.017	0.041	0.002
HDPE 5					0.004	0.026	0.589	<0.001	0.18	0.009	0.01	<0.001	0.002	0.132
HDPE 8						0.589	0.026	<0.001	0.002	0.002	<0.001	<0.001	0.002	0.24
HDPE S							0.132	<0.001	0.002	0.002	<0.001	<0.001	0.002	0.394
HDPE L								<0.001	0.18	0.009	0.01	<0.001	0.002	0.24
P. St									0.001	0.003	<0.001	0.795	0.022	<0.001
Vinyl 5										0.026	0.174	<0.001	0.026	0.002
Vinyl 8											0.281	<0.001	0.699	0.002
Alum												<0.001	0.482	<0.001
G.St													0.002	<0.001
Cop. 5														0.002
Cop.8														

Footnote: Values below detection limit (DL) were substituted with the half of detection limit value. For zinc DL was 0.02 mg/L. (For vinyl gutter at pH 5 there was only one data point above DL at two month of exposure).

Con = Concrete pipe, all data combined (short and long exposure times, both pH 5 and pH 8)
PVC S = PVC pipe during short exposure time, both pH 5 and pH 8 are combined;
PVC L = PVC pipe during long exposure time, both pH 5 and pH 8 are combined;
HDPE 5 = HDPE pipe at pH 5 (short and long exposure times are combined);
HDPE 8 = HDPE pipe at pH 8 (short and long exposure times are combined)
HDPE S = HDPE pipe during short exposure time, both pH 5 and pH 8 are combined
HDPE L = HDPE pipe during short exposure time, both pH 5 and pH 8 are combined
P.St = Steel pipe, all data combined (short and long exposure times, both pH 5 and pH 8)
Vin 5 = Vinyl gutter at pH 5 (short and long exposure times are combined)
Vin 8 = Vinyl gutter at pH 8 (short and long exposure times are combined)
Al = Aluminum gutter, all data combined (short and long exposure times, both pH 5 and pH 8)
G.St = Steel gutter, all data combined (short and long exposure times, both pH 5 and pH 8)
Cop.5 = Copper gutter at pH 5 (short and long exposure times are combined);
Cop.8 = Copper gutter at pH 8 (short and long exposure times are combined)

Table A.8.2. Mann-Whitney test P-values for zinc releases under natural pH conditions.

	Con	PVC	HDPE S B	HDPE S R	HDPE L B	HDPE L R	P. St S	P. St L	Vinyl	Alum	G. St S	G. St L	Cop
Con		<0.001	all ND	0.011	all ND	0.011	<0.001	<0.001	0.006	<0.001	0.027	<0.001	0.977
PVC			0.011	0.011	0.011	0.011	<0.001	<0.001	<0.001	0.885	0.027	<0.001	0.088
HDPE S B				0.1	all ND	0.100	0.024	0.024	0.011	0.718	0.167	0.024	0.219
HDPE S R					0.100	0.100	0.024	0.024	0.011	0.427	0.167	0.024	0.036
HDPE L B						1.000	0.024	0.024	0.011	0.718	0.167	0.024	0.219
HDPE L R							0.024	0.024	0.011	0.718	0.167	0.024	0.219
P. St S								0.002	<0.001	0.001	0.24	0.026	0.001
P. St L									<0.001	<0.001	0.002	0.818	<0.001
Vinyl										0.003	<0.001	<0.001	0.795
Alum											0.002	<0.001	0.214
G. St S												0.015	0.035
G. St L													<0.001
Cop													

Footnote: Values below detection limit were substituted with the half of detection limit value. The detection limit for zinc was 0.02 mg/L.

Con = Concrete pipe, all data combined (short and long exposure times, both bay and river waters)
PVC = PVC pipe, all data combined (short and long exposure time, both bay and river waters)
HDPE S B = HDPE pipe, short exposure time, bay water
HDPE S R = HDPE pipe, short exposure time, river water
HDPE L B = HDPE pipe, long exposure time, bay water
HDPE L R = HDPE pipe, long exposure time, river water
P.St S = Steel pipe, short exposure time, both bay and river waters combined
P.St L = Steel pipe, long exposure times, both bay and river waters combined
Vin = Vinyl gutter, all data combined (short and long exposure times, both bay and river waters)
Al = Aluminum gutter, all data combined (short and long exposure times, both bay and river waters)
G.St S = Steel gutter, short exposure times, both bay and river waters combined
G. St L= Steel gutter, long exposure times, both bay and river waters combined
Cop = Copper gutter, all data combined (short and long exposure times, both bay and river waters)

Table A.8.3. Mann-Whitney test P-values for copper releases under controlled pH conditions.

	Con	PVC S	PVC L	HDPE S	HDPE L	P.St	Vin S 5	Vin S 8	Vin L 5	Vin L 8	Alum S	Alum L	G. St S 5	G. St S 8	G. St S 8	G. St L 8	Cop 5	Cop 8
Con		<0.001	<0.001	all ND	<0.001	<0.001	all ND	all ND	0.011	0.425	all ND	<0.001	all ND	all ND	all ND	0.011	<0.001	<0.001
PVC S			0.002	0.065	0.009	0.013	0.024	0.024	0.024	0.024	0.002	0.002	0.048	0.048	0.167	0.024	0.002	0.002
PVC L				0.002	0.002	0.002	0.024	0.024	0.024	0.024	0.002	0.002	0.024	0.024	0.024	0.024	0.002	0.31
HDPE S					0.065	<0.001	all ND	all ND	0.024	0.024	all ND	0.002	all ND	all ND	all ND	0.024	0.002	0.002
HDPE L						0.814	0.167	0.167	0.024	0.048	0.065	0.002	0.548	0.548	0.548	0.048	0.002	0.002
P.St							0.219	0.219	0.036	0.07	0.1	0.006	0.219	0.219	0.717	0.07	<0.001	0.002
Vin S 5								all ND	0.1000	0.700	all ND	0.024	all ND	all ND	all ND	0.4	0.024	0.024
Vin S 8									0.1000	0.700	all ND	0.024	all ND	all ND	all ND	0.4	0.024	0.024
Vin L 5										0.100	0.024	0.905	0.100	0.100	0.100	0.100	0.024	0.095
Vin L 8											0.262	0.024	0.100	0.100	0.100	0.7	0.024	0.024
Alum S												0.002	all ND	all ND	all ND	0.095	0.002	0.002
Alum L													0.024	0.024	0.024	0.024	0.002	0.065
G. St S 5														all ND	all ND	0.100	0.024	0.024
G. St S 8															all ND	0.100	0.024	0.024
G. St L pH5																0.100	0.024	0.024
G. St L 8																	0.024	0.024
Cop 5																		0.065
Cop 8																		

Footnote: Values below detection limit were substituted with the half of detection limit value. Detection limit for copper was 0.02 mg/L. Copper was not detected for concrete and HDPE pipes. Also, copper was not detected for vinyl gutter during short time exposure at both pH 5 and 8, for aluminum gutter during short time of exposure, for steel gutter during short time exposure at pH 5 and pH 8, as well as for steel gutter during long time of exposure at pH 5. (For steel pipe there was only one data point above DL at one month of exposure).

Con = Concrete pipe, all data combined (short and long exposure times, both pH 5 and pH 8)

PVC. S = PVC pipe during short exposure time, both pH 5 and pH 8 are combined

PVC.L = PVC pipe during long exposure time, both pH 5 and pH 8 are combined
HDPE. S = HDPE pipe during short exposure time, both pH 5 and pH 8 are combined
HDPE.L = HDPE pipe during long exposure time, both pH 5 and pH 8 are combined
P.St = Steel pipe, all data combined (short and long exposure times, both pH 5 and pH 8)
Vin.S5 = Vinyl gutter during short time exposure at pH 5
Vin.S8 = Vinyl gutter during short time exposure at pH 8
Vin.L5 = Vinyl gutter during long time exposure at pH 5
Vin.L8 = Vinyl gutter during long time exposure at pH 8
Al.S = Aluminum gutter during short exposure time, both pH 5 and pH 8 are combined
Al.L = Aluminum gutter during long exposure time, both pH 5 and pH 8 are combined
G.St.S5 = Steel gutter during short time exposure at pH 5
G.St.S8 = Steel gutter during short time exposure at pH 8
G.St.L5 = Steel gutter during long time exposure at pH 5
G.St.L8 = Steel gutter during long time exposure at pH 8
Cop.5 = Copper gutter at pH 5 (short and long exposure times are combined)
Cop.8 = Copper gutter at pH 8 (short and long exposure times are combined)

Table A.8.4. Mann-Whitney test P-values for copper releases under natural pH conditions.

	Con	**PVC**	**HDPE**	**P. St**	**Vin**	**Alum**	**G. St**	**Cop Bay**	**Cop River**	**Cop S**	**Cop L**
Con		all ND	all ND	all ND	all ND	all ND	all ND	<0.001	<0.001	<0.001	<0.001
PVC			all ND	all ND	all ND	all ND	all ND	<0.001	<0.001	<0.001	<0.001
HDPE				all ND	all ND	all ND	all ND	<0.001	<0.001	<0.001	<0.001
P.St					all ND	all ND	all ND	<0.001	<0.001	<0.001	<0.001
Vin						all ND	all ND	<0.001	<0.001	<0.001	<0.001
Alum							all ND	<0.001	<0.001	<0.001	<0.001
G. St								0.002	0.003	0.004	0.001
Cop Bay									0.093	0.093	0.937
Cop Riv										0.699	0.026
Cop S											0.041
Cop L											

Footnote: Values below detection limit were substituted with the half of detection limit value. The detection limit for copper was 0.02 mg/L. Copper was not detected for concrete, PVC, HDPE, and steel pipes, and for vinyl, Aluminum, and steel gutters.

Con = Concrete pipe, all data combined (short and long exposure times, both bay and river waters)
PVC = PVC pipe, all data combined (short and long exposure times, both bay and river waters)
HDPE = HDPE, all data combined (short and long exposure times, both bay and river waters)
P.St = Steel pipe, all data combined (short and long exposure times, both bay and river waters)
Vin. = Vinyl gutter, all data combined (short and long exposure times, both bay and river waters)
Al = Aluminum gutter, all data combined (short and long exposure times, both bay and river waters)
G.St = Steel gutter, all data combined (short and long exposure times, both bay and river waters)
Cop.B = Copper gutter, bay water (short and long exposure times are combined)
Cop.R = Copper gutter, river water (short and long exposure times are combined)
Cop.S = Copper gutter, short exposure time (bay and river waters are combined)
Cop.L = Copper gutter, long exposure time (bay and river waters are combined)

Table A.8.5. Mann-Whitney test P-values for lead releases under controlled pH conditions.

	Con	**PVC**	**HDPE**	**P. St S**	**P. St L**	**Vin**	**Alum**	**G. St S pH5**	**G. St S pH8**	**G. St L pH5**	**G. St L pH8**	**Cop**
Con		all ND	all ND	all ND	0.027	all ND	all ND	all ND	0.011	0.011	0.011	all ND
PVC			all ND	all ND	0.017	all ND	all ND	all ND	0.011	0.011	0.011	all ND
HDPE				all ND	<0.001	all ND	all ND	all ND	0.011	0.011	0.011	all ND
P. St S					0.065	all ND	all ND	all ND	0.024	0.024	0.024	all ND
P. St L						0.027	0.027	0.167	0.167	0.167	0.167	0.027
Vin							all ND	all ND	0.425	0.011	0.011	all ND
Alum								all ND	0.425	0.011	0.011	all ND
G. St S pH5									0.400	0.100	0.100	all ND
G. St S pH8										0.100	0.100	0.425
G. St L pH5											0.100	0.011
G. St L pH8												0.011
Cop												

Footnote: Values below detection limit were substituted with the half of detection limit value. Detection limit for lead was 0.005 mg/L. Lead was not detected for concrete, PVC, HDPE pipes, as well as for steel pipe during short time exposure (both pH combined). Also, lead was not detected for Vinyl, Aluminum gutter, copper gutters, as well as for steel gutter during short time exposure at pH 5.

Con = Concrete pipe, all data combined (short and long exposure times, both pH 5 and pH 8)
PVC = PVC pipe, all data combined (short and long exposure times, both pH 5 and pH 8)
HDPE = HDPE pipe, all data combined (short and long exposure times, both pH 5 and pH 8)
P. St. S = Steel pipe during short exposure time, both pH 5 and pH 8 are combined
P. St. L = Steel pipe during long exposure time, both pH 5 and pH 8 are combined
Vin. = Vinyl gutter, all data combined (short and long exposure times, both pH 5 and pH 8)
Al = Aluminum gutter, all data combined (short and long exposure times, both pH 5 and pH 8)
G.St. S5 = Steel gutter during short time exposure at pH 5
G.St. S8 = Steel gutter during short time exposure at pH 8
G.St. L5 = Steel gutter during long time exposure at pH 5
G.St.L8 = Steel gutter during long time exposure at pH 8
Cop = Copper gutter, all data combined (short and long exposure times, both pH 5 and pH 8)

Table A.8.6 Mann-Whitney test P-values for lead releases under natural pH conditions.

	Con	**PVC**	**HDPE**	**P. St S Bay**	**P. St S Riv**	**P. St L Bay**	**P. St L Riv**	**Vin**	**Alum**	**G. St**	**Cop**
Con		all ND	all ND	0.05	all ND	all ND	0.425	all ND	all ND	0.04	all ND
PVC			all ND	0.011	all ND	all ND	0.425	all ND	all ND	<0.001	all ND
HDPE				0.011	all ND	all ND	0.011	all ND	all ND	<0.001	all ND
P. St S Bay					0.1	0.1	1	0.011	0.011	0.17	0.011
P. St S Riv						all ND	0.7	all ND	all ND	0.011	all ND
P. St L Bay							0.4	all ND	all ND	0.011	all ND
P. St L Riv								0.425	0.425	0.942	0.425
Vin									all ND	0.583	all ND
Alum										0.506	all ND
G. St											0.506
Cop											

Footnote: Values below detection limit were substituted with the half of detection limit value. For lead DL = 0.005 mg/L. Lead was not detected for concrete, PVC, HDPE pipes, as well as for steel pipe during long exposure time in bay water samples and during short exposure time in river water samples. Also, lead was not detected for vinyl, Aluminum gutter, copper gutters.

Con = Concrete pipe, all data combined (short and long exposure times, both bay and river waters)
PVC = PVC pipe, all data combined (short and long exposure times, both bay and river waters)
HDPE = HDPE pipe, all data combined (short and long exposure times, both bay and river waters)
P. St. S B = Steel pipe during short exposure time, bay water
P. St. S R = Steel pipe during short exposure time, river water
P. St. L B = Steel pipe during long exposure time, bay water
P. St. L R = Steel pipe during long exposure time, river water
Vin = Vinyl gutter, all data combined (short and long exposure times, both bay and river waters)
Al = Aluminum gutter, all data combined (short and long exposure times, both bay and river waters)
G. St = Steel gutter, all data combined (short and long time exposure, both bay and river waters)
Cop = Copper gutter, all data combined (short and long exposure times, both bay and river waters)

APPENDIX B: LINEAR REGRESSION ANALYSIS. MODEL FITTING

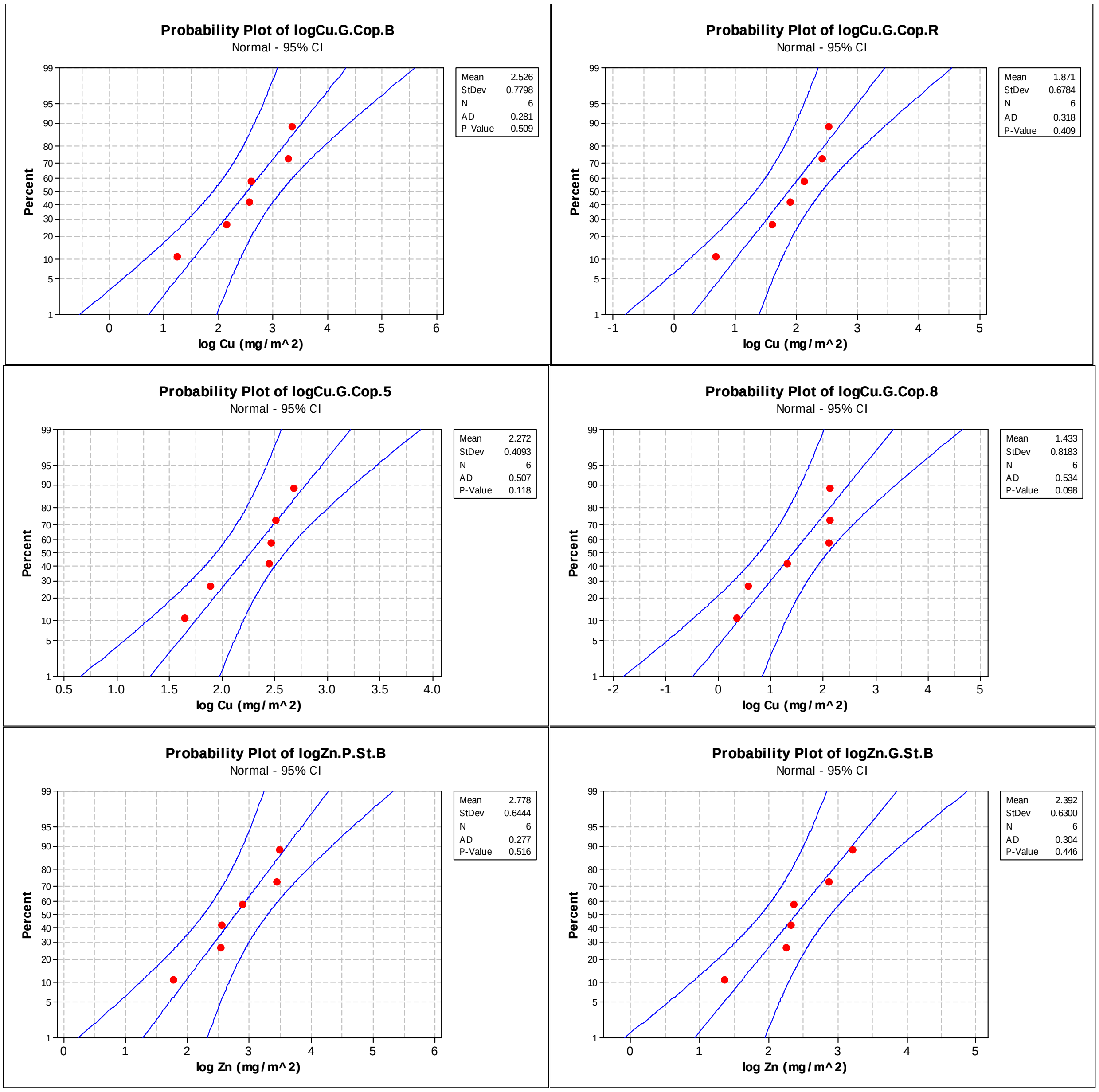


Figure B.1.1 Normal probability plots. Metal releases from pipe and gutter sections under various water conditions.

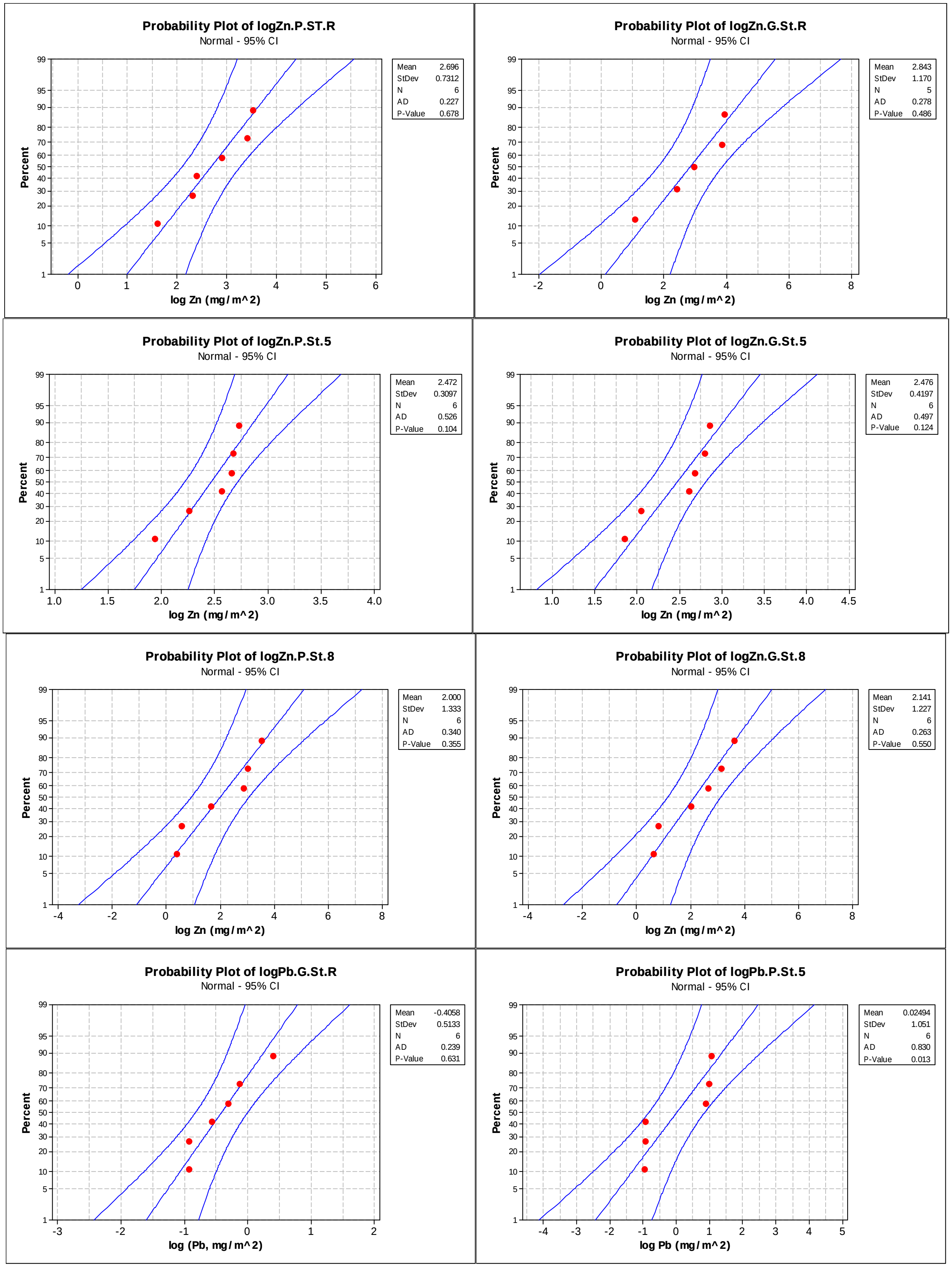


Figure B.1.1. - *Continued*

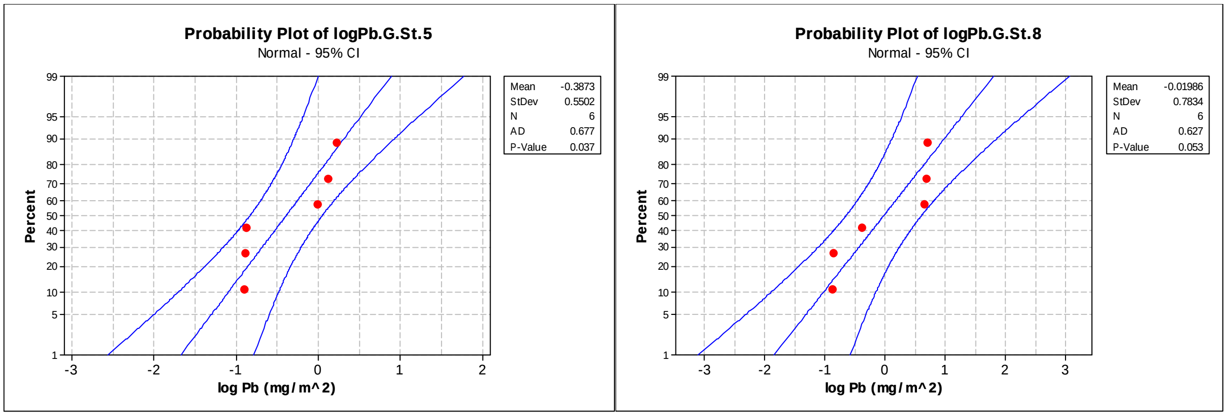


Figure B.1.1. - *Continued*

Table B.1.1 Check for the significance of the regression equations.

Pollutant, Material, Condition	**One –Way ANOVA**	**DF**	**Sum of Squares**	**Mean Square**	**F**	**P-value**
Log Cu, Copper Gutter, Bay Water	Regression	1	2.8310	2.8310	54.07	0.002
	Residual Error	4	0.2094	0.0524		
	Total	5	3.0405			
Log Cu, Copper Gutter, River Water	Regression	1	2.2653	2.2653	250.78	0.000
	Residual Error	4	0.0361	0.0090		
	Total	5	2.3014			
Log Cu, Copper Gutter, pH 5 Water (One Segment Linear Equation)	Regression	1	0.54266	0.54266	7.36	0.053
	Residual Error	4	0.29505	0.07376		
	Total	5	0.83771			
Log Cu, Copper Gutter, pH 5 Water (2 Segment Linear Equation)	Regression	3	0.8308	0.2769	80.5405	0.0123
	Residual Error	2	0.0069	0.0034		
	Total	5	0.8377	0.1675		
Log Cu, Copper Gutter, pH 8 Water	Regression	1	3.32599	3.32599	597.33	0.000
	Residual Error	4	0.02227	0.00557		
	Total	5	3.34826			
Log Zn, Steel Pipe, Bay Water	Regression	1	1.8710	1.8710	36.51	0.004
	Residual Error	4	0.2050	0.0512		
	Total	5	2.0760			
Log Zn, Steel Gutter, Bay Water	Regression	1	1.5804	1.5804	15.64	0.017
	Residual Error	4	0.4043	0.1011		
	Total	5	1.9846			
Log Zn, Steel Pipe, River Water	Regression	1	2.3555	2.3555	29.62	0.006
	Residual Error	4	0.3181	0.0795		
	Total	5	2.6736			

Table B.1.1.-*Continued*

Pollutant, Material, Condition	**One –Way ANOVA**	**DF**	**Sum of Squares**	**Mean Square**	**F**	**P-value**
Log Zn, Steel Gutter, River Water (Linear Equation, Intercept Zero)	Regression	1	44.526	44.526	131.51	0.000
	Residual Error	4	1.354	0.339		
	Total	5	45.881			
Log Zn, Steel Pipe, pH 5 Water	Regression	1	0.36222	0.36222	12.34	0.025
	Residual Error	4	0.11743	0.02936		
	Total	5	0.47965			
Log Zn, Steel Gutter, pH 5 Water	Regression	1	0.62254	0.62254	9.64	0.036
	Residual Error	4	0.25832	0.06458		
	Total	5	0.88086			
Log Zn, Steel Pipe, pH 8 Water	Regression	1	8.7937	8.7937	380.26	0.000
	Residual Error	4	0.0925	0.0231		
	Total	5	8.8862			
Log Zn, Steel Gutter, pH 8 Water	Regression	1	6.8464	6.8464	40.38	0.003
	Residual Error	4	0.6782	0.1695		
	Total	5	7.5246			
Log Pb, Steel Gutter, River Water	Regression	1	0.97268	0.97268	11.29	0.028
	Residual Error	4	0.34466	0.08616		
	Total	5	1.31734			
Log Pb, Steel Pipe, pH 5 Water	Regression	1	4.7644	4.7644	25.01	0.007
	Residual Error	4	0.7621	0.1905		
	Total	5	5.5264			
Log Pb, Steel Gutter, pH 5 Water	Regression	1	1.3002	1.3002	24.40	0.008
	Residual Error	4	0.2132	0.0533		
	Total	5	1.5134			

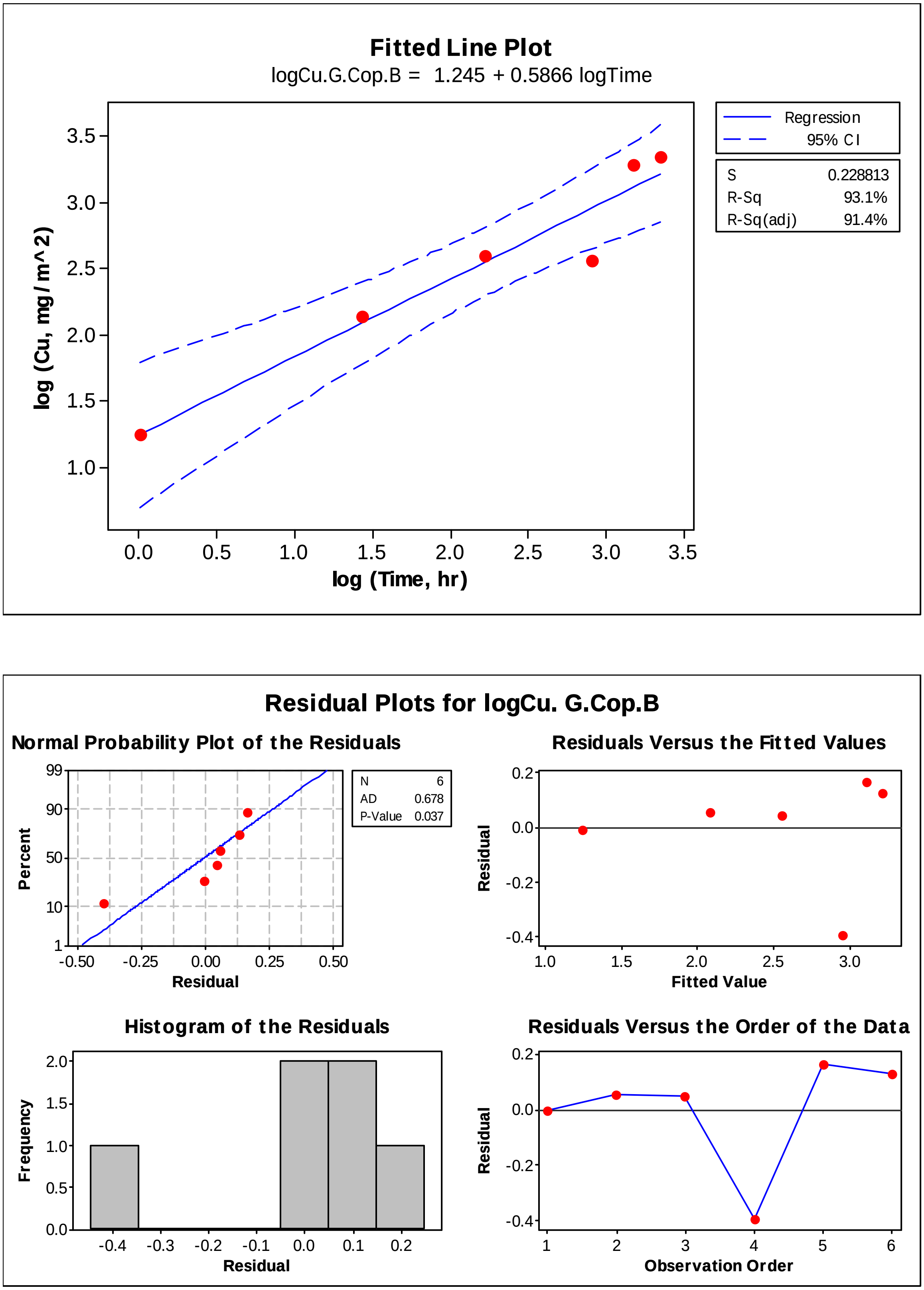


Figure B.1.2 Empirical estimation (linear equation) of copper release from copper gutter section submerged into bay waters as a function of time.

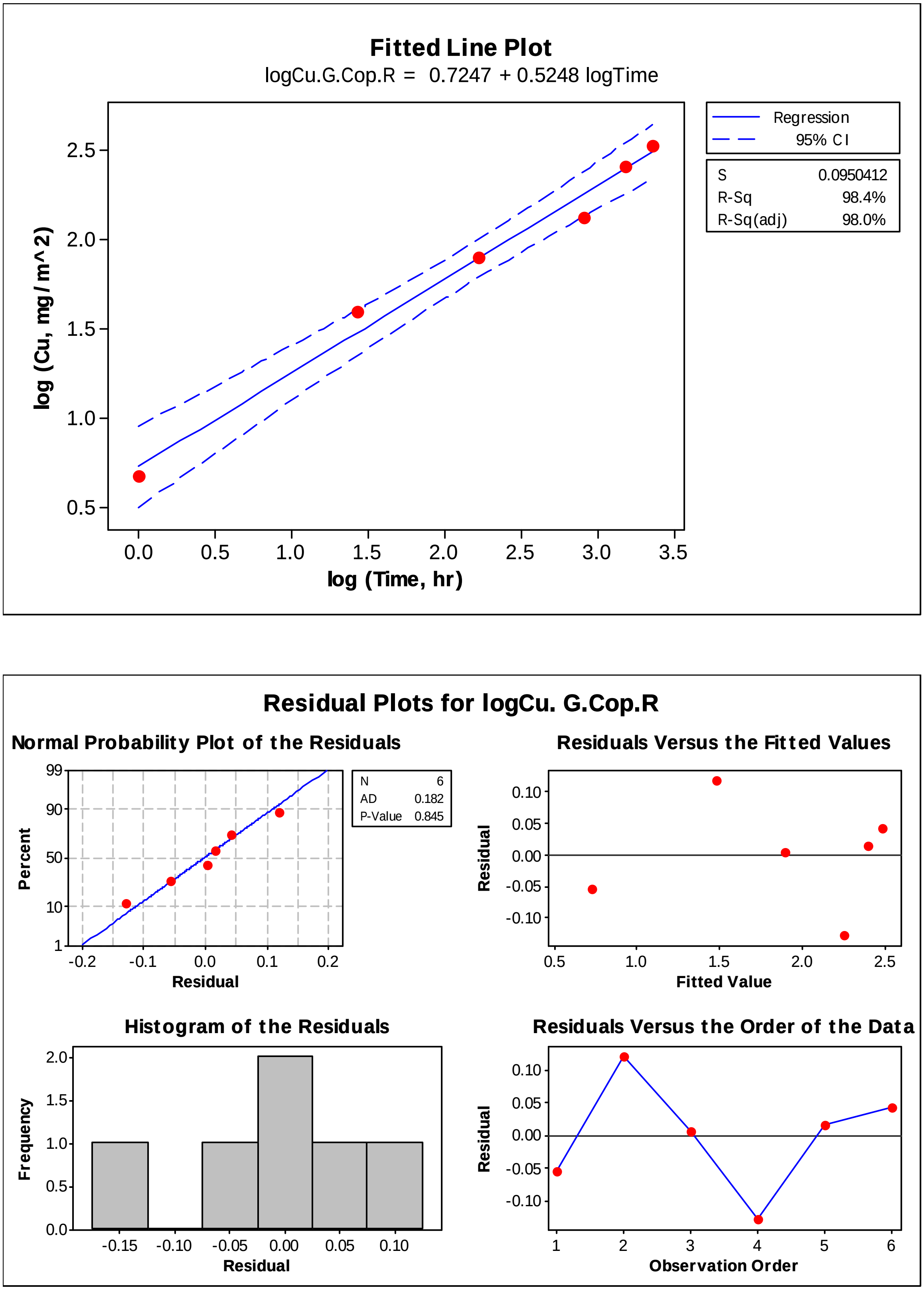


Figure B.1.3 Empirical estimation (linear equation) of copper release from copper gutter section submerged into river waters as a function of time.

Fitted Line Plot

1st Order Polynomial: logCu. G.Cop.5 = 1.916 + 0.202*logTime

2 Segment Linear Regression:

t1 = min(t); t2 = max(t)

Segment1: LogCu. G.Cop5 = (1.6428*(1.025-logTime) + 2.7152*(logTime-t1))/(1.025-t1)

Segment2: LogCu. G.Cop5 = (2.7152*(t2-logTime) + 2.4546*(logTime-1.0247))/(t2-1.025)

f = if(t <= 1.0247, Segment1(t), Segment2(t))

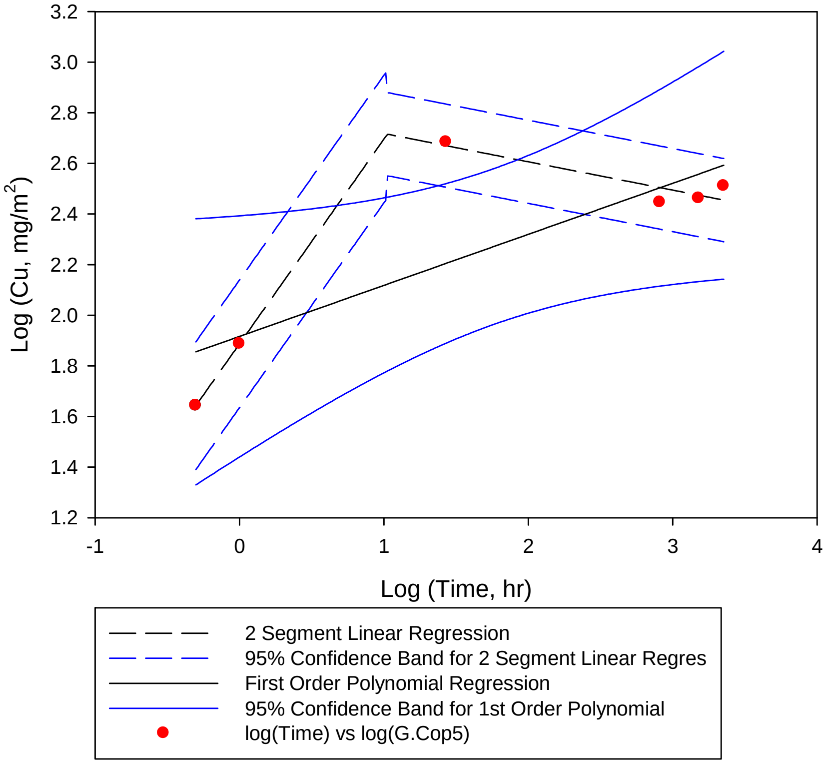
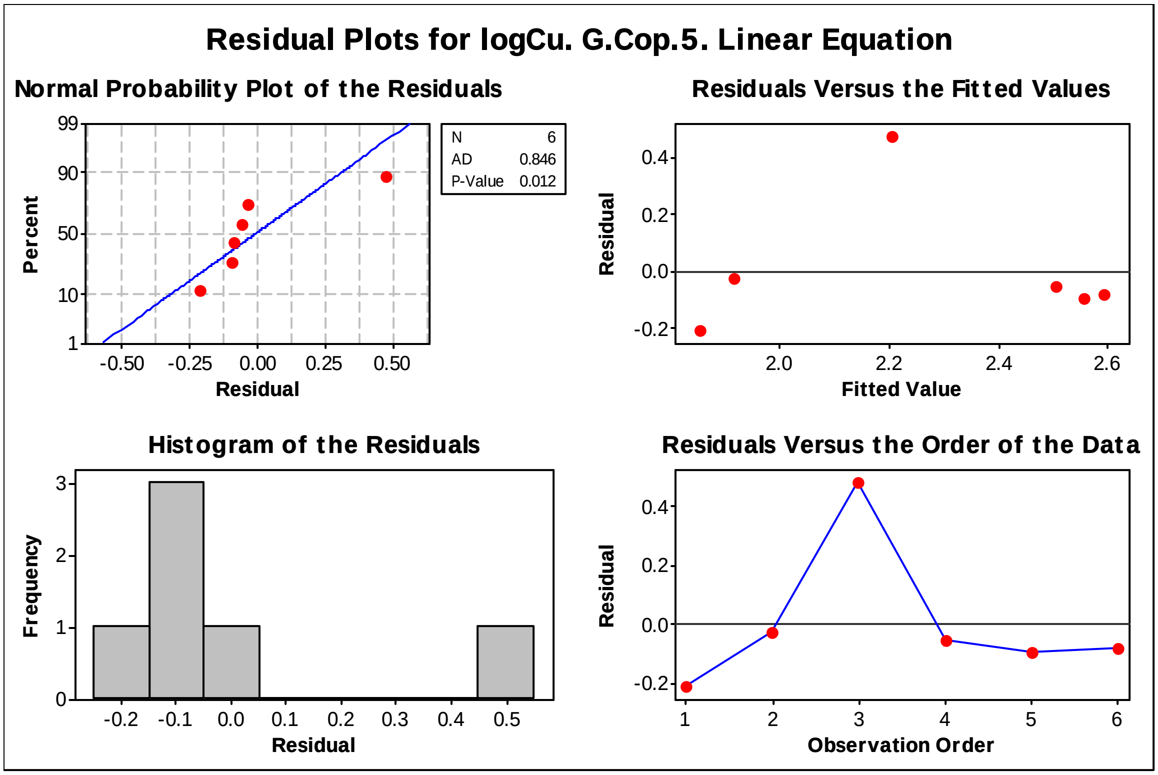


Figure B.1.4 Empirical estimation (linear and 2 segment linear equations) of copper release from copper gutter section submerged into pH 5 waters as a function of time.



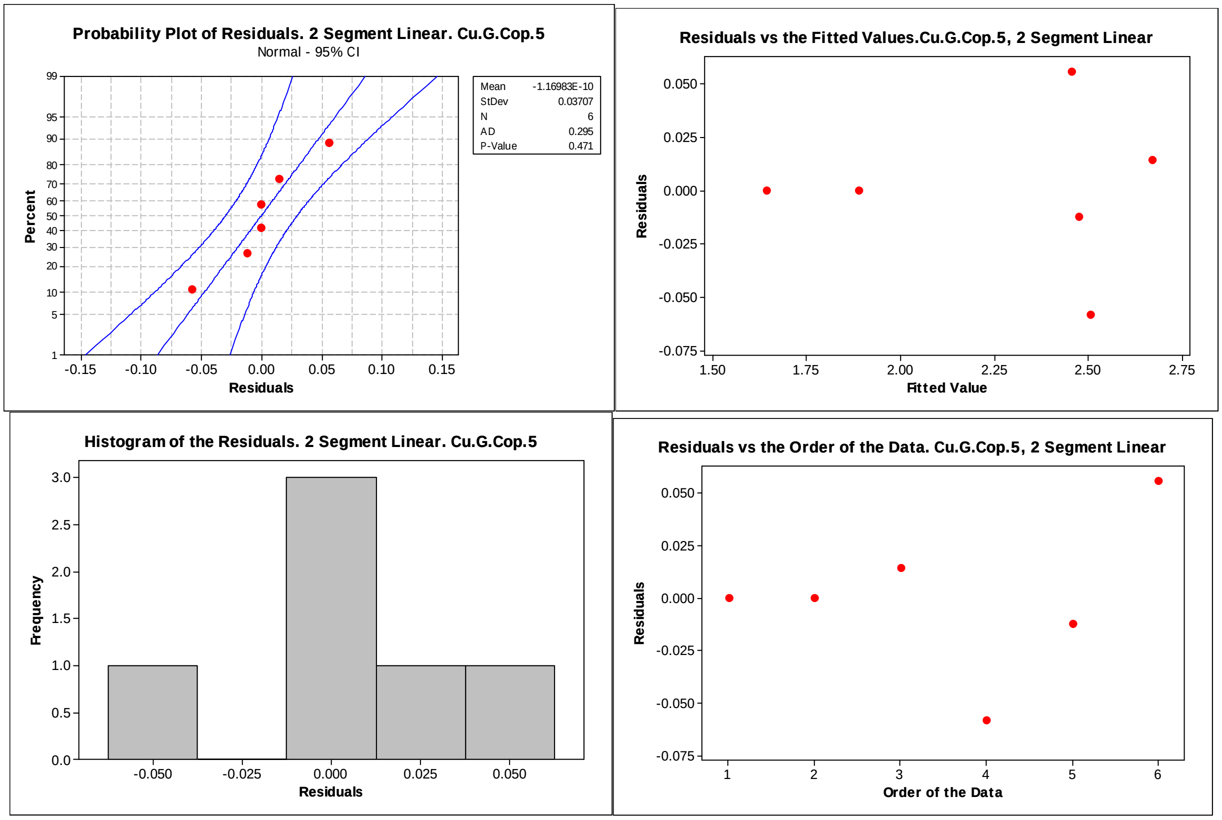
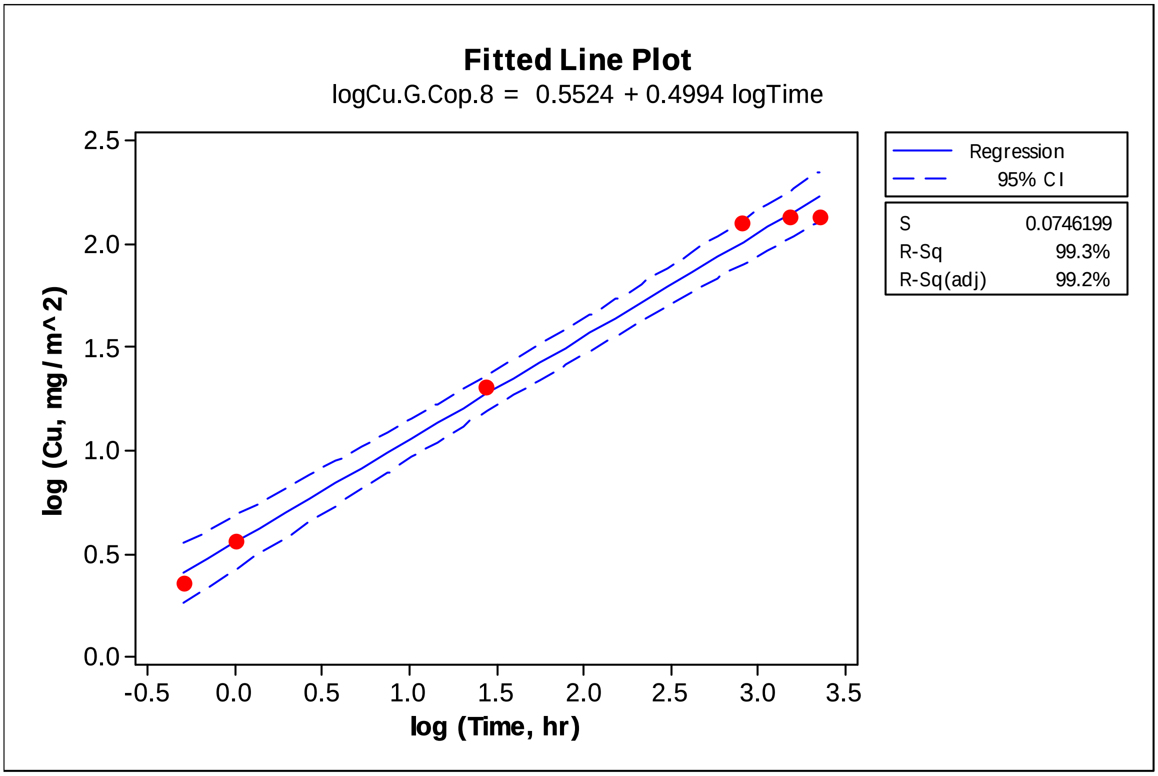


Figure B.1.4 - *Continued*



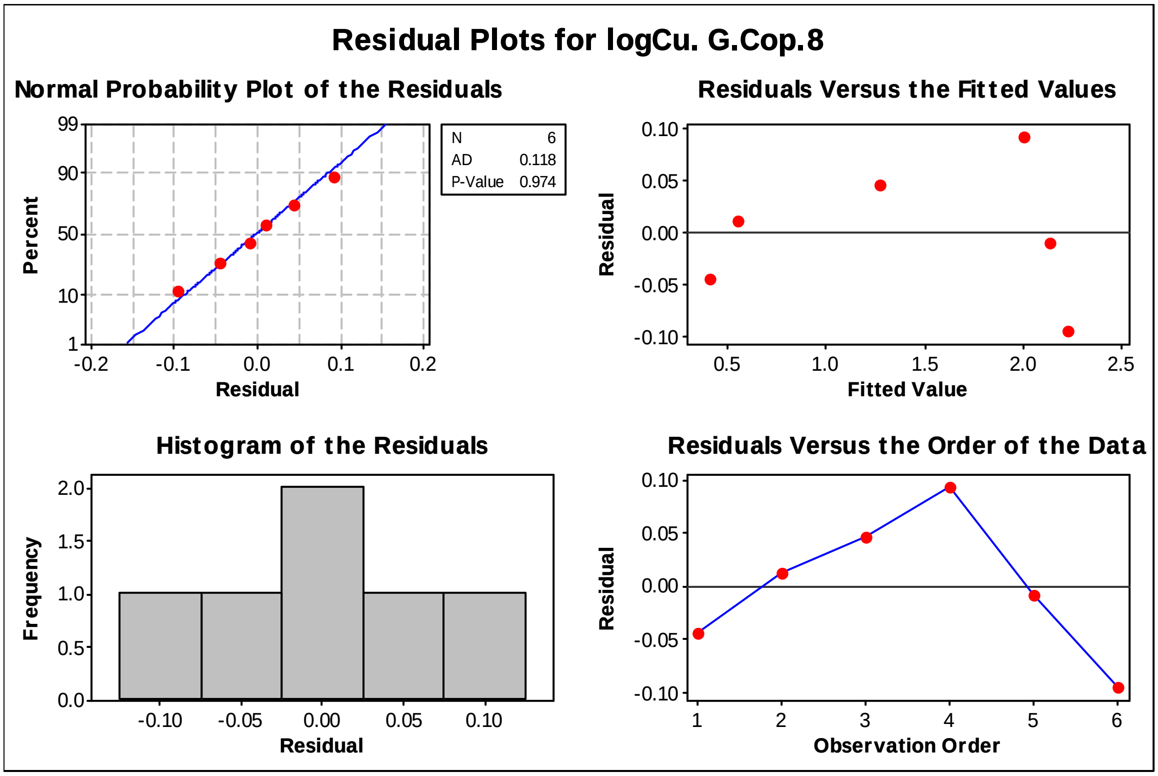
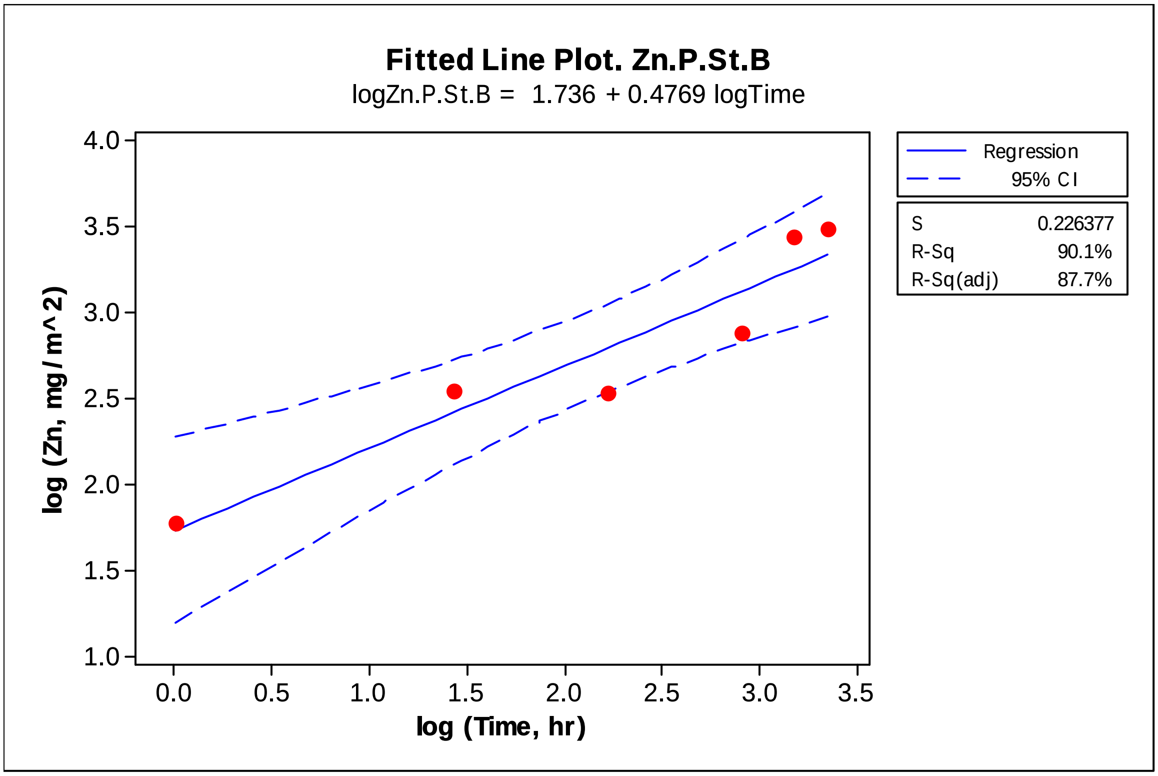


Figure B.1.5 Empirical estimation (linear equation) of copper release from copper gutter section submerged into pH 8 waters as a function of time.



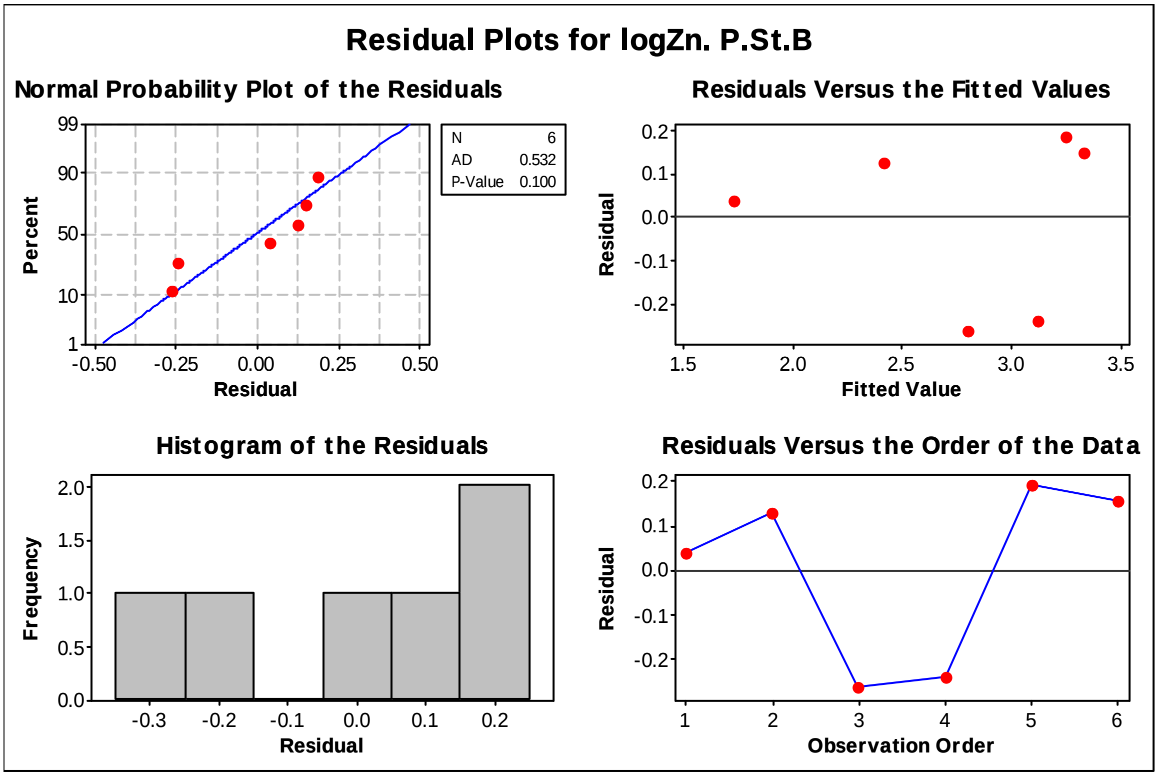
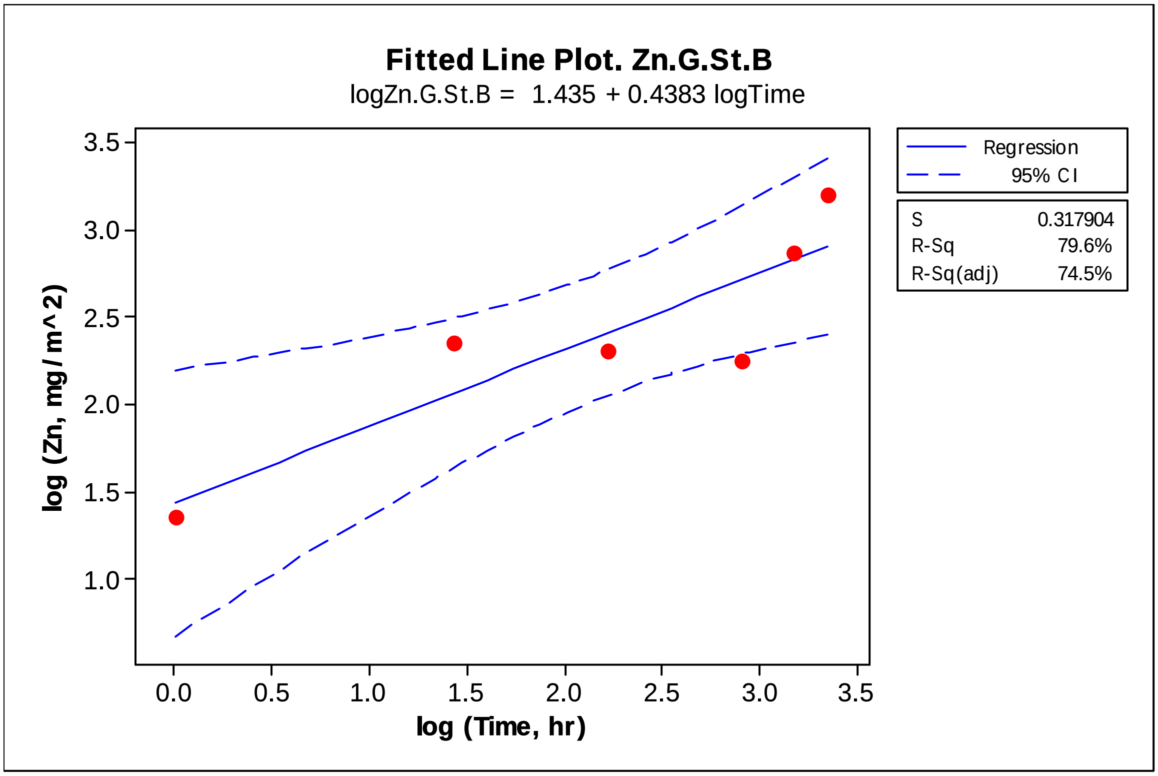


Figure B.1.6 Empirical estimation (linear equation) of zinc release from galvanized steel pipe section submerged into bay waters as a function of time.



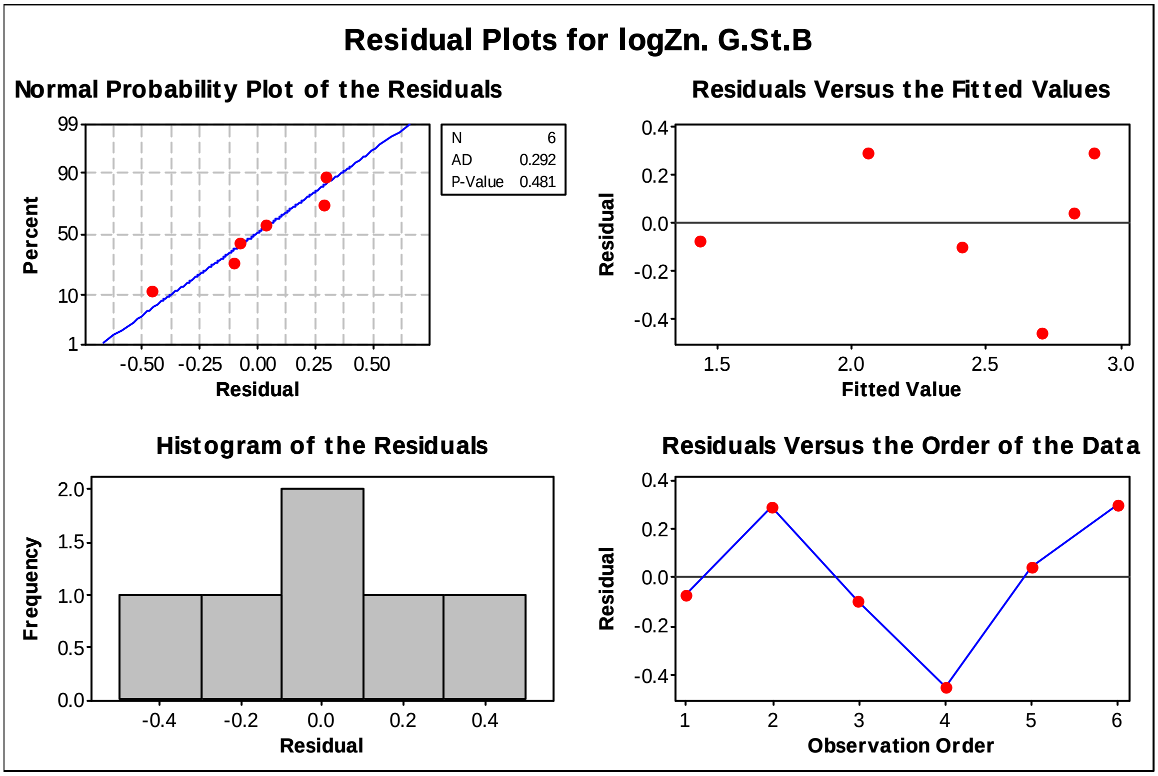
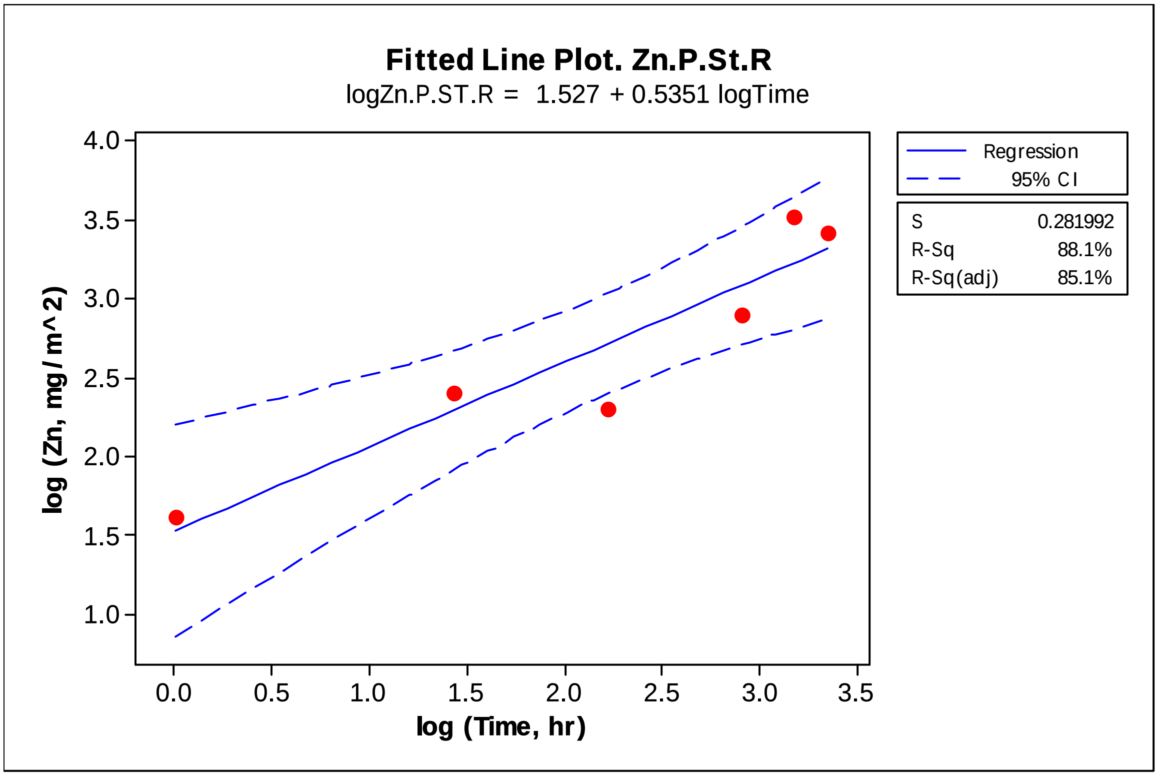


Figure B.1.7 Empirical estimation (linear equation) of zinc release from galvanized steel gutter section submerged into bay waters as a function of time.



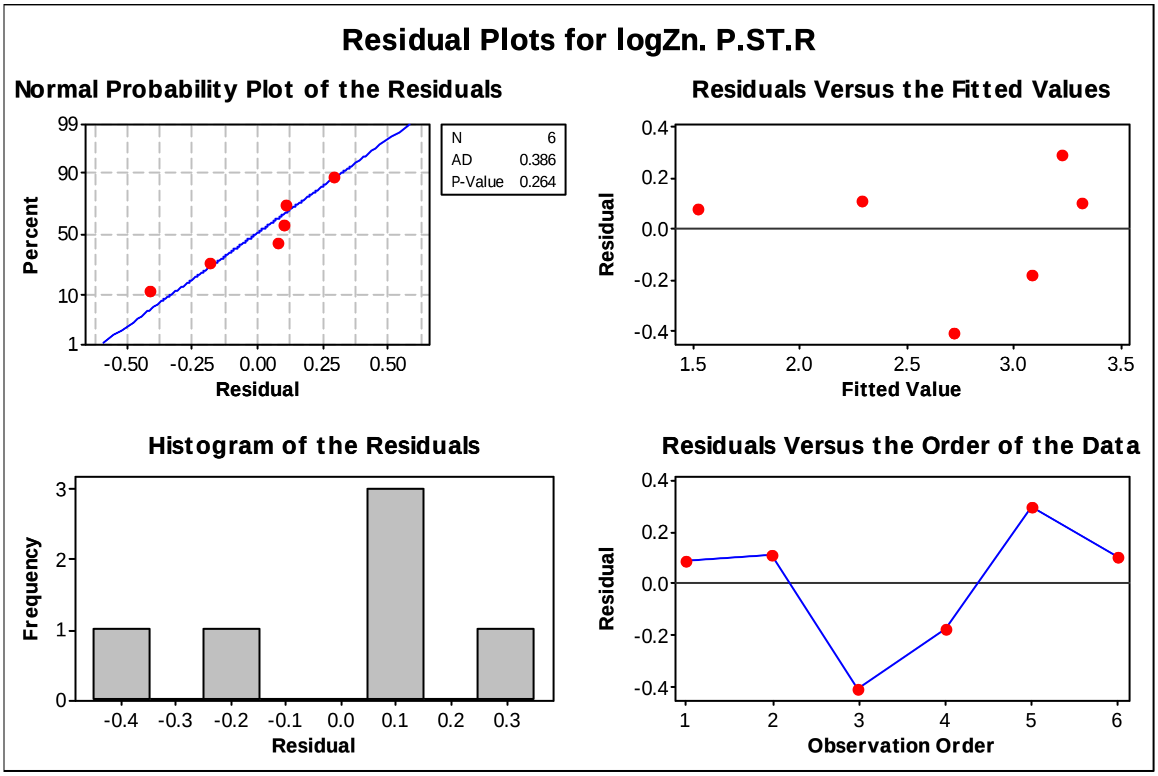


Figure B.1.8 Empirical estimation (linear equation) of zinc release from galvanized steel pipe section submerged into river waters as a function of time.

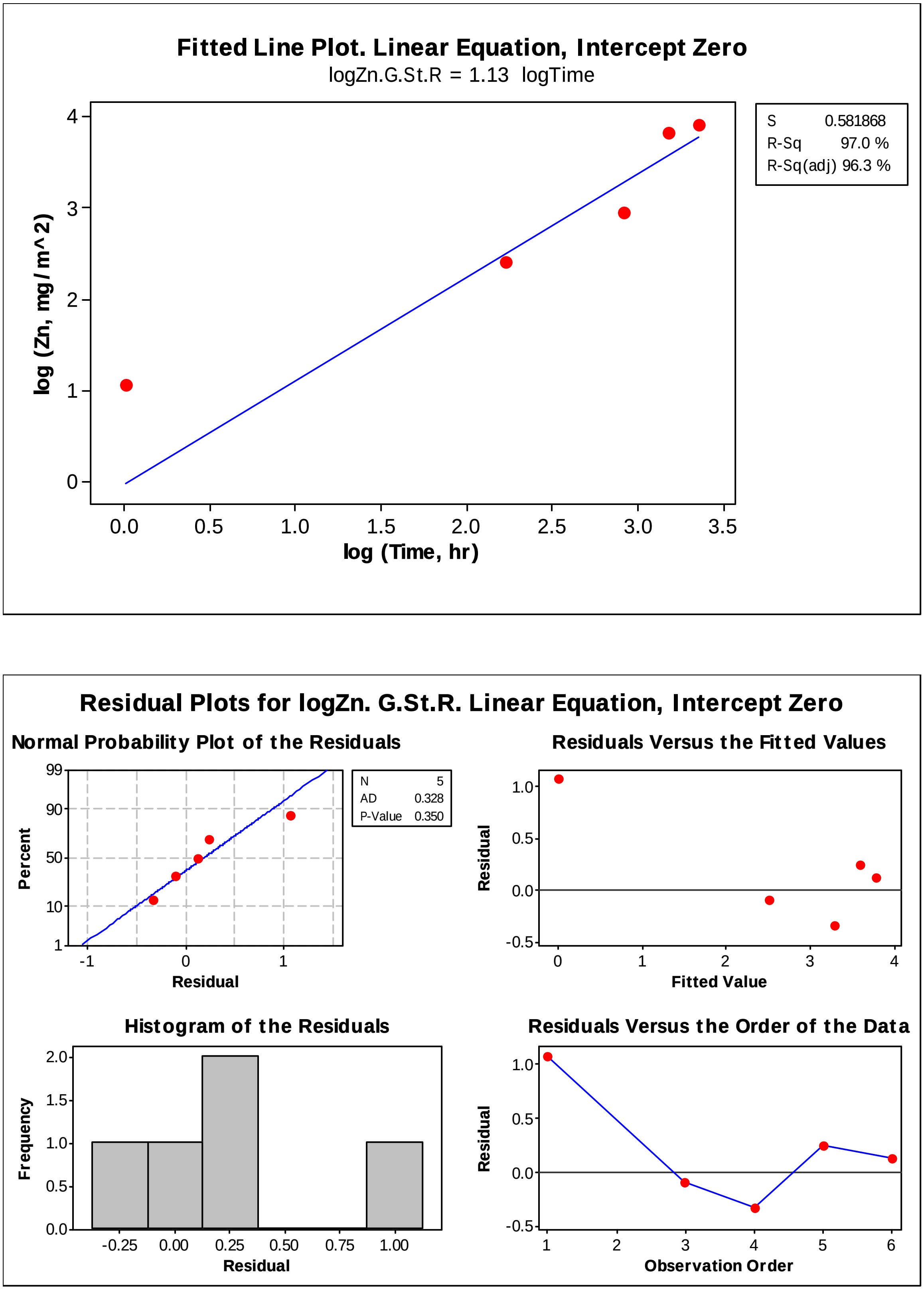


Figure B.1.9 Empirical estimation (linear equation) of zinc release from galvanized steel gutter section submerged into river waters as a function of time.

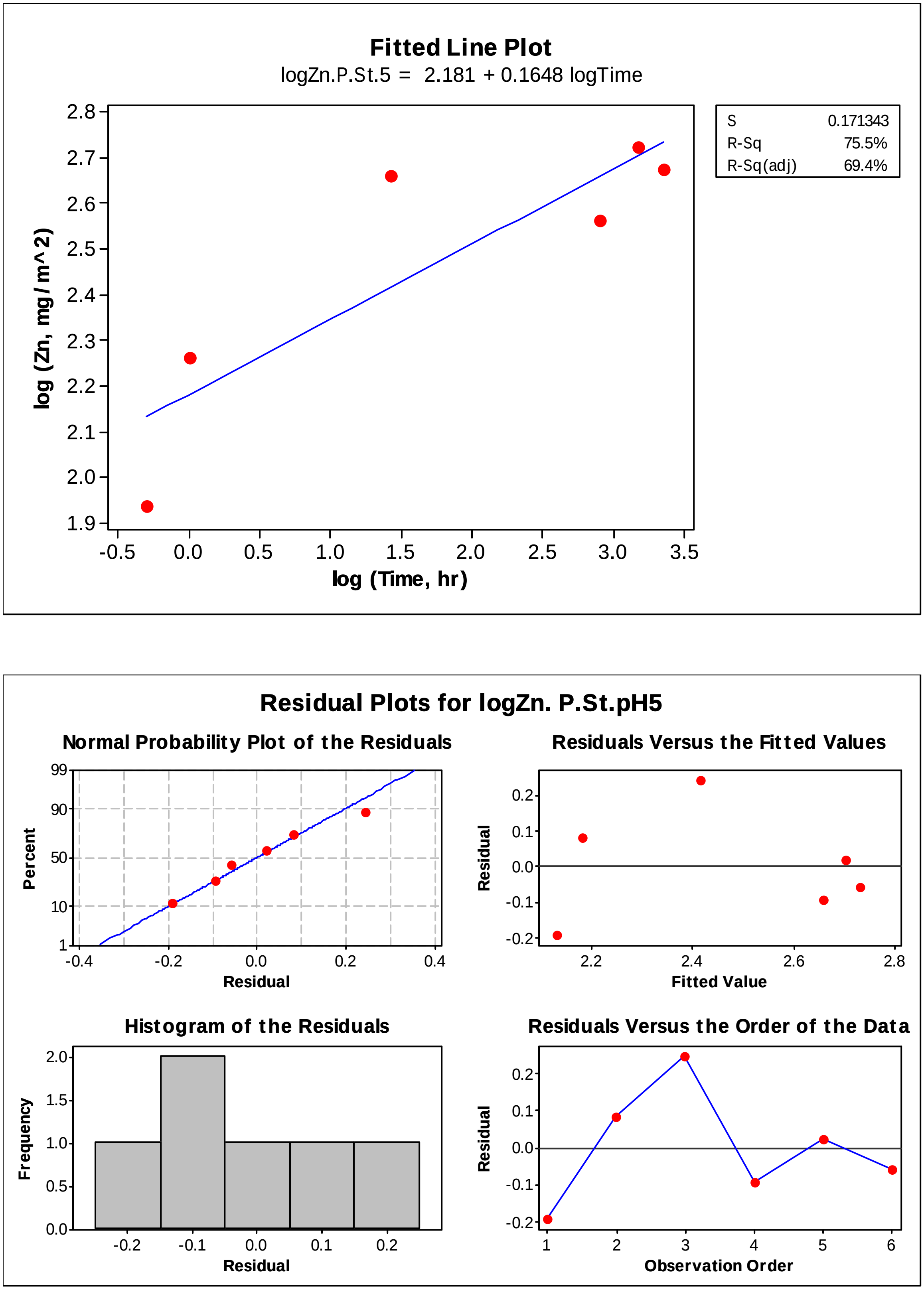
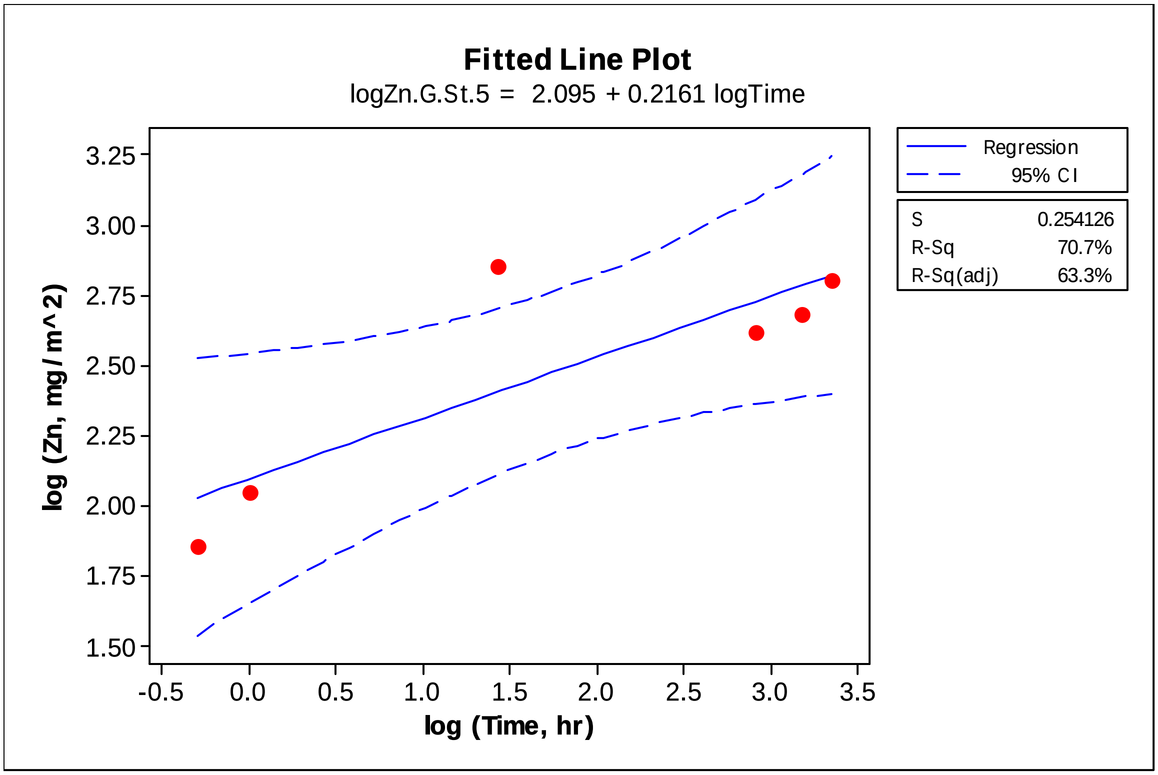


Figure B.1.10 Empirical estimation (linear equation) of zinc release from galvanized steel pipe section submerged into pH 5 waters as a function of time.



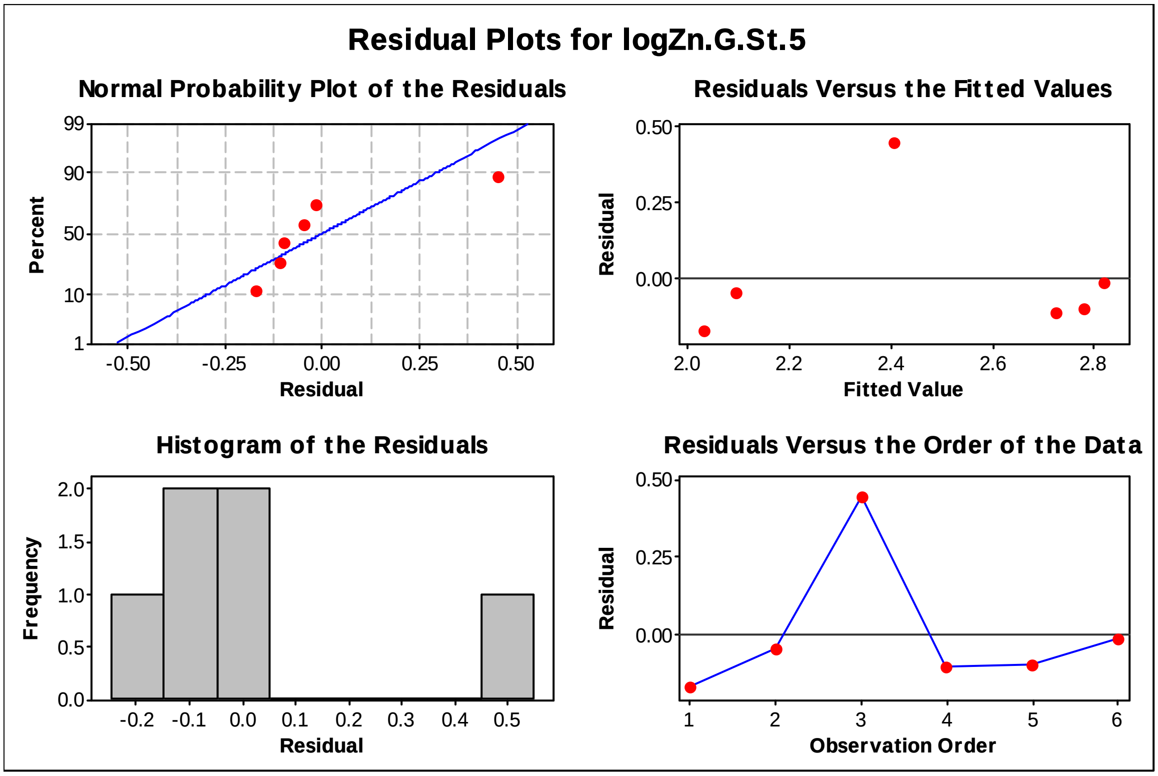
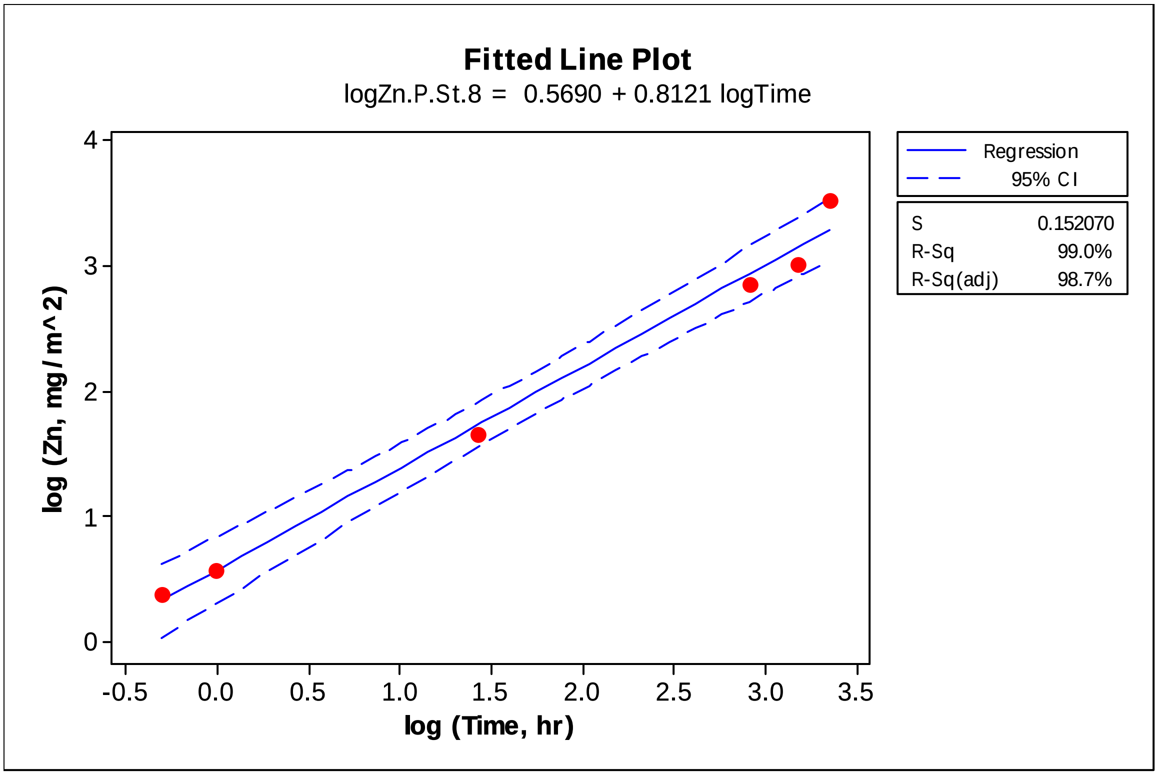


Figure B.1.11 Empirical estimation (linear equation) of zinc release from galvanized steel gutter section submerged into pH 5 waters as a function of time.



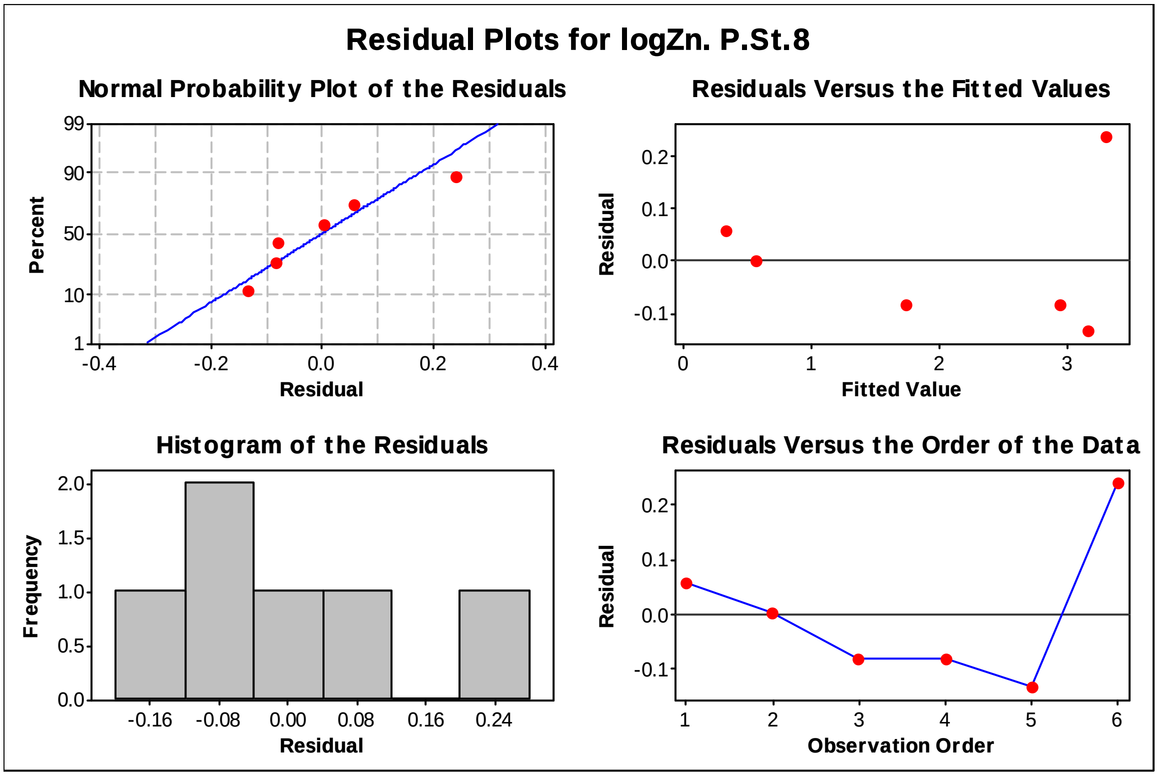
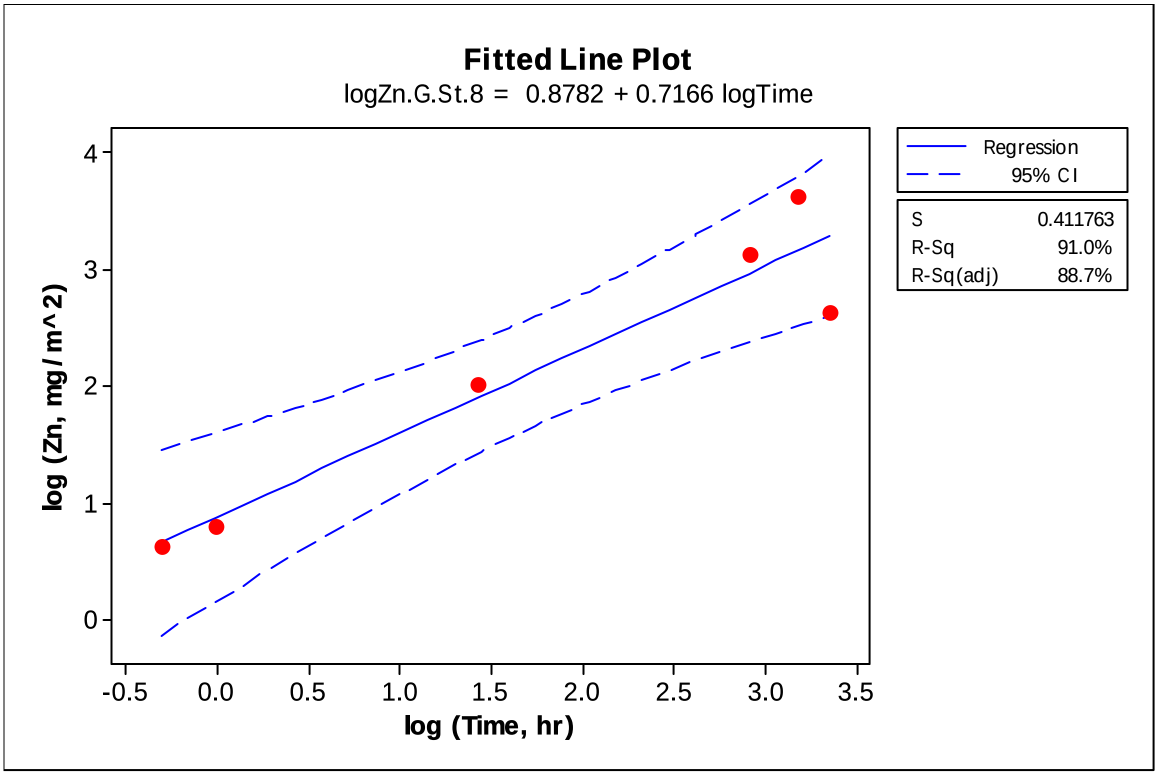


Figure B.1.12 Empirical estimation (linear equation) of zinc release from galvanized steel pipe section submerged into pH 8 waters as a function of time.



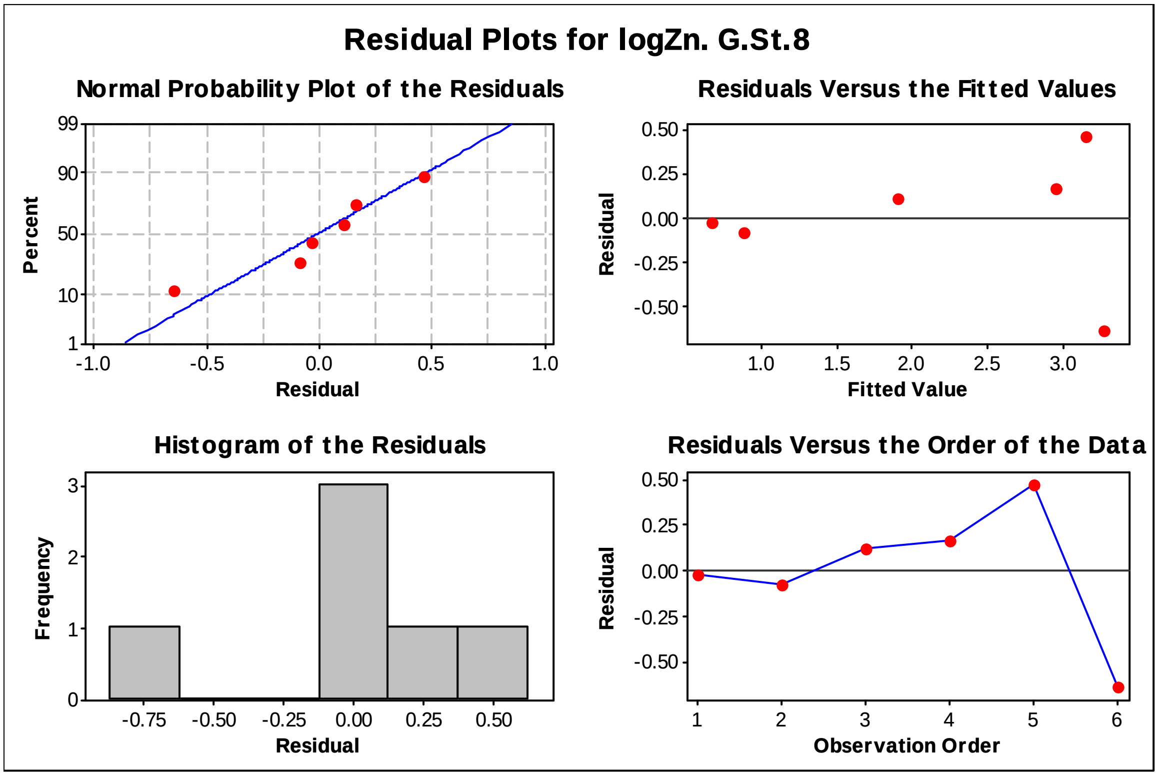


Figure B.1.13 Empirical estimation (linear equation) of zinc release from galvanized steel gutter section submerged into pH 8 waters as a function of time.

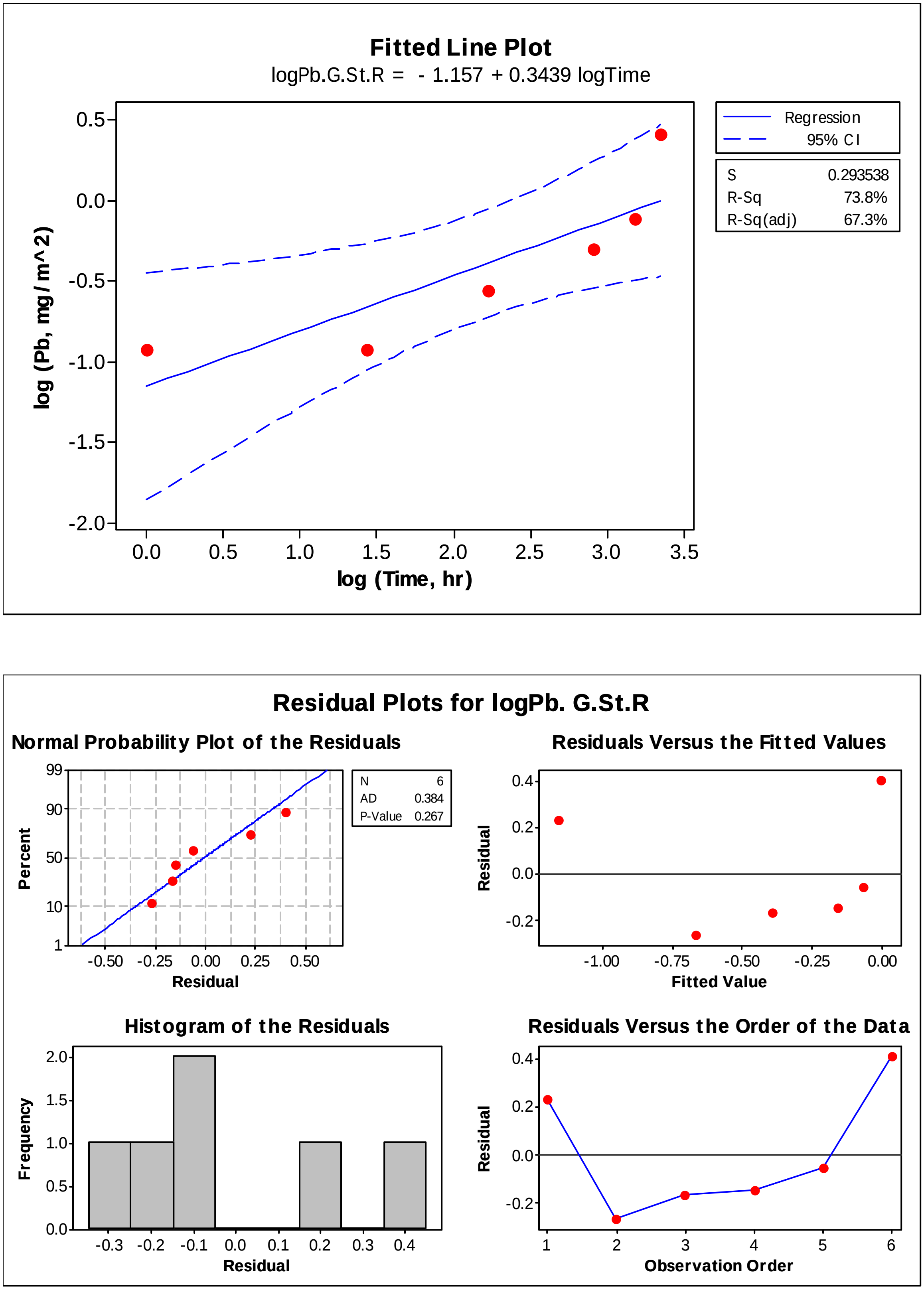
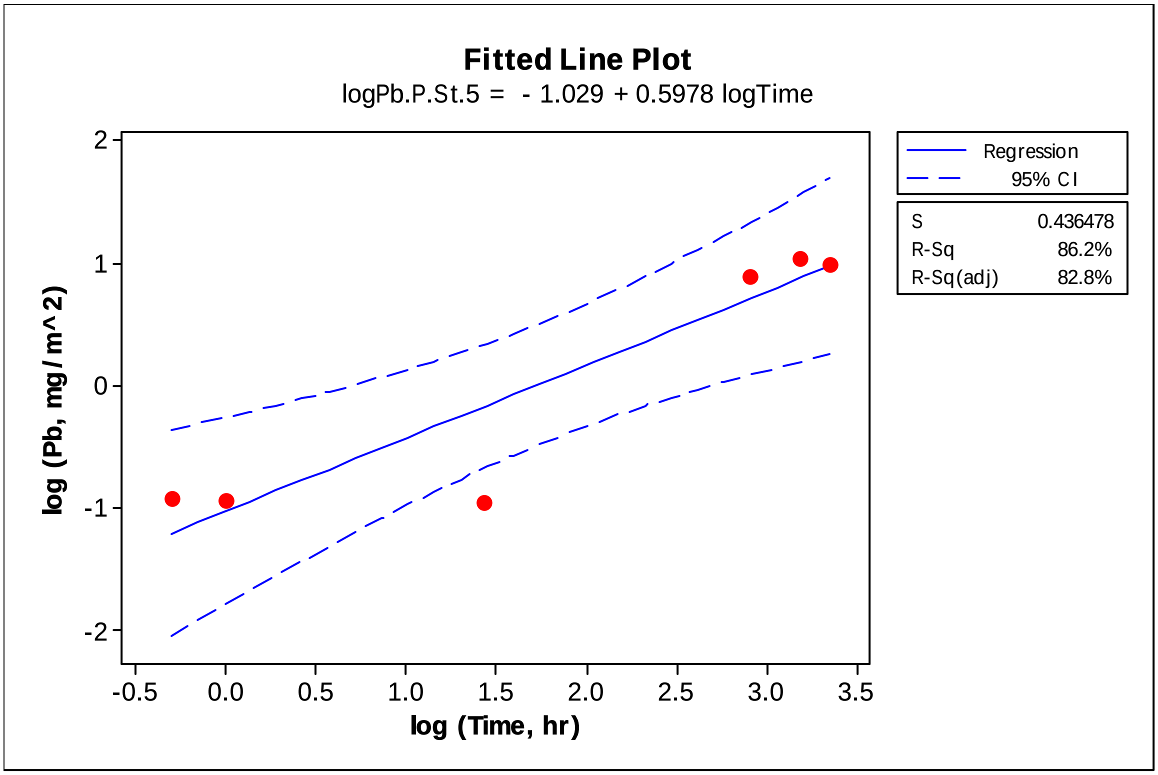


Figure B.1.14 Empirical estimation (linear equation) of lead release from galvanized steel gutter section submerged into river waters as a function of time.



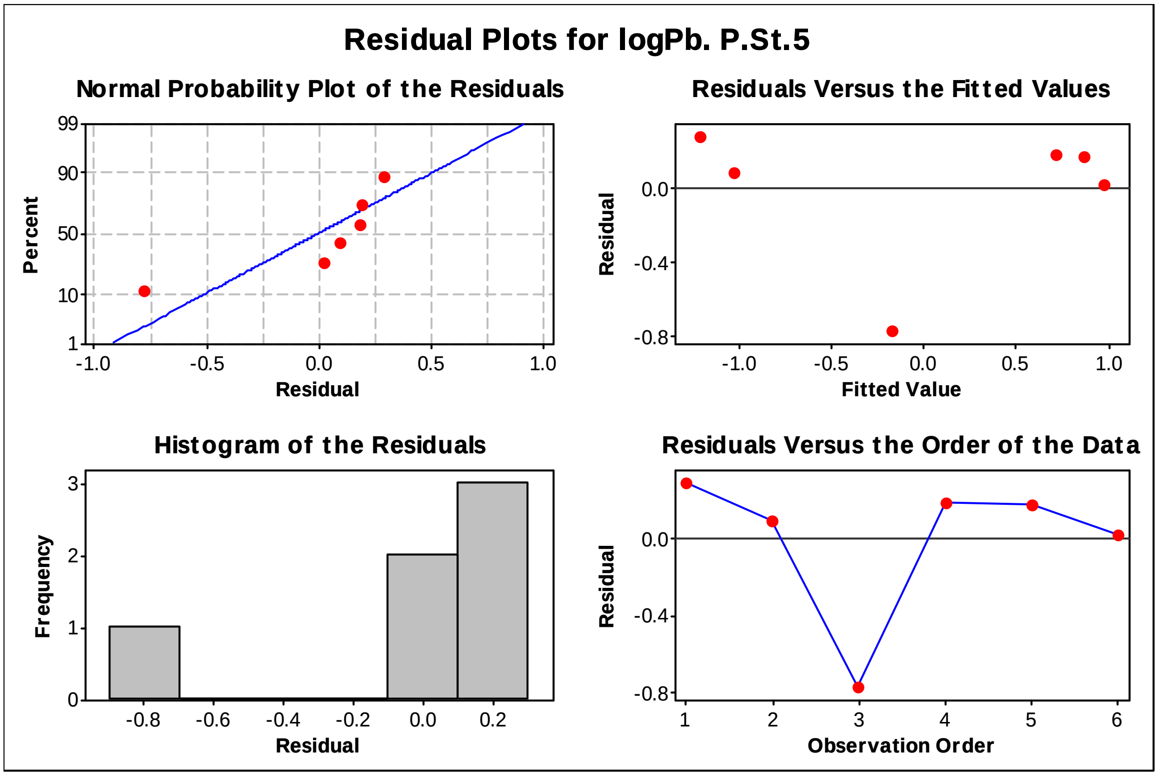
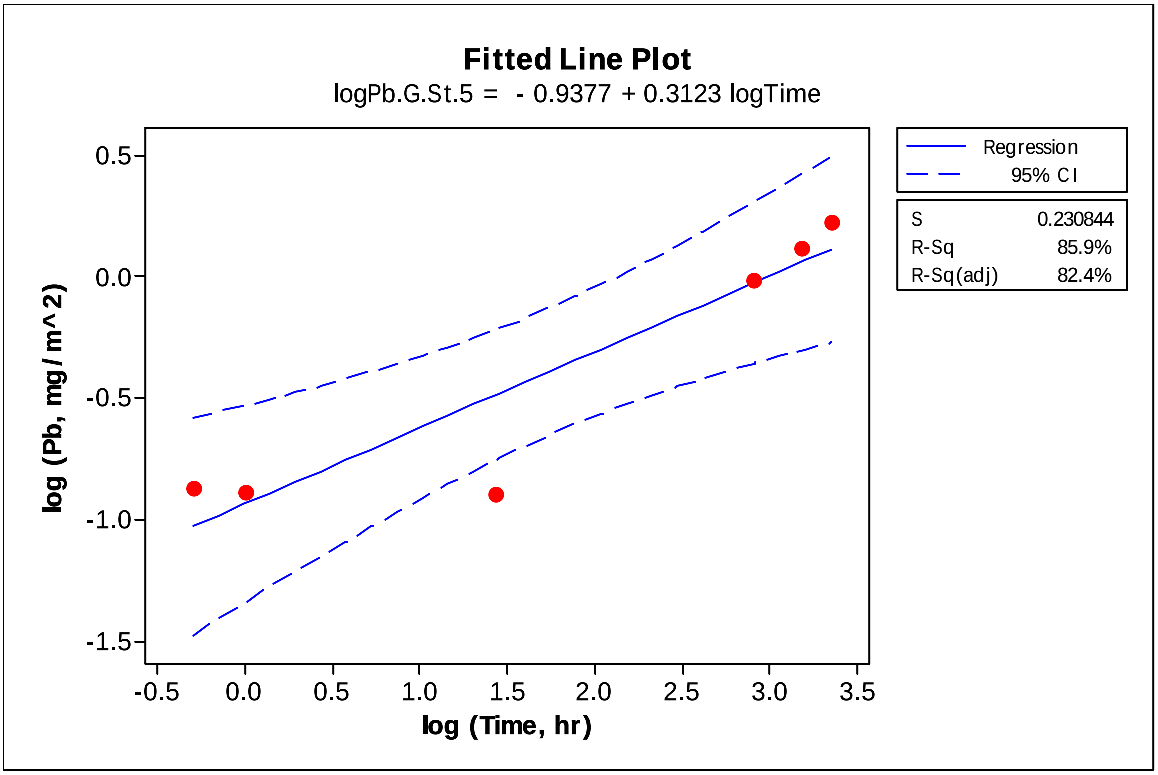


Figure B.1.15 Empirical estimation (linear equation) of lead release from galvanized steel pipe section submerged into pH 5 waters as a function of time.



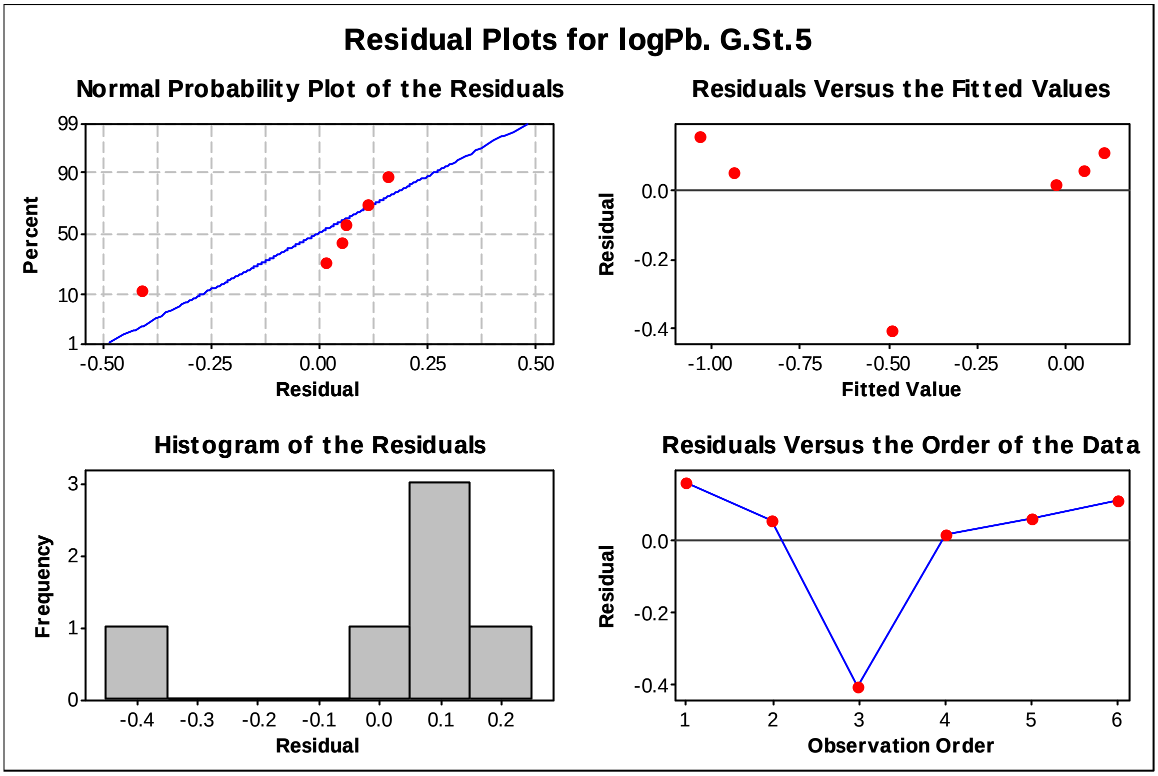


Figure B.1.16 Empirical estimation (linear equation) of lead release from galvanized steel gutter section submerged into pH 5 waters as a function of time.

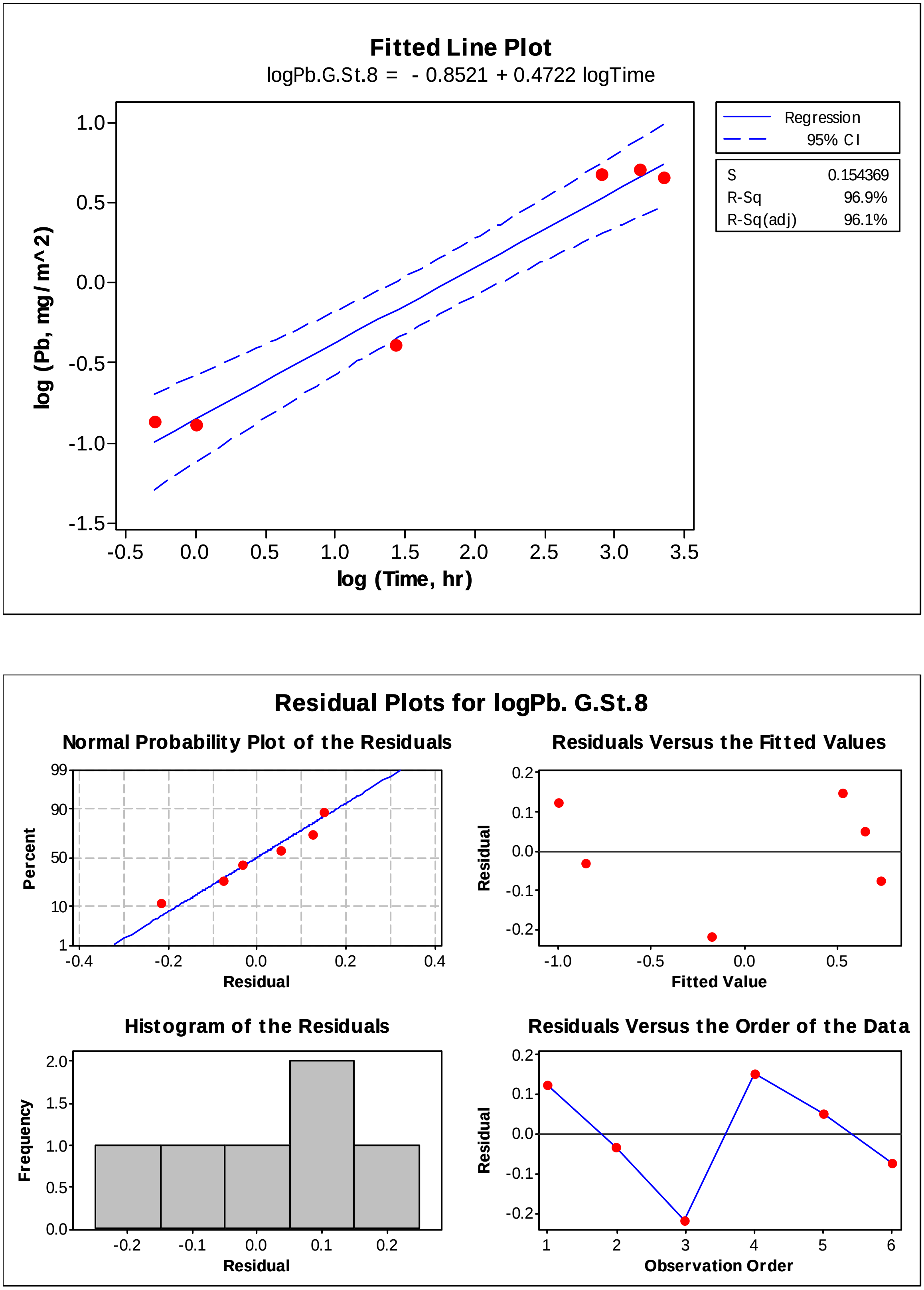


Figure B.1.17 Empirical estimation (linear equation) of lead release from galvanized steel gutter section submerged into pH 8 waters as a function of time.

APPENDIX C: MEDUSA RESULTS

Steel Pipe, pH 5 Water, After Three Months of Exposure

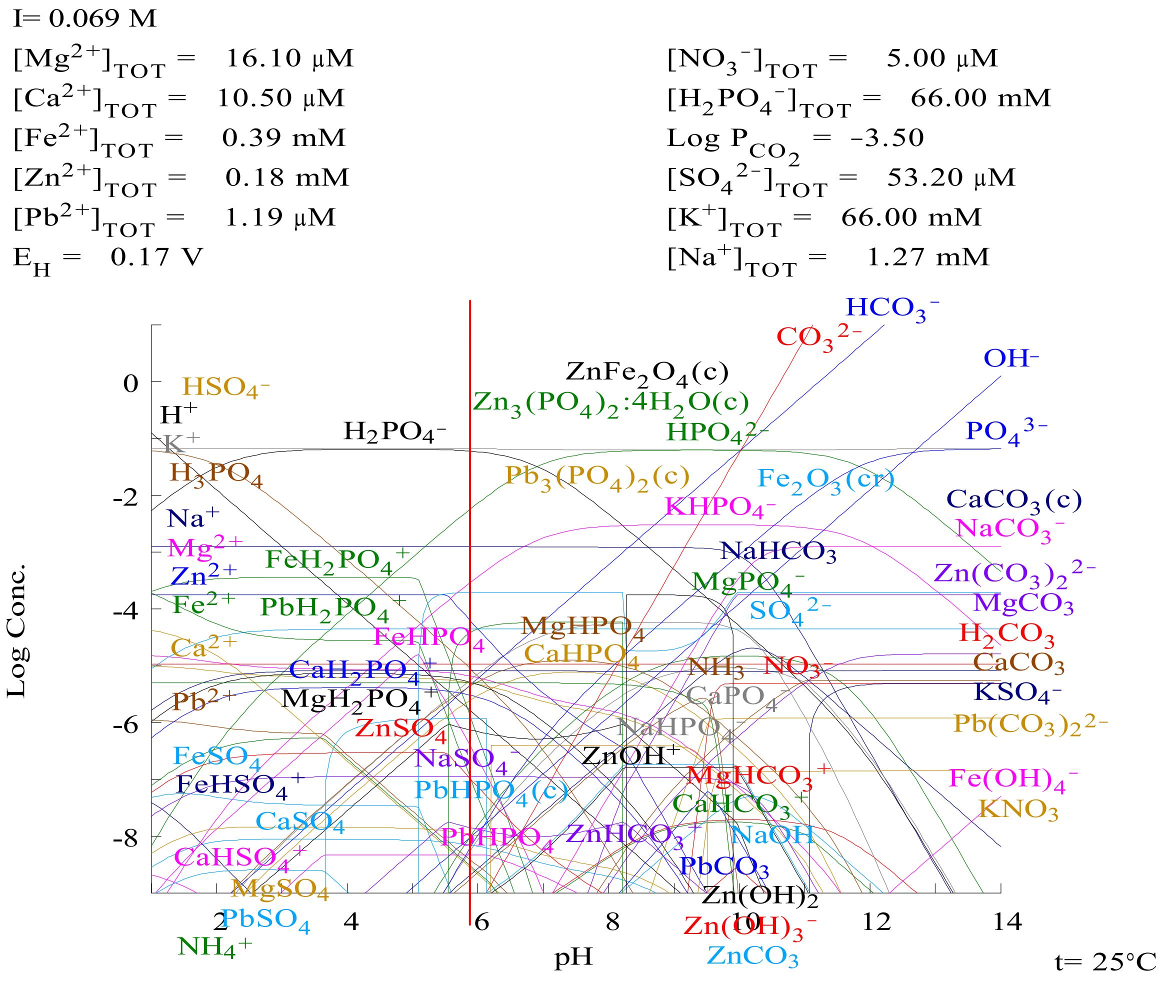


Figure C.1 Phase diagram for steel pipe section immersed into pH 5 water after three months of exposure.

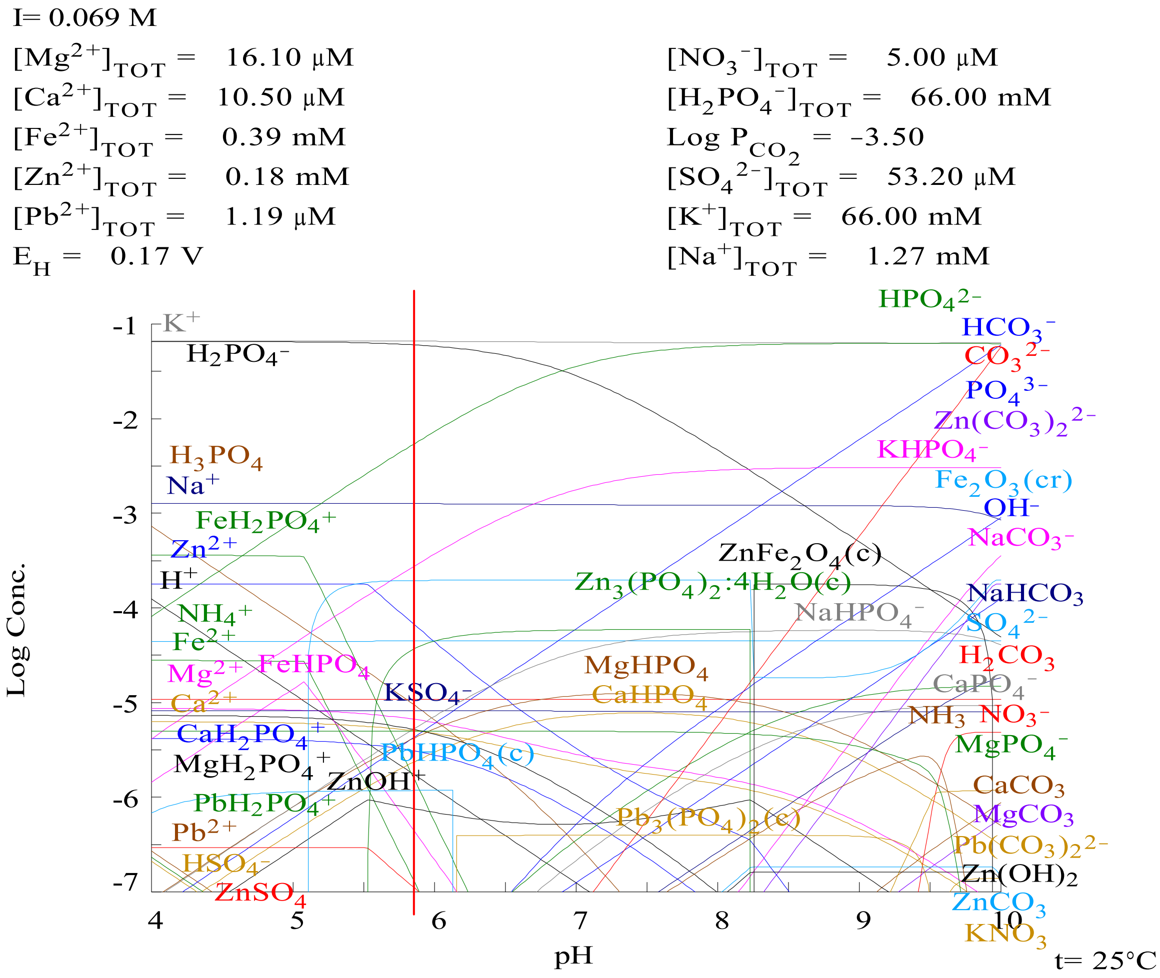


Figure C.2 Phase diagram for steel pipe section immersed into pH 5 water after three months of exposure. Study area.

Table C.1. The predominant species of zinc.Steel pipe section, pH 5 water, three months exposure.

Component	Log Concentration (mol/L)	Concentration (mol/L)	Zn Concentration (mg/L as Zn)	Cumulative Percentage of Zn
$Zn_3(PO_4)_2{:}4H_2O(c)$	-4.47	3.37E-05	6.62	56.54
Zn^{2+}	-4.11	7.69E-05	5.03	99.48
$ZnOH^+$	-6.11	7.80E-07	5.10E-02	99.92
$ZnSO_4$	-6.90	1.27E-07	8.31E-03	99.99

Table C.2. The predominant species of lead.Steel pipe section, pH 5 water, three months exposure.

Component	Log Concentration (mol/L)	Concentration (mol/L)	Pb Concentration (mg/L as Pb)	Cumulative Percentage of Pb
$PbHPO_4$(c)	-5.93	1.18E-06	0.24	98.925
$PbHPO_4$	-8.33	4.67E-09	9.68E-04	99.317
Pb^{2+}	-8.35	4.49E-09	9.30E-04	99.694
$PbH_2PO_4^+$	-8.45	3.58E-09	7.43E-04	99.995

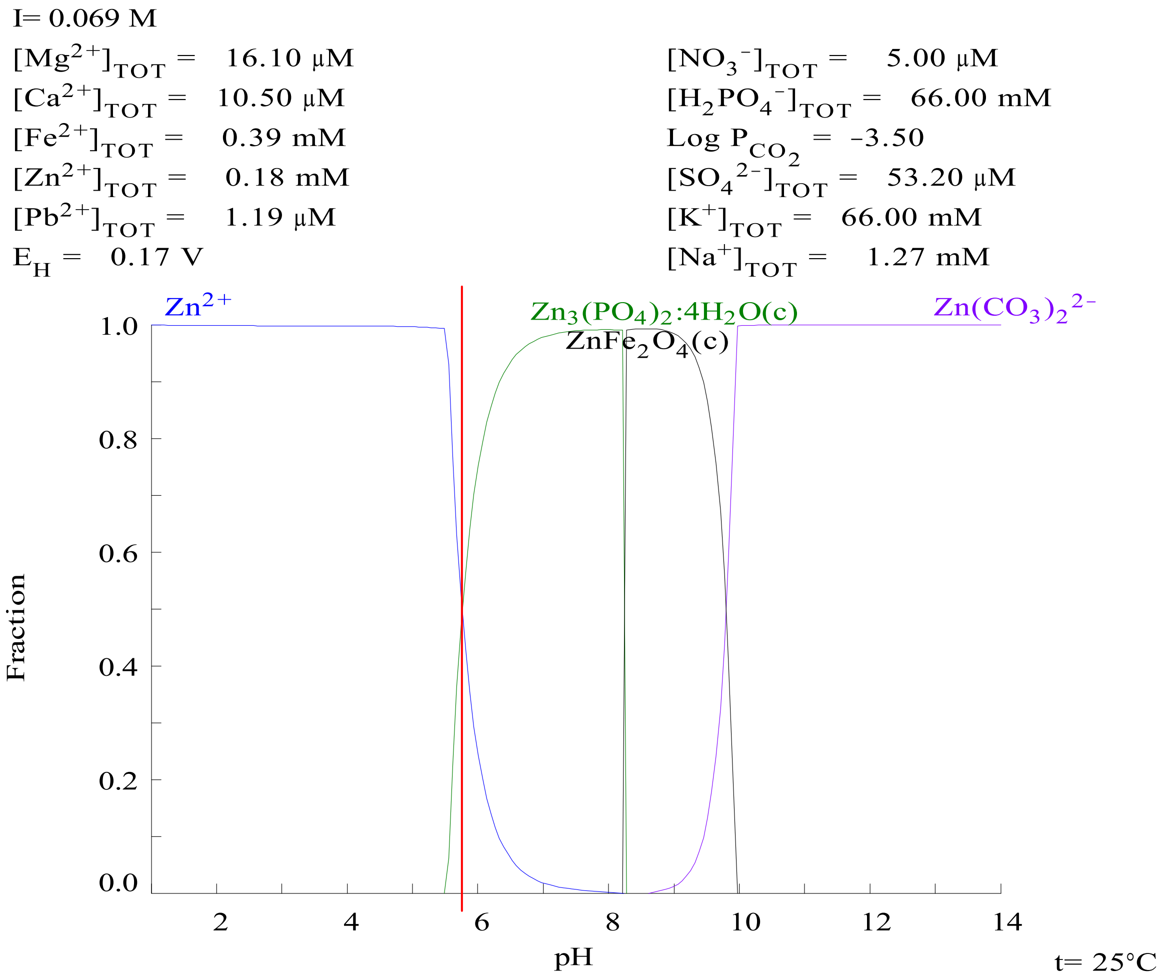


Figure C.3 Fraction diagram of zinc for steel pipe section immersed into pH 5 water after three months of exposure.

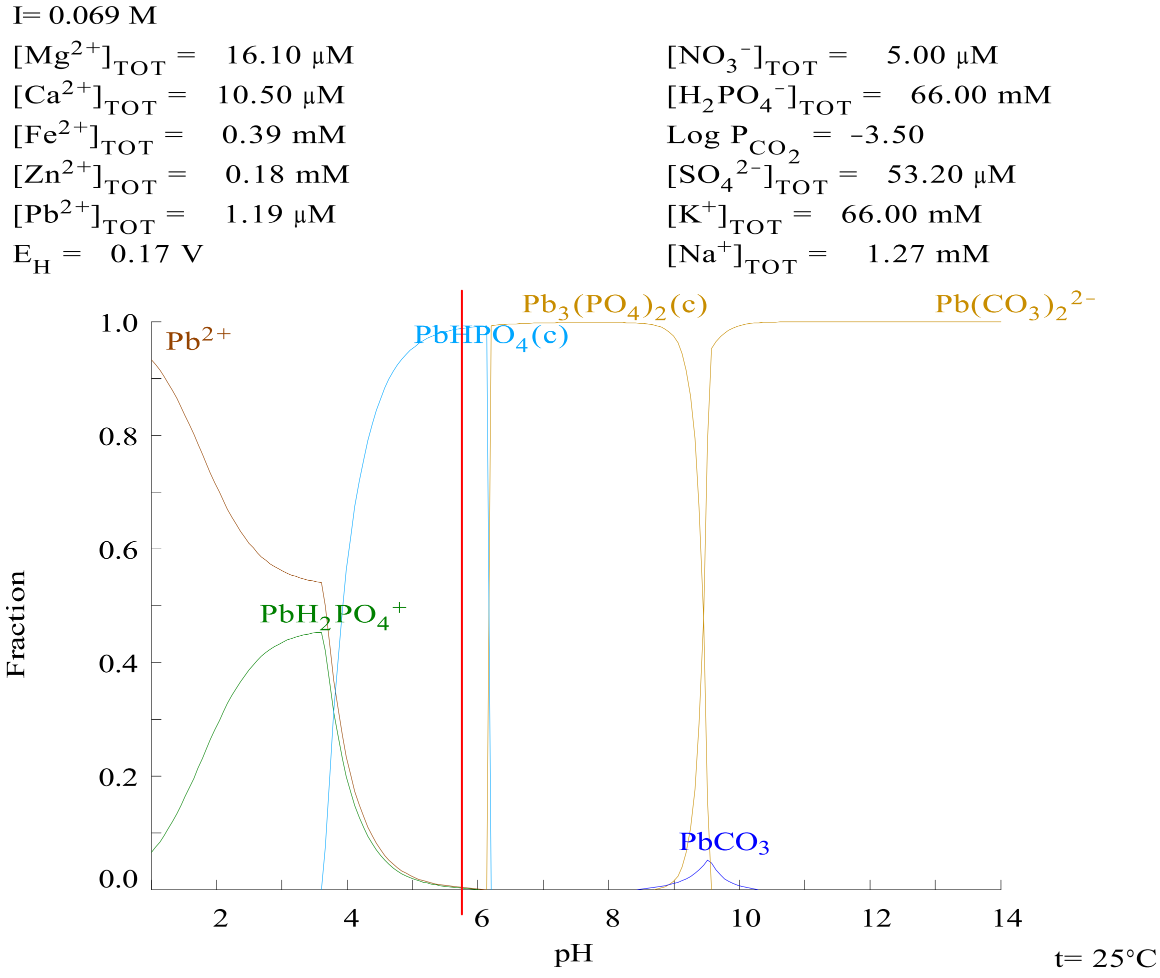


Figure C.4 Fraction diagram of lead for steel pipe section immersed into pH 5 water after three months of exposure.

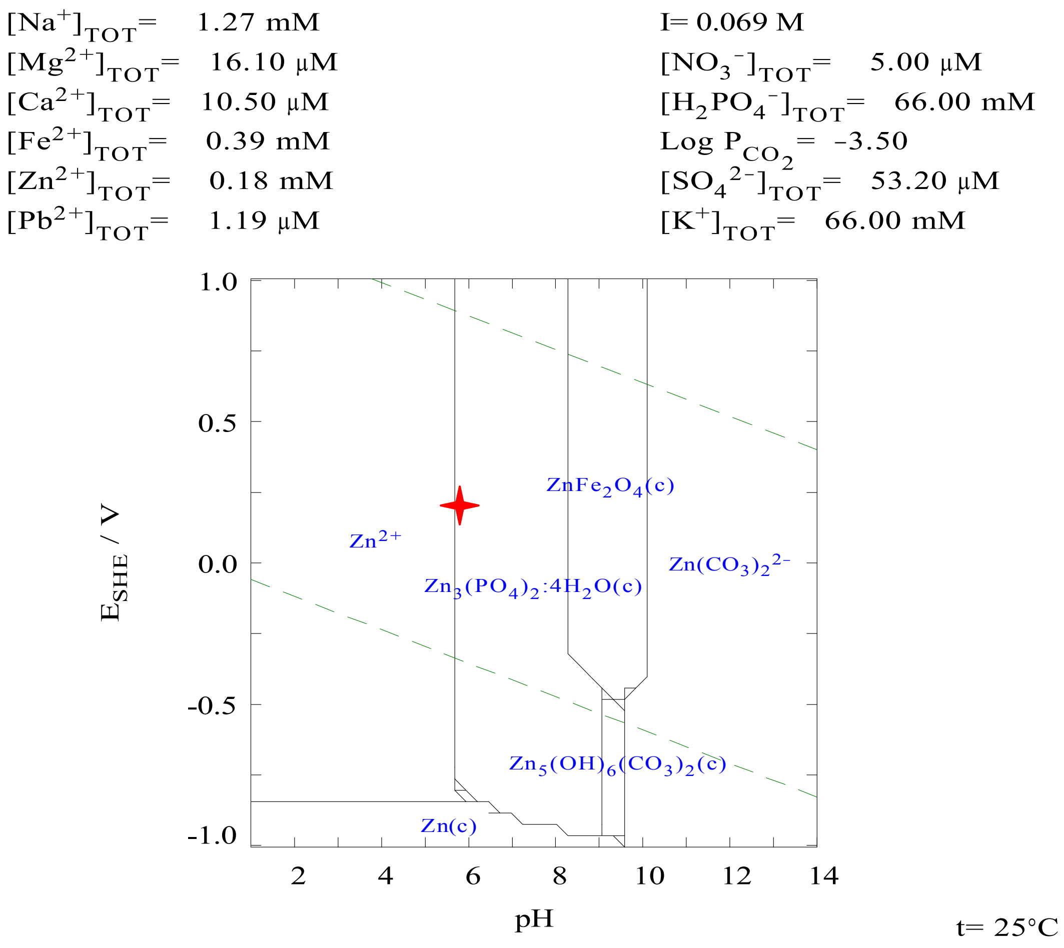


Figure C.5 Pourbaix diagram of zinc for steel pipe section immersed into pH 5 water after three months of exposure.

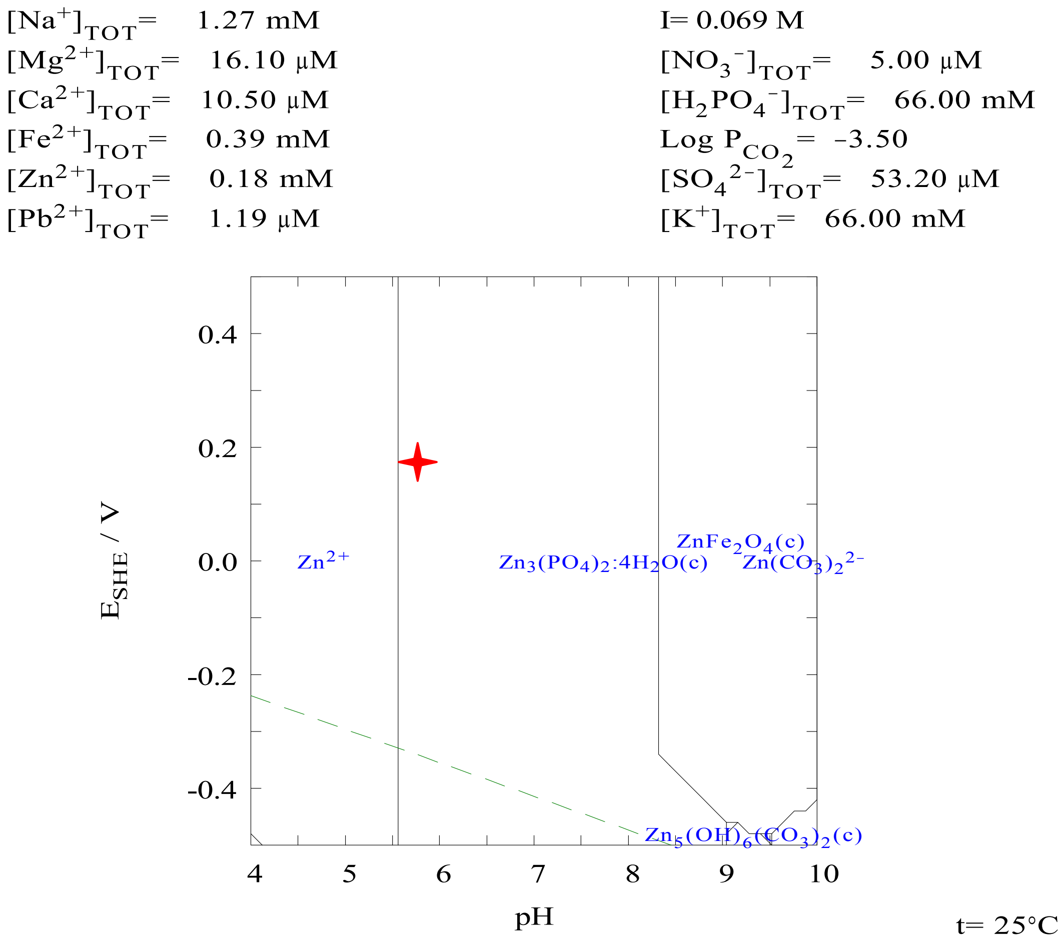


Figure C.6 Pourbaix diagram of zinc for steel pipe section immersed into pH 5 water after three months of exposure. Study area.

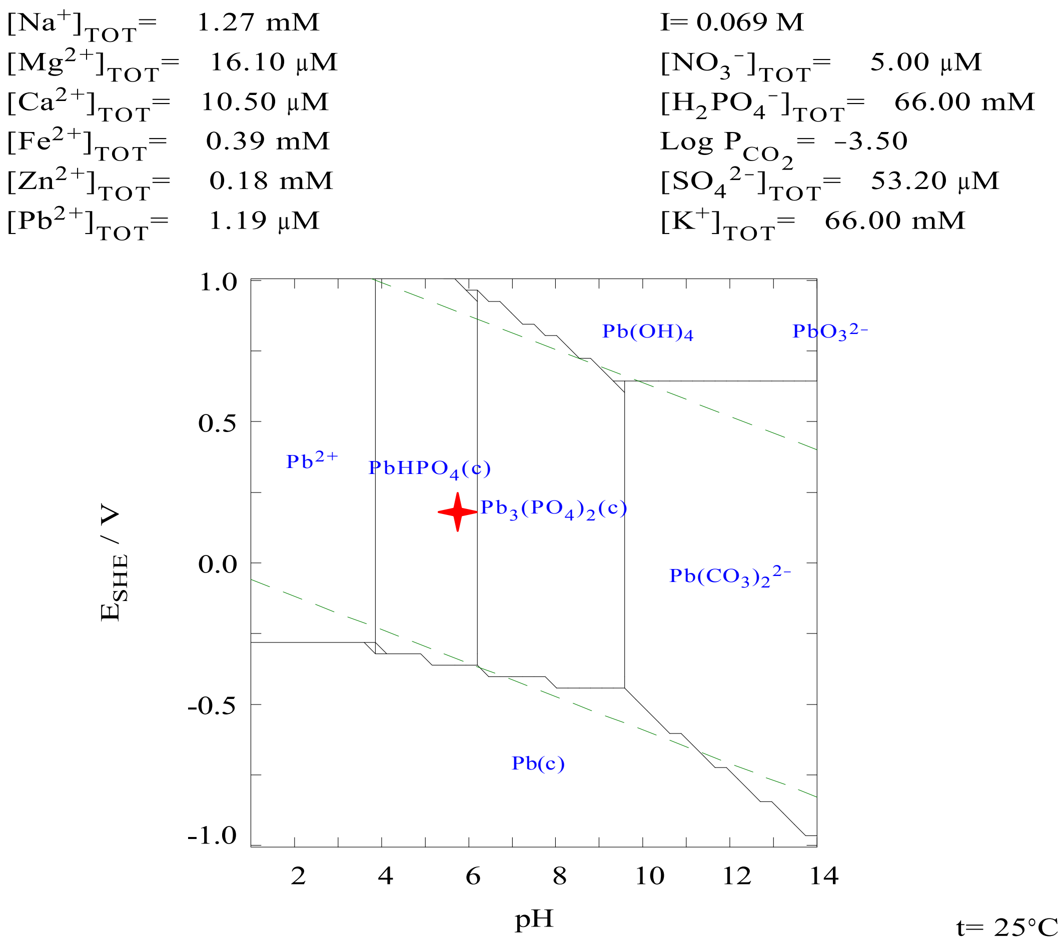


Figure C.7 Pourbaix diagram of lead for steel pipe section immersed into pH 5 water after three months of exposure.

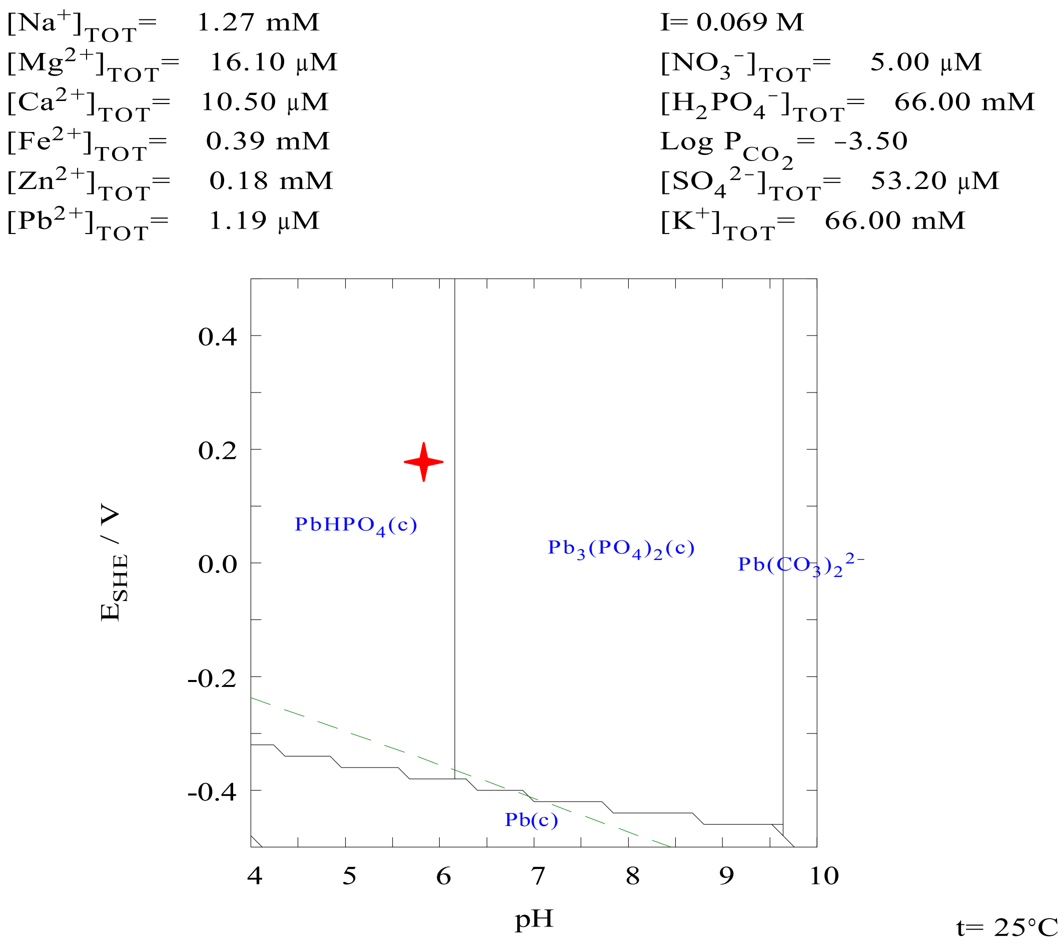


Figure C.8 Pourbaix diagram of lead for steel pipe section immersed into pH 5 water after three months of exposure. Study area.

Steel Gutter, pH 5 Water, After Three Months of Exposure

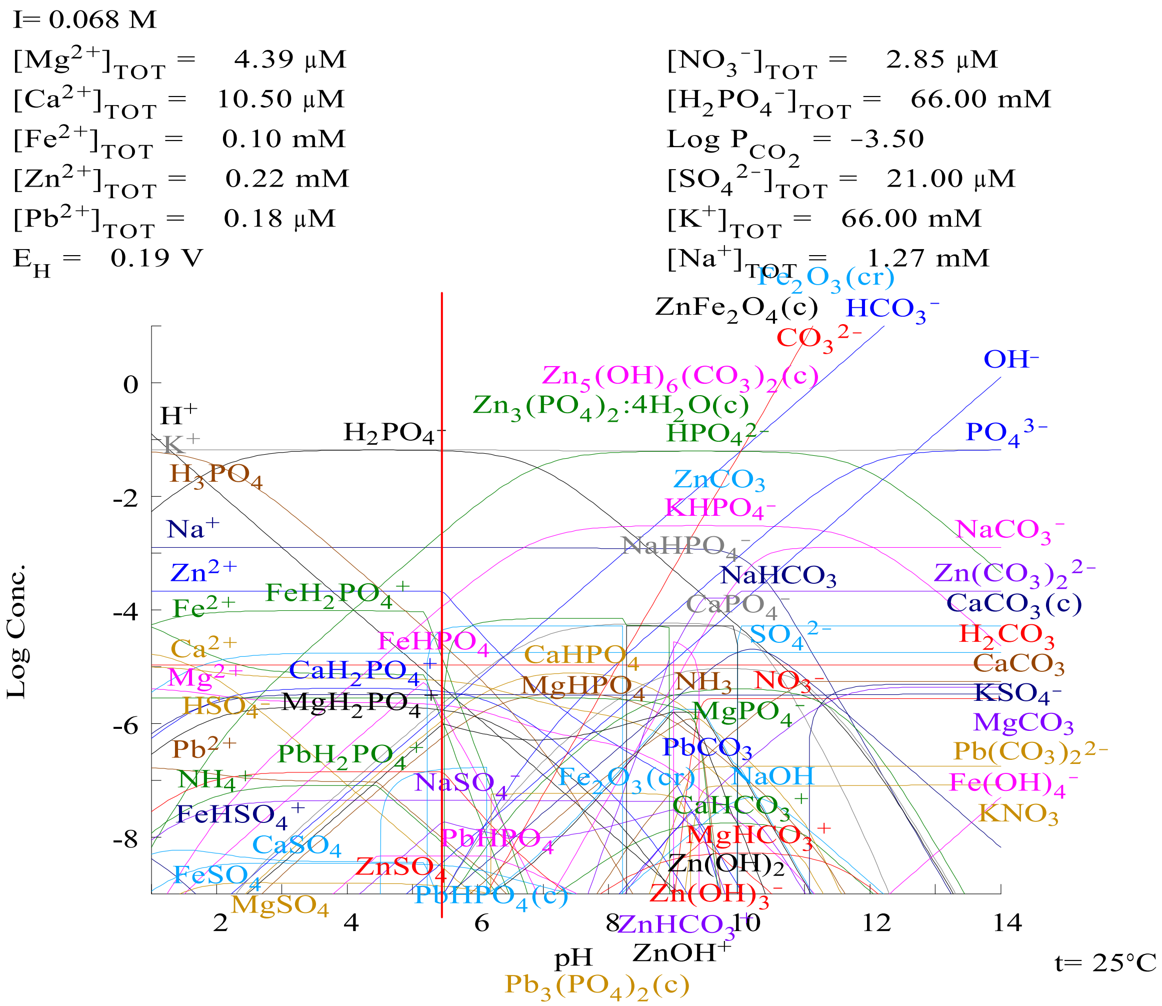


Figure C.9 Phase diagram for steel gutter section immersed into pH 5 water after three months of exposure.

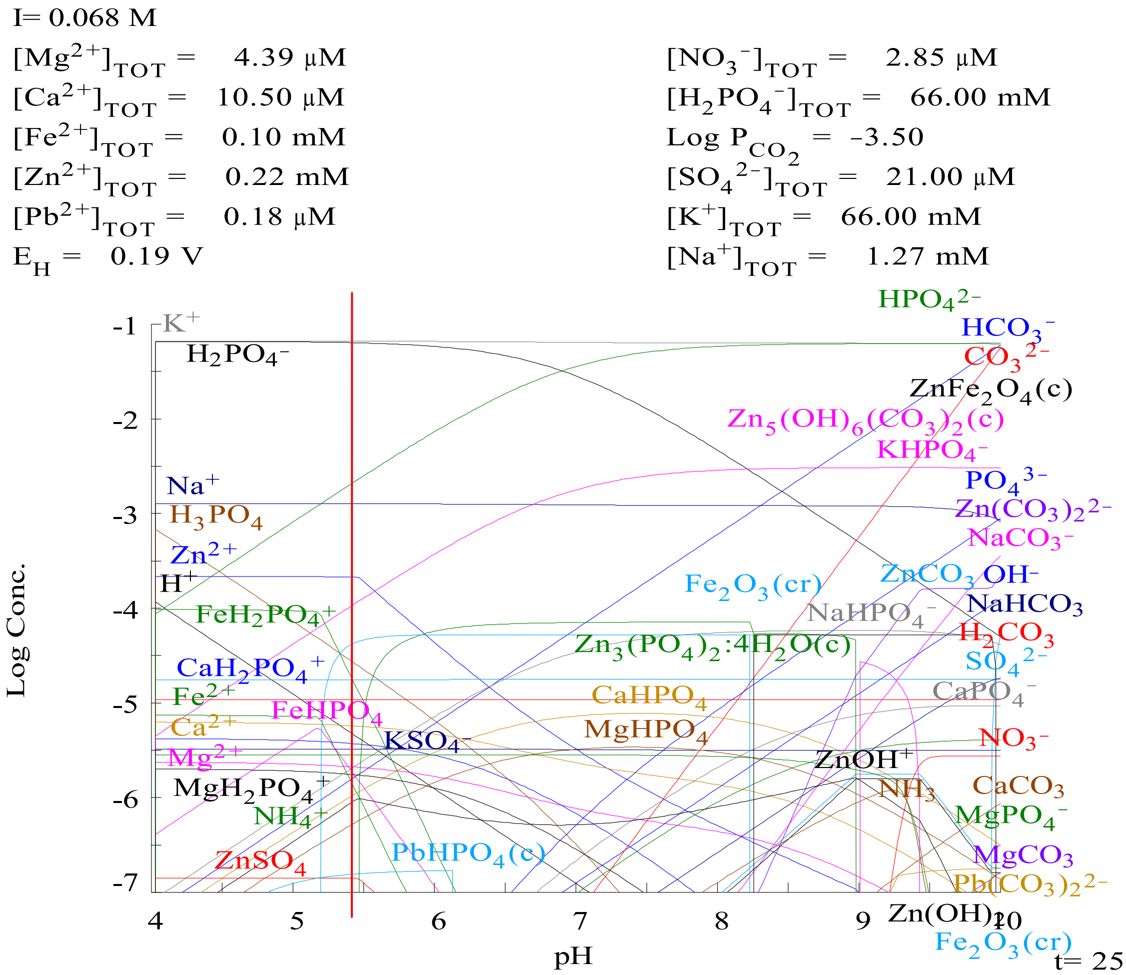


Figure C.10. Phase diagram for steel gutter section immersed into pH 5 water after three months of exposure. Study area.

Table C.3. The predominant species of zinc. Steel gutter section, pH 5 water, three months exposure.

Component	Log Concentration (mol/L)	Concentration (mol/L)	Zn Concentration (mg/L as Zn)	Cumulative Percentage of Zn
Zn^{2+}	-3.67	2.15E-04	14.06	99.51
$ZnOH^+$	-6.05	8.92E-07	5.83E-02	99.93
$ZnSO_4$	-6.85	1.41E-07	9.22E-03	99.99

Table C.4. The predominant species of lead. Steel gutter section, pH 5 water, three months exposure.

Component	Log Concentration (mol/L)	Concentration (mol/L)	Pb Concentration (mg/L as Pb)	Cumulative Percentage of Pb
$PbHPO_4$(c)	-6.81	1.55E-07	3.21E-02	86.63
Pb^{2+}	-7.98	1.04E-08	2.16E-03	92.45
$PbH_2PO_4^+$	-8.06	8.79E-09	1.82E-03	97.36
$PbHPO_4$	-8.33	4.67E-09	9.68E-04	99.97

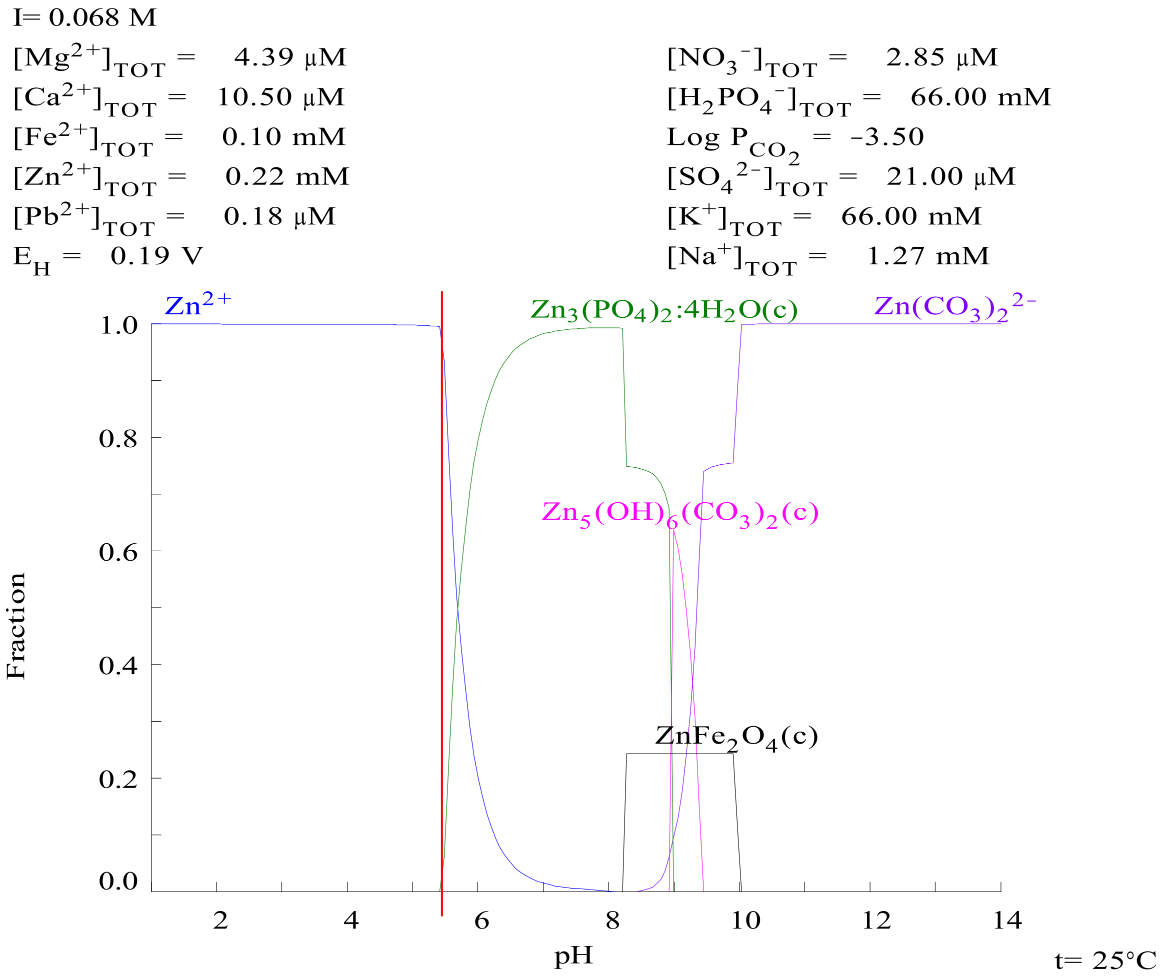


Figure C.11 Fraction diagram of zinc for steel gutter section immersed into pH 5 water after three months of exposure.

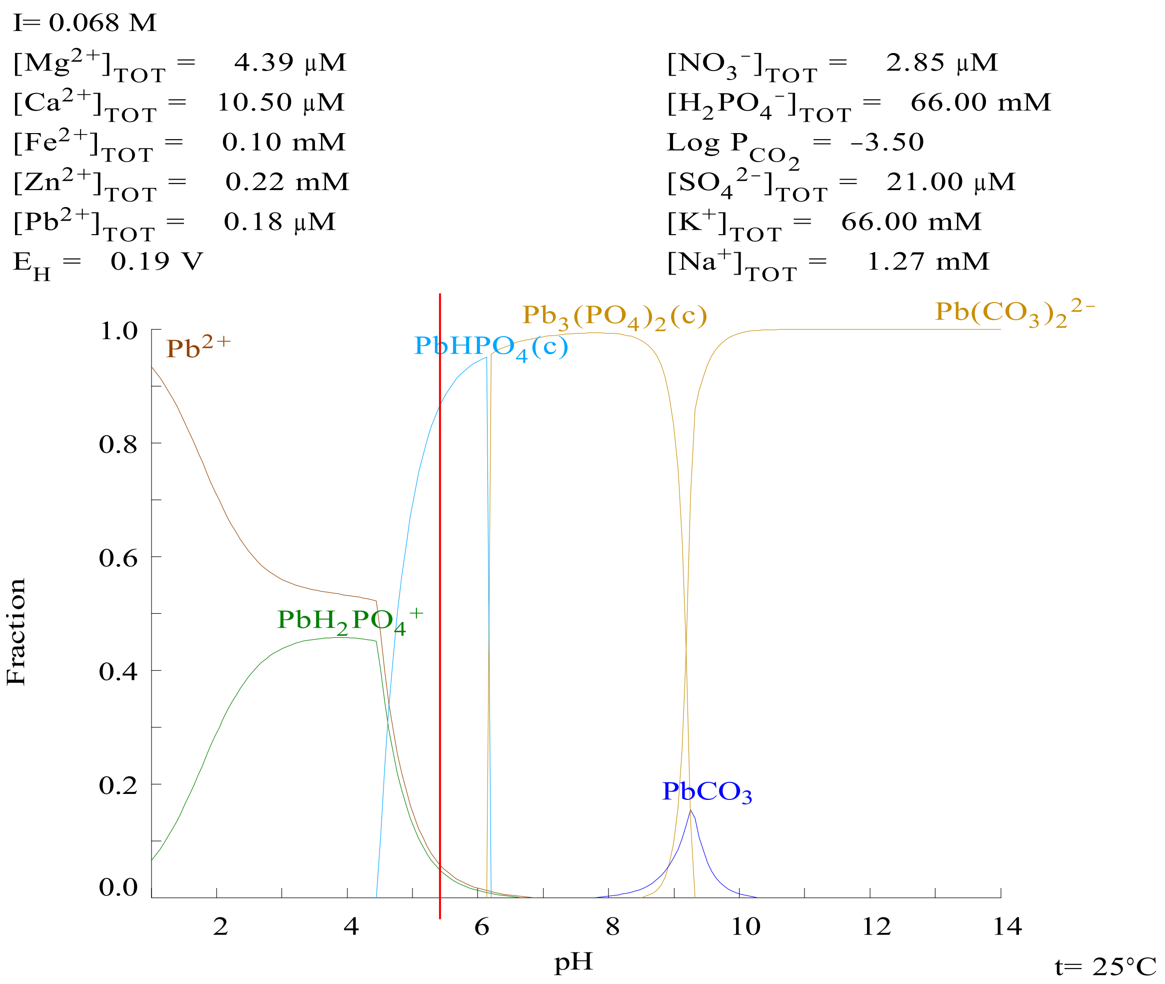


Figure C.12 Fraction diagram of lead for steel gutter section immersed into pH 5 water after three months of exposure.

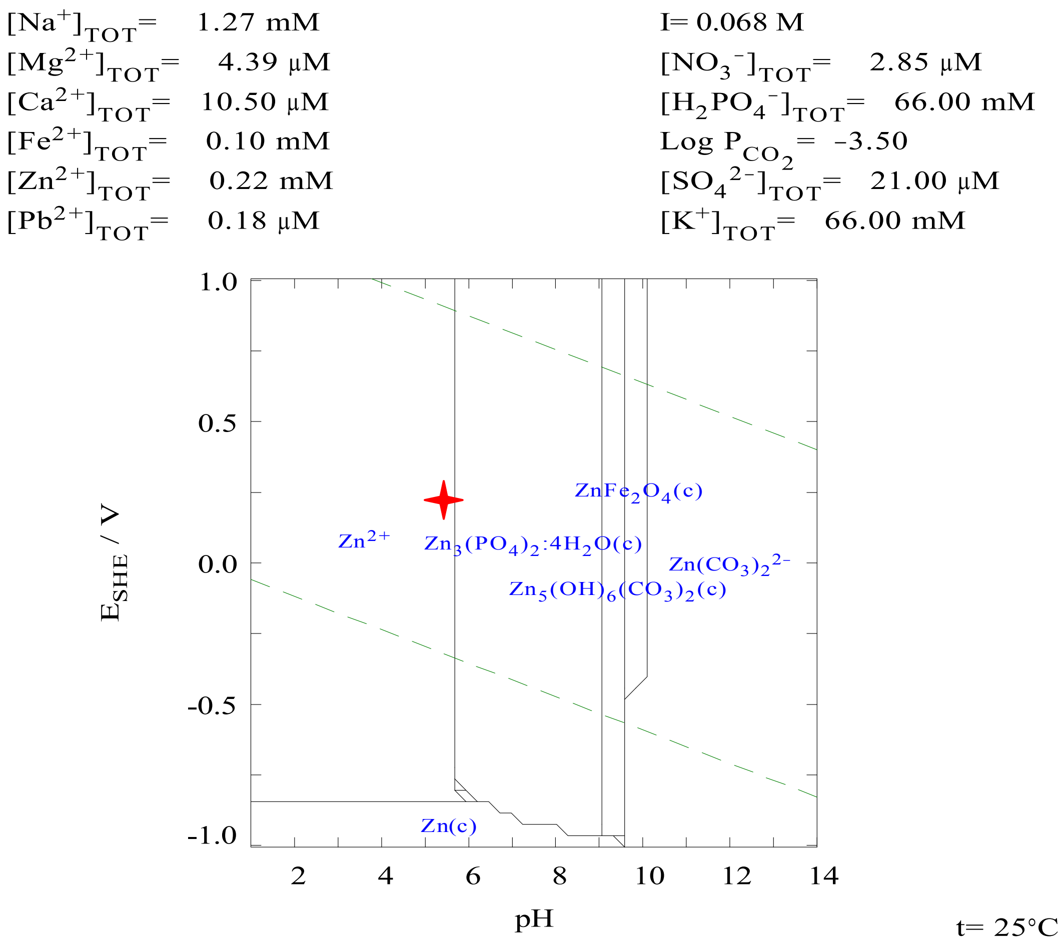


Figure C.13 Pourbaix diagram of zinc for steel gutter section immersed into pH 5 water after three months of exposure.

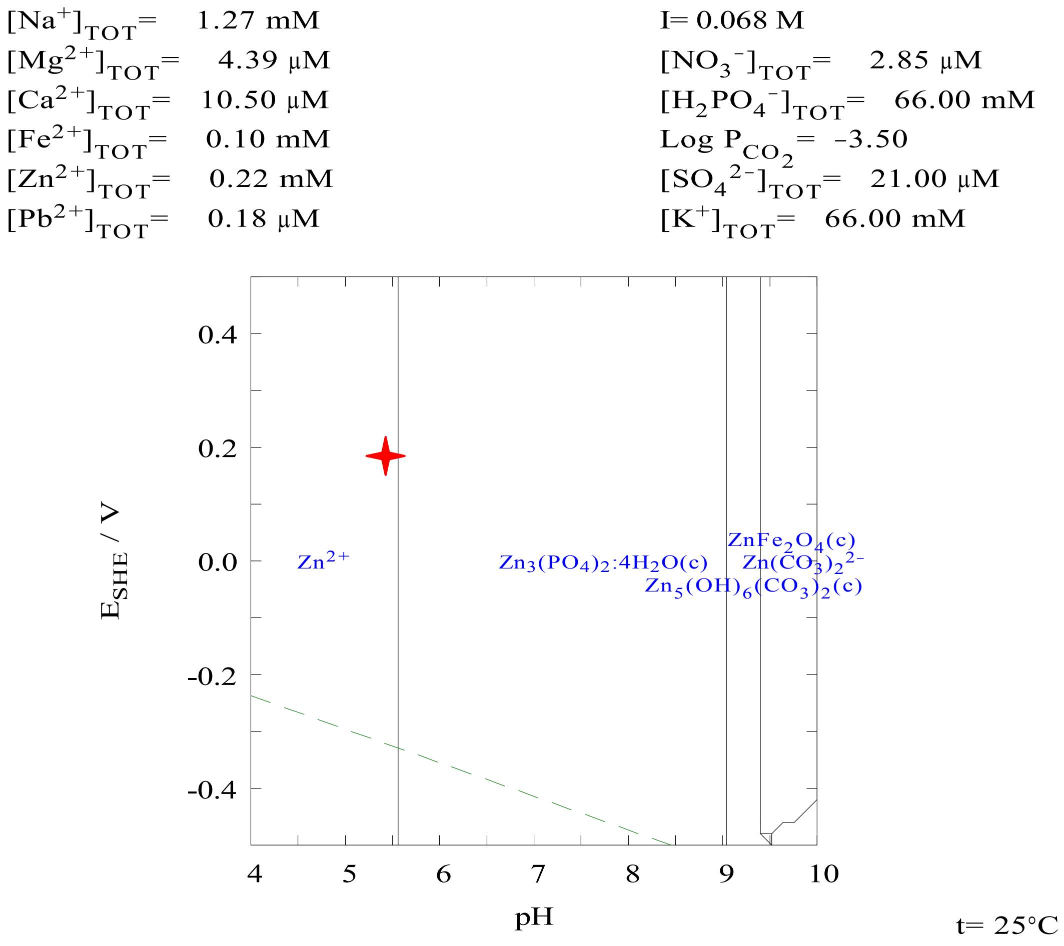


Figure C.14. Pourbaix diagram of zinc for steel gutter section immersed into pH 5 water after three months of exposure. Study area.

$[Na^+]_{TOT}=$ 1.27 mM

$[Mg^{2+}]_{TOT}=$ 4.39 μM

$[Ca^{2+}]_{TOT}=$ 10.50 μM

$[Fe^{2+}]_{TOT}=$ 0.10 mM

$[Zn^{2+}]_{TOT}=$ 0.22 mM

$[Pb^{2+}]_{TOT}=$ 0.18 μM

I= 0.068 M

$[NO_3^-]_{TOT}=$ 2.85 μM

$[H_2PO_4^-]_{TOT}=$ 66.00 mM

Log $P_{CO_2}=$ -3.50

$[SO_4^{2-}]_{TOT}=$ 21.00 μM

$[K^+]_{TOT}=$ 66.00 mM

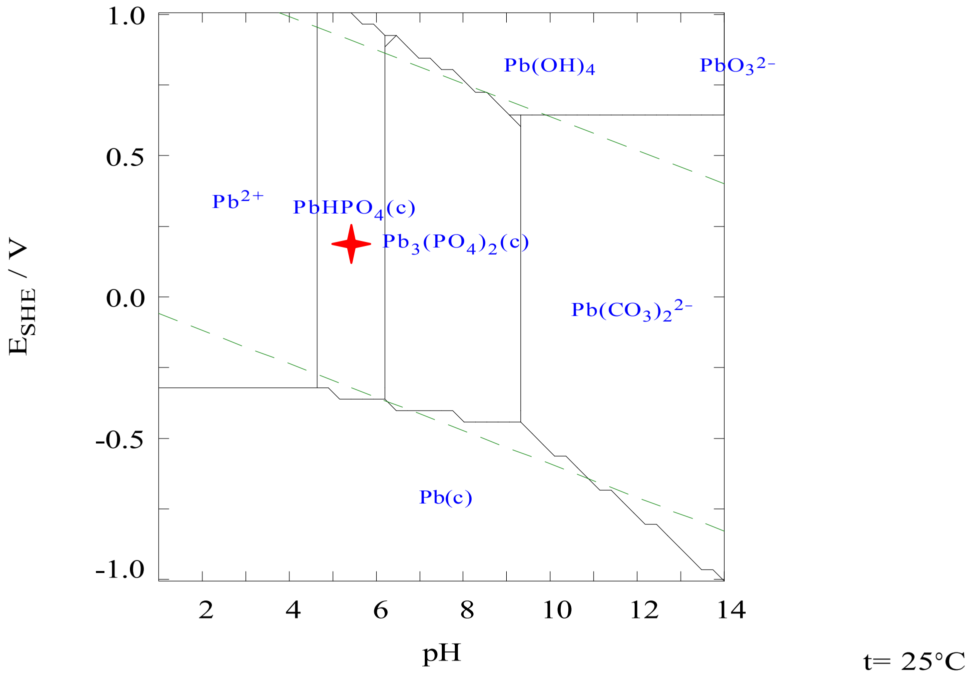


Figure C.15. Pourbaix diagram of lead for steel gutter section immersed into pH 5 water after three months of exposure.

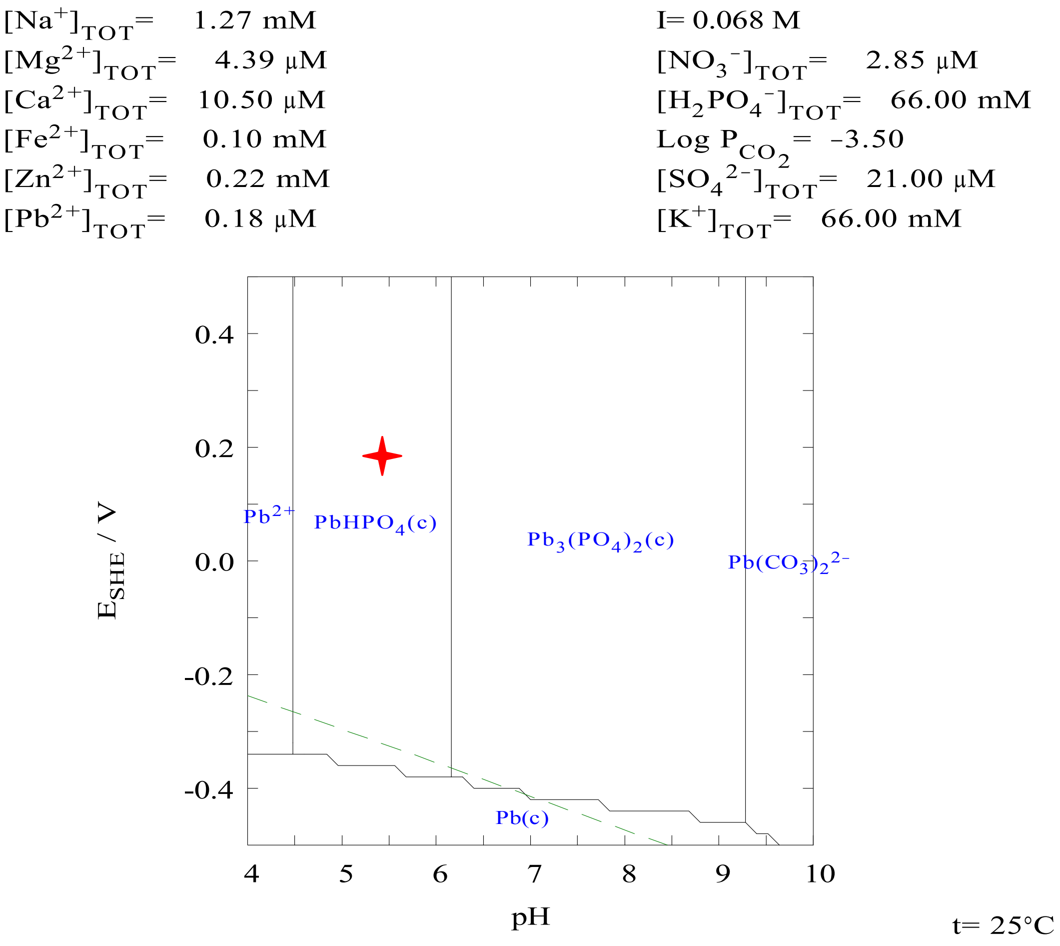


Figure 16.Pourbaix diagram of lead for steel gutter section immersed into pH 5 water after three months of exposure. Study area.

Steel Pipe, pH 8 Water, After Three Months of Exposure

$[Mg^{2+}]_{TOT}$ = 5.93 µM
$[Ca^{2+}]_{TOT}$ = 3.70 µM
$[Fe^{2+}]_{TOT}$ = 21.10 µM
$[Zn^{2+}]_{TOT}$ = 1.29 mM
$[Cu^{2+}]_{TOT}$ = 0.47 µM
$[Pb^{2+}]_{TOT}$ = 3.03 µM
E_H = 0.11 V

I= 0.196 M
$[HPO_4^{2-}]_{TOT}$ = 64.60 mM
$[NO_3^-]_{TOT}$ = 41.90 µM
Log P_{CO_2} = -3.50
$[SO_4^{2-}]_{TOT}$ = 23.70 µM
$[K^+]_{TOT}$ = 2.07 mM
$[Na^+]_{TOT}$ = 129.00 mM

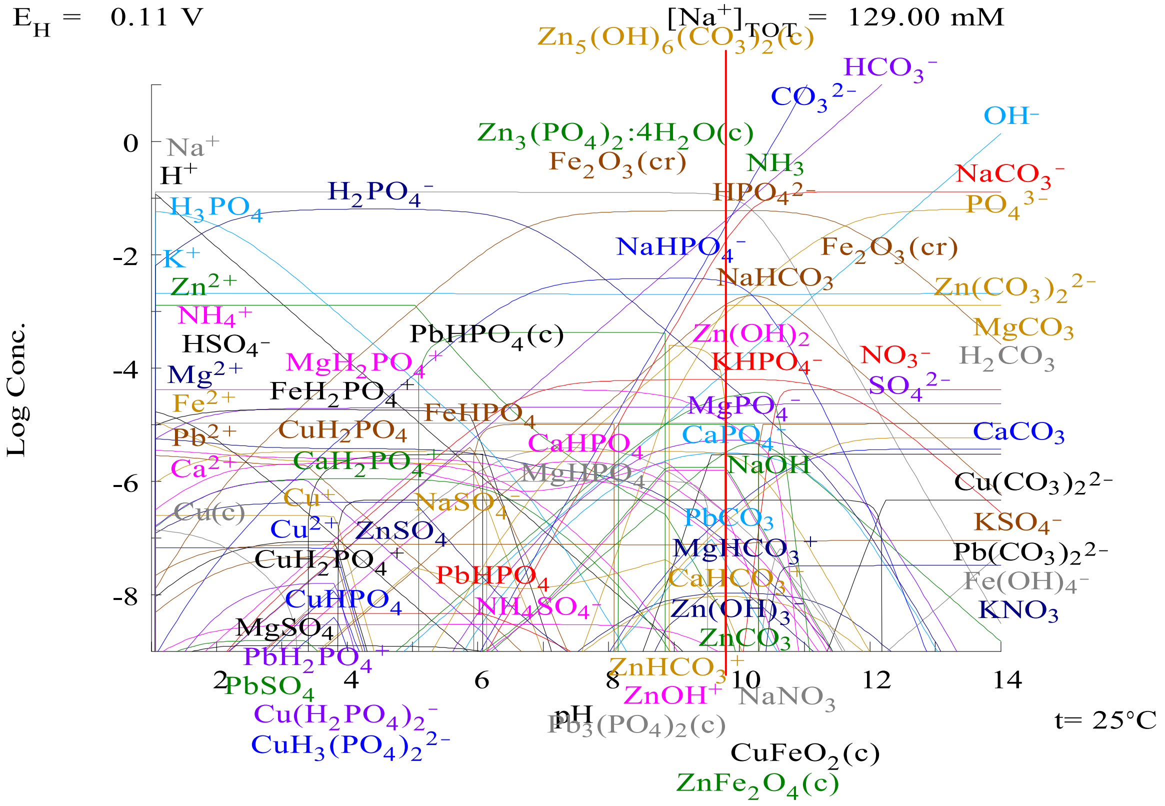


Figure C.17 Phase diagram for steel pipe section immersed into pH 8 water after three months of exposure.

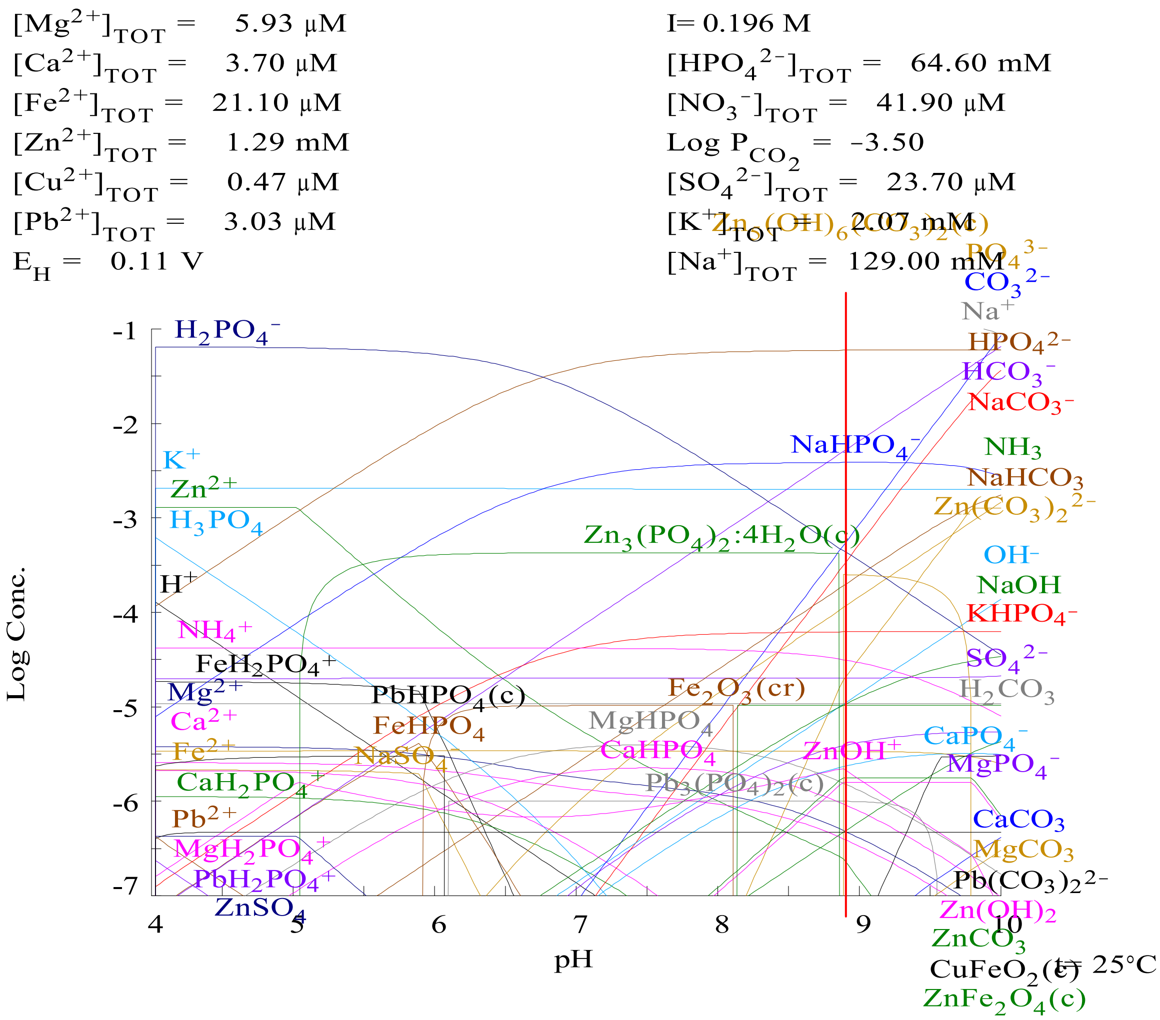


Figure C.18 Phase diagram for steel pipe section immersed into pH 8 water after three months of exposure. Study area.

Table C.5. The predominant species of zinc. Steel pipe section, pH 8 water, three months exposure.

Component	Log Concentration (mol/L)	Concentration (mol/L)	Zn Concentration (mg/L as Zn)	Cumulative Percentage of Zn
$Zn_3(PO_4)_2{:}4H_2O(c)$	-3.38	4.19E-04	82.28	97.51
$Zn(CO_3)_2^{2-}$	-4.79	1.61E-05	1.06	98.76
$ZnFe_2O_4(c)$	-4.99	1.03E-05	0.67	99.56
$ZnOH^+$	-5.66	2.20E-06	0.14	99.73
$ZnCO_3$	-5.78	1.68E-06	0.11	99.86
$Zn(OH)_2$	-5.83	1.49E-06	9.75E-02	99.98
Zn^{2+}	-6.58	2.61E-07	1.70E-02	99.997

Table C.6. The predominant species of copper. Steel pipe section, pH 8 water, three months exposure.

Component	Log Concentration (mol/L)	Concentration (mol/L)	Cu Concentration (mg/L as Cu)	Cumulative Percentage of Cu
$CuFeO_2$(c)	-6.33	4.72E-07	3.00E-02	99.999999
$CuH_2(PO_4)_2^{2-}$	-14.48	3.33E-15	2.12E-10	99.99999989
$CuCO_3$	-15.70	1.98E-16	1.26E-11	99.99999993

Footnote: Cu^+ was calculated to be 2.69E-13 mg/L; Cu^{2+} was calculated to be 7.26E-14 mg/L

Table C.7. The predominant species of lead. Steel pipe section, pH 8 water, three months exposure.

Component	Log Concentration (mol/L)	Concentration (mol/L)	Pb Concentration (mg/L as Pb)	Cumulative Percentage of Pb
$Pb_3(PO_4)_2$(c)	-6.00	1.00E-06	0.62	99.19
$Pb(CO_3)_2^{2-}$	-7.89	1.29E-08	2.67E-03	99.61
$PbCO_3$	-7.94	1.14E-08	2.36E-03	99.99

Footnote: Pb^{2+} was calculated to be 4.22E-06 mg/L

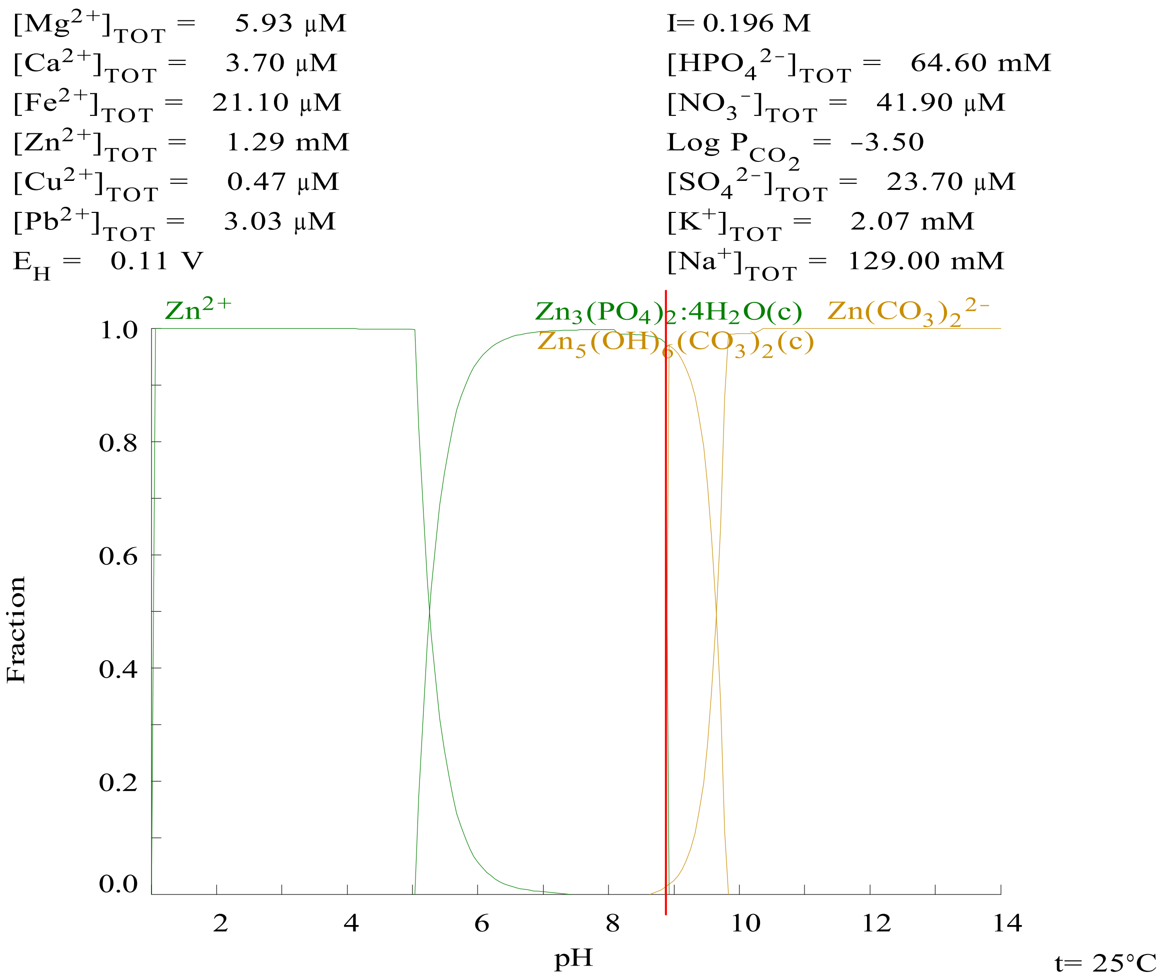


Figure C.19 Fraction diagram of zinc for steel pipe section immersed into pH 8 water after three months of exposure.

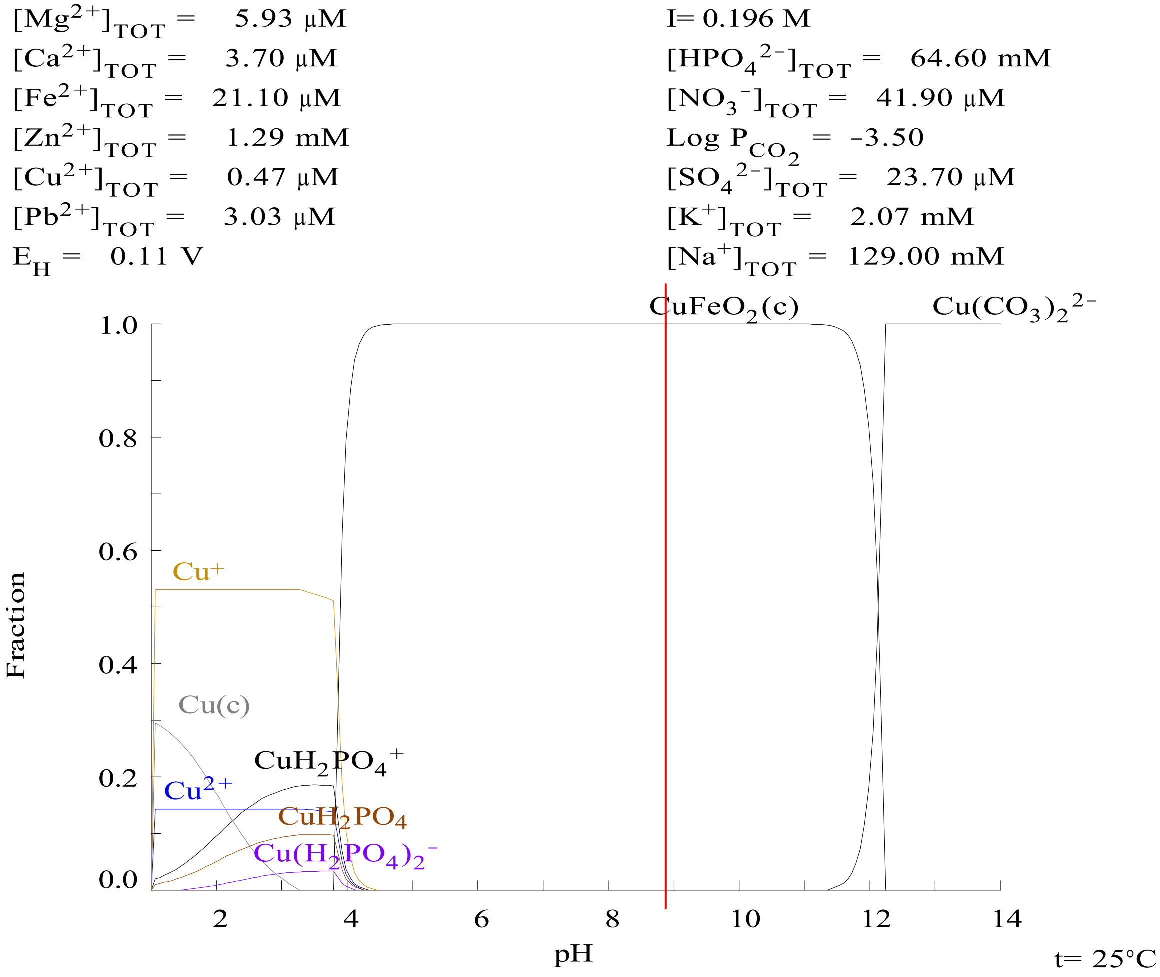


Figure C.20 Fraction diagram of copper for steel pipe section immersed into pH 8 water after three months of exposure.

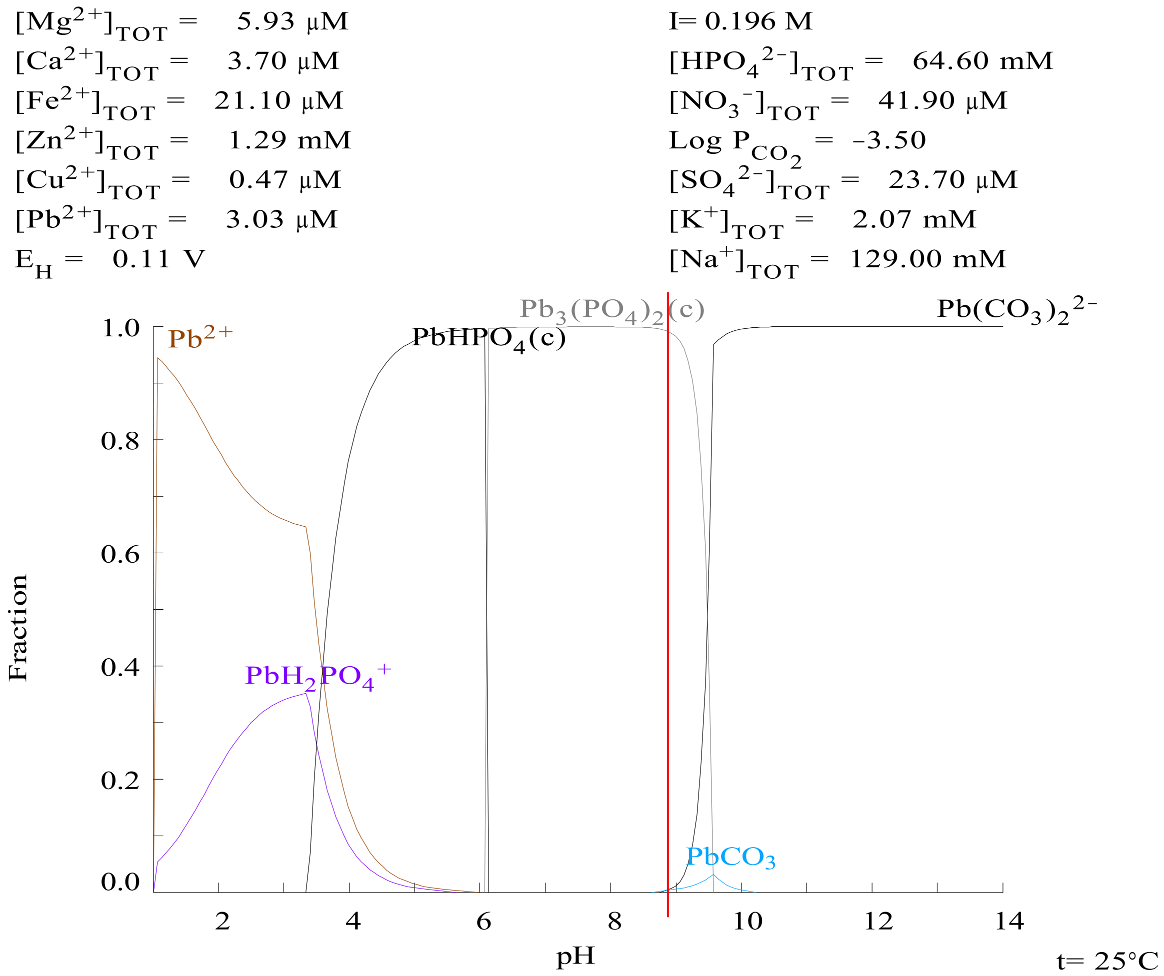


Figure C.21 Fraction diagram of lead for steel pipe section immersed into pH 8 water after three months of exposure.

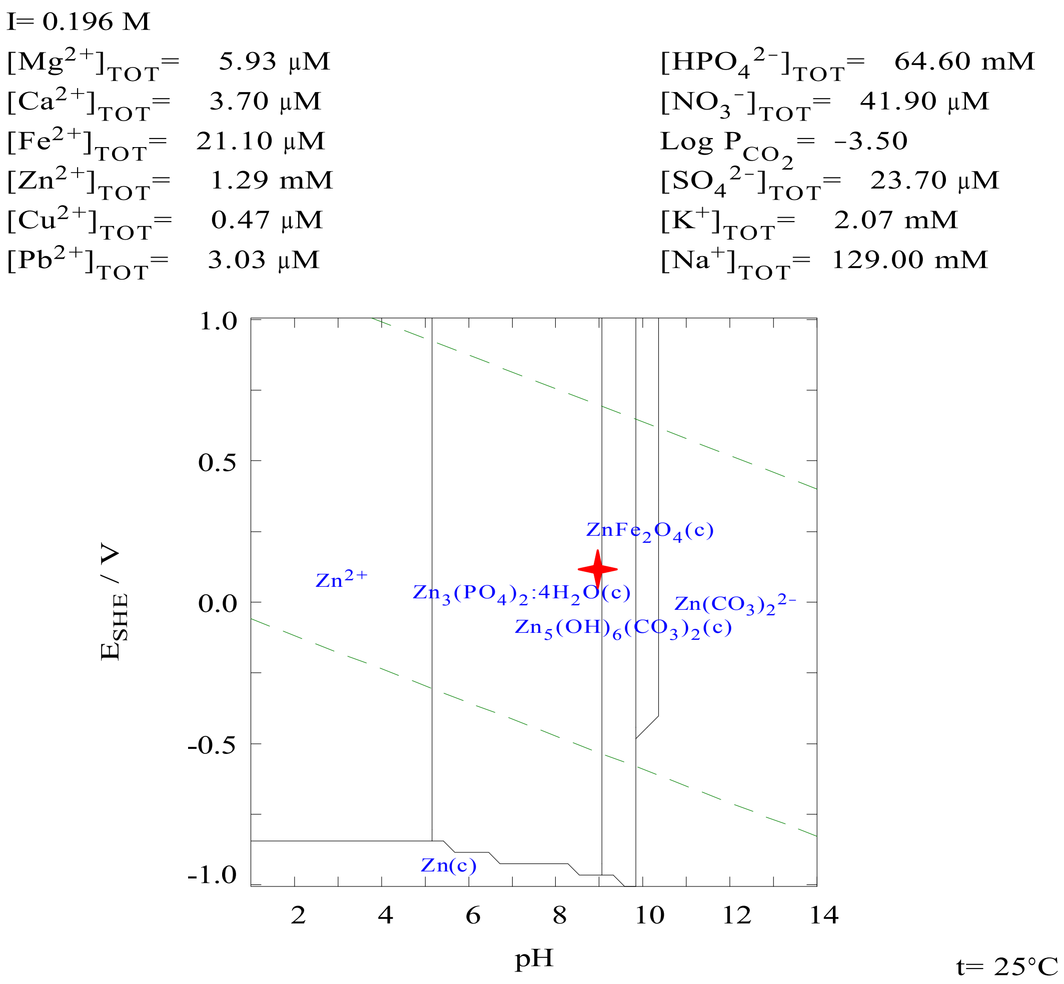


Figure C.22. Pourbaix diagram of zinc for steel pipe section immersed into pH 8 water after three months of exposure.

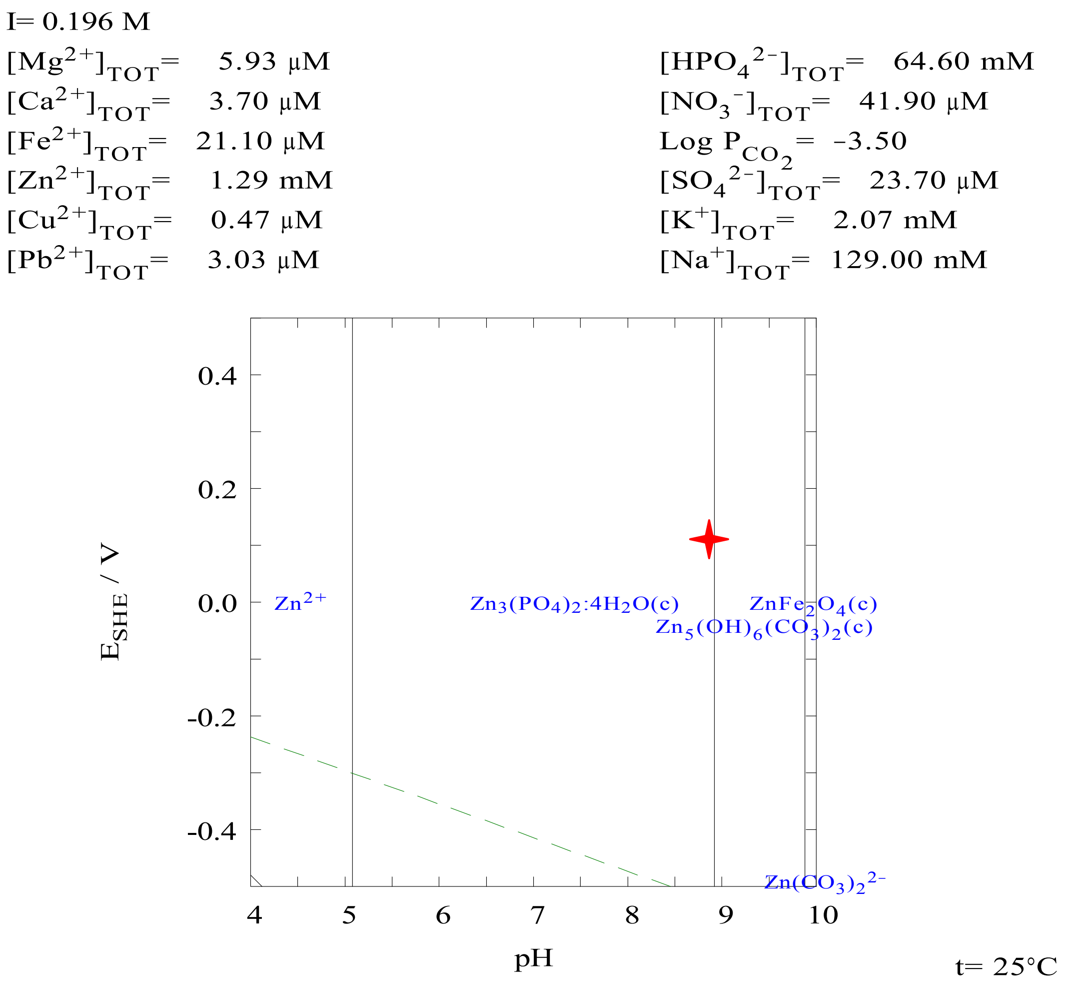


Figure C.23. Pourbaix diagram of zinc for steel pipe section immersed into pH 8 water after three months of exposure. Study area.

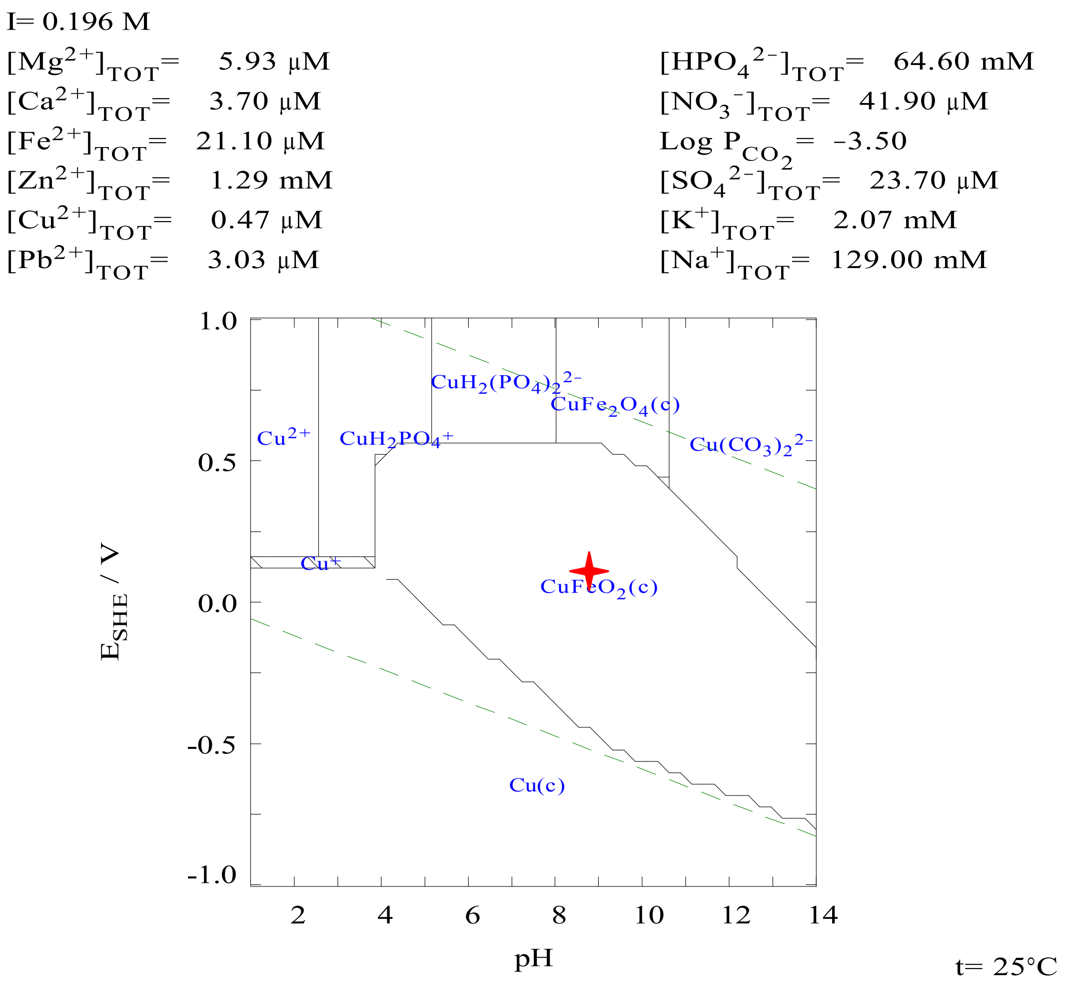


Figure C.24. Pourbaix diagram of copper for steel pipe section immersed into pH 8 water after three months of exposure.

I= 0.196 M

$[Mg^{2+}]_{TOT}$= 5.93 μM

$[Ca^{2+}]_{TOT}$= 3.70 μM

$[Fe^{2+}]_{TOT}$= 21.10 μM

$[Zn^{2+}]_{TOT}$= 1.29 mM

$[Cu^{2+}]_{TOT}$= 0.47 μM

$[Pb^{2+}]_{TOT}$= 3.03 μM

$[HPO_4^{2-}]_{TOT}$= 64.60 mM

$[NO_3^{-}]_{TOT}$= 41.90 μM

Log P_{CO_2}= -3.50

$[SO_4^{2-}]_{TOT}$= 23.70 μM

$[K^{+}]_{TOT}$= 2.07 mM

$[Na^{+}]_{TOT}$= 129.00 mM

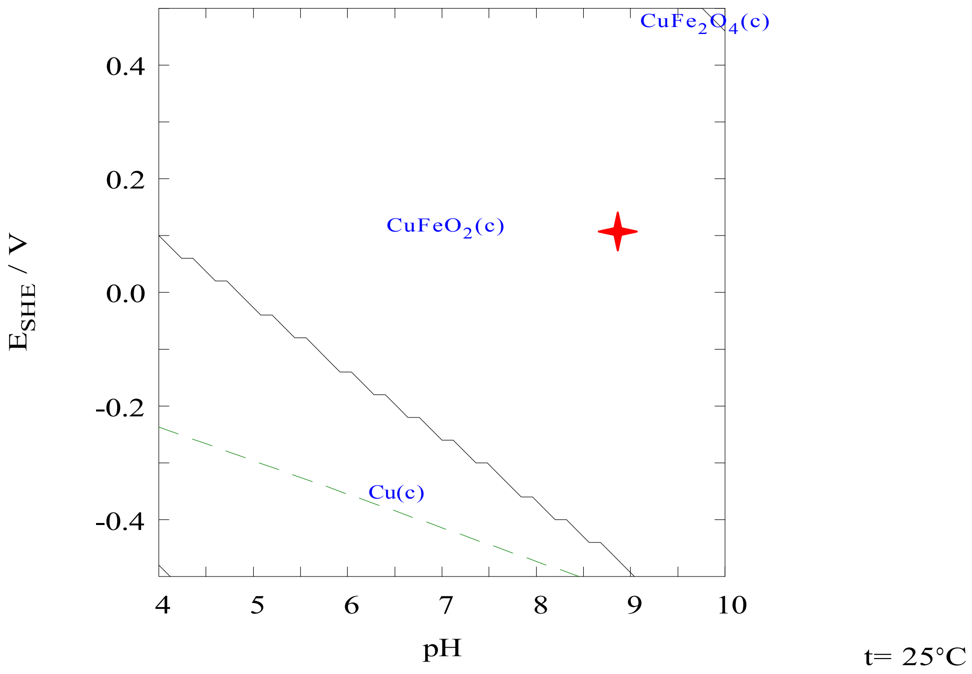


Figure C.25. Pourbaix diagram of copper for steel pipe section immersed into pH 8 water after three months of exposure. Study area.

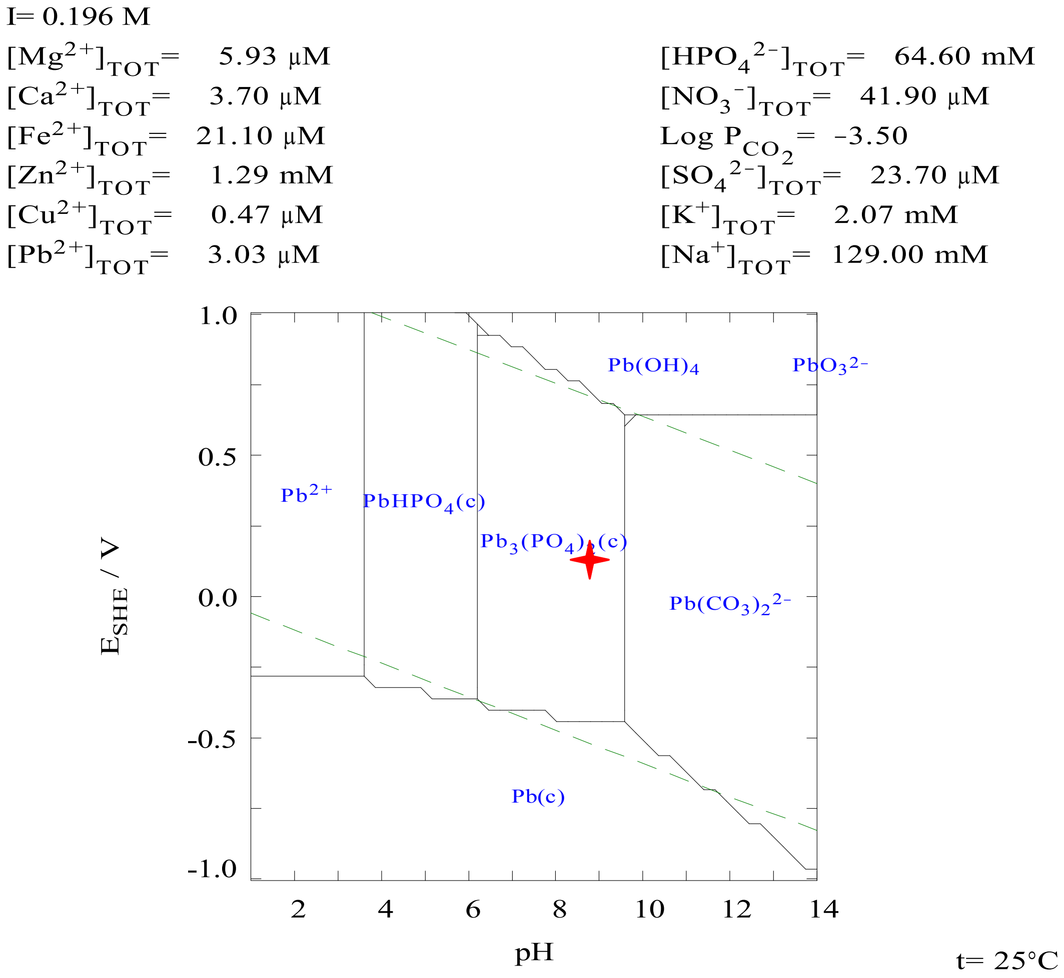


Figure C.26. Pourbaix diagram of lead for steel pipe section immersed into pH 8 water after three months of exposure.

I= 0.196 M

$[Mg^{2+}]_{TOT}$= 5.93 μM
$[Ca^{2+}]_{TOT}$= 3.70 μM
$[Fe^{2+}]_{TOT}$= 21.10 μM
$[Zn^{2+}]_{TOT}$= 1.29 mM
$[Cu^{2+}]_{TOT}$= 0.47 μM
$[Pb^{2+}]_{TOT}$= 3.03 μM

$[HPO_4^{2-}]_{TOT}$= 64.60 mM
$[NO_3^{-}]_{TOT}$= 41.90 μM
Log P_{CO_2}= -3.50
$[SO_4^{2-}]_{TOT}$= 23.70 μM
$[K^{+}]_{TOT}$= 2.07 mM
$[Na^{+}]_{TOT}$= 129.00 mM

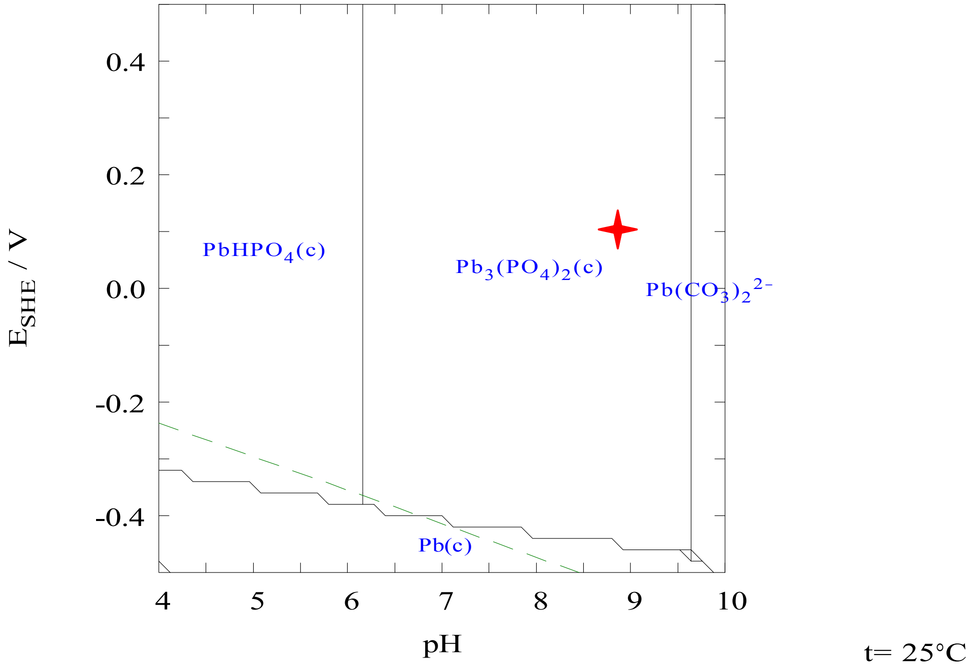


Figure C.27. Pourbaix diagram of lead for steel pipe section immersed into pH 8 water after three months of exposure. Study area.

Steel Gutter, pH 8 Water, After Three Months of Exposure

I= 0.196 M

$[Ca^{2+}]_{TOT}$ = 4.71 µM

$[Fe^{2+}]_{TOT}$ = 6.09 µM

$[Al^{3+}]_{TOT}$ = 7.41 µM

$[Zn^{2+}]_{TOT}$ = 0.15 mM

$[Cu^{2+}]_{TOT}$ = 0.47 µM

$[Pb^{2+}]_{TOT}$ = 0.48 µM

E_H = 0.12 V

$[HPO_4^{2-}]_{TOT}$ = 64.60 mM

$[NO_3^-]_{TOT}$ = 37.10 µM

Log P_{CO_2} = -3.50

$[SO_4^{2-}]_{TOT}$ = 7.18 µM

$[K^+]_{TOT}$ = 2.07 mM

$[Na^+]_{TOT}$ = 129.00 mM

$[Mg^{2+}]_{TOT}$ = 5.93 µM

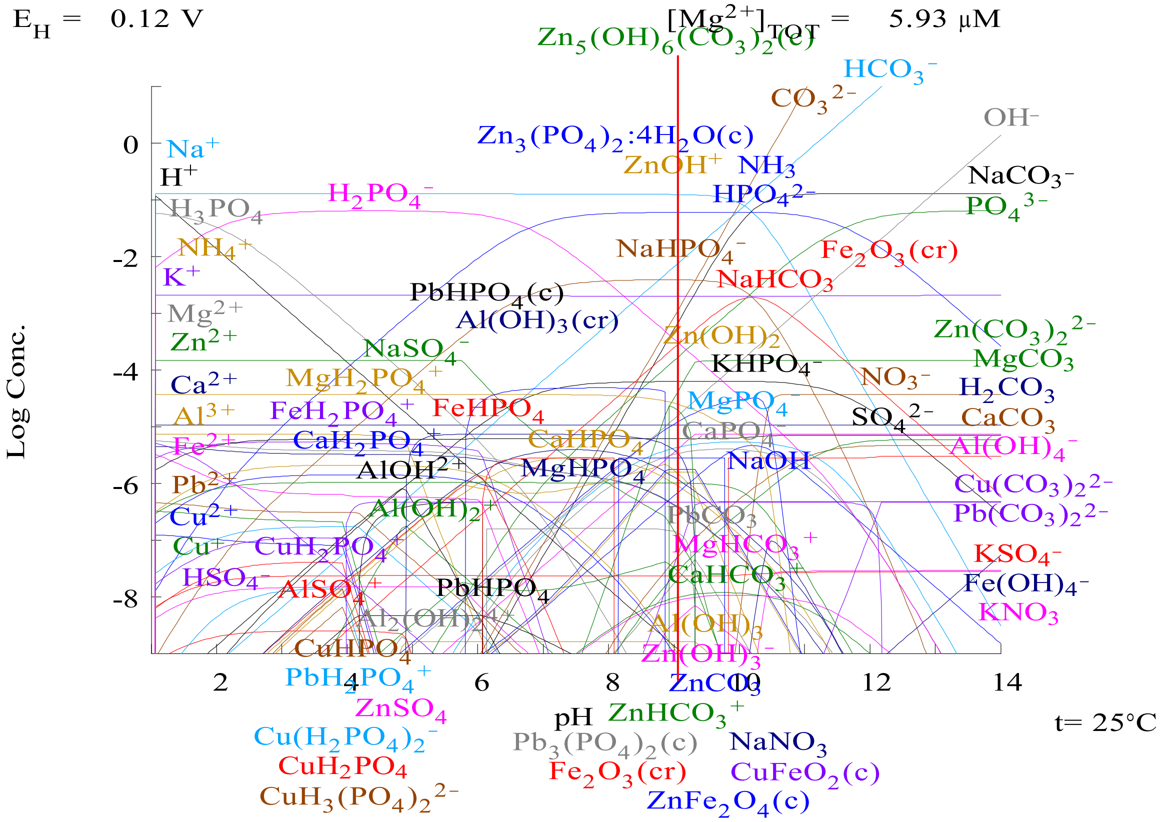


Figure C.28. Phase diagram for steel gutter section immersed into pH 8 water after three months of exposure.

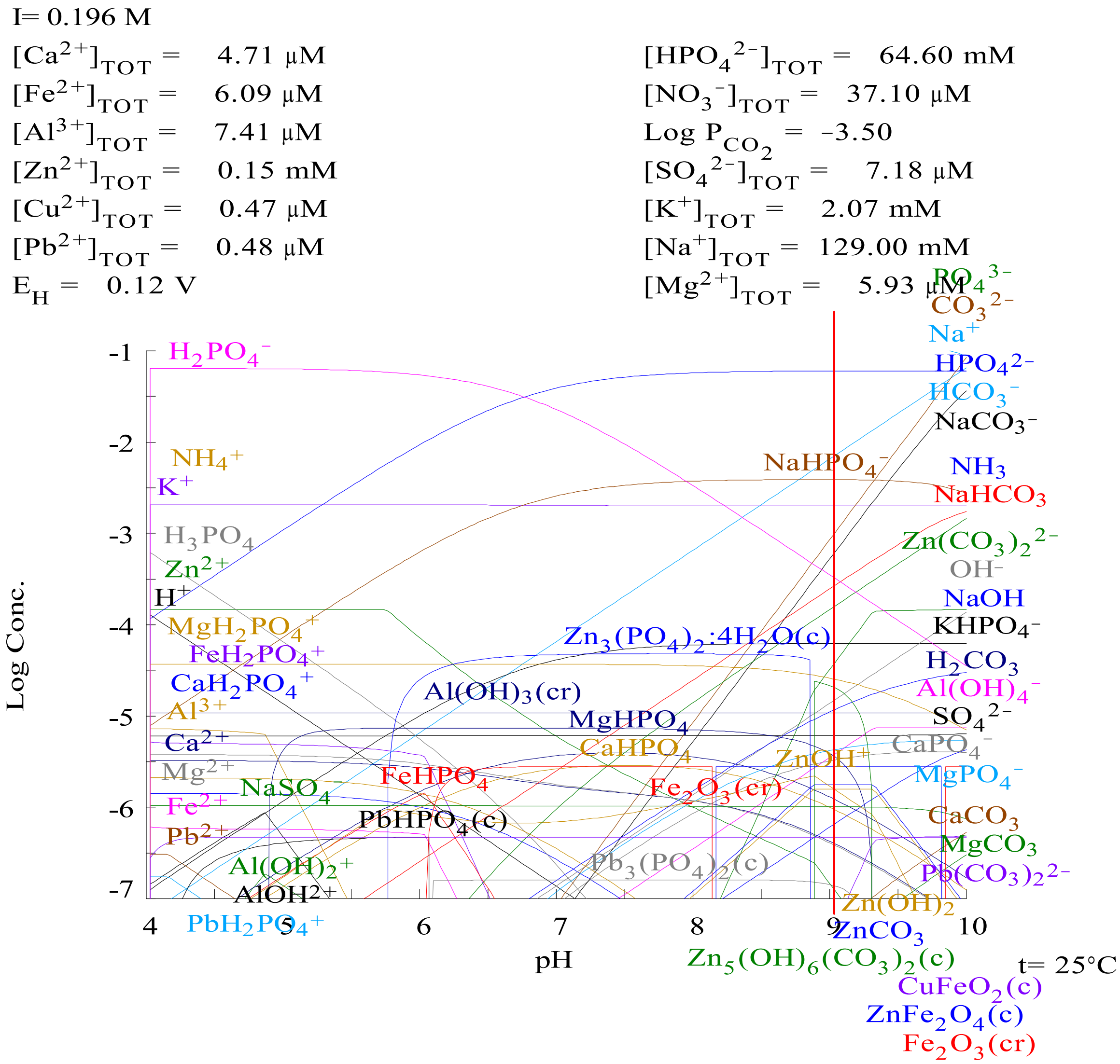


Figure C.29. Phase diagram for steel gutter section immersed into pH 8 water after three months of exposure. Study area.

Table C.8. The predominant species of zinc. Steel gutter section, pH 8 water, three months exposure.

Component	Log Concentration (mol/L)	Concentration (mol/L)	Zn Concentration (mg/L as Zn)	Cumulative Percentage of Zn
$Zn_5(OH)_6(CO_3)_2$(c)	-4.71	1.96E-05	6.42	66.31
$Zn(CO_3)_2^{2-}$	-4.38	4.21E-05	2.75	94.73
$ZnFe_2O_4$(c)	-5.55	2.81E-06	0.18	96.63
$ZnCO_3$	-5.75	1.78E-06	0.12	97.83
$Zn(OH)_2$	-5.80	1.58E-06	1.03E-01	98.90
$ZnOH^+$	-5.83	1.49E-06	9.74E-02	99.90

Footnote: Zn^{2+} was calculated to be 7.37E-03mg/L.

Table C.9. The predominant species of copper. Steel gutter section, pH 8 water, three months exposure.

Component	Log Concentration (mol/L)	Concentration (mol/L)	Cu Concentration (mg/L as Cu)	Cumulative Percentage of Cu
$CuFeO_2$(c)	-6.33	4.72E-07	3.00E-02	99.9999990
$CuH_2(PO_4)_2^{2-}$	-14.49	3.21E-15	2.04E-10	99.9999997
$Cu(CO_3)_2^{2-}$	-15.20	6.31E-16	4.01E-11	99.9999998

Footnote: Cu^+ was calculated to be 1.77E-13 mg/L; Cu^{2+} was calculated to be 6.77E-14 mg/L

Table C.10. The predominant species of lead. Steel gutter section, pH 8 water, three months exposure.

Component	Log Concentration (mol/L)	Concentration (mol/L)	Pb Concentration (mg/L as Pb)	Cumulative Percentage of Pb
$Pb_3(PO_4)_2$(c)	-6.87	1.35E-07	8.40E-02	83.89
$Pb(CO3)_2^{2-}$	-7.24	5.70E-08	1.18E-02	95.69
$PbCO_3$	-7.69	2.05E-08	4.25E-03	99.94

Footnote: Pb^{2+} was calculated to be 3.09E-06 mg/L.

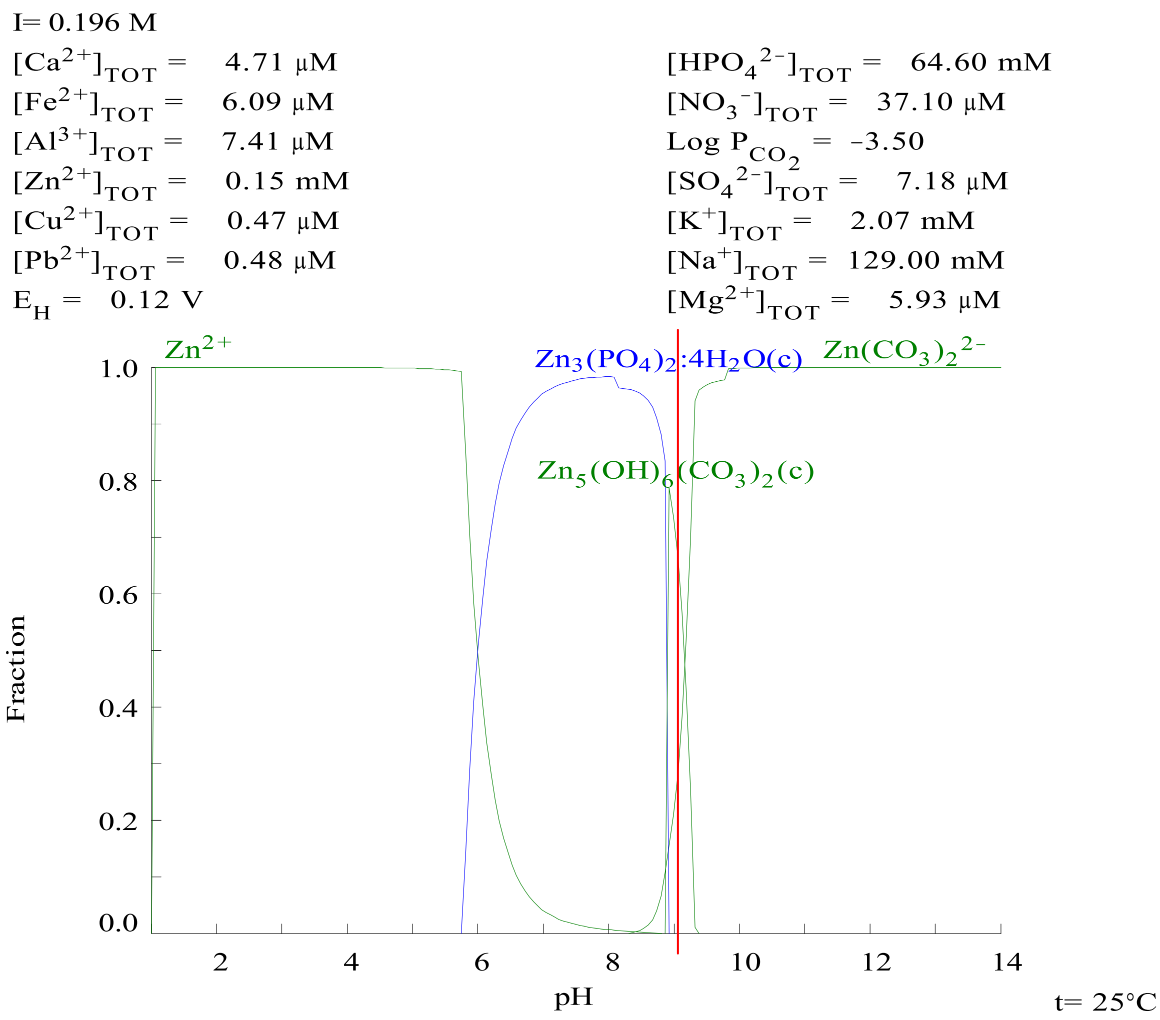


Figure C.30. Fraction diagram of zinc for steel gutter section immersed into pH 8 water after three months of exposure.

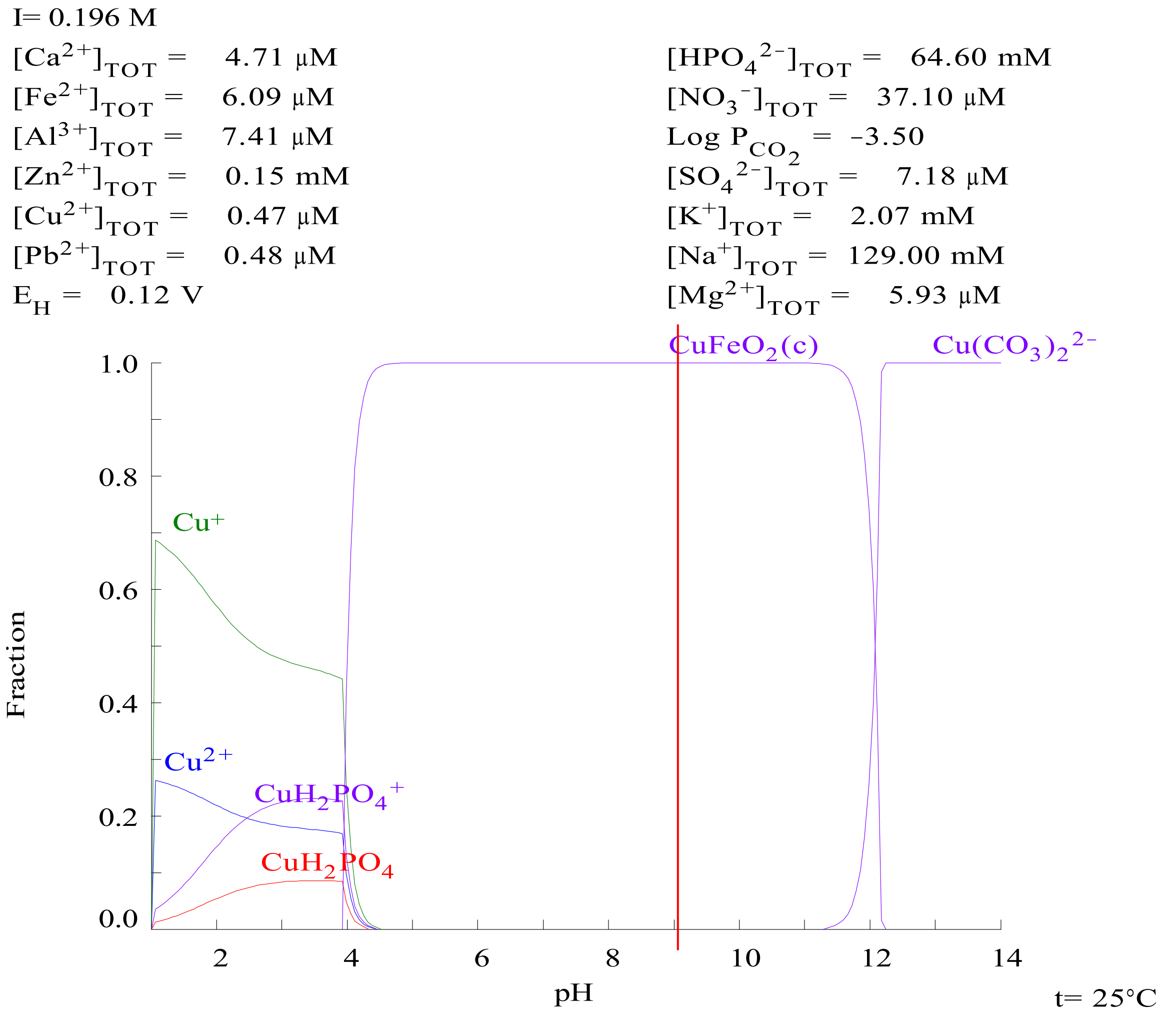


Figure C.31. Fraction diagram of copper for steel gutter section immersed into pH 8 water after three months of exposure.

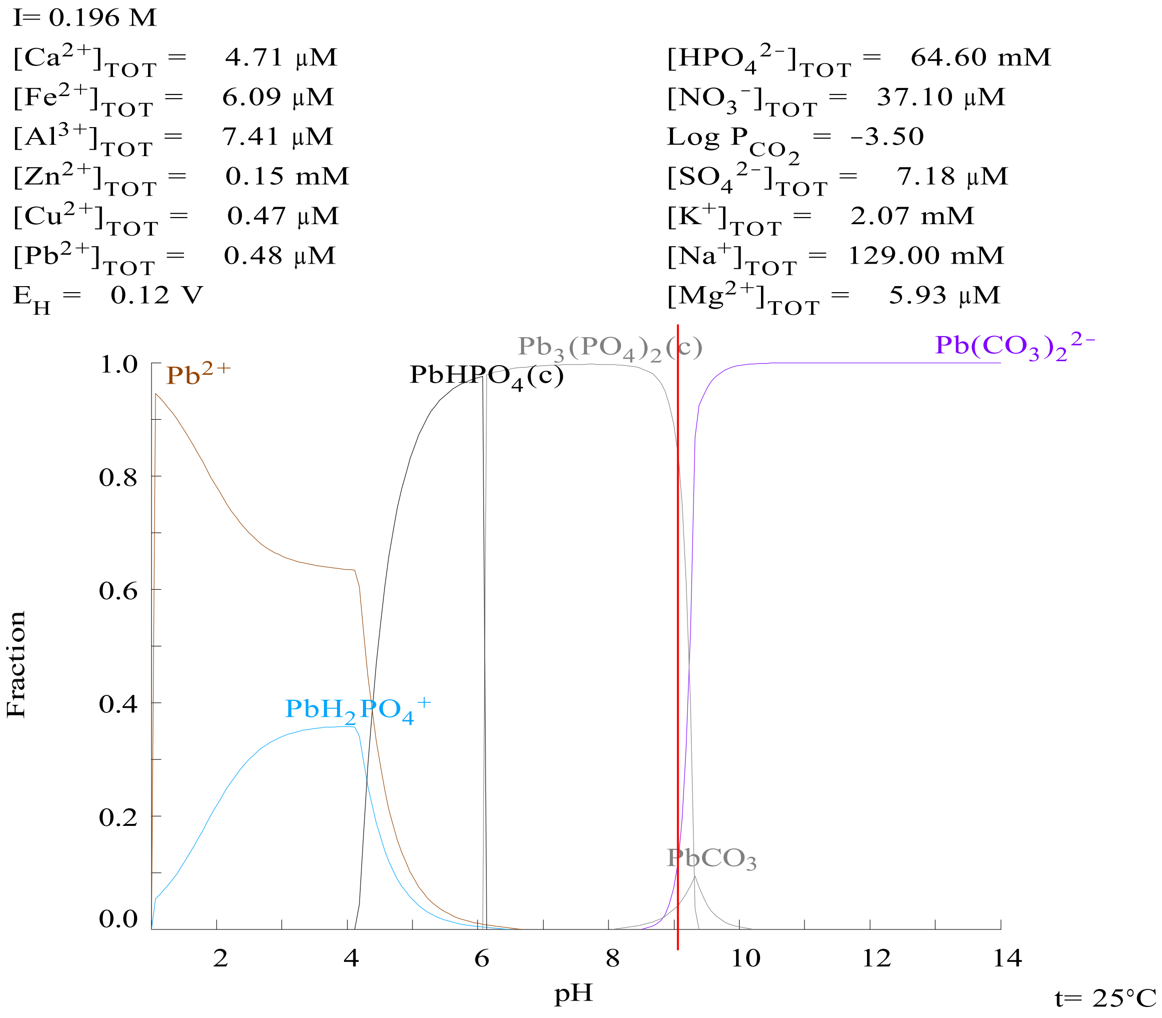


Figure C.32. Fraction diagram of lead for steel gutter section immersed into pH 8 water after three months of exposure.

$[Mg^{2+}]_{TOT}$= 5.93 µM
$[Ca^{2+}]_{TOT}$= 4.71 µM
$[Fe^{2+}]_{TOT}$= 6.09 µM
$[Al^{3+}]_{TOT}$= 7.41 µM
$[Zn^{2+}]_{TOT}$= 0.15 mM
$[Cu^{2+}]_{TOT}$= 0.47 µM
$[Pb^{2+}]_{TOT}$= 0.48 µM

I= 0.196 M
$[HPO_4^{2-}]_{TOT}$= 64.60 mM
$[NO_3^{-}]_{TOT}$= 37.10 µM
Log P_{CO_2}= -3.50
$[SO_4^{2-}]_{TOT}$= 7.18 µM
$[K^{+}]_{TOT}$= 2.07 mM
$[Na^{+}]_{TOT}$= 129.00 mM

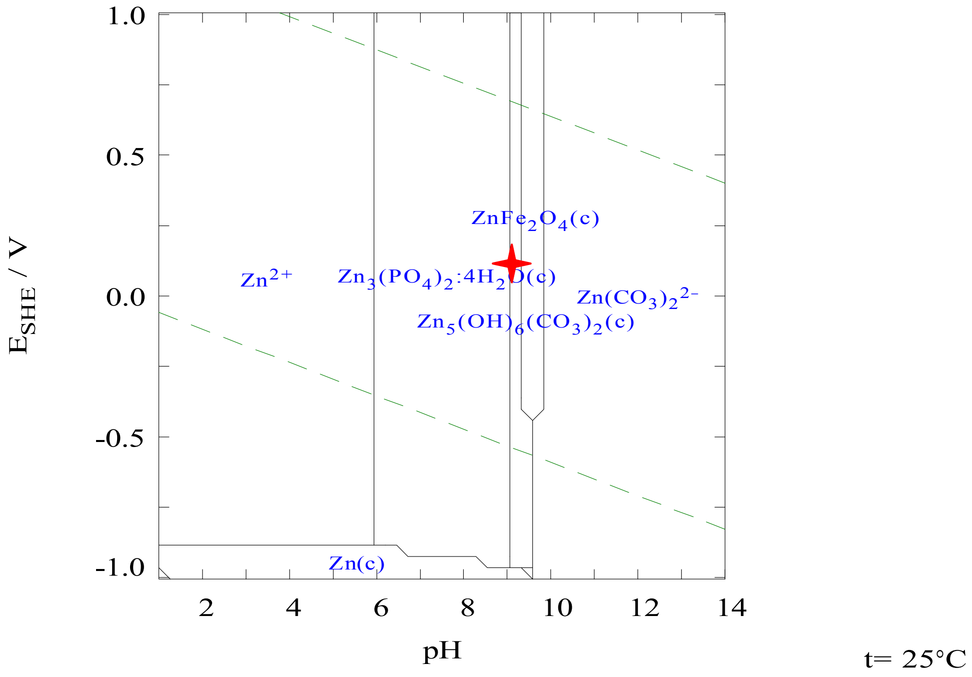


Figure C.33. Pourbaix diagram of zinc for steel gutter section immersed into pH 8 water after three months of exposure.

$[Mg^{2+}]_{TOT}=$ 5.93 µM
$[Ca^{2+}]_{TOT}=$ 4.71 µM
$[Fe^{2+}]_{TOT}=$ 6.09 µM
$[Al^{3+}]_{TOT}=$ 7.41 µM
$[Zn^{2+}]_{TOT}=$ 0.15 mM
$[Cu^{2+}]_{TOT}=$ 0.47 µM
$[Pb^{2+}]_{TOT}=$ 0.48 µM

I= 0.196 M
$[HPO_4^{2-}]_{TOT}=$ 64.60 mM
$[NO_3^{-}]_{TOT}=$ 37.10 µM
Log $P_{CO_2}=$ -3.50
$[SO_4^{2-}]_{TOT}=$ 7.18 µM
$[K^{+}]_{TOT}=$ 2.07 mM
$[Na^{+}]_{TOT}=$ 129.00 mM

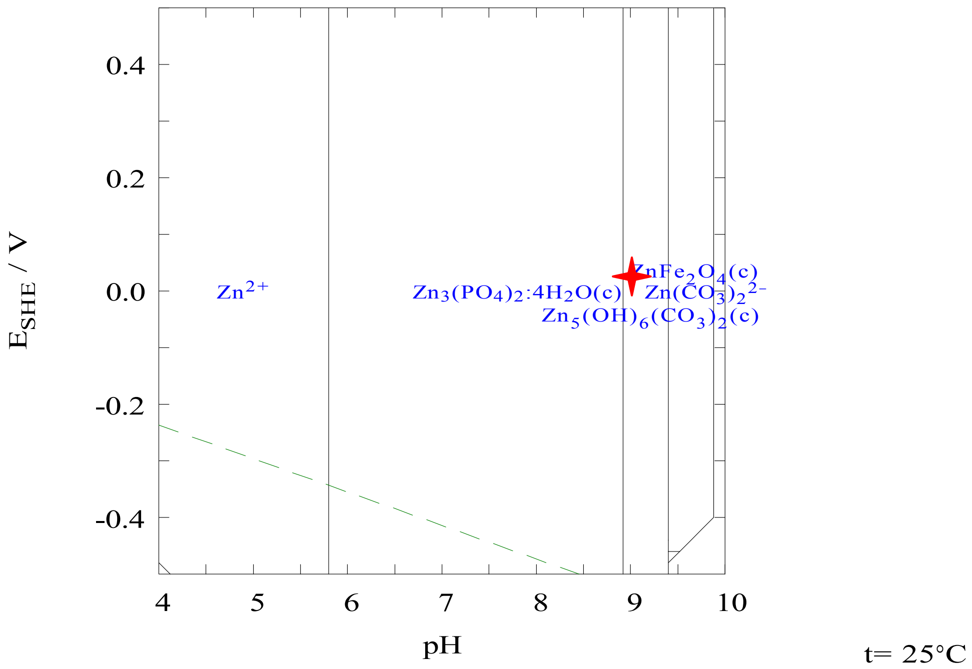


Figure C.34. Pourbaix diagram of zinc for steel gutter section immersed into pH 8 water after three months of exposure. Study area.

$[Mg^{2+}]_{TOT}$= 5.93 µM
$[Ca^{2+}]_{TOT}$= 4.71 µM
$[Fe^{2+}]_{TOT}$= 6.09 µM
$[Al^{3+}]_{TOT}$= 7.41 µM
$[Zn^{2+}]_{TOT}$= 0.15 mM
$[Cu^{2+}]_{TOT}$= 0.47 µM
$[Pb^{2+}]_{TOT}$= 0.48 µM

I= 0.196 M
$[HPO_4^{2-}]_{TOT}$= 64.60 mM
$[NO_3^{-}]_{TOT}$= 37.10 µM
Log P_{CO_2} = -3.50
$[SO_4^{2-}]_{TOT}$= 7.18 µM
$[K^{+}]_{TOT}$= 2.07 mM
$[Na^{+}]_{TOT}$= 129.00 mM

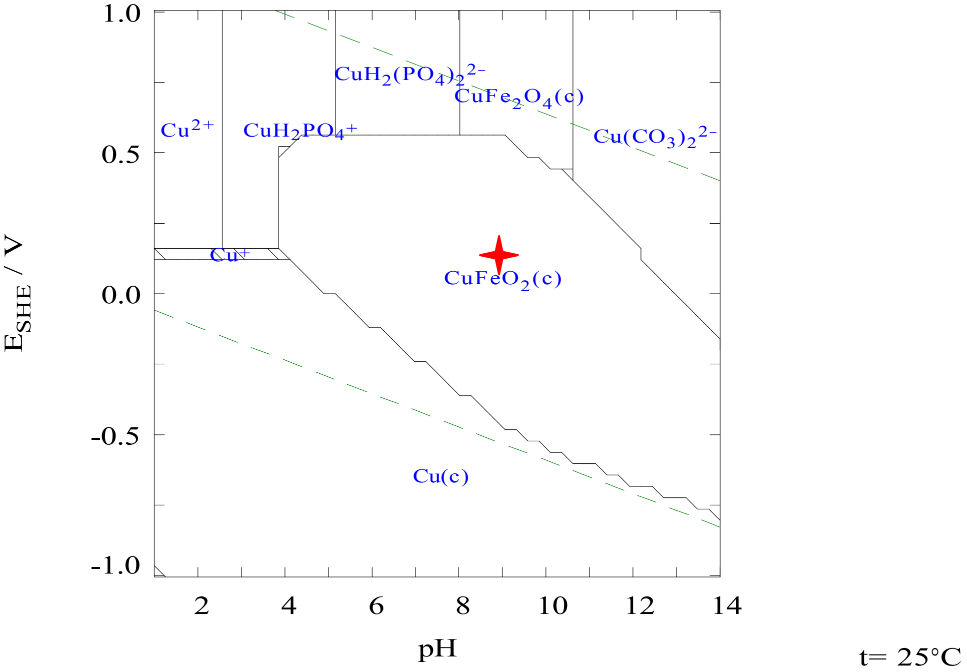


Figure C.35. Pourbaix diagram of copper for steel gutter section immersed into pH 8 water after three months of exposure.

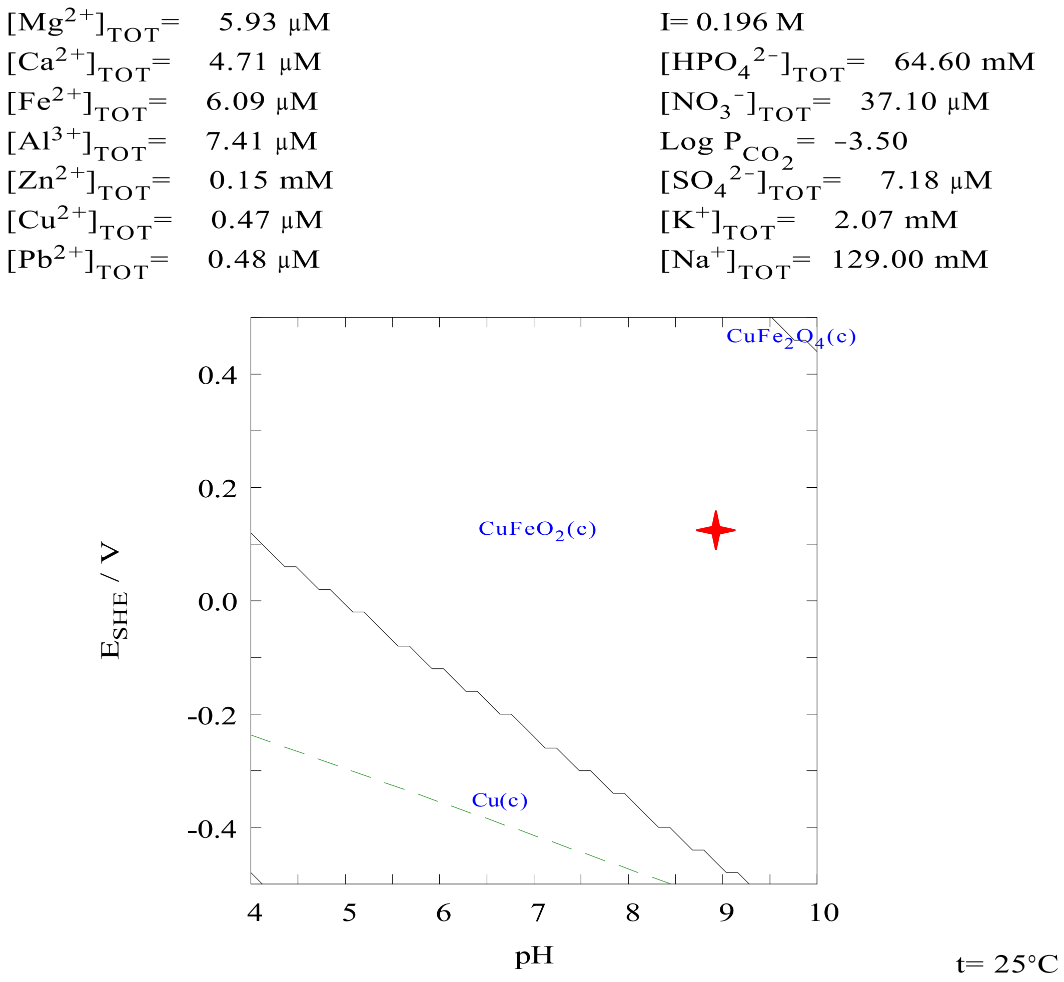


Figure C.36. Pourbaix diagram of copper for steel gutter section immersed into pH 8 water after three months of exposure. Study area.

$[Mg^{2+}]_{TOT}$= 5.93 µM
$[Ca^{2+}]_{TOT}$= 4.71 µM
$[Fe^{2+}]_{TOT}$= 6.09 µM
$[Al^{3+}]_{TOT}$= 7.41 µM
$[Zn^{2+}]_{TOT}$= 0.15 mM
$[Cu^{2+}]_{TOT}$= 0.47 µM
$[Pb^{2+}]_{TOT}$= 0.48 µM

I= 0.196 M
$[HPO_4^{2-}]_{TOT}$= 64.60 mM
$[NO_3^{-}]_{TOT}$= 37.10 µM
Log P_{CO_2} = -3.50
$[SO_4^{2-}]_{TOT}$= 7.18 µM
$[K^{+}]_{TOT}$= 2.07 mM
$[Na^{+}]_{TOT}$= 129.00 mM

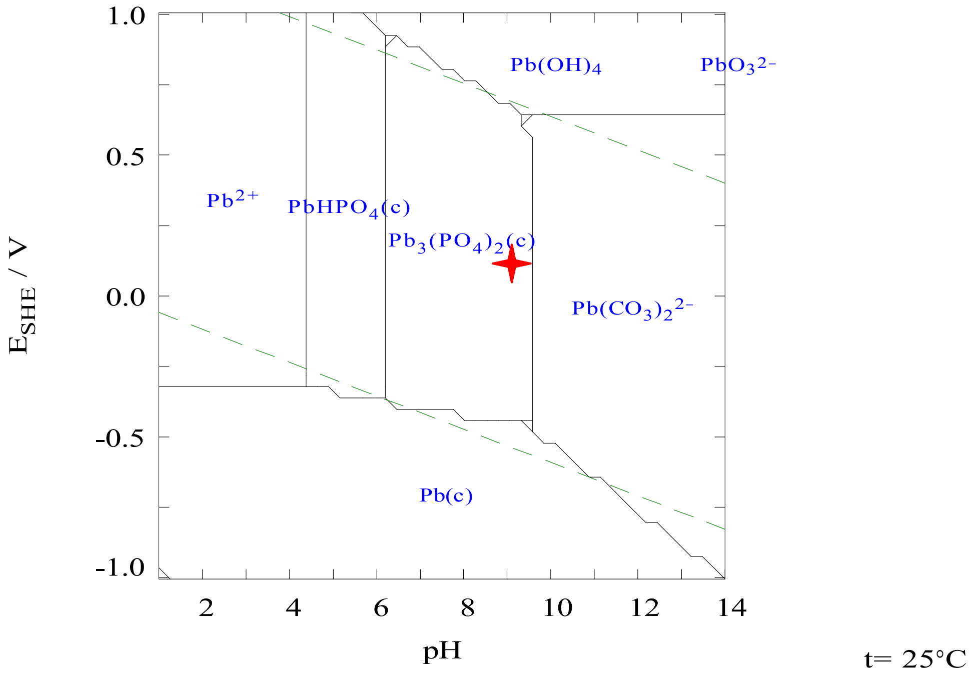


Figure C.37. Pourbaix diagram of lead for steel gutter section immersed into pH 8 water after three months of exposure.

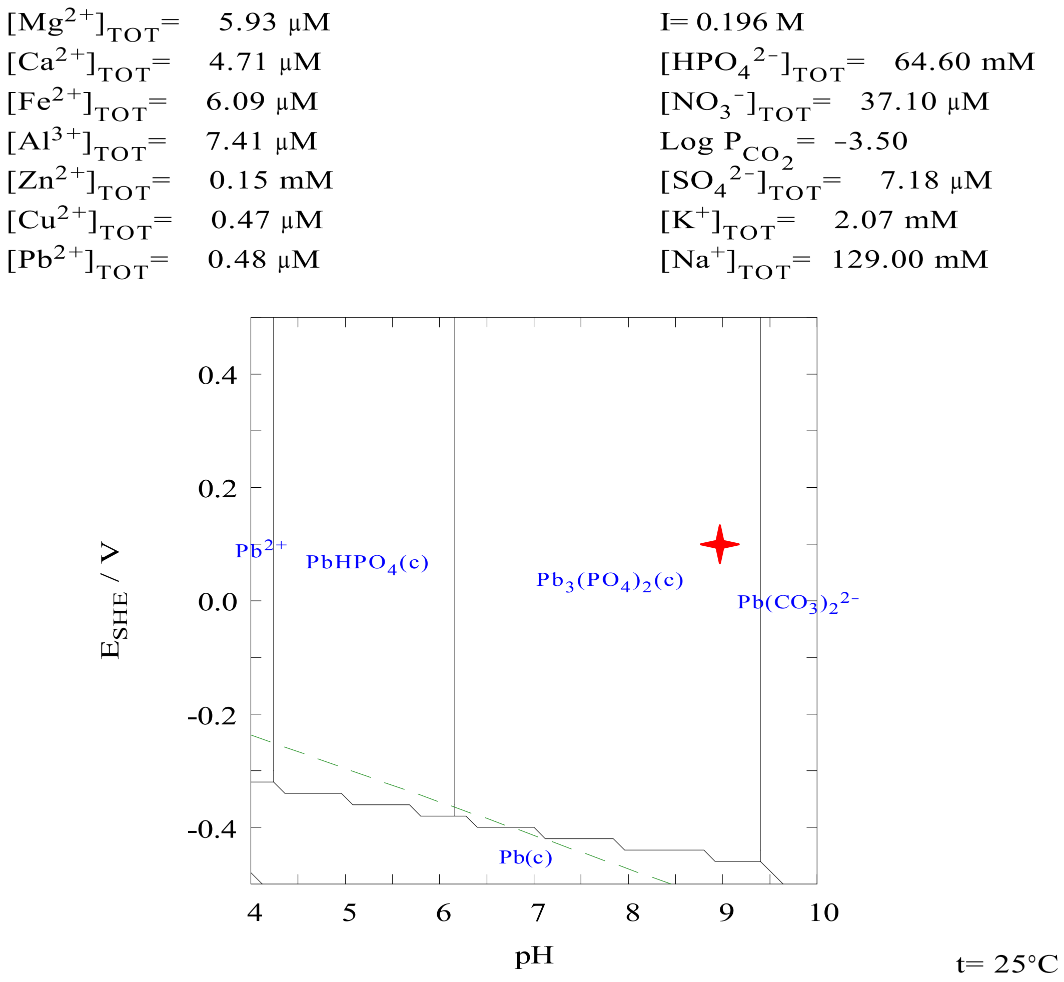


Figure C.38. Pourbaix diagram of lead for steel gutter section immersed into pH 8 water after three months of exposure. Study area.

Copper Gutter, pH 5 Water, After Three Months of Exposure

I= 0.068 M
$[Mg^{2+}]_{TOT}$ = 5.22 µM
$[Ca^{2+}]_{TOT}$ = 0.10 µM
$[Fe^{2+}]_{TOT}$ = 2.69 µM
$[Zn^{2+}]_{TOT}$ = 1.99 µM
$[Cu^{2+}]_{TOT}$ = 80.30 µM
E_H = 0.25 V

$[H_2PO_4^-]_{TOT}$ = 66.00 mM
$[NO_3^-]_{TOT}$ = 3.23 µM
Log P_{CO_2} = -3.50
$[SO_4^{2-}]_{TOT}$ = 27.60 µM
$[K^+]_{TOT}$ = 66.00 mM
$[Na^+]_{TOT}$ = 1.27 mM

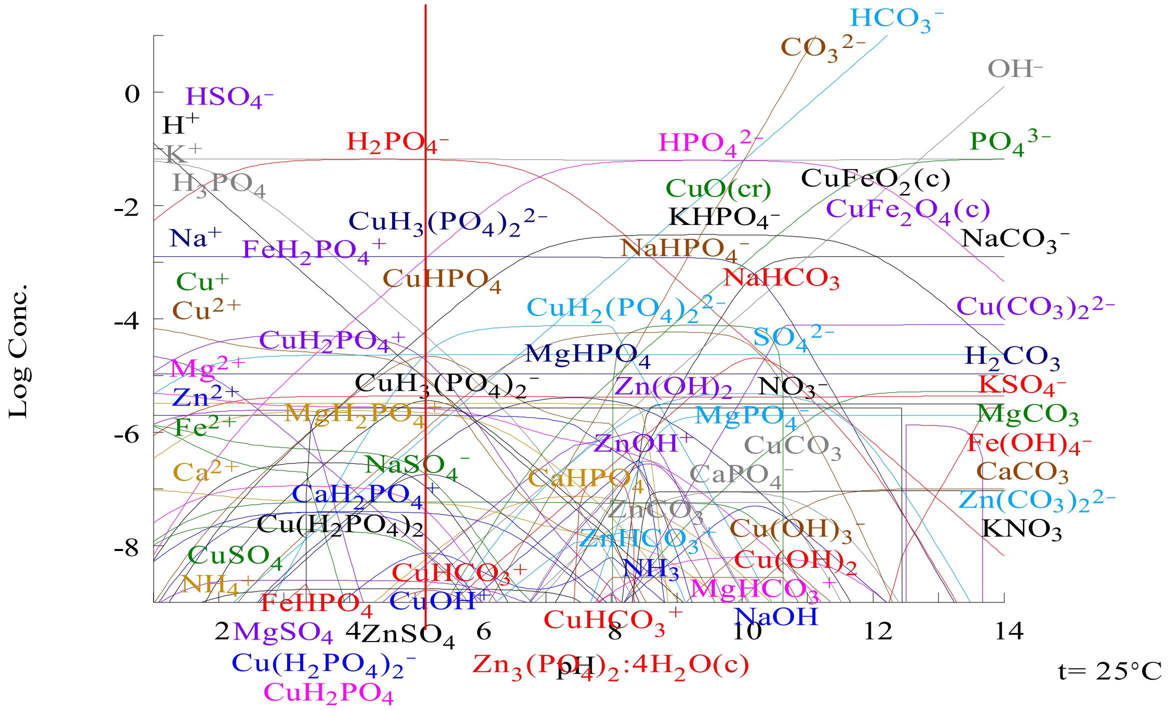


Figure C.39. Phase diagram for copper gutter section immersed into pH 5 water after three months of exposure.

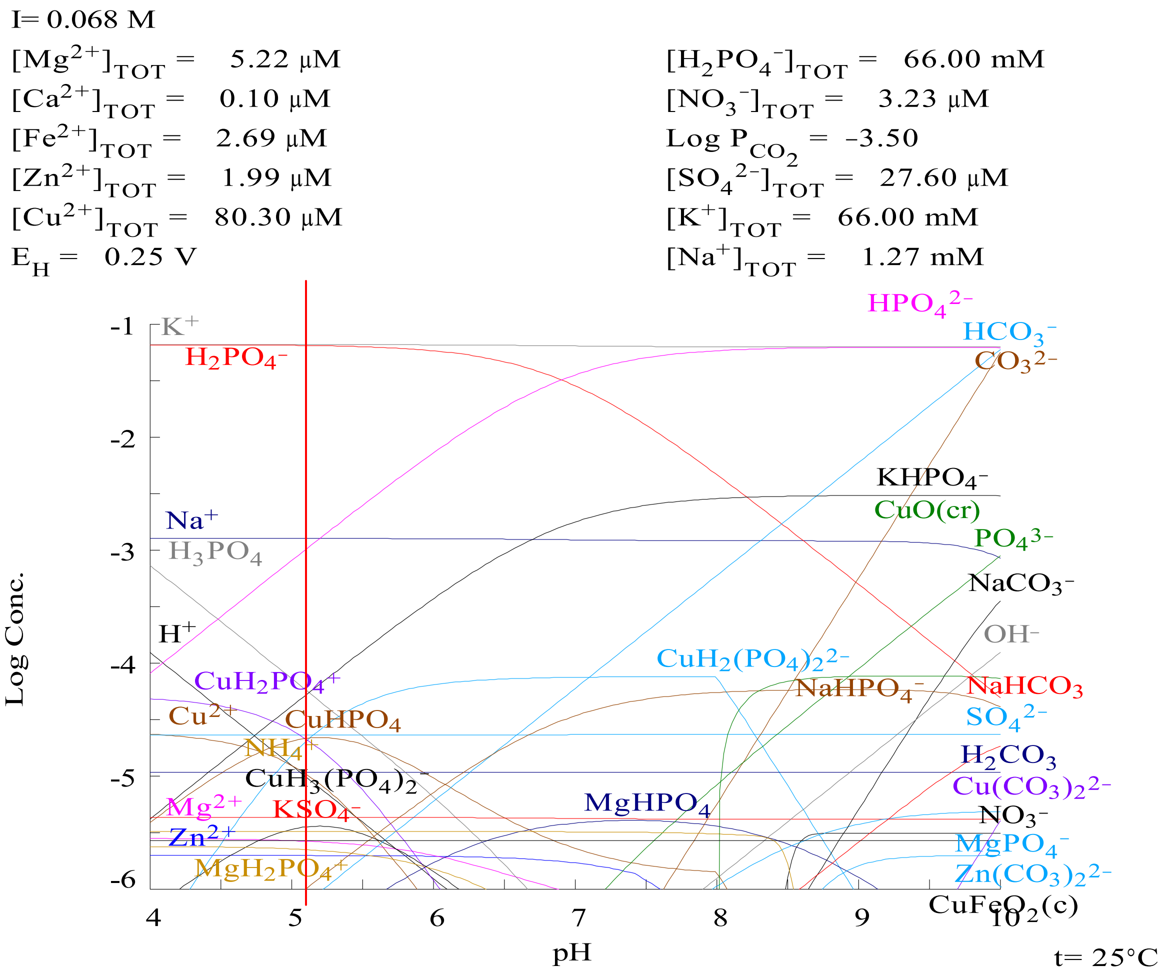


Figure C.40. Phase diagram for copper gutter section immersed into pH 5 water after three months of exposure. Study area.

Table C.11. The predominant species of zinc. Copper gutter section, pH 5 water, three months exposure.

Component	Log Concentration (mol/L)	Concentration (mol/L)	Zn Concentration (mg/L as Zn)	Cumulative Percentage of Zn
Zn^{2+}	-5.70	1.98E-06	0.13	99.71
$ZnOH^{+}$	-8.41	3.89E-09	2.55E-04	99.91

Table C.12. The predominant species of copper. Copper gutter section, pH 5 water, three months exposure.

Component	Log Concentration (mol/L)	Concentration (mol/L)	Cu Concentration (mg/L as Cu)	Cumulative Percentage of Cu
$CuH_2PO_4^+$	-4.67	2.16E-05	1.37	26.85
$CuHPO_4$	-4.67	2.15E-05	1.37	53.62
$CuH_2(PO_4)_2^{2-}$	-4.70	1.98E-05	1.26	78.32
Cu^{2+}	-4.98	1.06E-05	0.67	91.49
$CuH_3(PO_4)_2^-$	-5.45	3.55E-06	0.23	95.91
$CuFeO_2(c)$	-5.57	2.69E-06	0.17	99.26
Cu^+	-6.69	2.05E-07	1.30E-02	99.52
$CuH_3(PO_4)_2^{2-}$	-6.75	1.79E-07	1.14E-02	99.74
$Cu(H_2PO_4)_2$	-6.90	1.26E-07	7.98E-03	99.899
CuH_2PO_4	-7.32	4.76E-08	3.02E-03	99.958

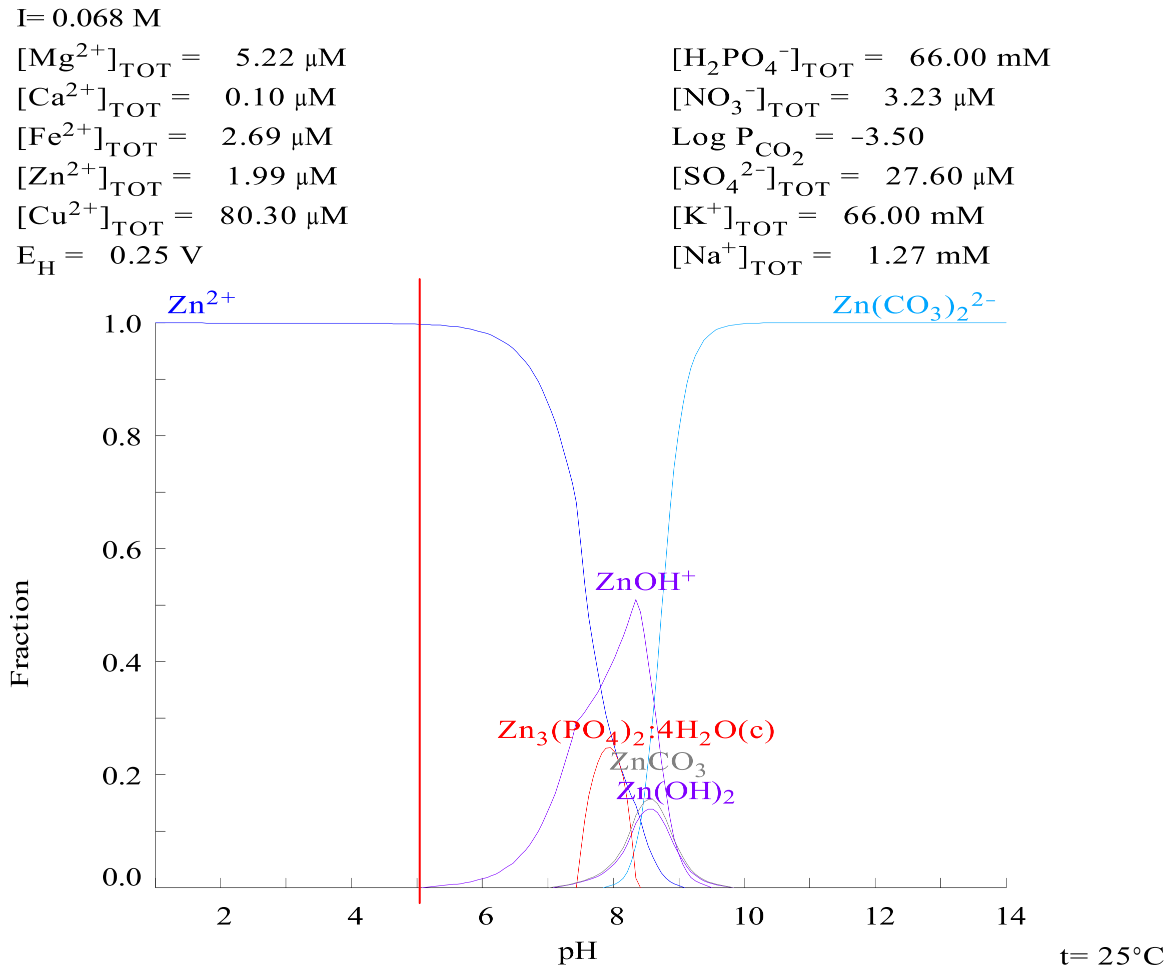


Figure C.41. Fraction diagram of zinc for copper gutter section immersed into pH 5 water after three months of exposure.

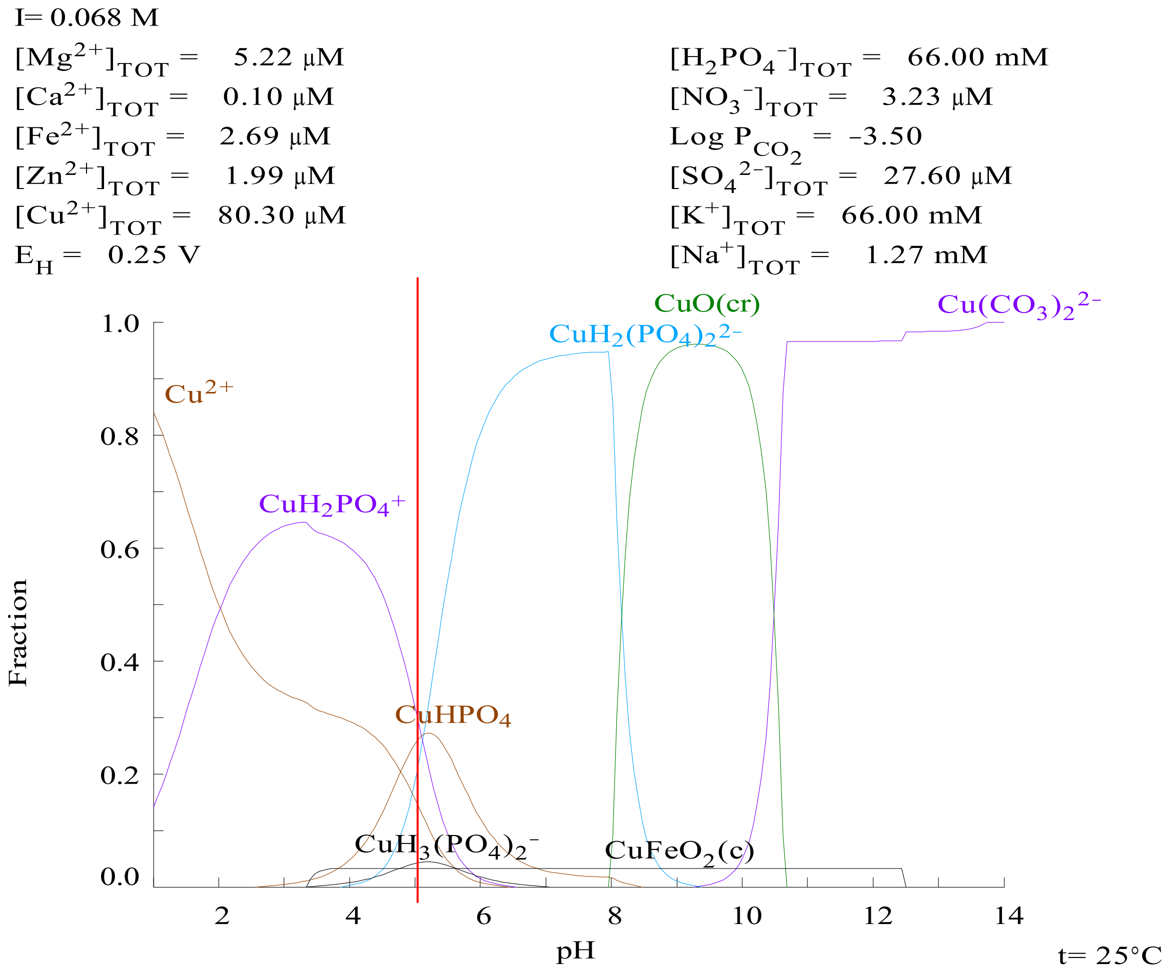


Figure C.42. Fraction diagram of copper for copper gutter section immersed into pH 5 water after three months of exposure.

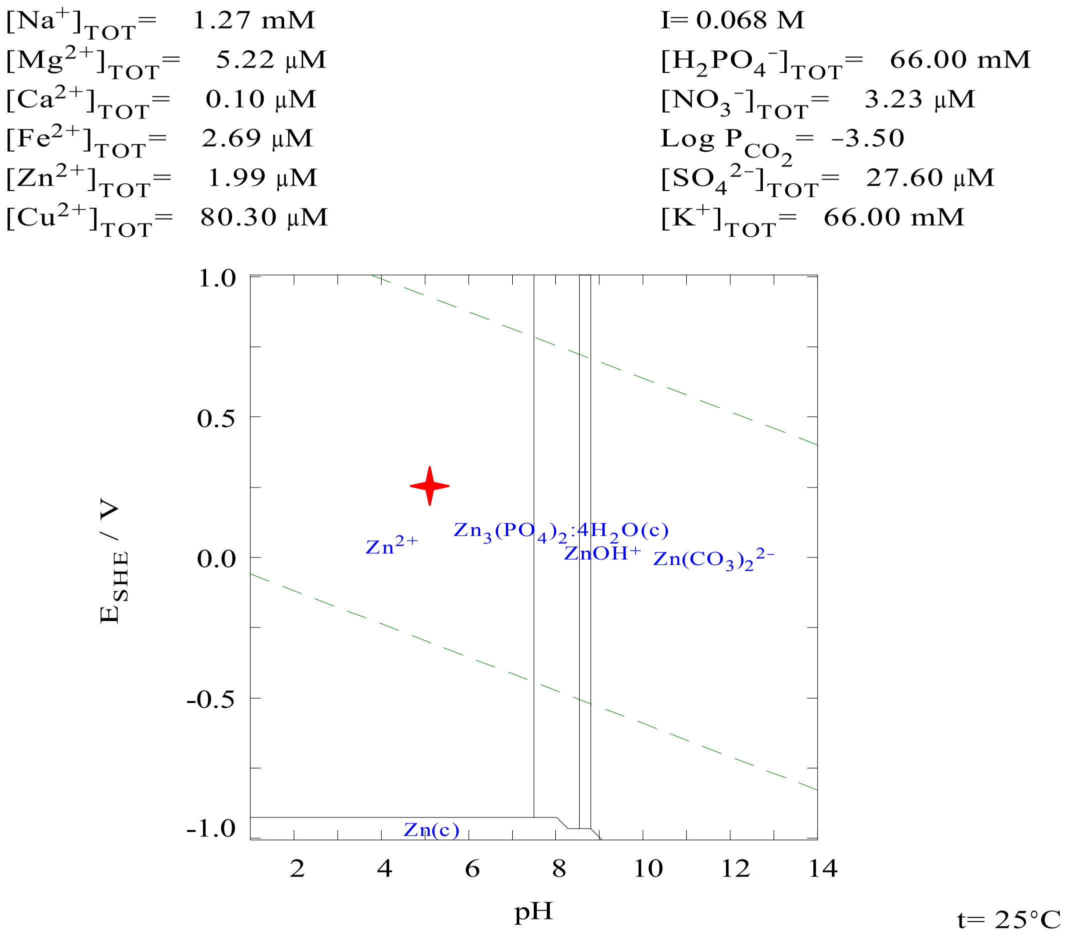


Figure C.43. Pourbaix diagram of zinc for copper gutter section immersed into pH 5 water after three months of exposure.

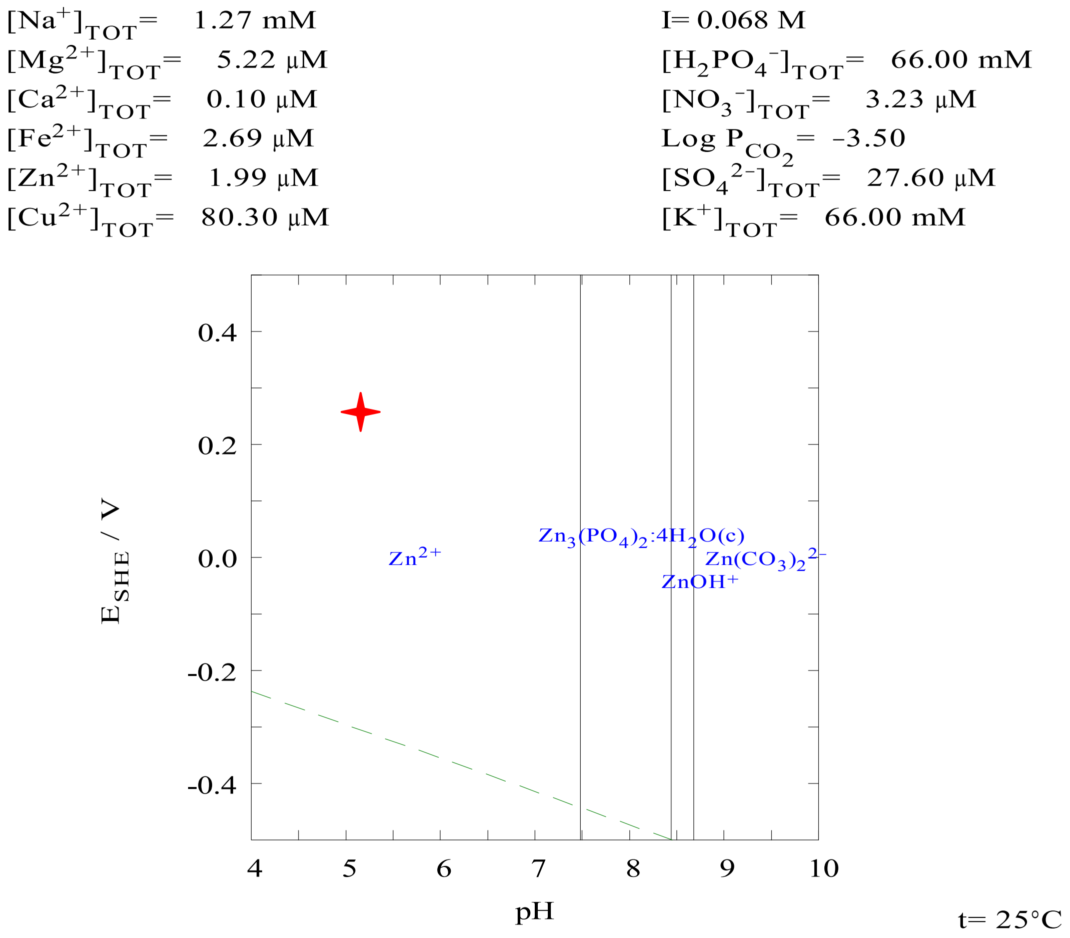


Figure C.44. Pourbaix diagram of zinc for copper gutter section immersed into pH 5 water after three months of exposure. Study area.

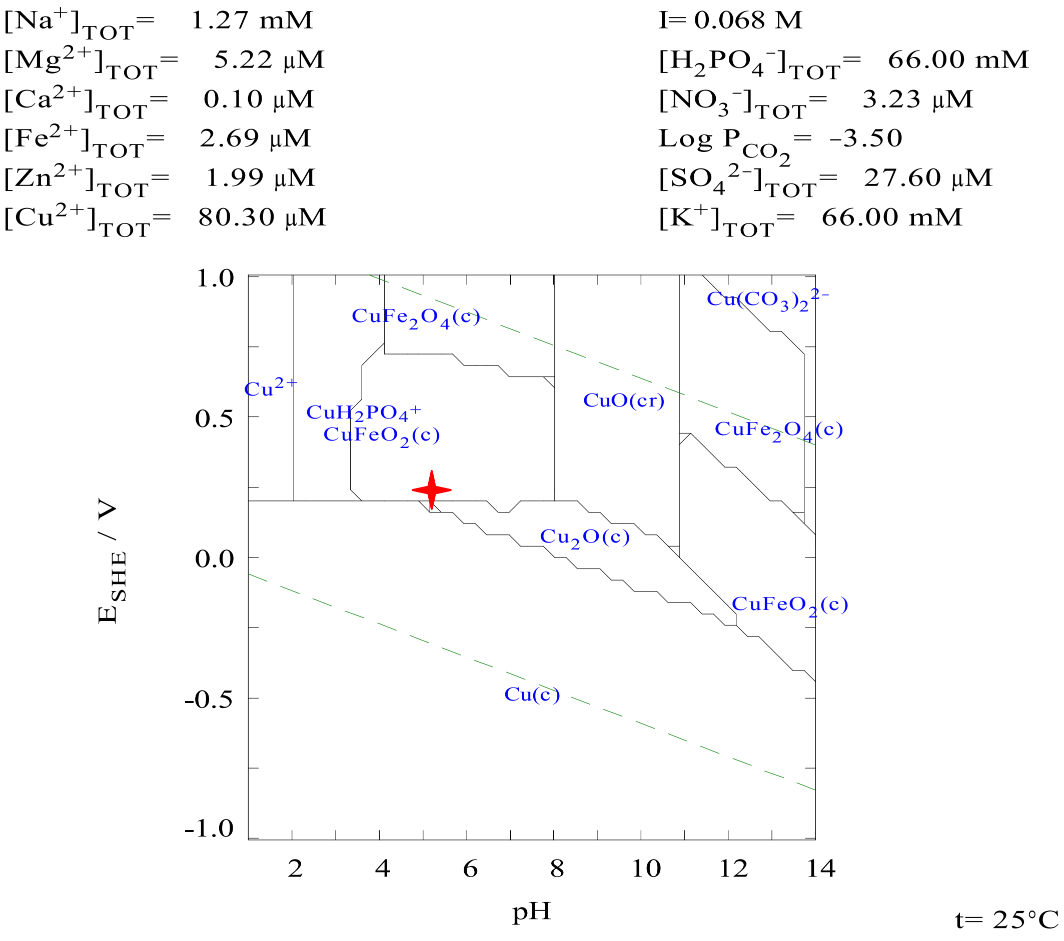


Figure C.45. Pourbaix diagram of copper for copper gutter section immersed into pH 5 water after three months of exposure.

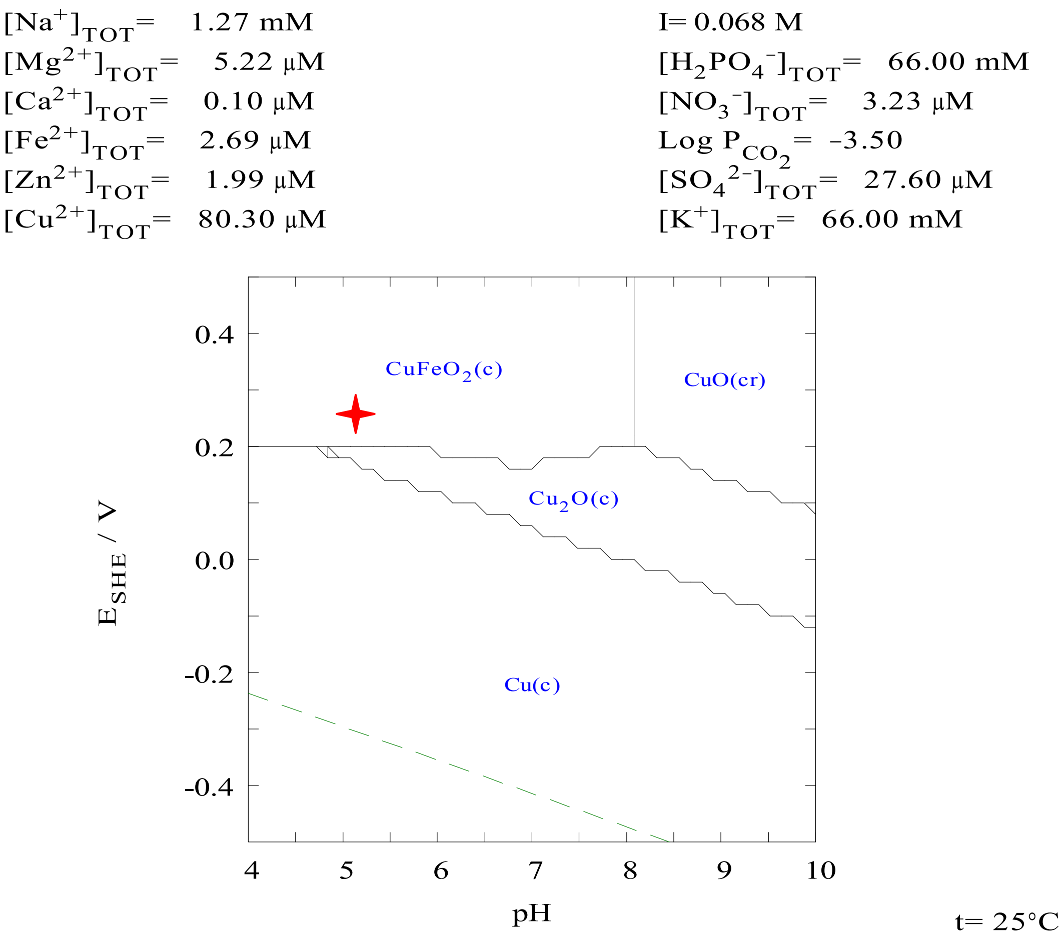


Figure C.46. Pourbaix diagram of copper for copper gutter section immersed into pH 5 water after three months of exposure. Study area.

Copper Gutter, pH 8 Water, After Three Months of Exposure

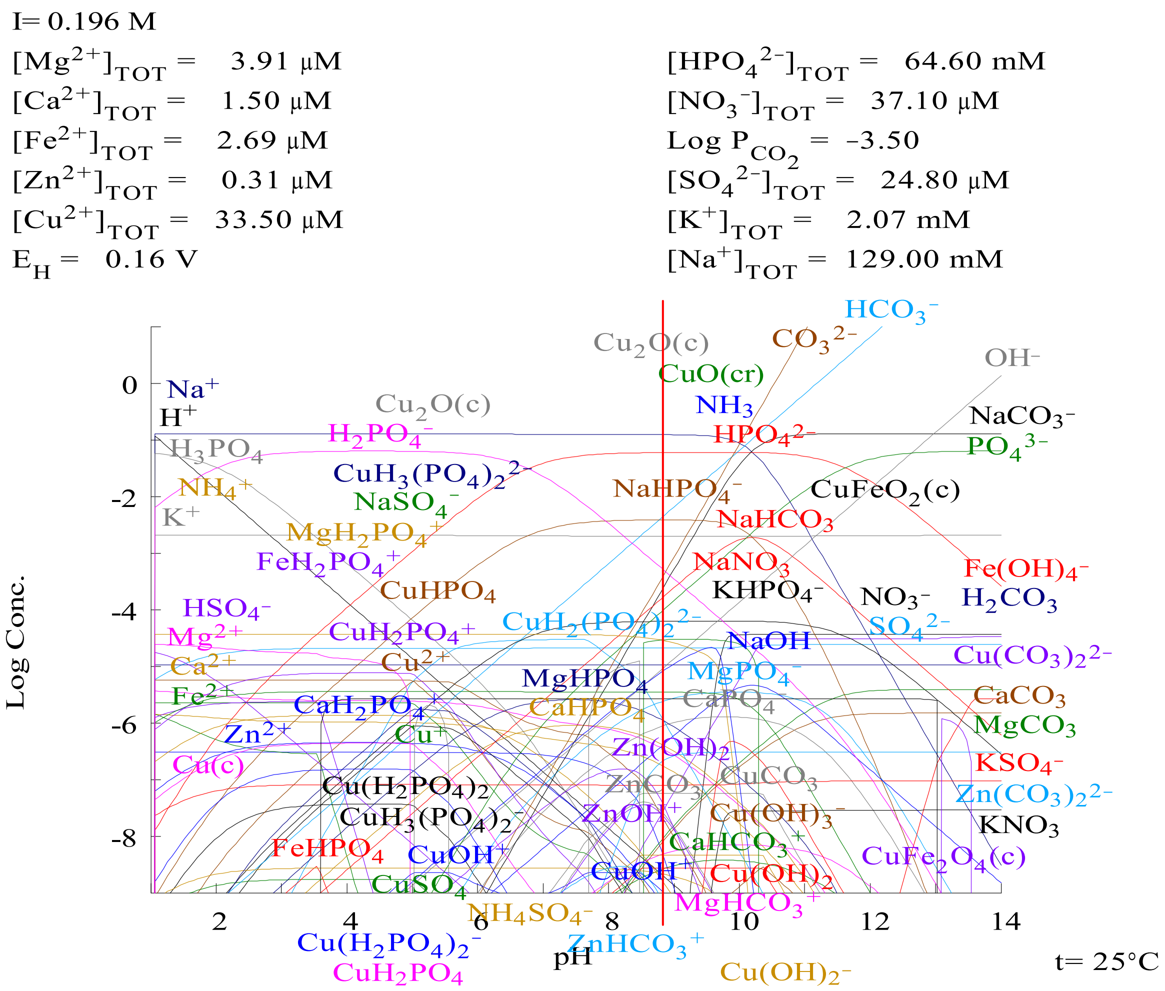


Figure C.47. Phase diagram for copper gutter section immersed into pH 8 water after three months of exposure.

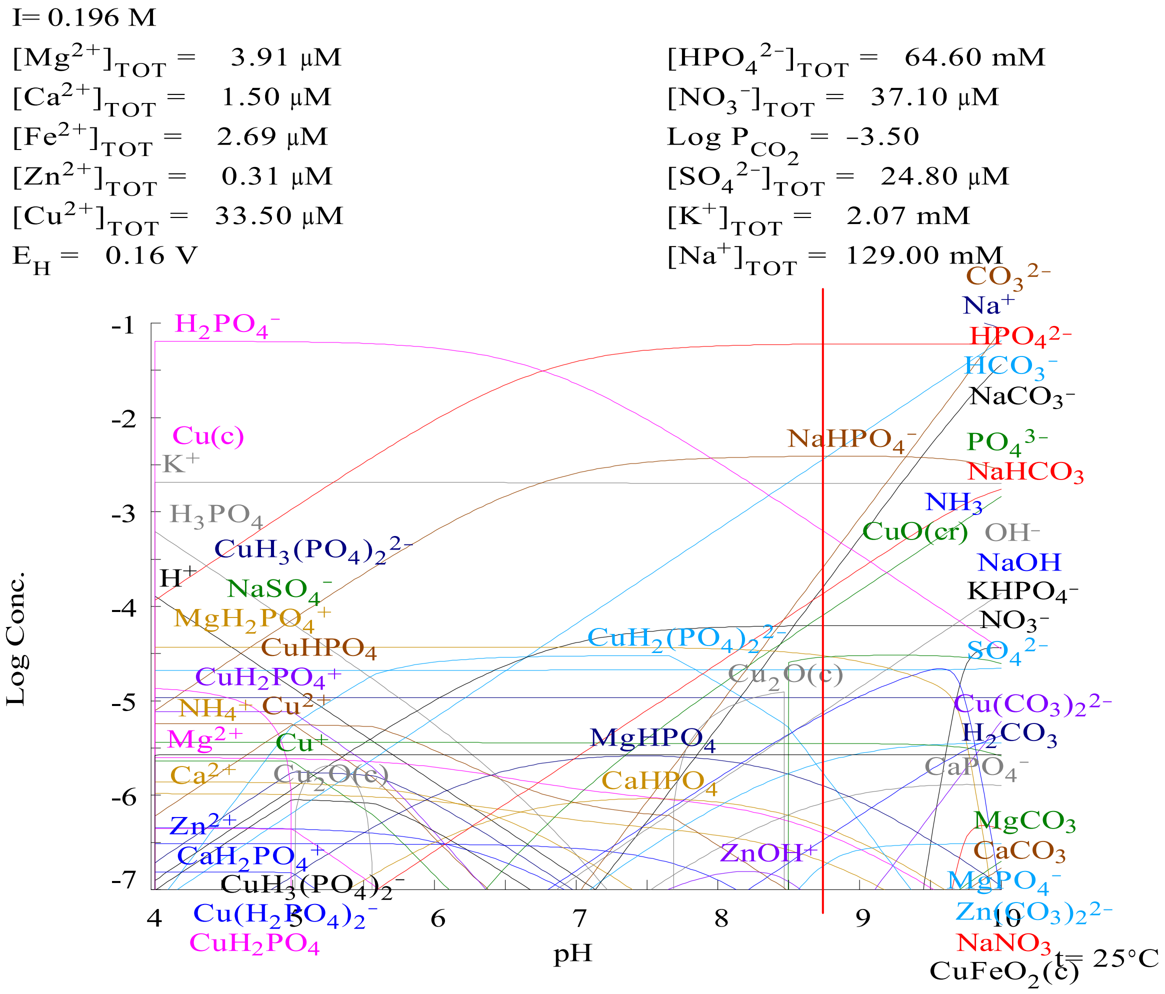


Figure C.48. Phase diagram for copper gutter section immersed into pH 8 water after three months of exposure. Study area.

Table C.13. The predominant species of zinc. Copper gutter section, pH 8 water, three months exposure.

Component	Log Concentration (mol/L)	Concentration (mol/L)	Zn Concentration (mg/L as Zn)	Cumulative Percentage of Zn
$Zn(CO_3)_2^{2-}$	-6.76	1.75E-07	1.14E-02	57.11
$ZnOH^+$	-7.23	5.84E-08	3.82E-03	76.19
$ZnCO_3$	-7.48	3.30E-08	2.16E-03	86.98
$Zn(OH)_2$	-7.53	2.94E-08	1.92E-03	96.57
Zn^{2+}	-8.03	9.34E-09	6.11E-04	99.62
$ZnHCO_3^+$	-8.95	1.11E-09	7.28E-05	99.99

Table C.14. The predominant species of copper. Copper gutter section, pH 8 water, three months exposure.

Component	Log Concentration (mol/L)	Concentration (mol/L)	Cu Concentration (mg/L as Cu)	Cumulative Percentage of Cu
CuO(cr)	-4.54	2.89E-05	1.84	86.26
$CuFeO_2$(c)	-5.57	2.69E-06	0.17	94.29
$CuH_2(PO_4)_2^{2-}$	-5.75	1.79E-06	0.11	99.65
$CuCO_3$	-7.24	5.72E-08	3.64E-03	99.82
$CuHPO_4$	-7.49	3.26E-08	2.07E-03	99.92

Footnote: Cu^+ was calculated to be 1.54E-05 mg/L; Cu^{2+} was calculated to be 3.82E-05 mg/L

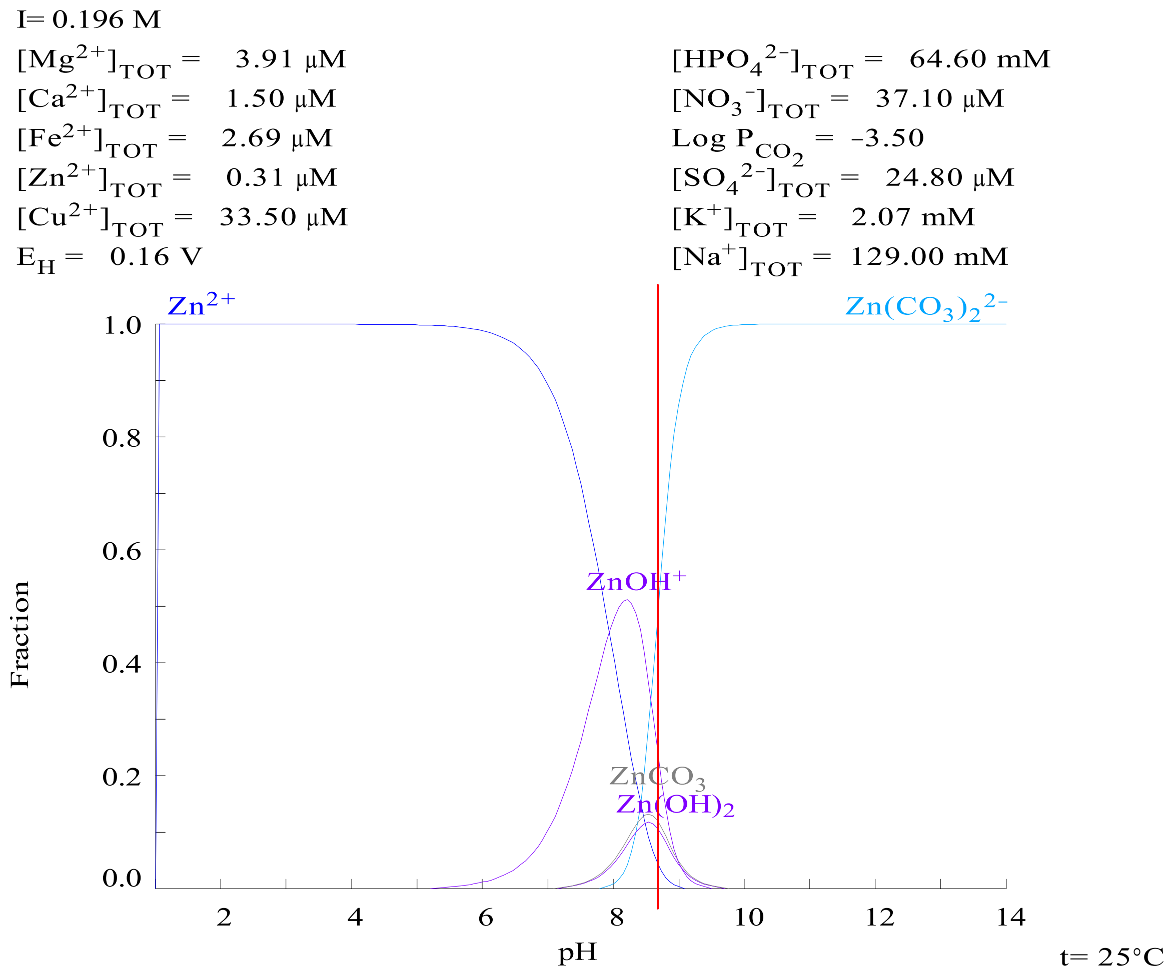


Figure C.49. Fraction diagram of zinc for copper gutter section immersed into pH 8 water after three months of exposure.

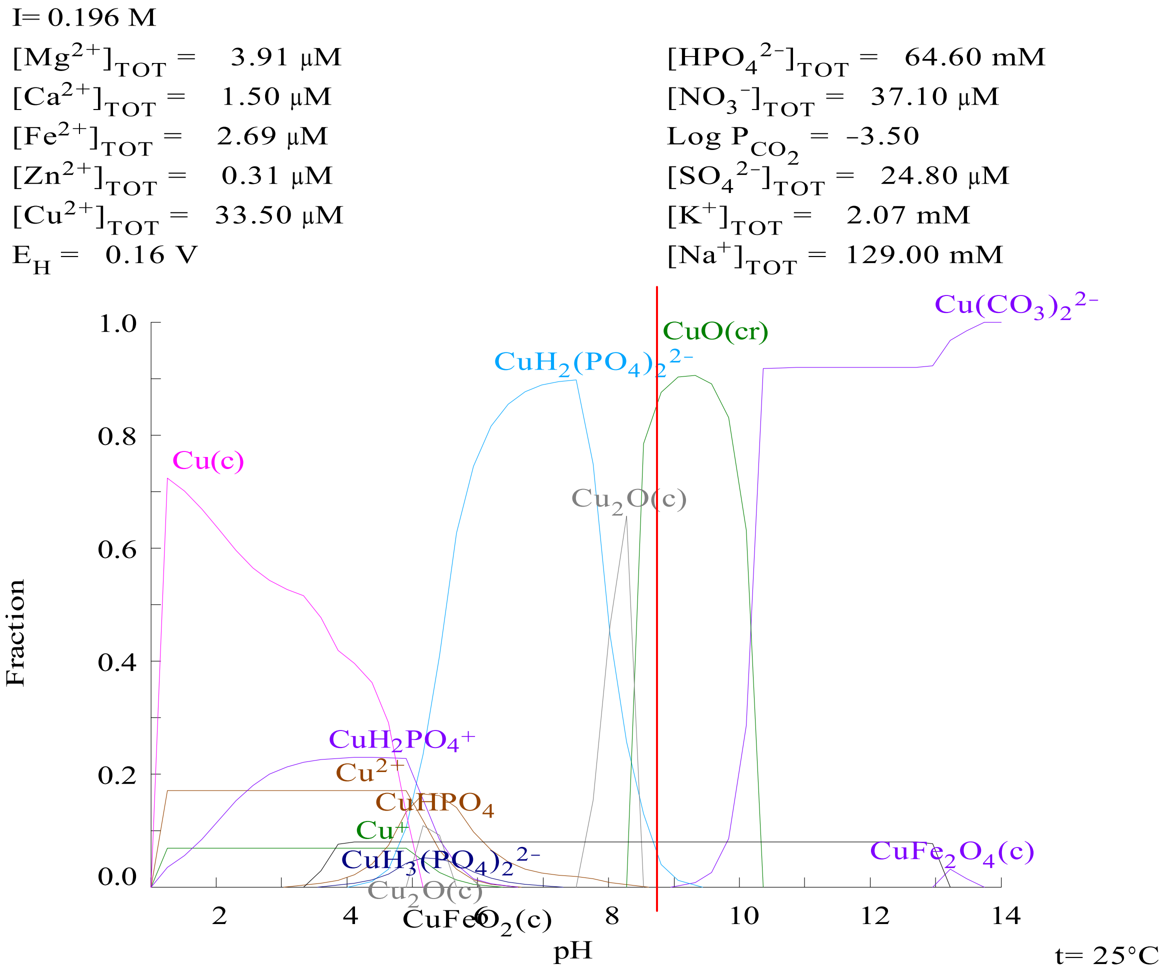


Figure C.50. Fraction diagram of copper for copper gutter section immersed into pH 8 water after three months of exposure.

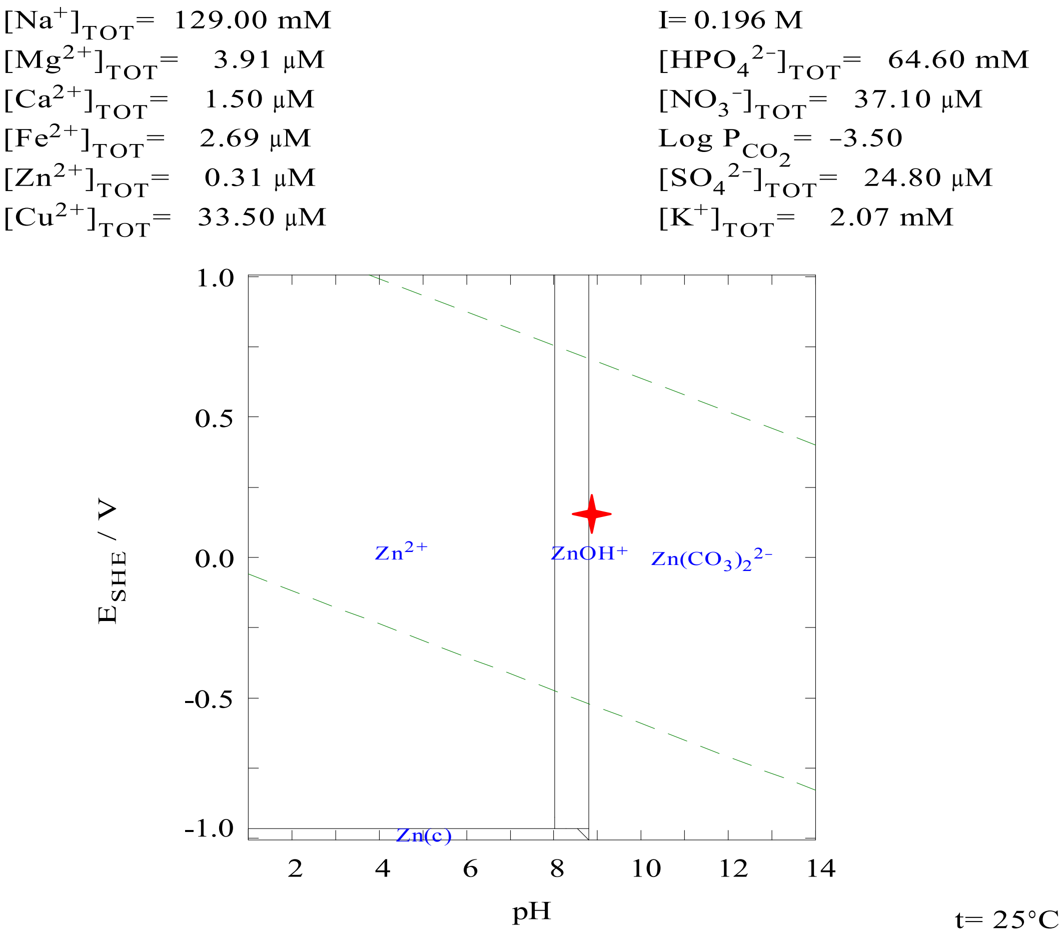


Figure C.51. Pourbaix diagram of zinc for copper gutter section immersed into pH 8 water after three months of exposure.

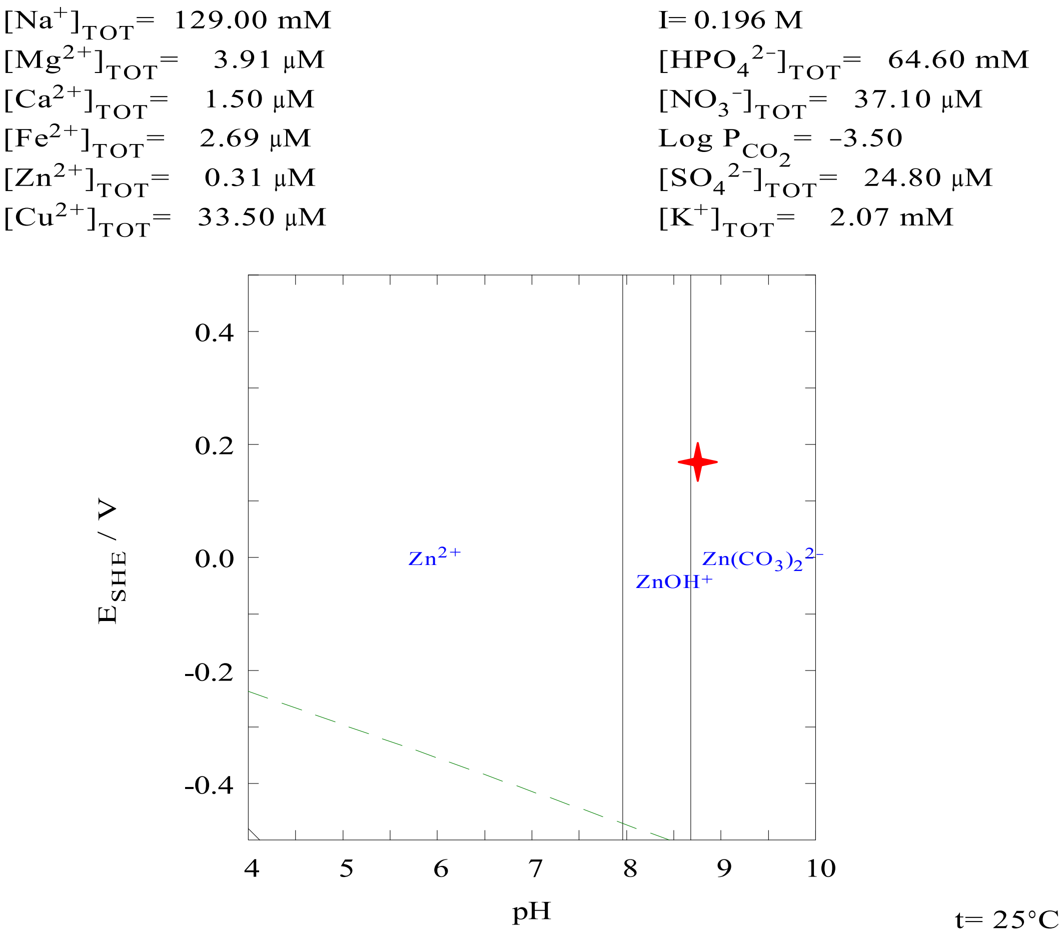


Figure C.52. Pourbaix diagram of zinc for copper gutter section immersed into pH 8 water after three months of exposure. Study area.

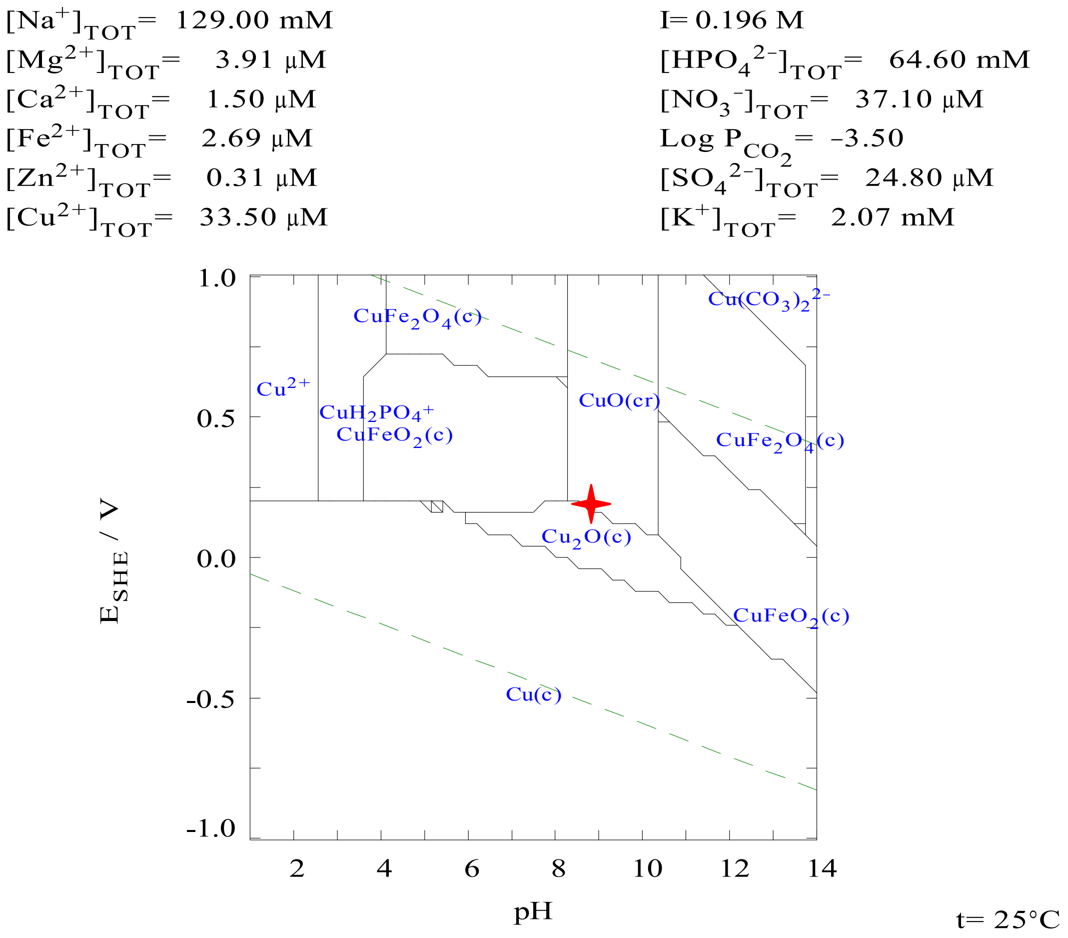


Figure C.53. Pourbaix diagram of copper for copper gutter section immersed into pH 8 water after three months of exposure.

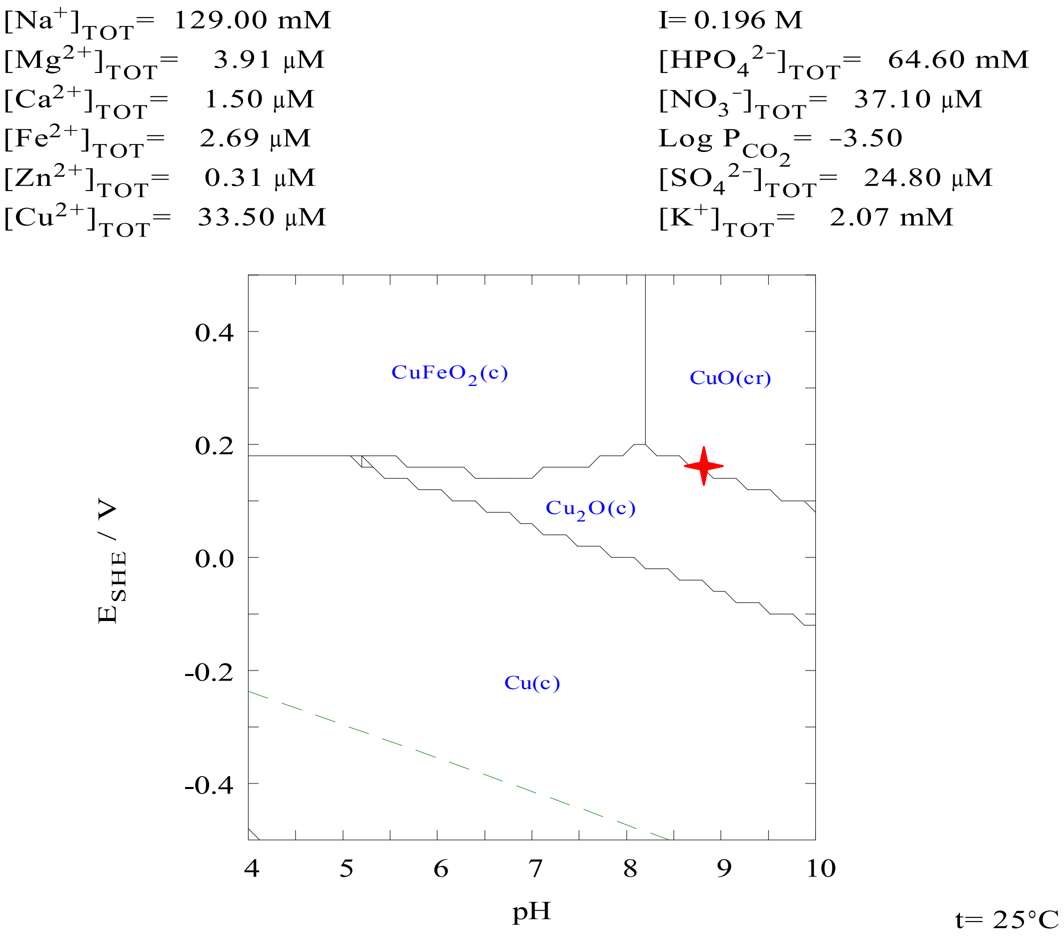


Figure C.54. Pourbaix diagram of copper for copper gutter section immersed into pH 8 water after three months of exposure. Study area.

Concrete Pipe, pH 8 Water, After Three Months of Exposure

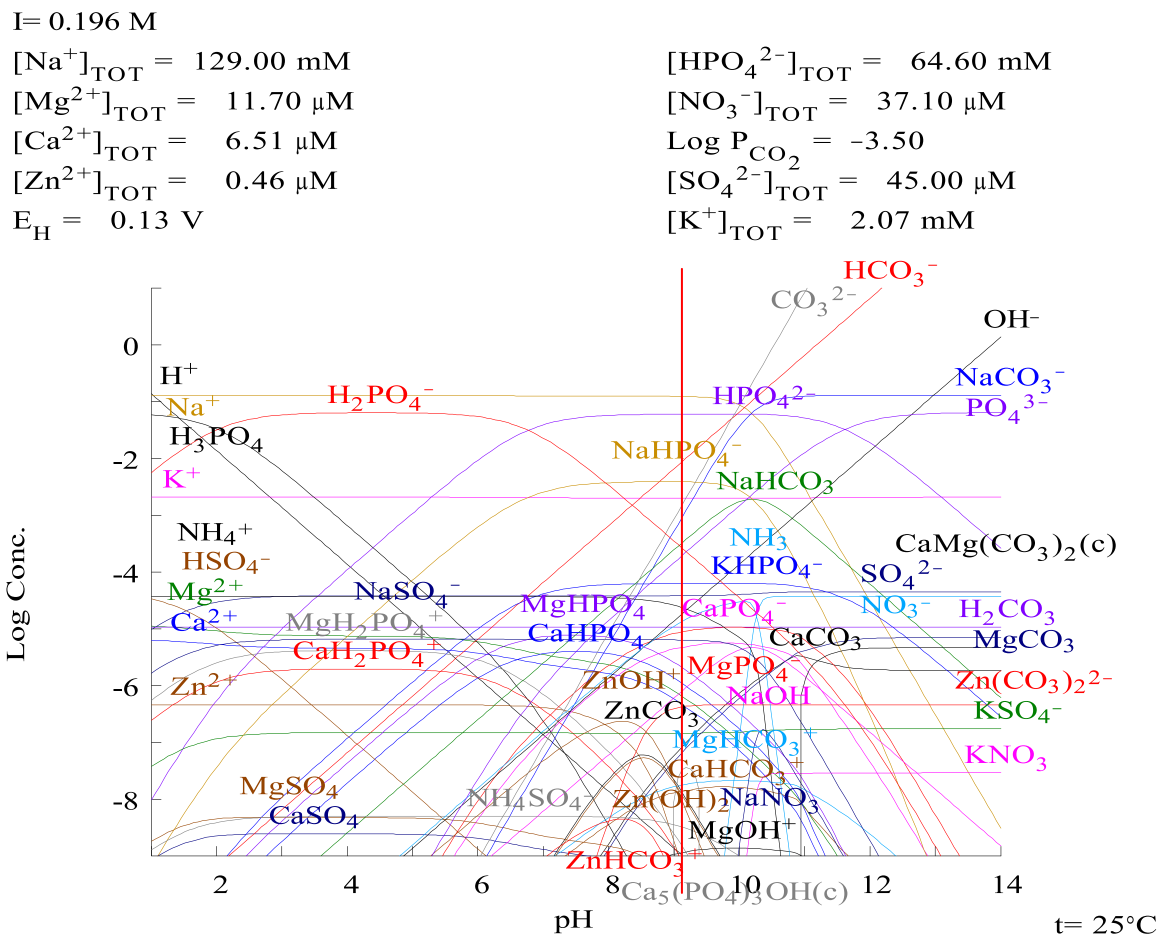


Figure C.55. Phase diagram for concrete pipe section immersed into pH 8 water after three months of exposure.

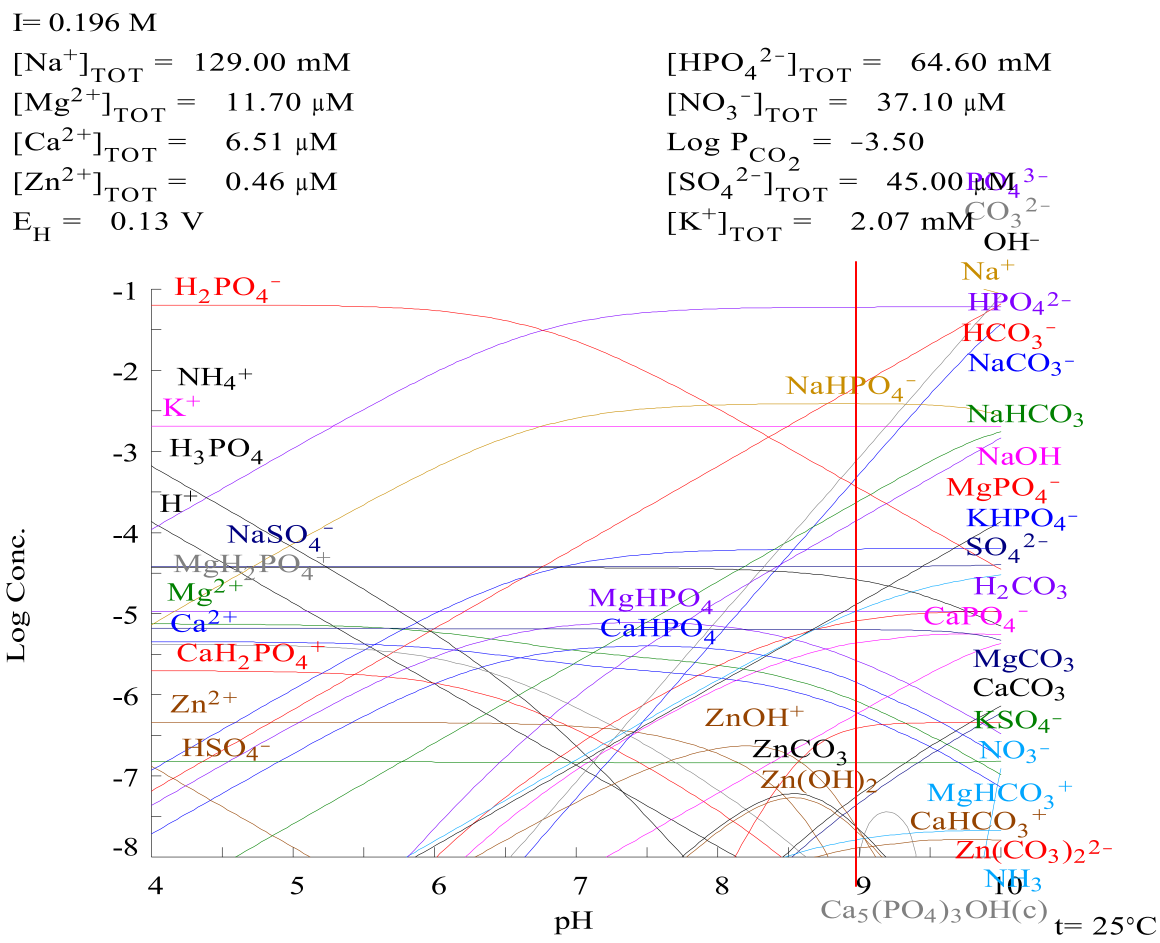


Figure C.56. Phase diagram for concrete pipe section immersed into pH 8 water after three months of exposure. Study area.

Table C.15. The predominant species of zinc. Concrete pipe section, pH 8 water, three months exposure.

Component	Log Concentration (mol/L)	Concentration (mol/L)	Zn Concentration (mg/L as Zn)	Cumulative Percentage of Zn
$Zn(CO_3)_2^{2-}$	-6.43	3.69E-07	2.42E-02	80.45
$ZnOH^+$	-7.49	3.21E-08	2.10E-03	87.44
$ZnCO_3$	-7.55	2.84E-08	1.86E-03	93.64
$Zn(OH)_2$	-7.60	2.53E-08	1.65E-03	99.14
Zn^{2+}	-8.48	3.28E-09	2.14E-04	99.86
$ZnHCO_3^+$	-9.21	6.12E-10	4.00E-05	99.99

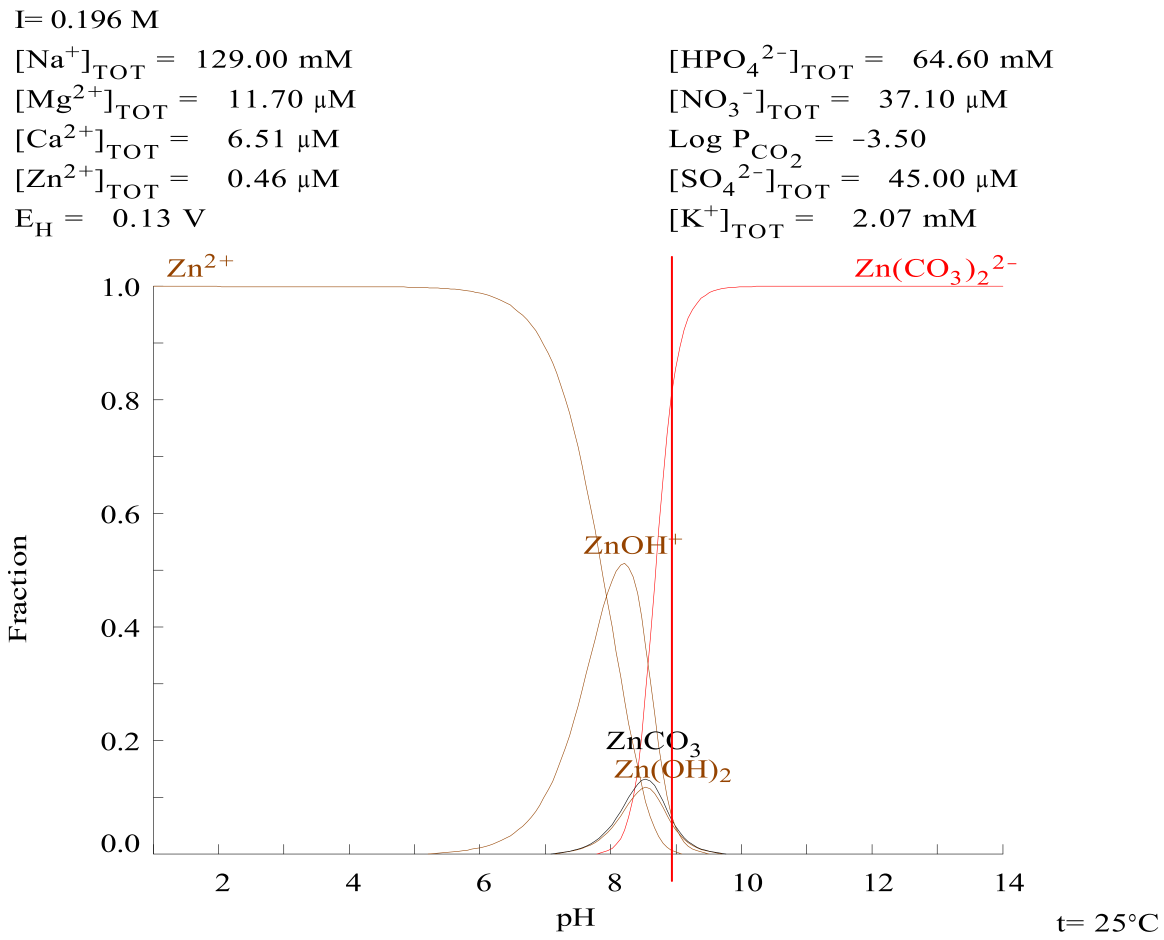


Figure C.57. Fraction diagram of zinc for concrete pipe section immersed into pH 8 water after three months of exposure.

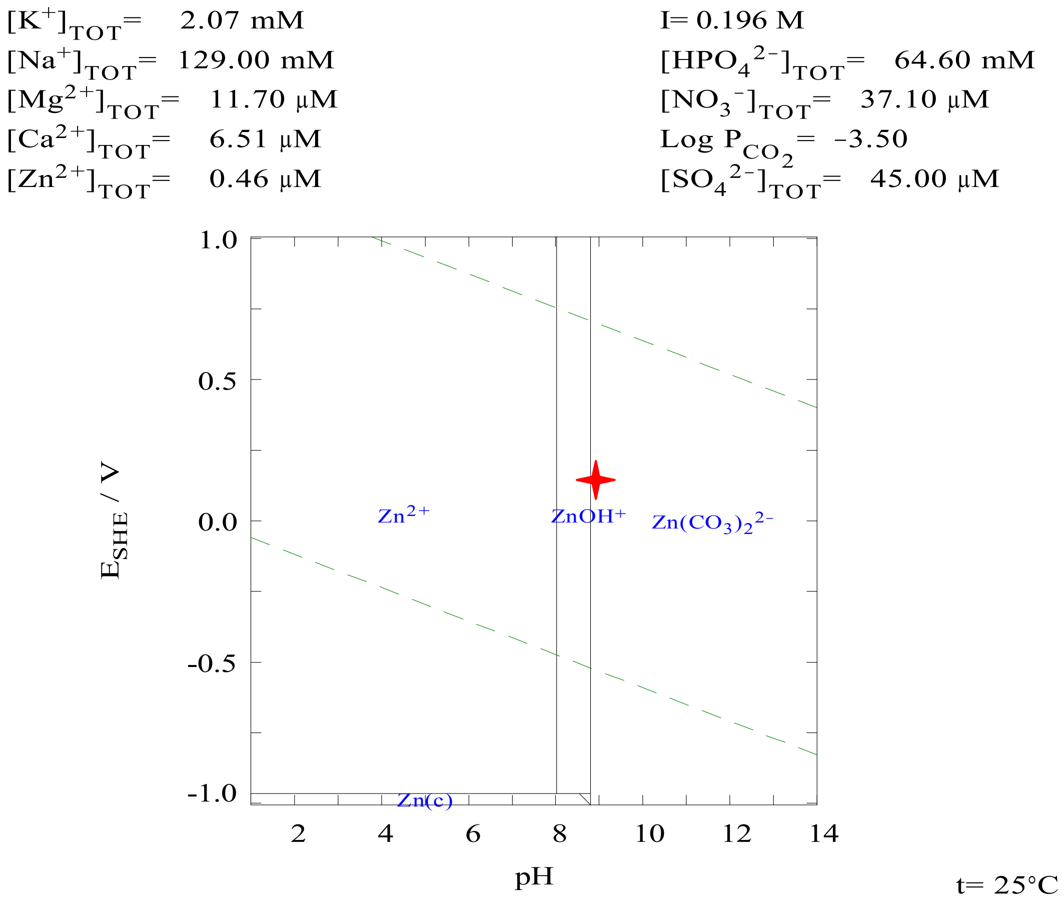


Figure C.58. Pourbaix diagram of zinc for concrete pipe section immersed into pH 8 water after three months of exposure.

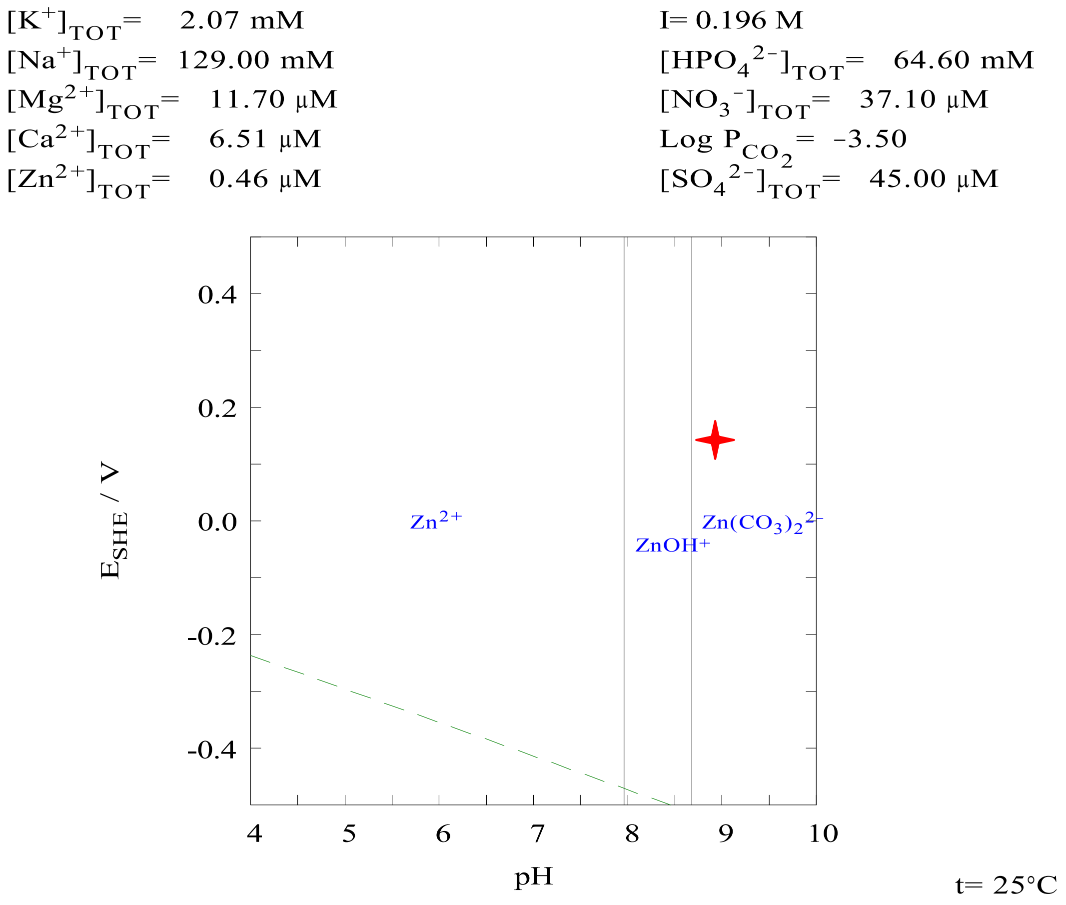


Figure C.59. Pourbaix diagram of zinc for concrete pipe section immersed into pH 8 water after three months of exposure. Study area.

PVC Pipe, pH 5 Water, After Three Months of Exposure

$[Mg^{2+}]_{TOT}$ = 37.90 μM
$[Ca^{2+}]_{TOT}$ = 0.61 mM
$[Fe^{2+}]_{TOT}$ = 2.15 μM
$[Al^{3+}]_{TOT}$ = 3.71 μM
$[Zn^{2+}]_{TOT}$ = 6.73 μM
$[Cu^{2+}]_{TOT}$ = 3.62 μM
E_H = 0.22 V

I= 0.070 M
$[NO_3^-]_{TOT}$ = 17.70 μM
$[H_2PO_4^-]_{TOT}$ = 66.00 mM
Log P_{CO_2} = -3.50
$[SO_4^{2-}]_{TOT}$ = 0.15 mM
$[K^+]_{TOT}$ = 66.00 mM
$[Na^+]_{TOT}$ = 1.27 mM

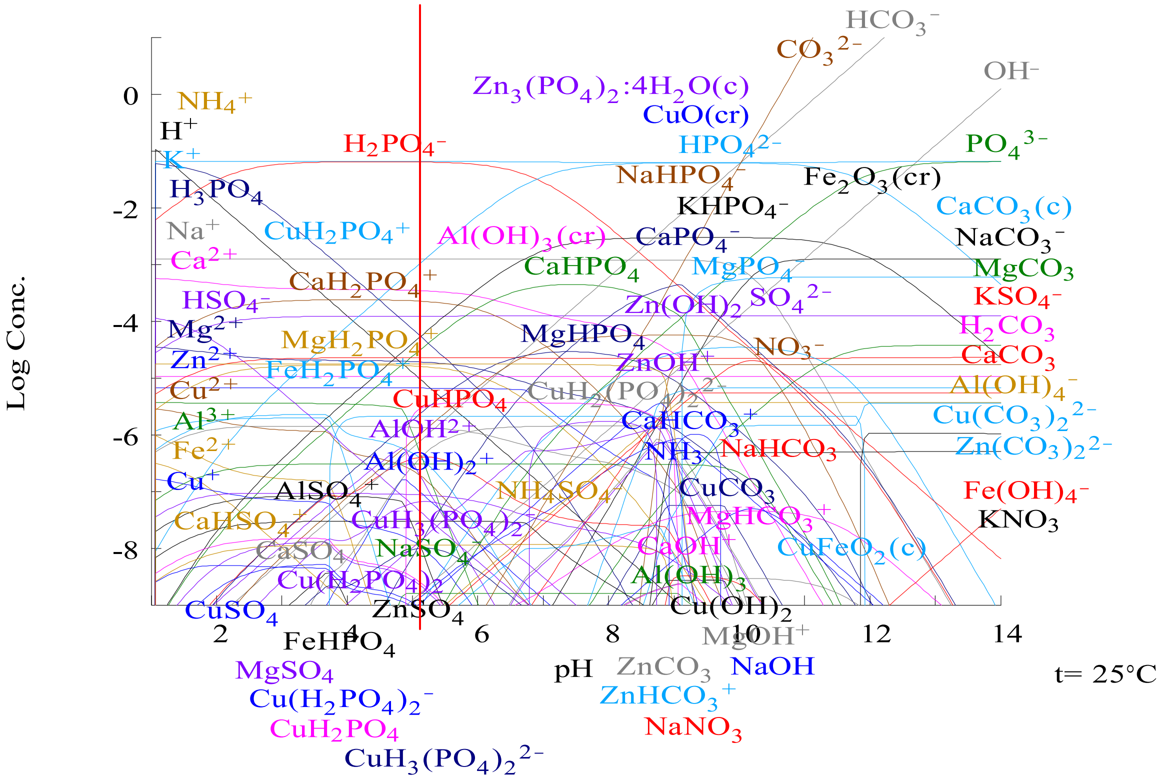


Figure C.60. Phase diagram for PVC pipe section immersed into pH 5 water after three months of exposure.

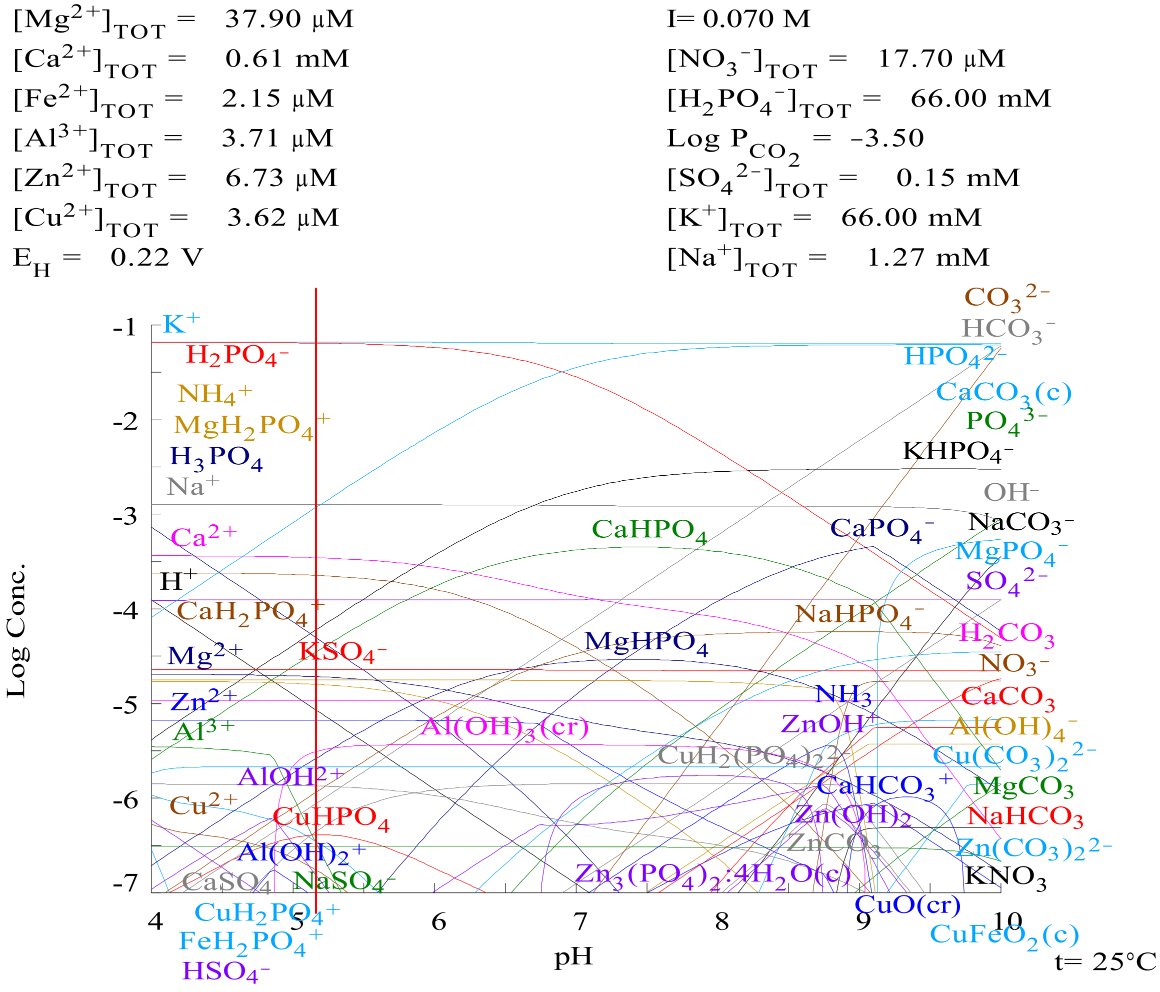


Figure C.61. Phase diagram for PVC pipe section immersed into pH 5 water after three months of exposure. Study area.

Table C.16. The predominant species of zinc. PVC pipe section, pH 5 water, three months exposure.

Component	Log Concentration (mol/L)	Concentration (mol/L)	Zn Concentration (mg/L as Zn)	Cumulative Percentage of Zn
Zn^{2+}	-5.18	6.68E-06	0.437	99.28
$ZnSO_4$	-7.52	3.04E-08	1.99E-03	99.73
$ZnOH^+$	-7.76	1.76E-08	1.15E-03	99.99

Table C.17. The predominant species of copper. PVC pipe section, pH 5 water, three months exposure.

Component	Log Concentration (mol/L)	Concentration (mol/L)	Cu Concentration (mg/L as Cu)	Cumulative Percentage of Cu
$CuFeO_2$(c)	-5.67	2.15E-06	0.14	59.39
$CuH_2(PO_4)_2^{2-}$	-6.29	5.10E-07	3.24E-02	73.49
$CuHPO_4$	-6.39	4.10E-07	2.61E-02	84.82
$CuH_2PO_4^+$	-6.51	3.06E-07	1.94E-02	93.26
Cu^{2+}	-6.82	1.53E-07	9.70E-03	97.48
$CuH_3(PO_4)_2^-$	-7.17	6.72E-08	4.27E-03	99.33
$CuH_3(PO_4)_2^{2-}$	-7.99	1.01E-08	6.45E-04	99.61
Cu^+	-8.06	8.75E-09	5.56E-04	99.86
CuH_2PO_4	-8.70	2.00E-09	1.27E-04	99.91

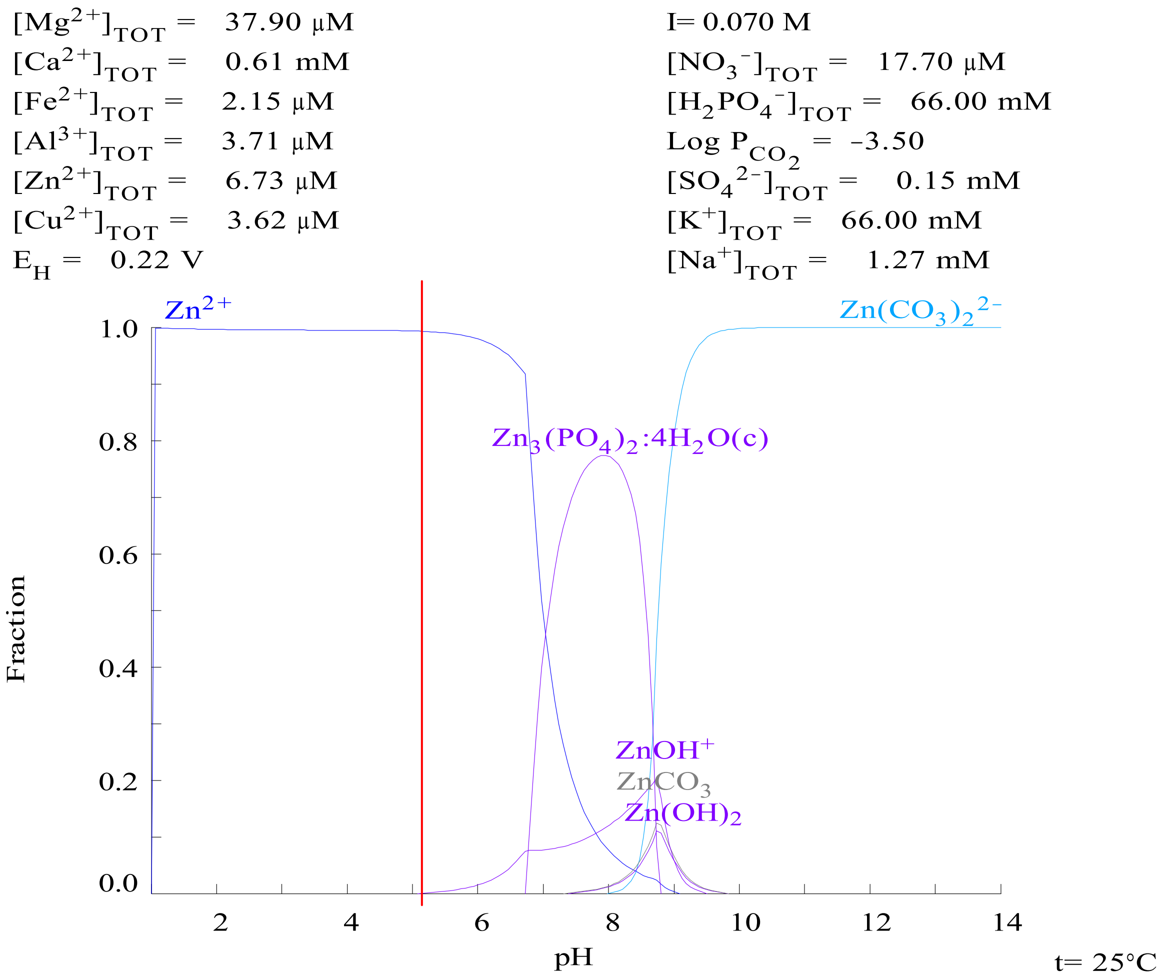


Figure C.62. Fraction diagram of zinc for PVC pipe section immersed into pH 5 water after three months of exposure.

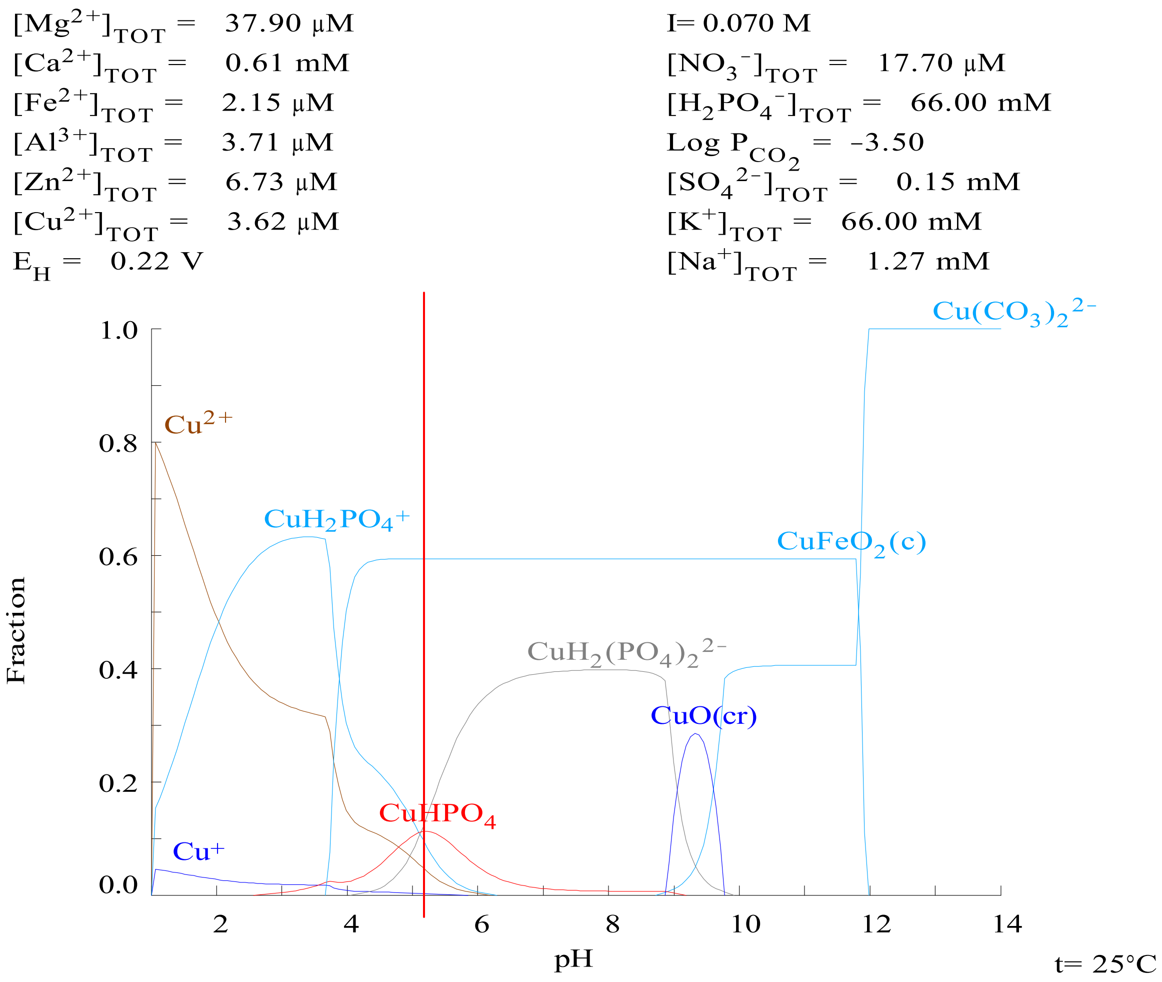


Figure C.63. Fraction diagram of copper for PVC pipe section immersed into pH 5 water after three months of exposure.

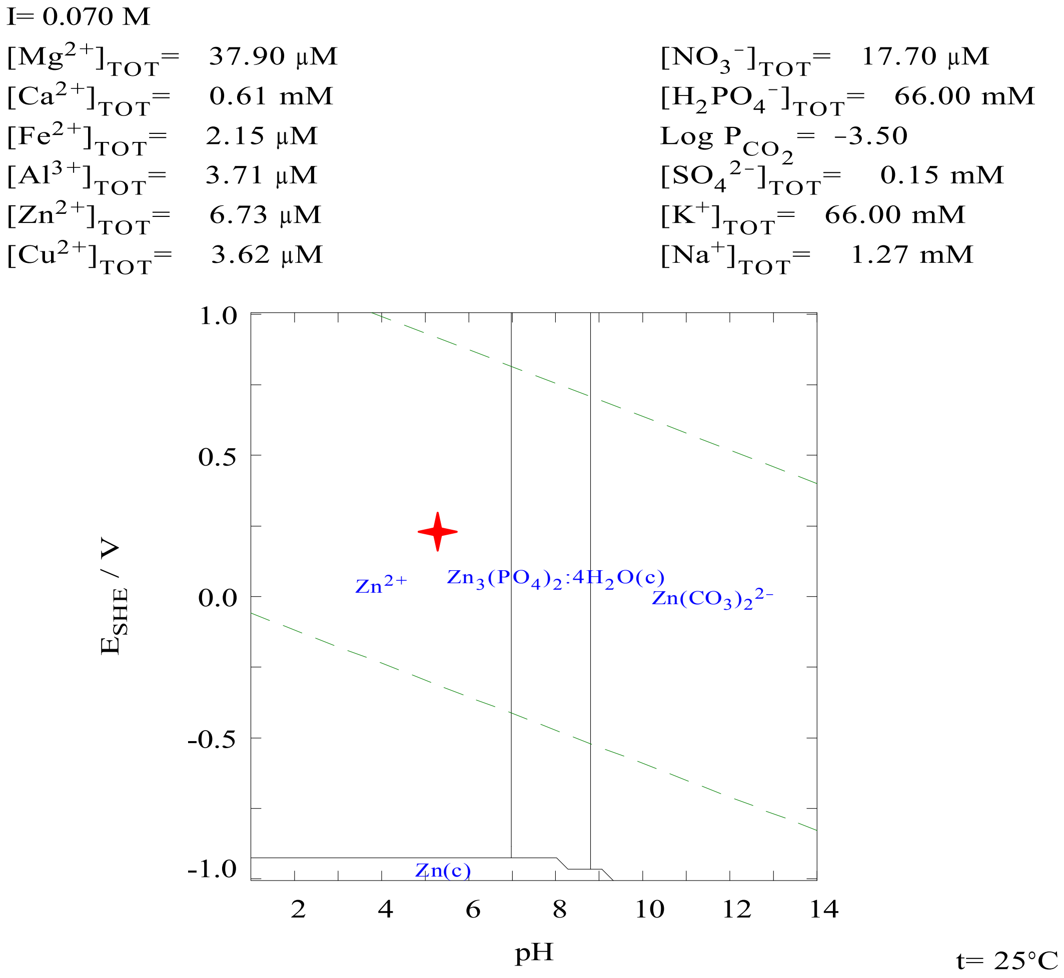


Figure C.64. Pourbaix diagram of zinc for PVC pipe section immersed into pH 5 water after three months of exposure.

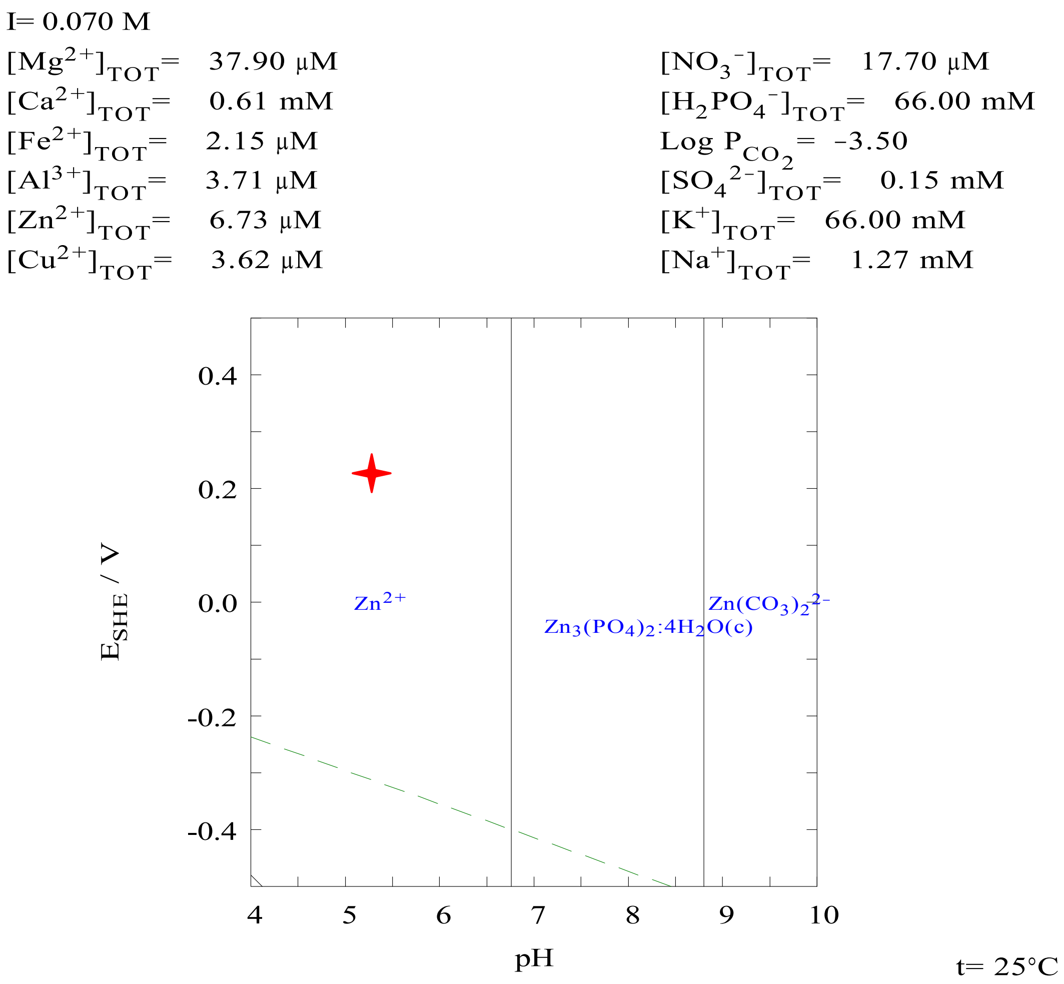


Figure C.65. Pourbaix diagram of zinc for PVC pipe section immersed into pH 5 water after three months of exposure. Study area.

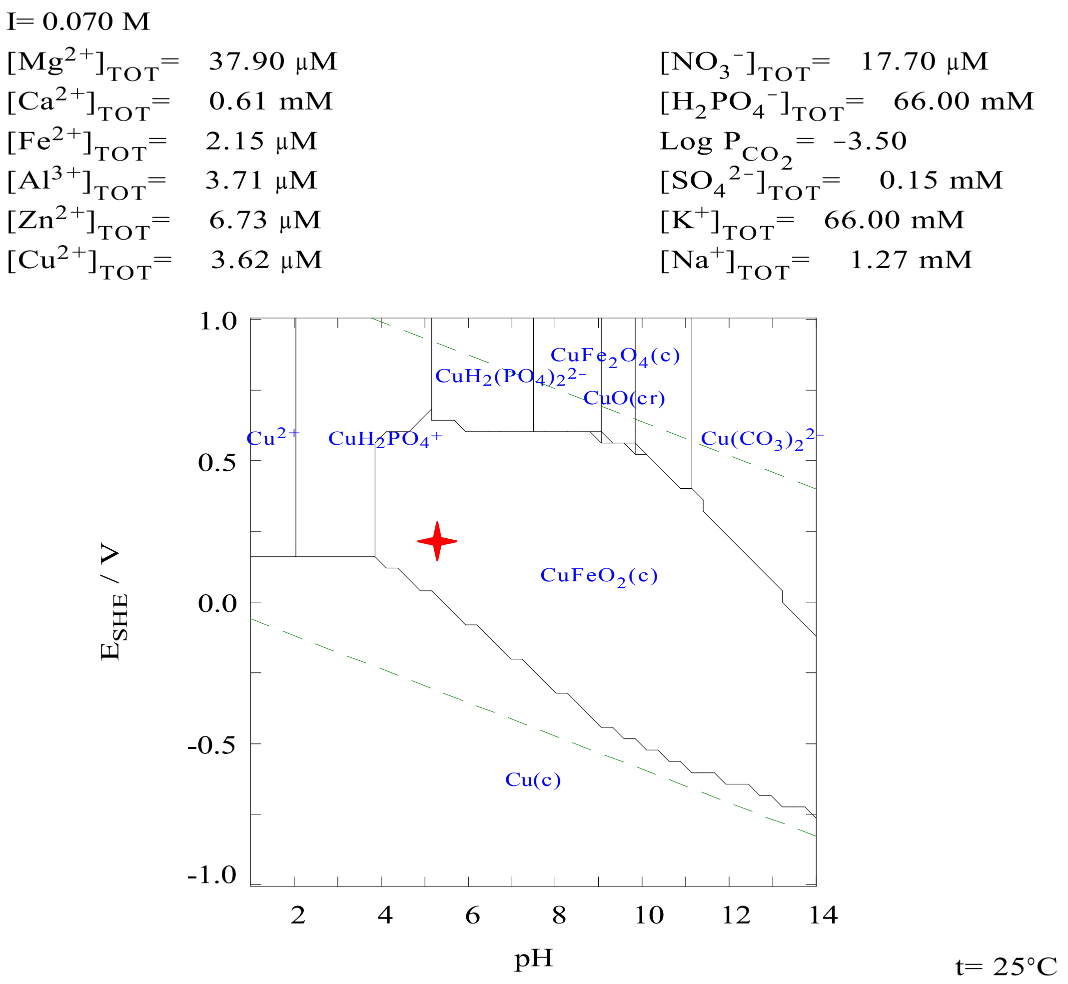


Figure C.66. Pourbaix diagram of copper for PVC pipe section immersed into pH 5 water after three months of exposure.

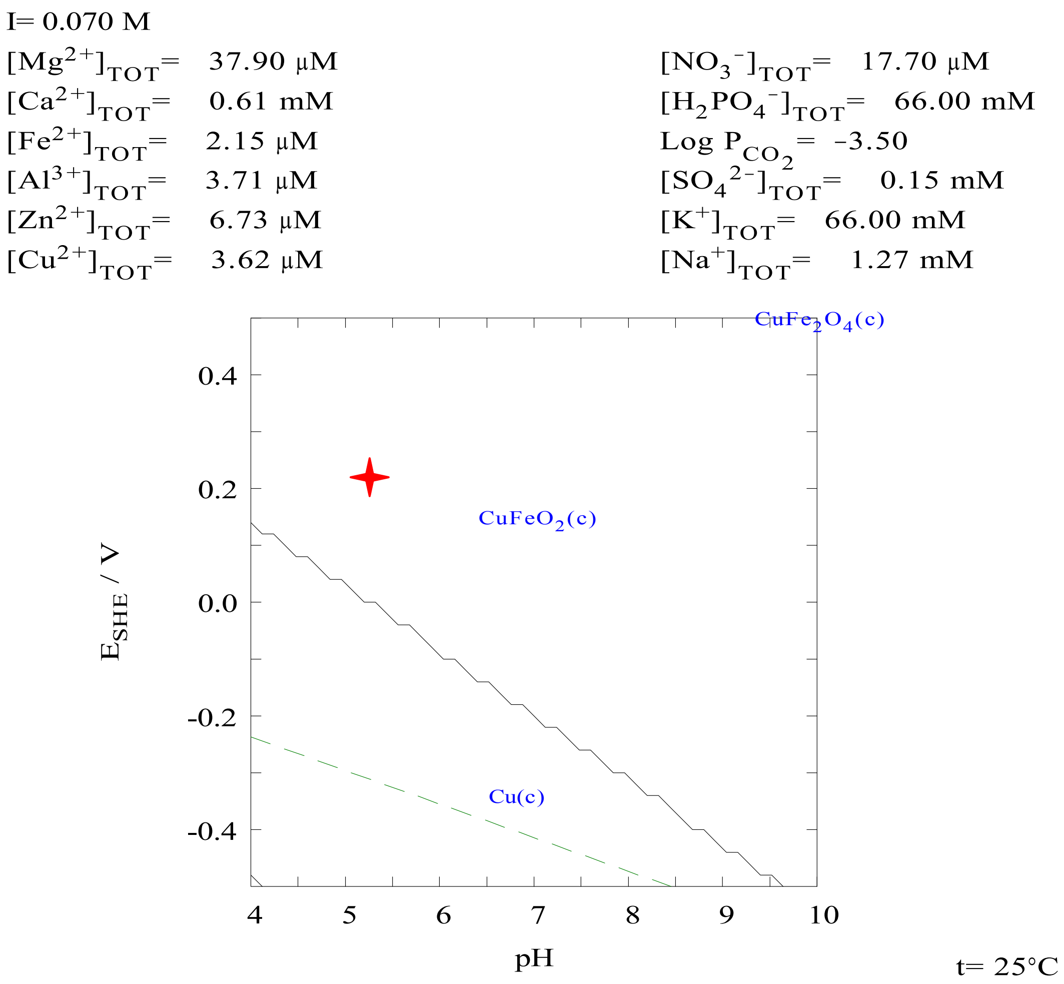


Figure C.67. Pourbaix diagram of copper for PVC pipe section immersed into pH 5 water after three months of exposure. Study area.

PVC Pipe, pH 8 Water, After Three Months of Exposure

$[Mg^{2+}]_{TOT}$ = 27.40 µM
$[Ca^{2+}]_{TOT}$ = 47.00 µM
$[Fe^{2+}]_{TOT}$ = 2.33 µM
$[Al^{3+}]_{TOT}$ = 3.71 µM
$[Zn^{2+}]_{TOT}$ = 10.40 µM
$[Cu^{2+}]_{TOT}$ = 3.30 µM
E_H = 0.13 V

I= 0.196 M
$[HPO_4^{2-}]_{TOT}$ = 64.60 mM
$[NO_3^-]_{TOT}$ = 46.80 µM
Log P_{CO_2} = -3.50
$[SO_4^{2-}]_{TOT}$ = 0.17 mM
$[K^+]_{TOT}$ = 2.07 mM
$[Na^+]_{TOT}$ = 129.00 mM

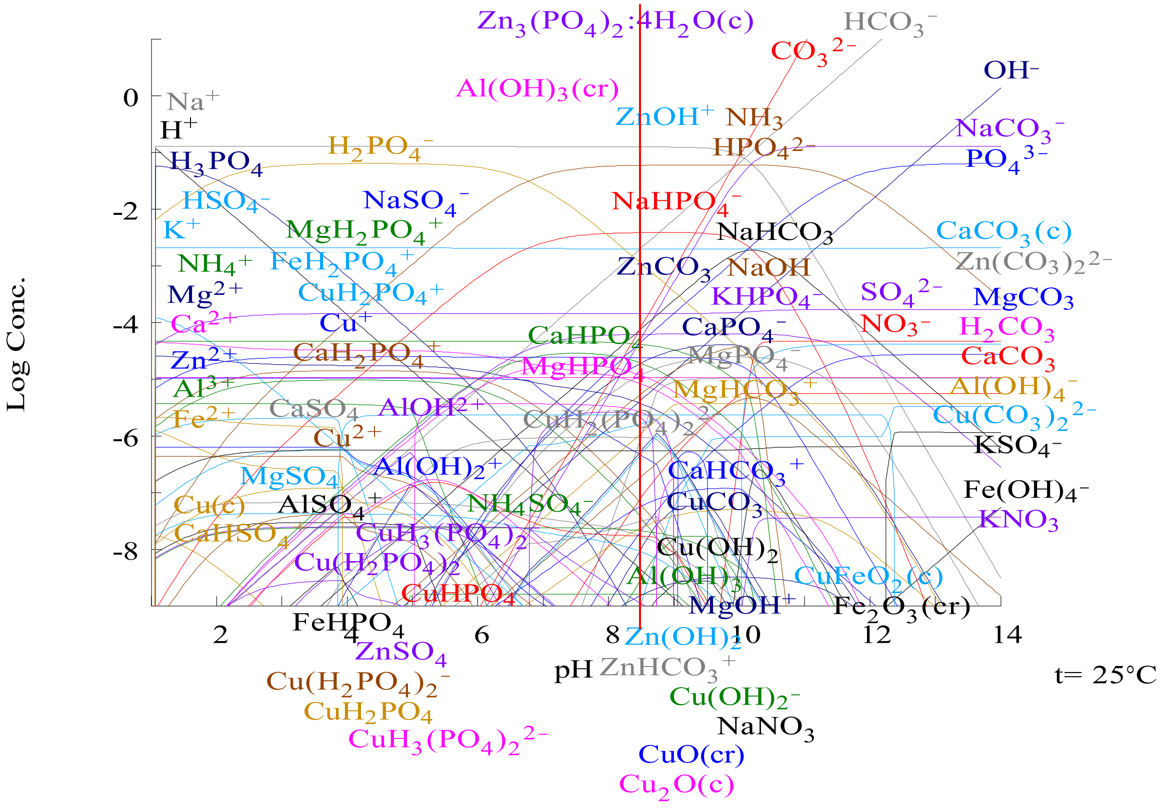


Figure C.68. Phase diagram for PVC pipe section immersed into pH 8 water after three months of exposure.

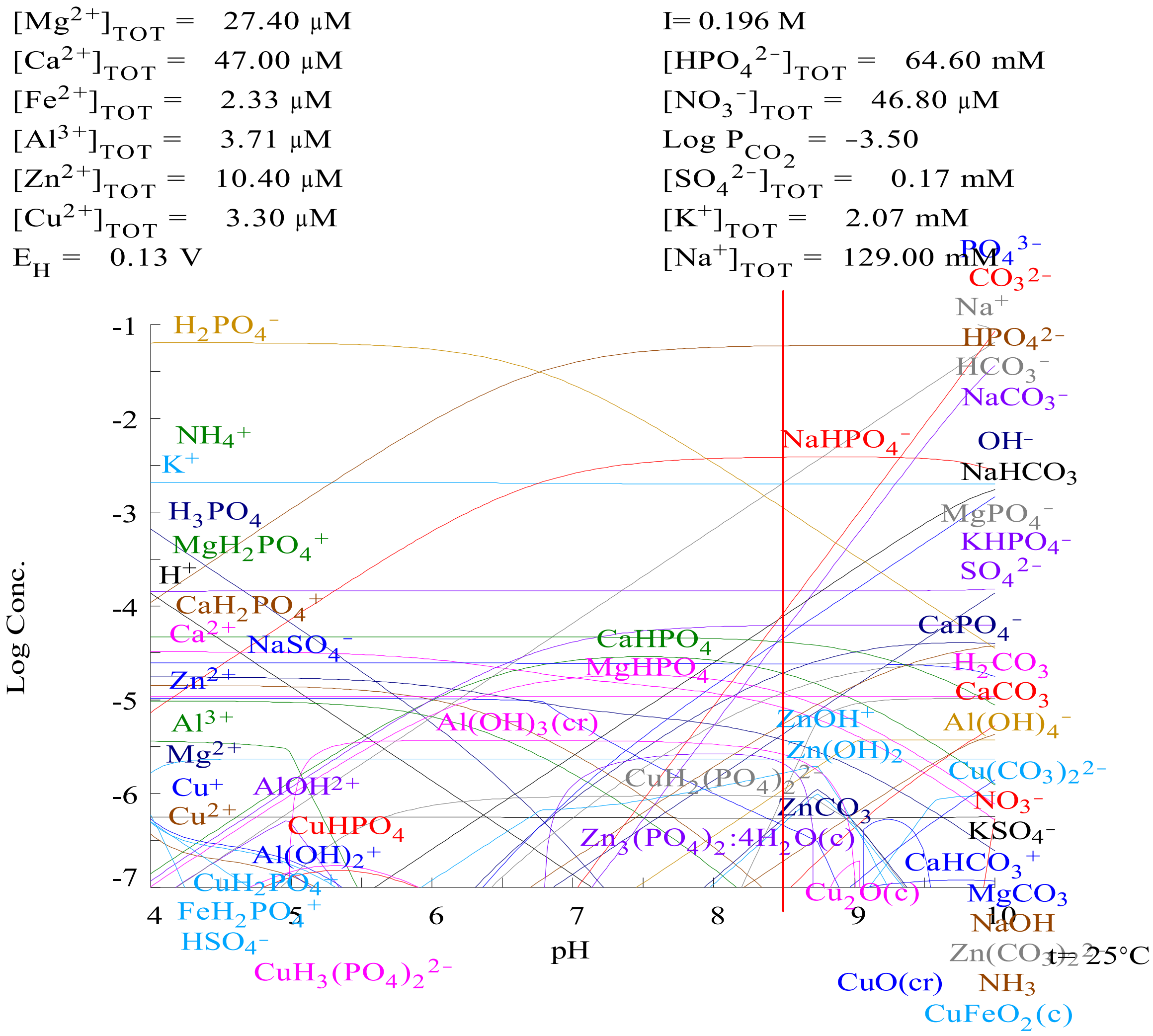


Figure C.69. Phase diagram for PVC pipe section immersed into pH 8 water after three months of exposure. Study area.

Table C.18. The predominant species of zinc. PVC pipe section, pH 8 water, three months exposure.

Component	Log Concentration (mol/L)	Concentration (mol/L)	Zn Concentration (mg/L as Zn)	Cumulative Percentage of Zn
$Zn_3(PO_4)_2:4H_2O(c)$	-5.66	2.17E-06	4.26E-01	62.55
$ZnOH^+$	-5.79	1.63E-06	1.06E-01	78.19
$Zn(CO_3)_2^{2-}$	-6.09	8.08E-07	5.28E-02	85.96
$ZnCO_3$	-6.30	5.05E-07	3.30E-02	90.82
Zn^{2+}	-6.32	4.73E-07	3.10E-02	95.37
$Zn(OH)_2$	-6.35	4.49E-07	2.94E-02	99.69
$ZnHCO_3^+$	-7.51	3.10E-08	2.03E-03	99.99

Table C.19. The predominant species of copper. PVC pipe section, pH 8 water, three months exposure.

Component	Log Concentration (mol/L)	Concentration (mol/L)	Cu Concentration (mg/L as Cu)	Cumulative Percentage of Cu
$CuFeO_2$(c)	-5.63	2.33E-06	1.48E-01	70.60
$CuH_2(PO_4)_2^{2-}$	-6.03	9.38E-07	5.96E-02	99.03
$CuHPO_4$	-7.76	1.72E-08	1.09E-03	99.55
$CuCO_3$	-8.04	9.19E-09	5.84E-04	99.83
$Cu(OH)_2^-$	-8.56	2.74E-09	1.74E-04	99.91

Footnote: Cu^+ was calculated to be 2.96E-05 mg/L; Cu^{2+} was calculated to be 2.03E-05 mg/L

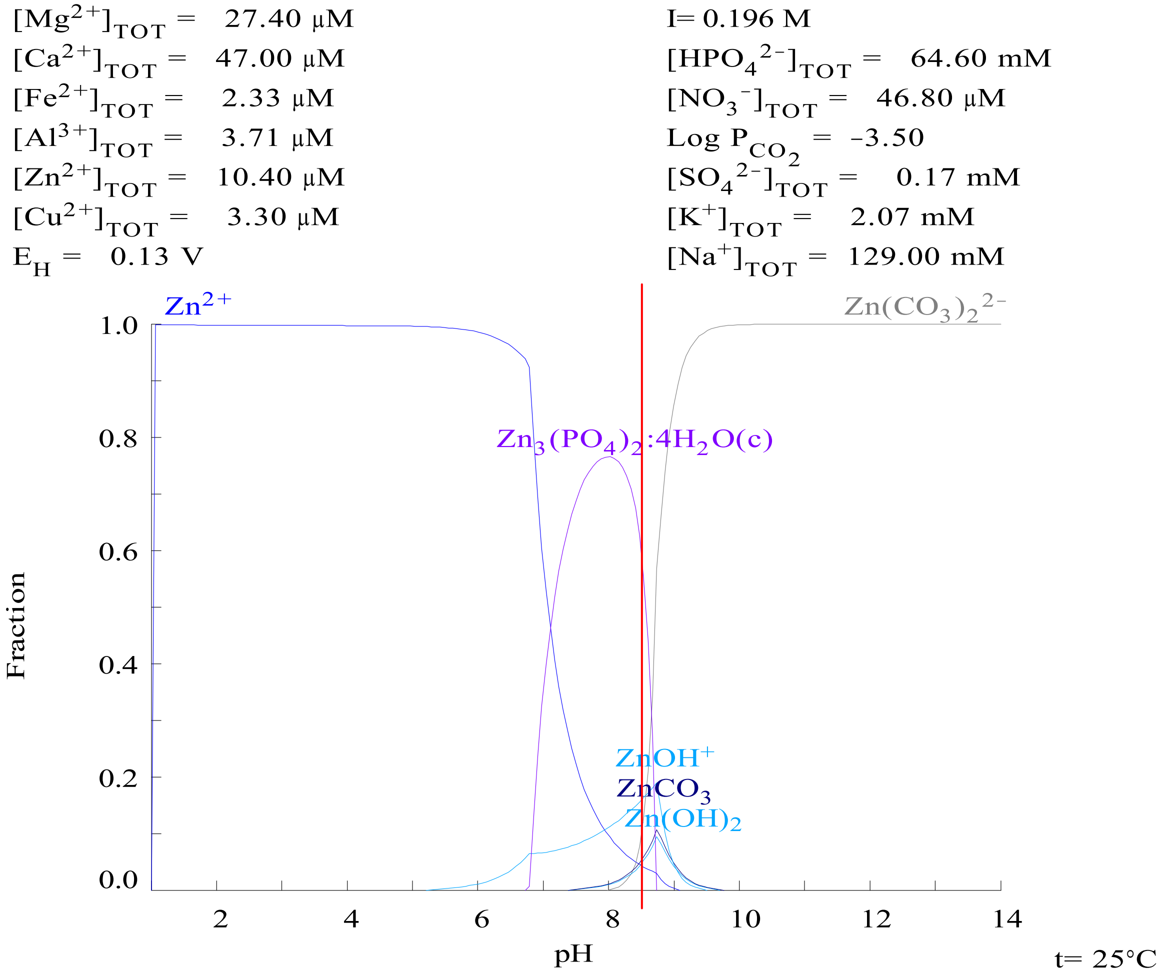


Figure C.70. Fraction diagram of zinc for PVC pipe section immersed into pH 8 water after three months of exposure.

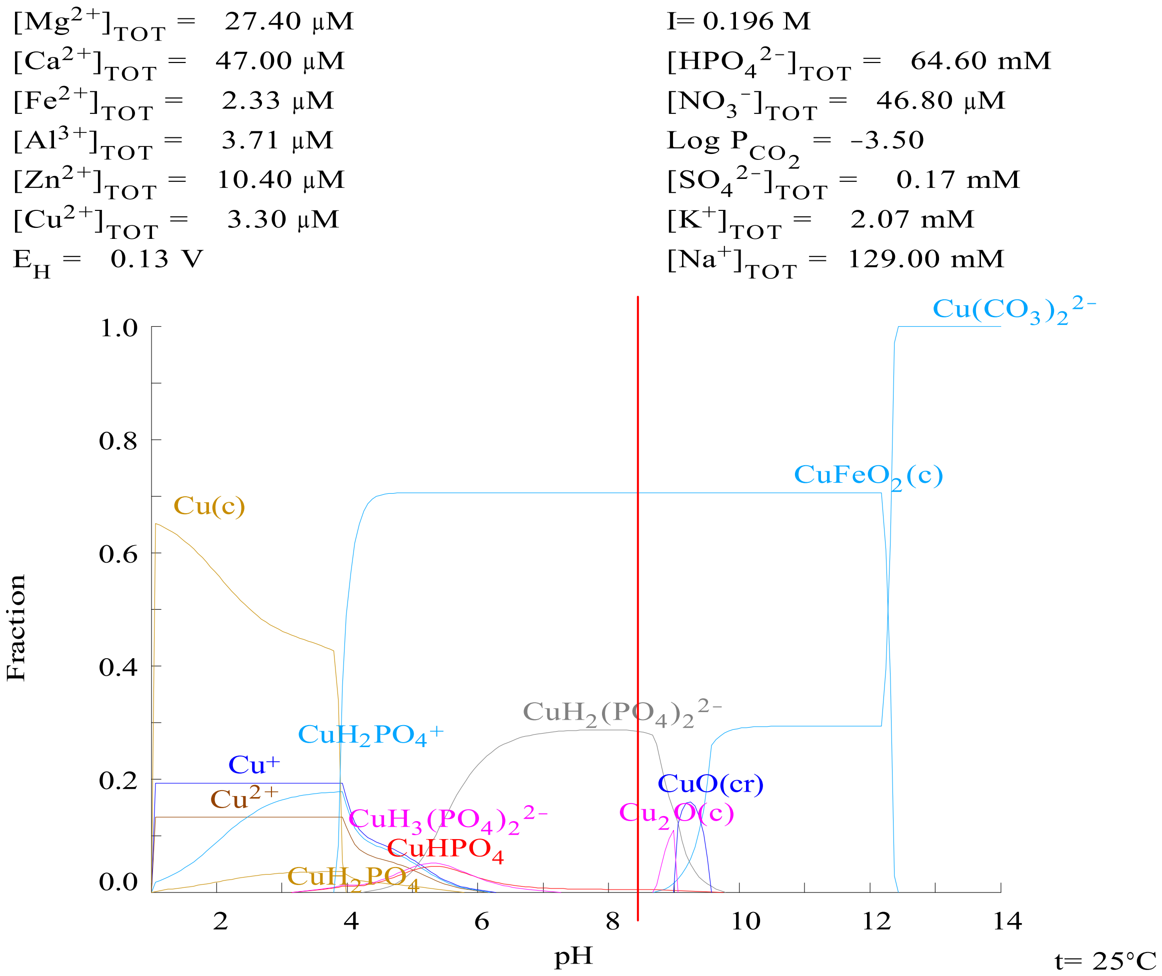


Figure C.71. Fraction diagram of copper for PVC pipe section immersed into pH 8 water after three months of exposure.

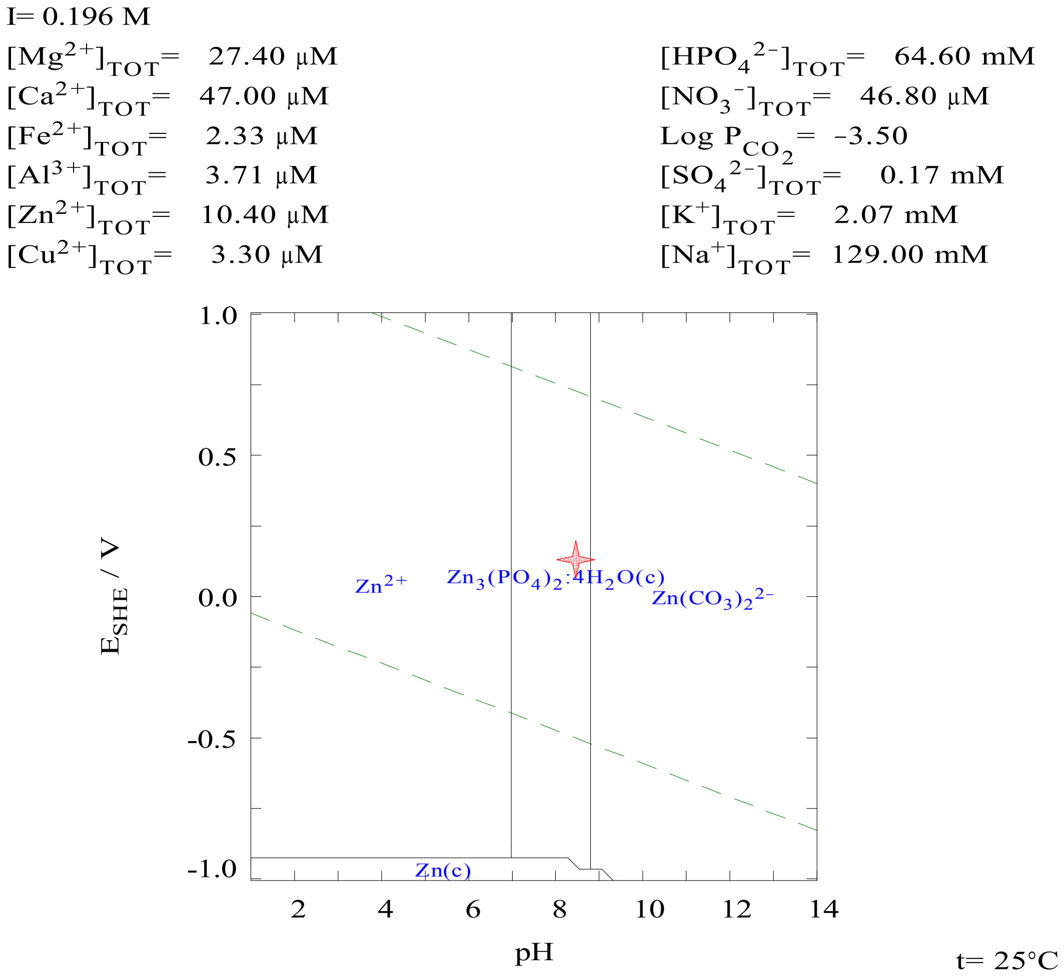


Figure C.72. Pourbaix diagram of zinc for PVC pipe section immersed into pH 8 water after three months of exposure.

I= 0.196 M
$[Mg^{2+}]_{TOT}$= 27.40 μM
$[Ca^{2+}]_{TOT}$= 47.00 μM
$[Fe^{2+}]_{TOT}$= 2.33 μM
$[Al^{3+}]_{TOT}$= 3.71 μM
$[Zn^{2+}]_{TOT}$= 10.40 μM
$[Cu^{2+}]_{TOT}$= 3.30 μM

$[HPO_4{}^{2-}]_{TOT}$= 64.60 mM
$[NO_3{}^{-}]_{TOT}$= 46.80 μM
Log P_{CO_2}= -3.50
$[SO_4{}^{2-}]_{TOT}$= 0.17 mM
$[K^{+}]_{TOT}$= 2.07 mM
$[Na^{+}]_{TOT}$= 129.00 mM

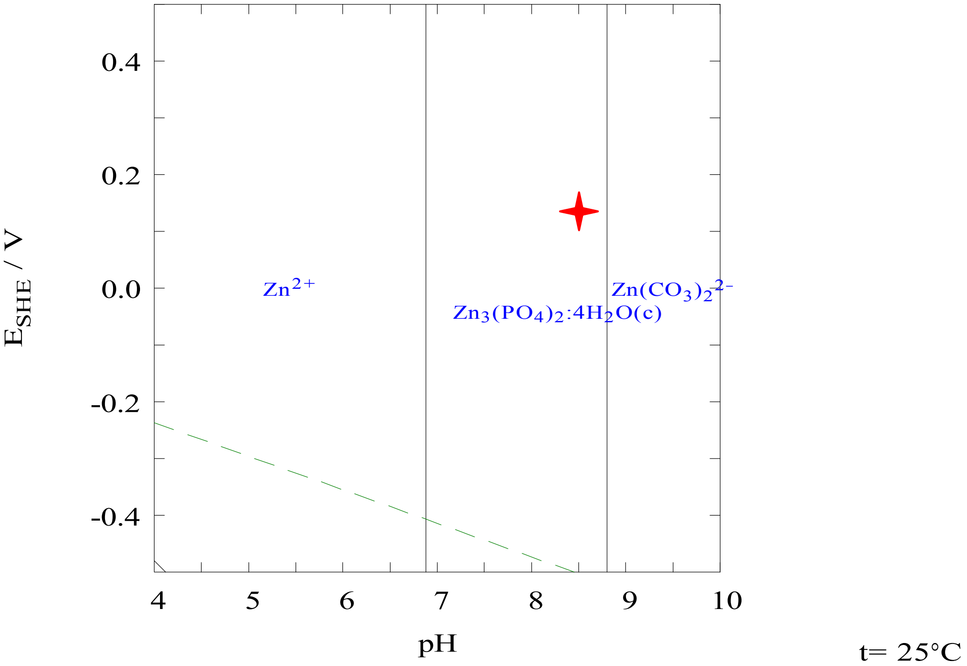


Figure C.73. Pourbaix diagram of zinc for PVC pipe section immersed into pH 8 water after three months of exposure. Study area.

I= 0.196 M

$[Mg^{2+}]_{TOT}$= 27.40 µM
$[Ca^{2+}]_{TOT}$= 47.00 µM
$[Fe^{2+}]_{TOT}$= 2.33 µM
$[Al^{3+}]_{TOT}$= 3.71 µM
$[Zn^{2+}]_{TOT}$= 10.40 µM
$[Cu^{2+}]_{TOT}$= 3.30 µM

$[HPO_4^{2-}]_{TOT}$= 64.60 mM
$[NO_3^{-}]_{TOT}$= 46.80 µM
Log P_{CO_2}= -3.50
$[SO_4^{2-}]_{TOT}$= 0.17 mM
$[K^{+}]_{TOT}$= 2.07 mM
$[Na^{+}]_{TOT}$= 129.00 mM

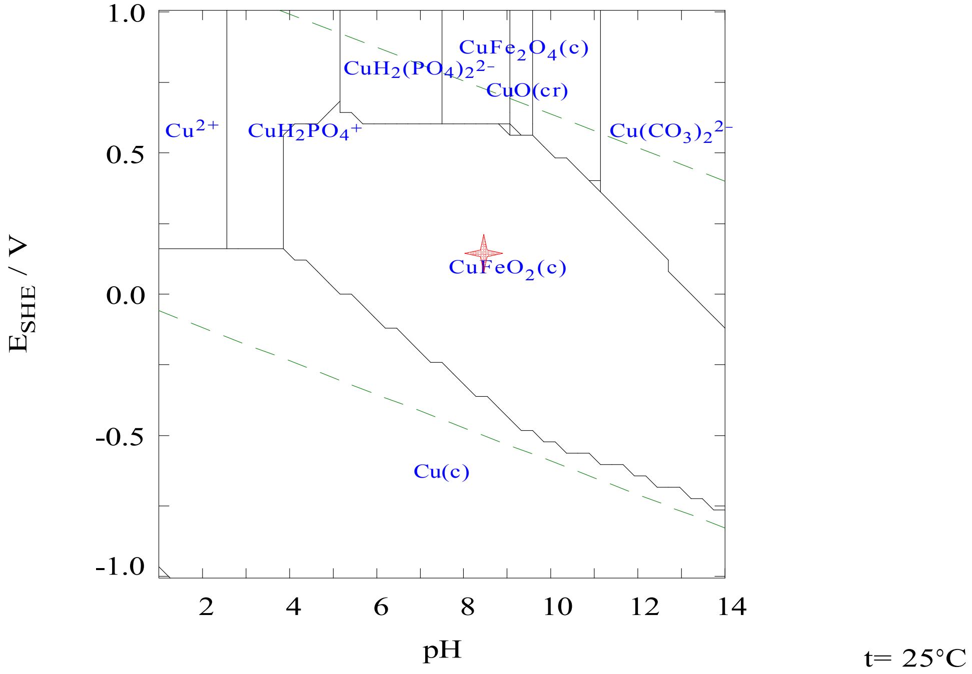


Figure C.74. Pourbaix diagram of copper for PVC pipe section immersed into pH 8 water after three months of exposure.

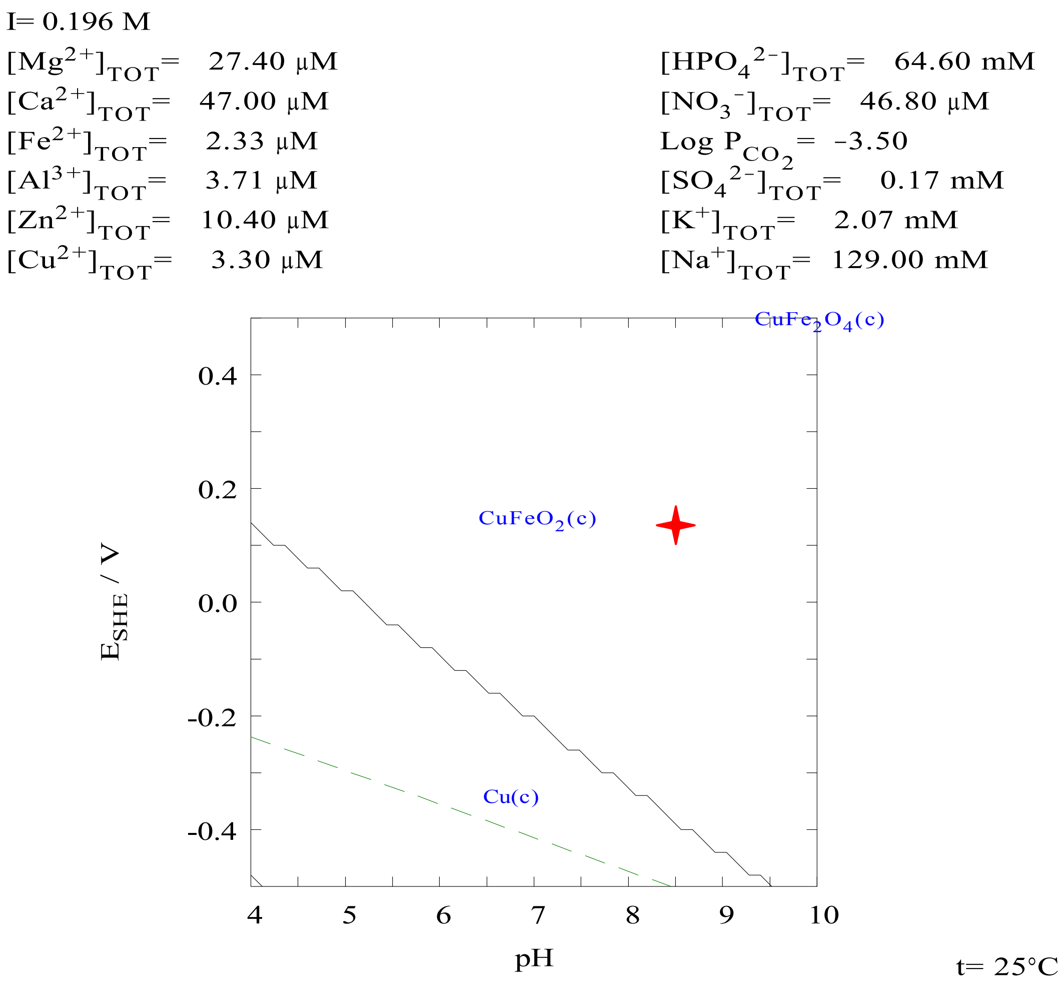


Figure C.75. Pourbaix diagram of copper for PVC pipe section immersed into pH 8 water after three months of exposure. Study area.

HDPE Pipe, pH 5 Water, After Three Months of Exposure

I= 0.068 M

$[Mg^{2+}]_{TOT}$ = 5.93 µM

$[Ca^{2+}]_{TOT}$ = 13.70 µM

$[Fe^{2+}]_{TOT}$ = 2.69 µM

$[Zn^{2+}]_{TOT}$ = 0.92 µM

$[Cu^{2+}]_{TOT}$ = 0.47 µM

E_H = 0.21 V

$[NO_3^-]_{TOT}$ = 6.43 µM

$[H_2PO_4^-]_{TOT}$ = 66.00 mM

Log P_{CO_2} = -3.50

$[SO_4^{2-}]_{TOT}$ = 16.60 µM

$[K^+]_{TOT}$ = 66.00 mM

$[Na^+]_{TOT}$ = 1.27 mM

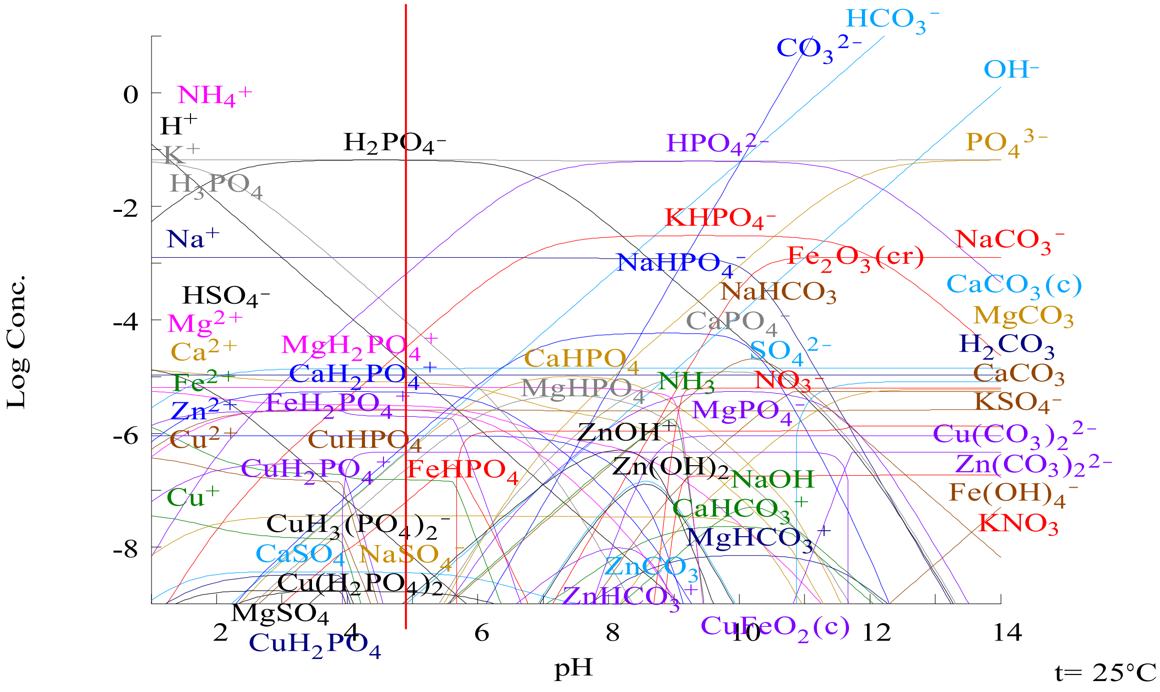


Figure C.76. Phase diagram for HDPE pipe section immersed into pH 5 water after three months of exposure.

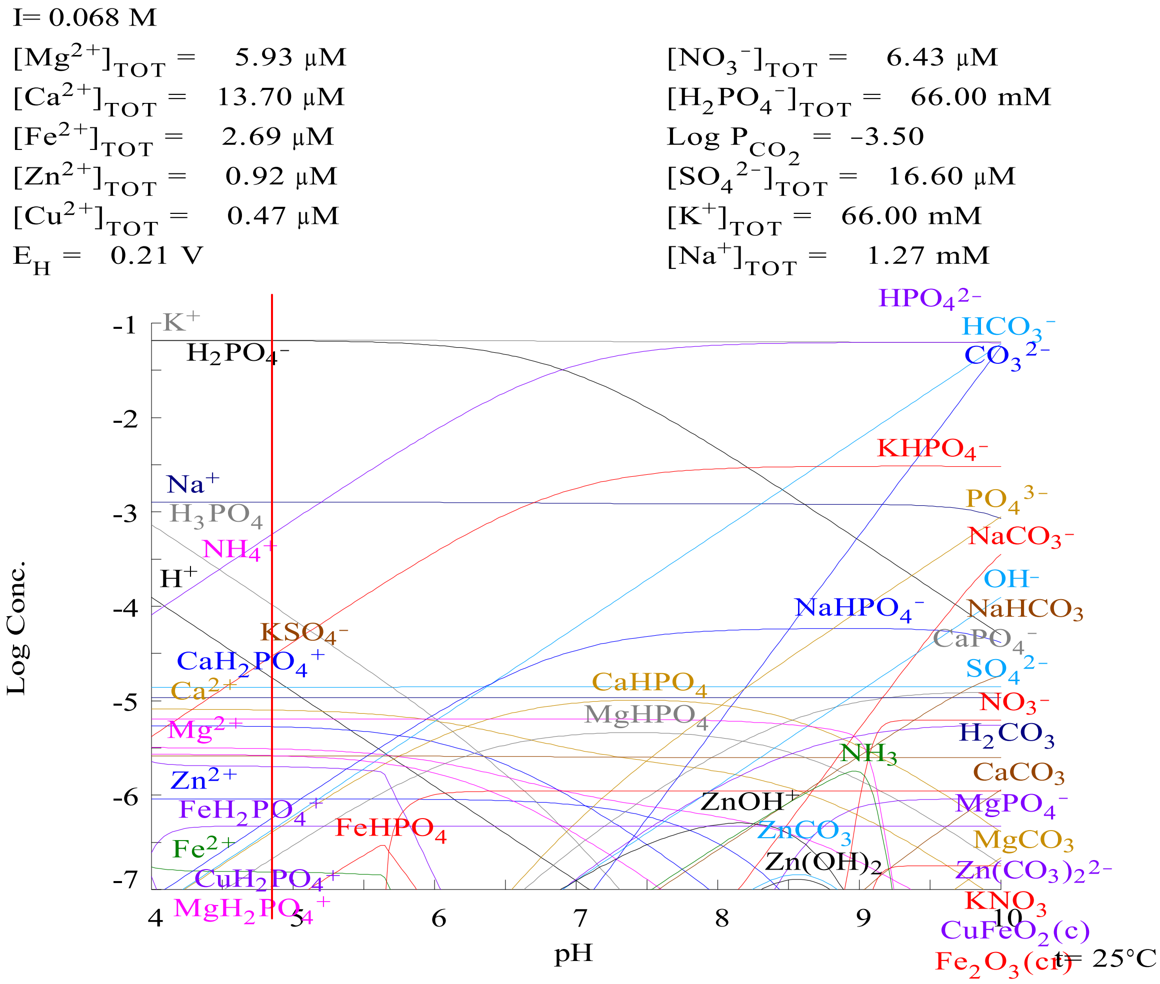


Figure C.77. Phase diagram for HDPE pipe section immersed into pH 5 water after three months of exposure. Study area.

Table C.20. The predominant species of zinc. HDPE pipe section, pH 5 water, three months exposure.

Component	Log Concentration (mol/L)	Concentration (mol/L)	Zn Concentration (mg/L as Zn)	Cumulative Percentage of Zn
Zn^{2+}	-6.04	9.17E-07	5.99E-02	99.84
$ZnOH^{+}$	-9.00	9.89E-10	6.47E-05	99.95
$ZnSO_4$	-9.32	4.78E-10	3.12E-05	99.998

Table C.21. The predominant species of copper. HDPE pipe section, pH 5 water, three months exposure.

Component	Log Concentration (mol/L)	Concentration (mol/L)	Cu Concentration (mg/L as Cu)	Cumulative Percentage of Cu
$CuFeO_2$(c)	-6.33	4.72E-07	0.029994	99.96
$CuH_2PO_4^+$	-10.15	7.09E-11	4.50E-06	99.98
$CuHPO_4$	-10.41	3.88E-11	2.47E-06	99.986
Cu^{2+}	-10.46	3.45E-11	2.19E-06	99.993

Footnote: Cu^+ was calculated to be 2.10E-07 mg/L.

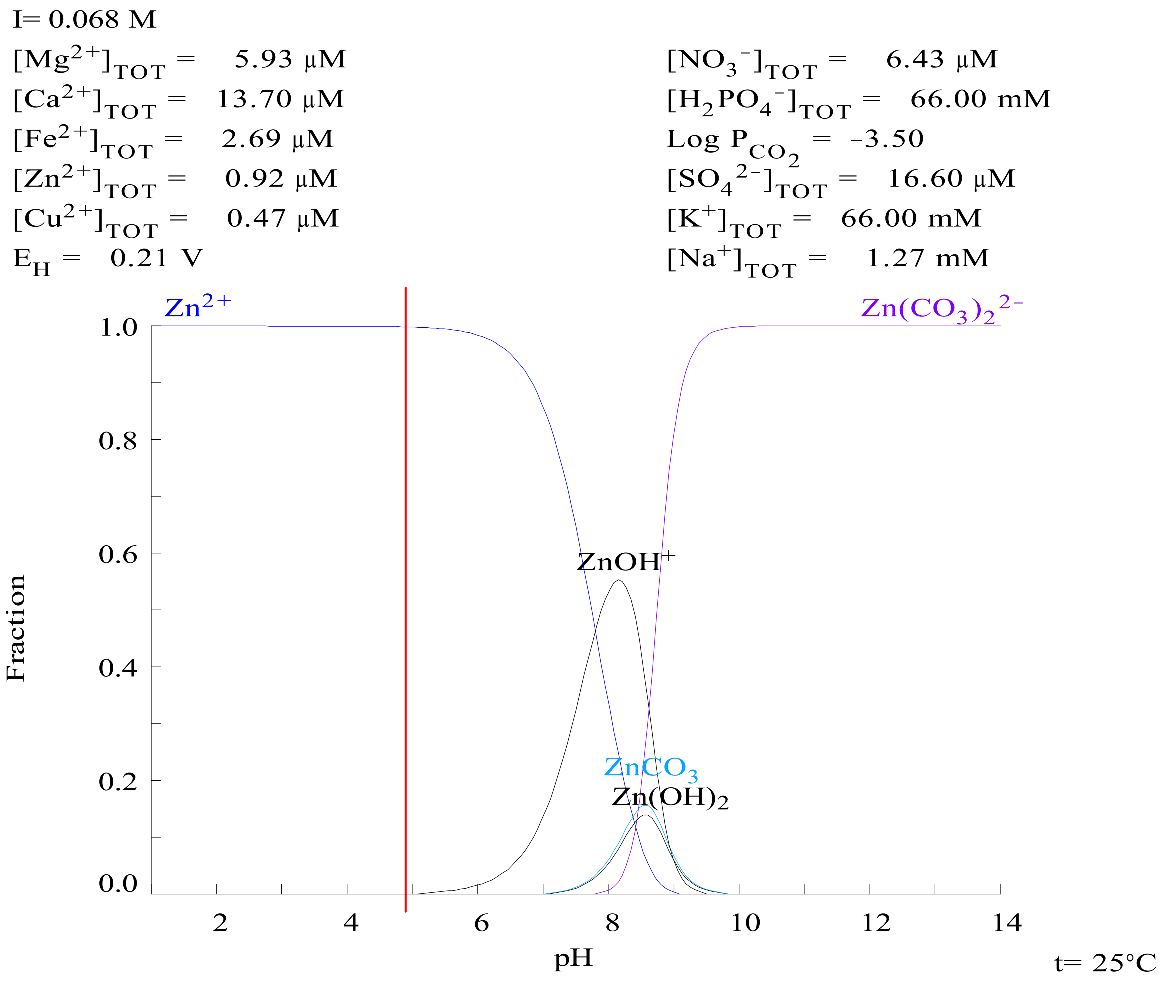


Figure C.78. Fraction diagram of zinc for HDPE pipe section immersed into pH 5 water after three months of exposure.

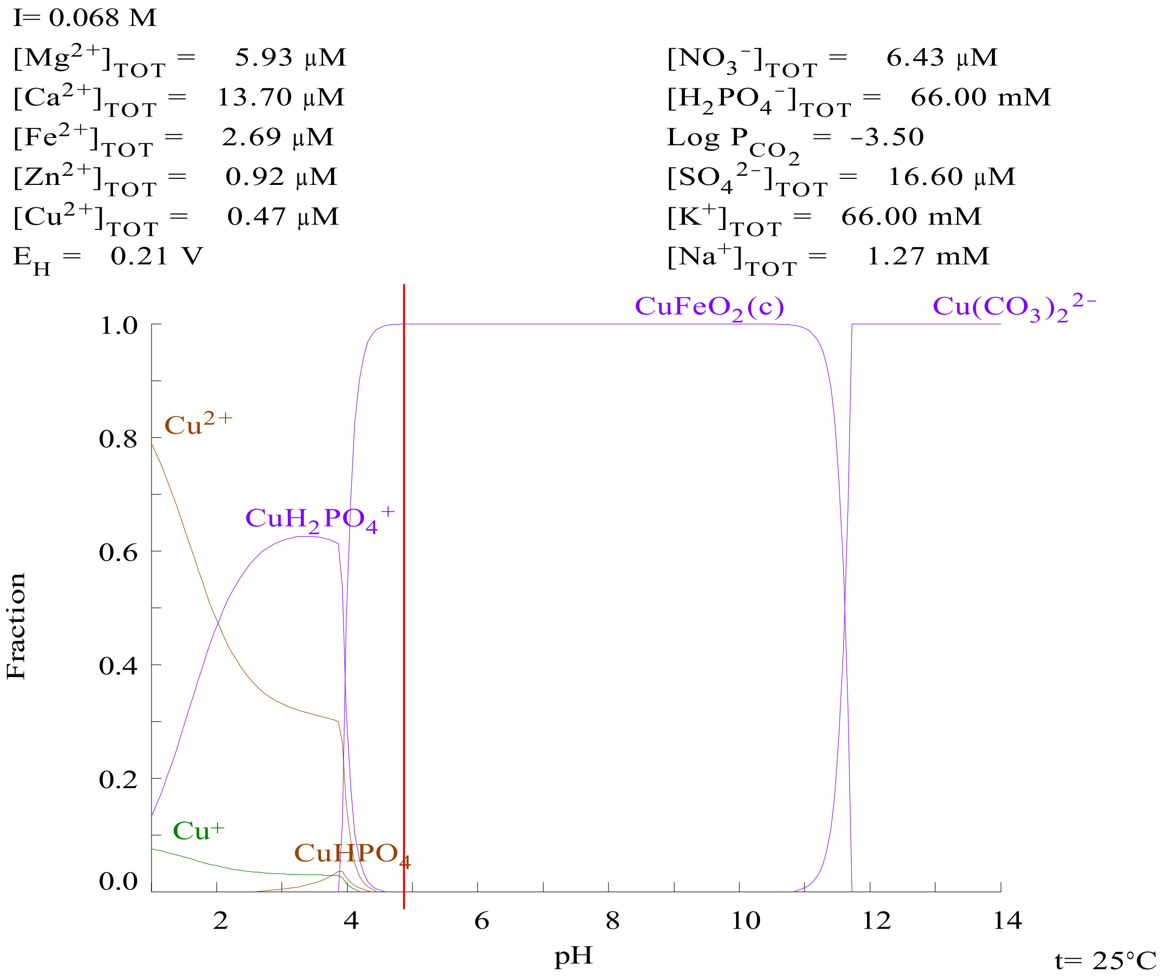


Figure C.79. Fraction diagram of copper for HDPE pipe section immersed into pH 5 water after three months of exposure.

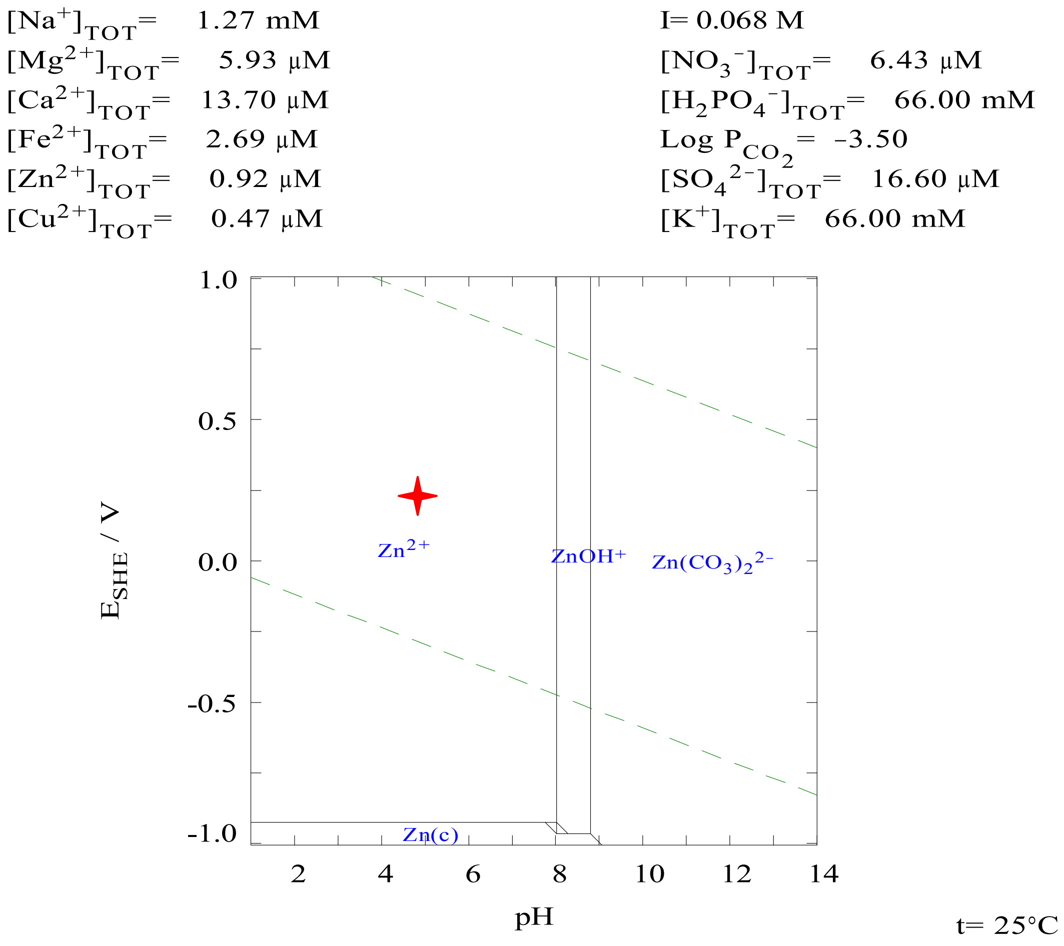


Figure C.80. Pourbaix diagram of zinc for HDPE pipe section immersed into pH 5 water after three months of exposure.

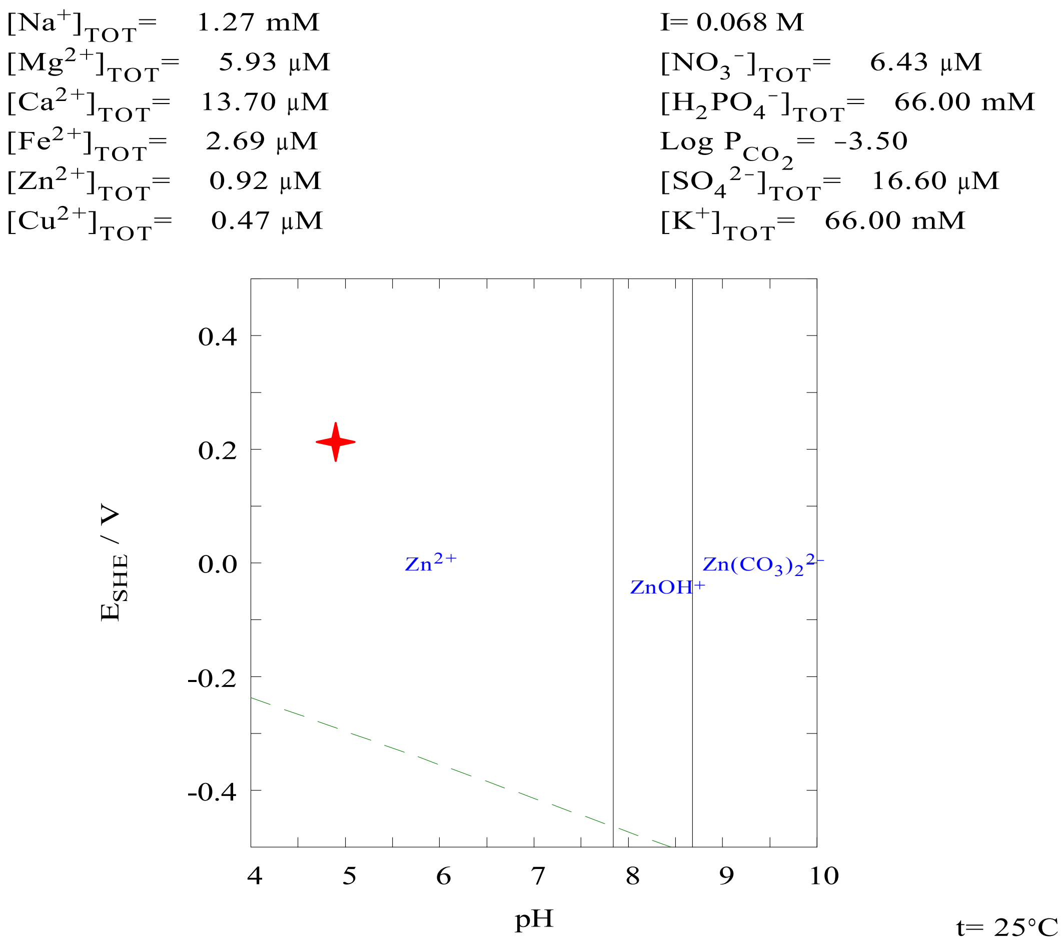


Figure C.81. Pourbaix diagram of zinc for HDPE pipe section immersed into pH 5 water after three months of exposure. Study area.

$[Na^+]_{TOT}$= 1.27 mM
$[Mg^{2+}]_{TOT}$= 5.93 µM
$[Ca^{2+}]_{TOT}$= 13.70 µM
$[Fe^{2+}]_{TOT}$= 2.69 µM
$[Zn^{2+}]_{TOT}$= 0.92 µM
$[Cu^{2+}]_{TOT}$= 0.47 µM

I= 0.068 M
$[NO_3^-]_{TOT}$= 6.43 µM
$[H_2PO_4^-]_{TOT}$= 66.00 mM
Log P_{CO_2}= -3.50
$[SO_4^{2-}]_{TOT}$= 16.60 µM
$[K^+]_{TOT}$= 66.00 mM

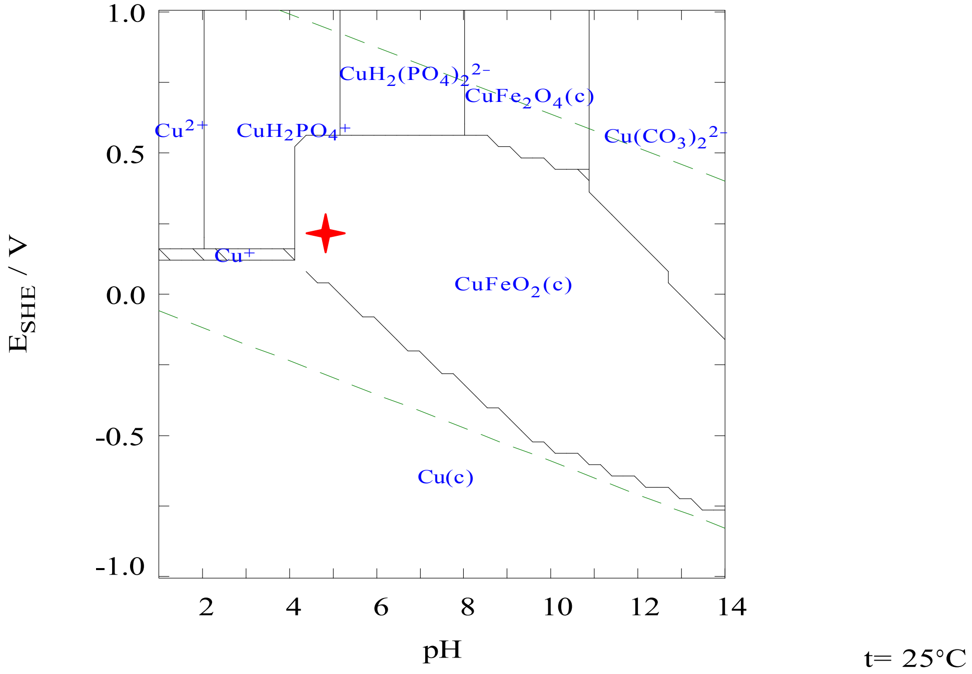


Figure C.82. Pourbaix diagram of copper for HDPE pipe section immersed into pH 5 water after three months of exposure.

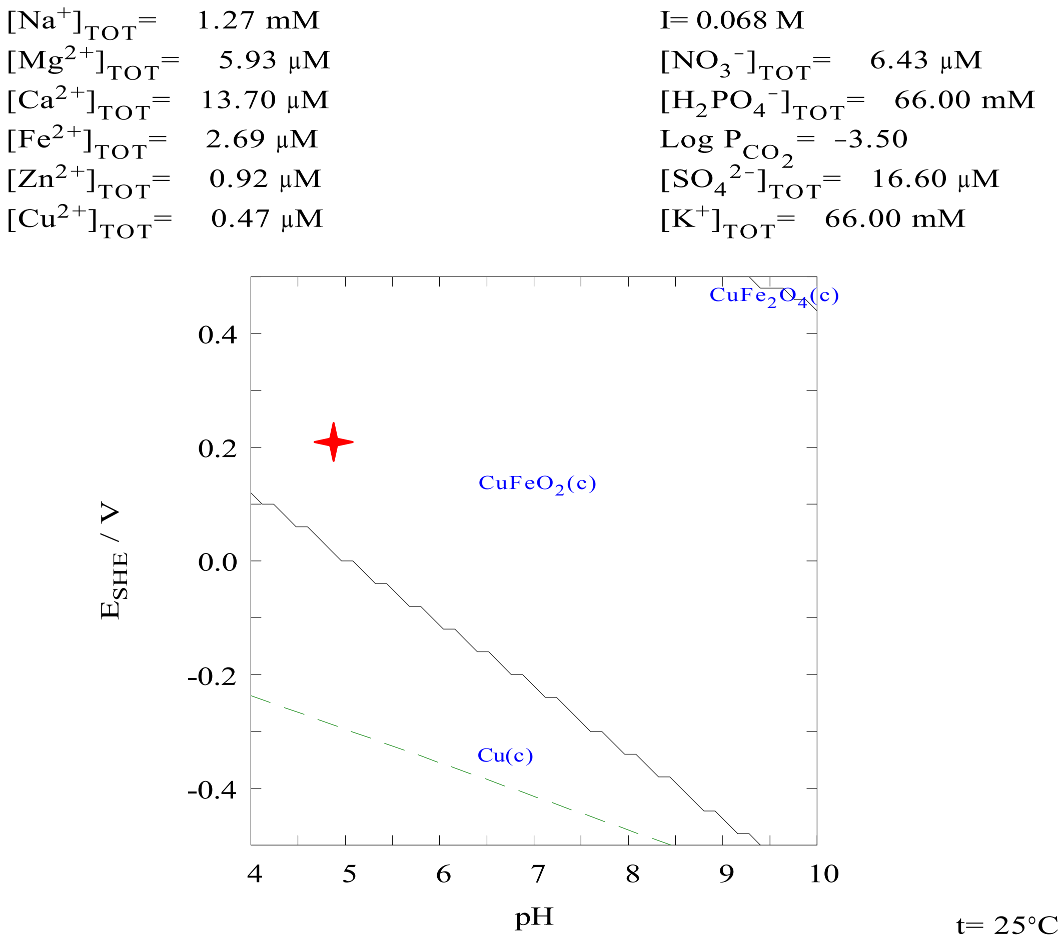


Figure C.83. Pourbaix diagram of copper for HDPE pipe section immersed into pH 5 water after three months of exposure. Study area.

HDPE Pipe, pH 8 Water, After Three Months of Exposure

$[Mg^{2+}]_{TOT}$ = 5.45 µM
$[Ca^{2+}]_{TOT}$ = 7.71 µM
$[Fe^{2+}]_{TOT}$ = 2.33 µM
$[Al^{3+}]_{TOT}$ = 7.41 µM
$[Zn^{2+}]_{TOT}$ = 0.76 µM
$[Cu^{2+}]_{TOT}$ = 0.47 µM
E_H = 0.13 V

I= 0.196 M
$[HPO_4^{2-}]_{TOT}$ = 64.60 mM
$[NO_3^-]_{TOT}$ = 33.90 µM
Log P_{CO_2} = -3.50
$[SO_4^{2-}]_{TOT}$ = 5.52 µM
$[K^+]_{TOT}$ = 2.07 mM
$[Na^+]_{TOT}$ = 129.00 mM

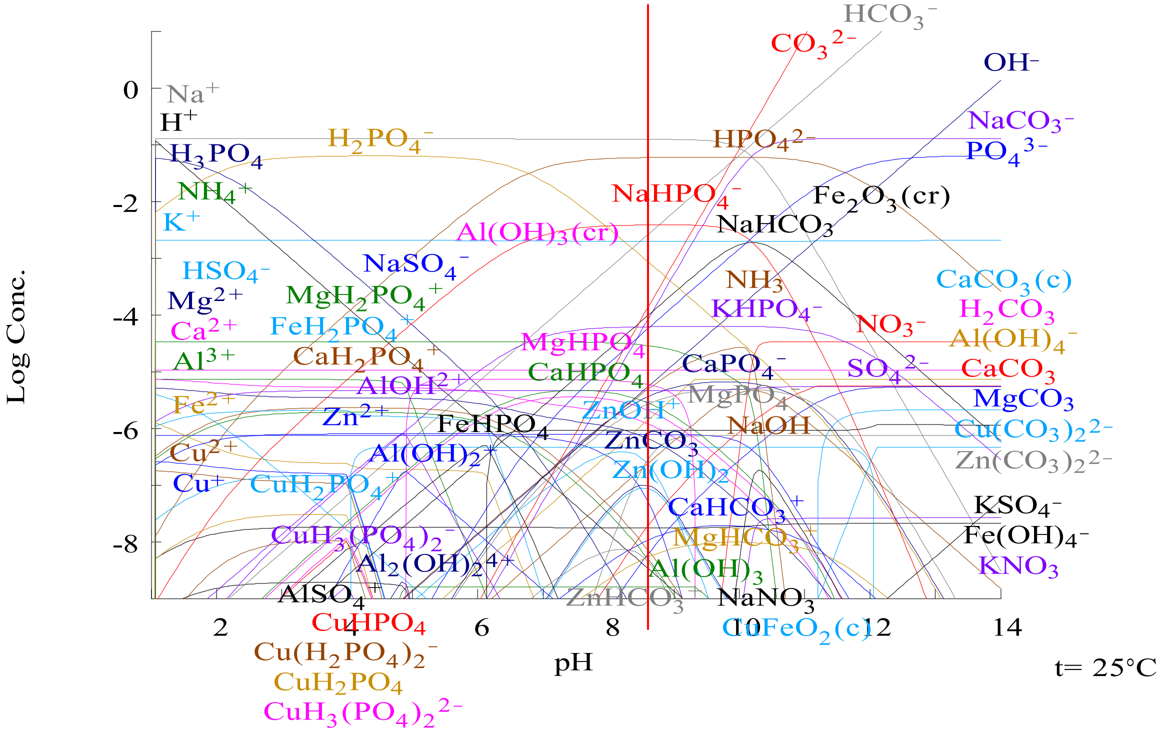


Figure C.84. Phase diagram for HDPE pipe section immersed into pH 8 water after three months of exposure.

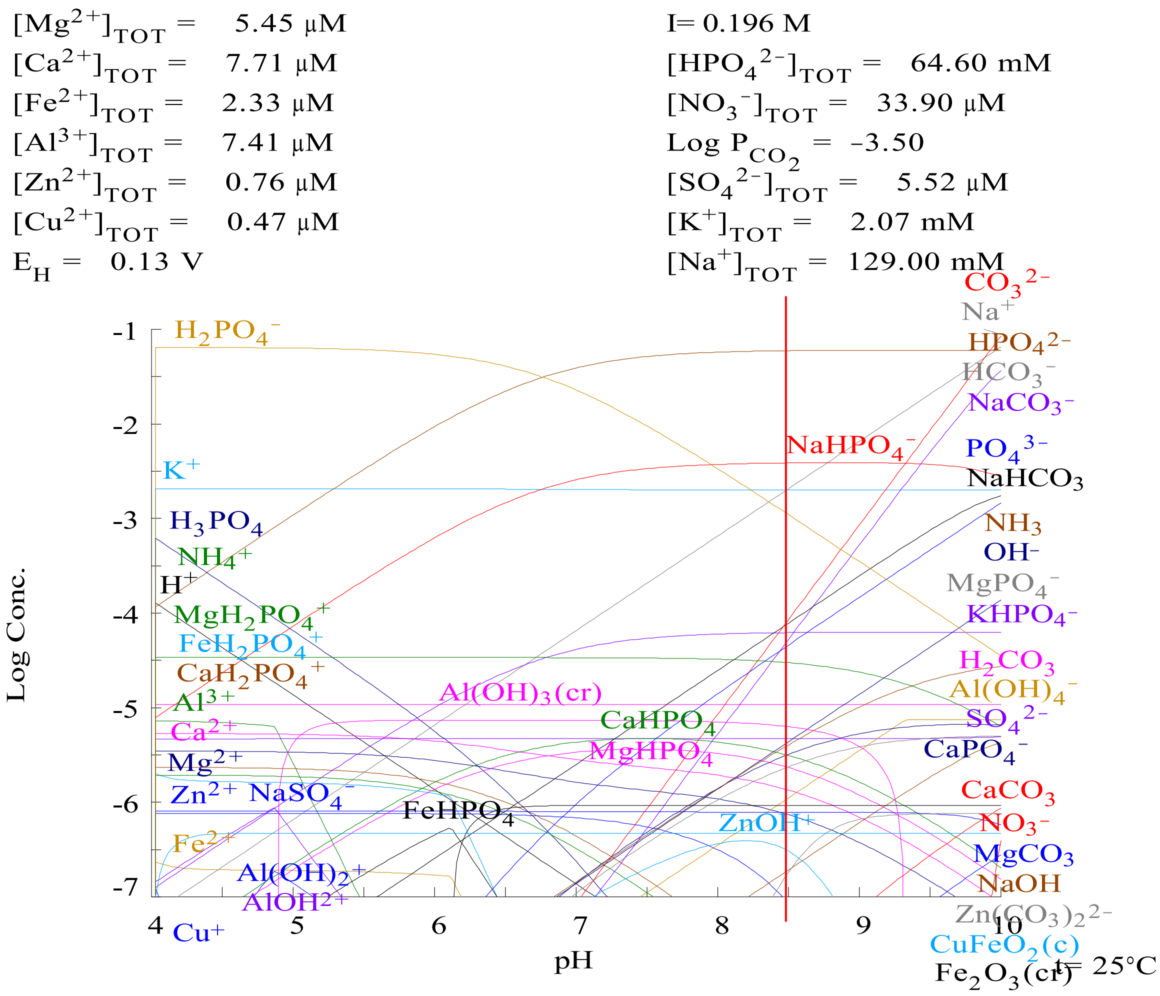


Figure C.85. Phase diagram for HDPE pipe section immersed into pH 8 water after three months of exposure. Study area.

Table C.22. The predominant species of zinc. HDPE pipe section, pH 8 water, three months exposure.

Component	Log Concentration (mol/L)	Concentration (mol/L)	Zn Concentration (mg/L as Zn)	Cumulative Percentage of Zn
$ZnOH^+$	-6.50	3.20E-07	2.09E-02	41.78
$Zn(CO_3)_2^{2-}$	-6.80	1.59E-07	1.04E-02	62.52
$ZnCO_3$	-7.00	9.93E-08	6.49E-03	75.50
Zn^{2+}	-7.03	9.30E-08	6.08E-03	87.66
$Zn(OH)_2$	-7.05	8.83E-08	5.77E-03	99.20
$ZnHCO_3^+$	-8.22	6.09E-09	3.98E-04	99.99

Table C.23. The predominant species of copper. HDPE pipe section, pH 8 water, three months exposure.

Component	Log Concentration (mol/L)	Concentration (mol/L)	Cu Concentration (mg/L as Cu)	Cumulative Percentage of Cu
$CuFeO_2(c)$	-6.33	4.72E-07	0.03	99.99999848
$CuH_2(PO_4)_2^{2-}$	-14.16	6.94E-15	4.41E-10	99.99999995

Footnote: Cu^+ was calculated to be 1.50E-13 mg/L; Cu^{2+} was calculated to be 2.18E-13 mg/L

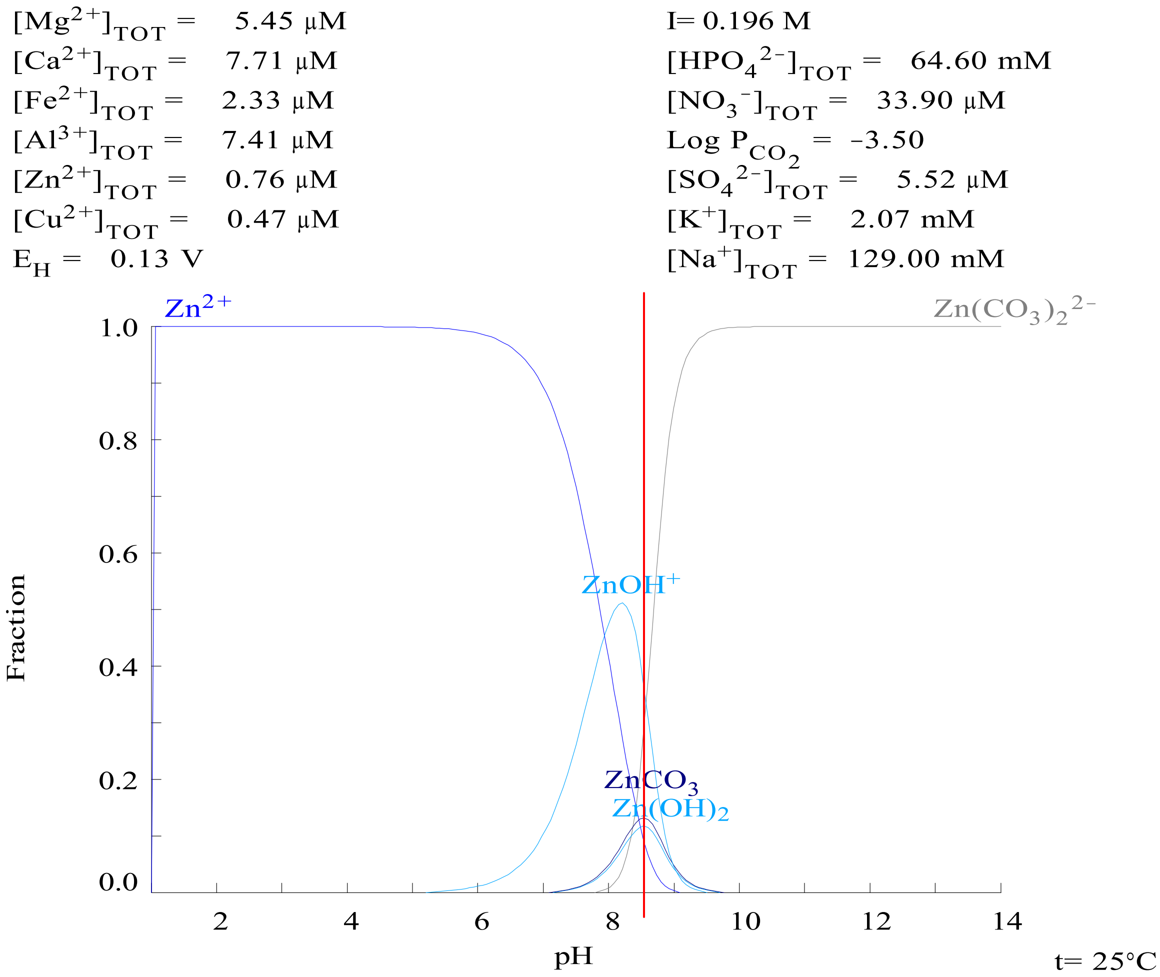


Figure C.86. Fraction diagram of zinc for HDPE pipe section immersed into pH 8 water after three months of exposure.

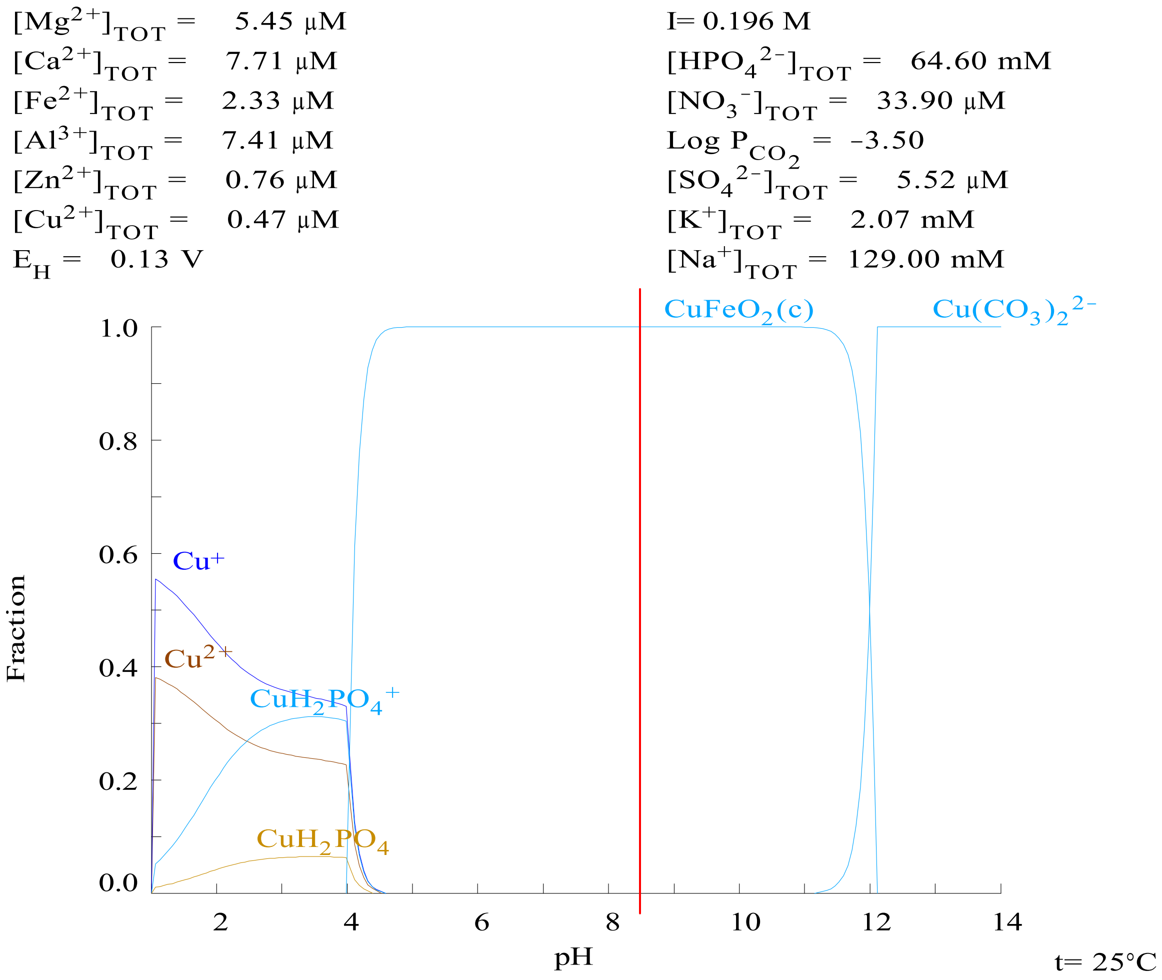


Figure C.87. Fraction diagram of copper for HDPE pipe section immersed into pH 8 water after three months of exposure.

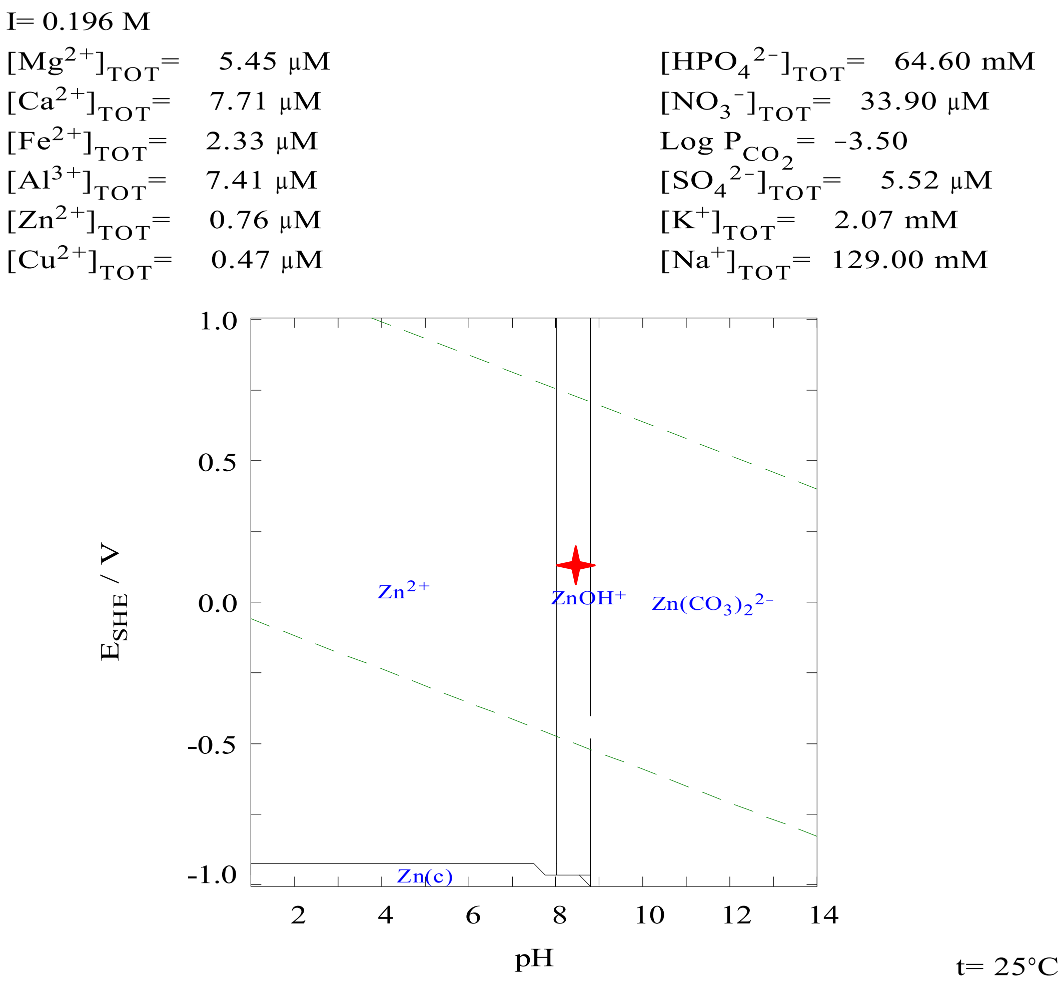


Figure C.88. Pourbaix diagram of zinc for HDPE pipe section immersed into pH 8 water after three months of exposure.

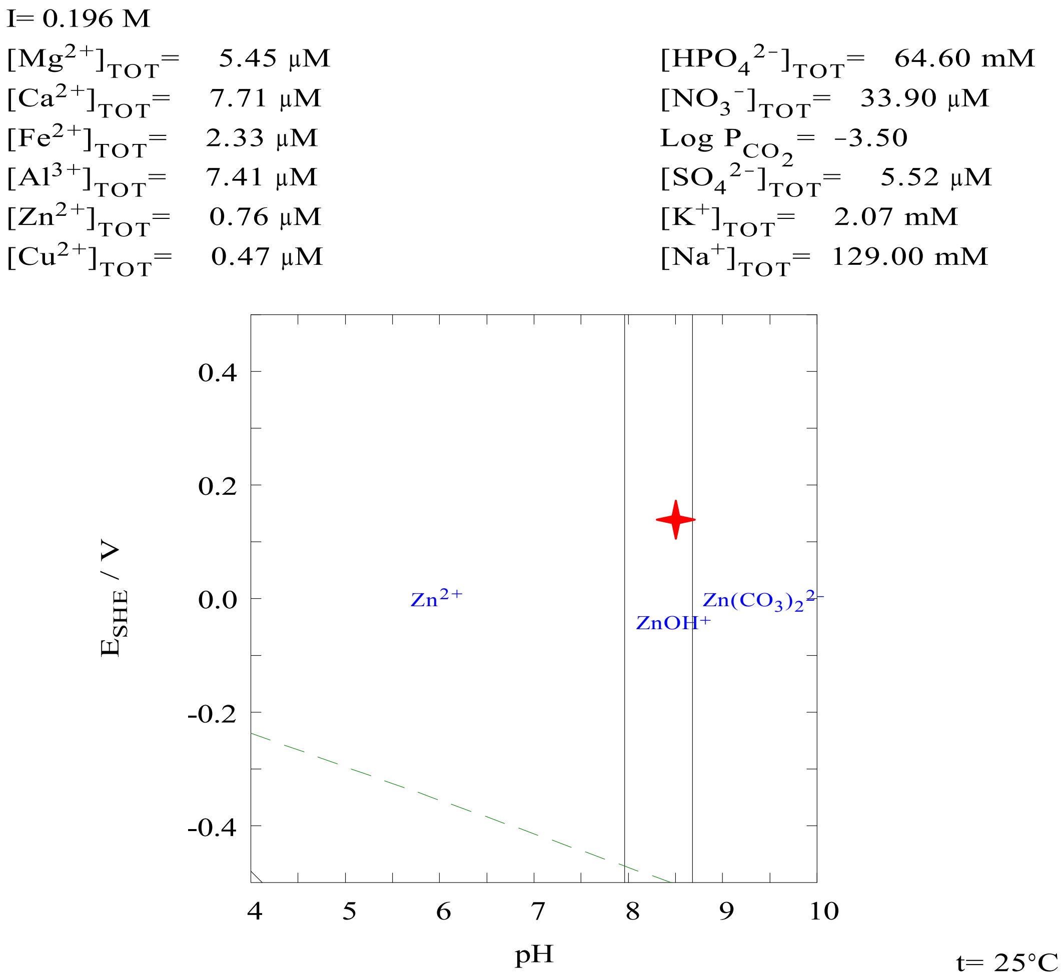


Figure C.89. Pourbaix diagram of zinc for HDPE pipe section immersed into pH 8 water after three months of exposure. Study area.

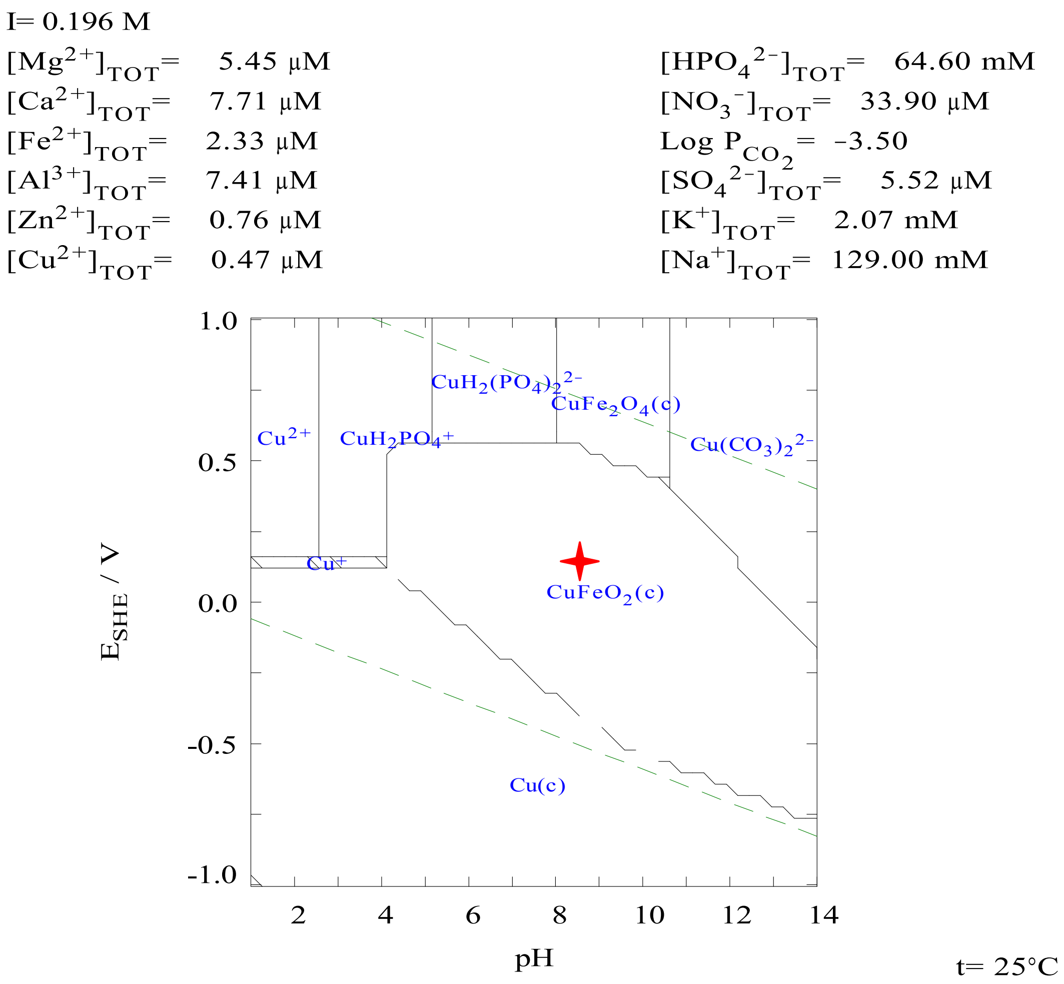


Figure C.90. Pourbaix diagram of copper for HDPE pipe section immersed into pH 8 water after three months of exposure.

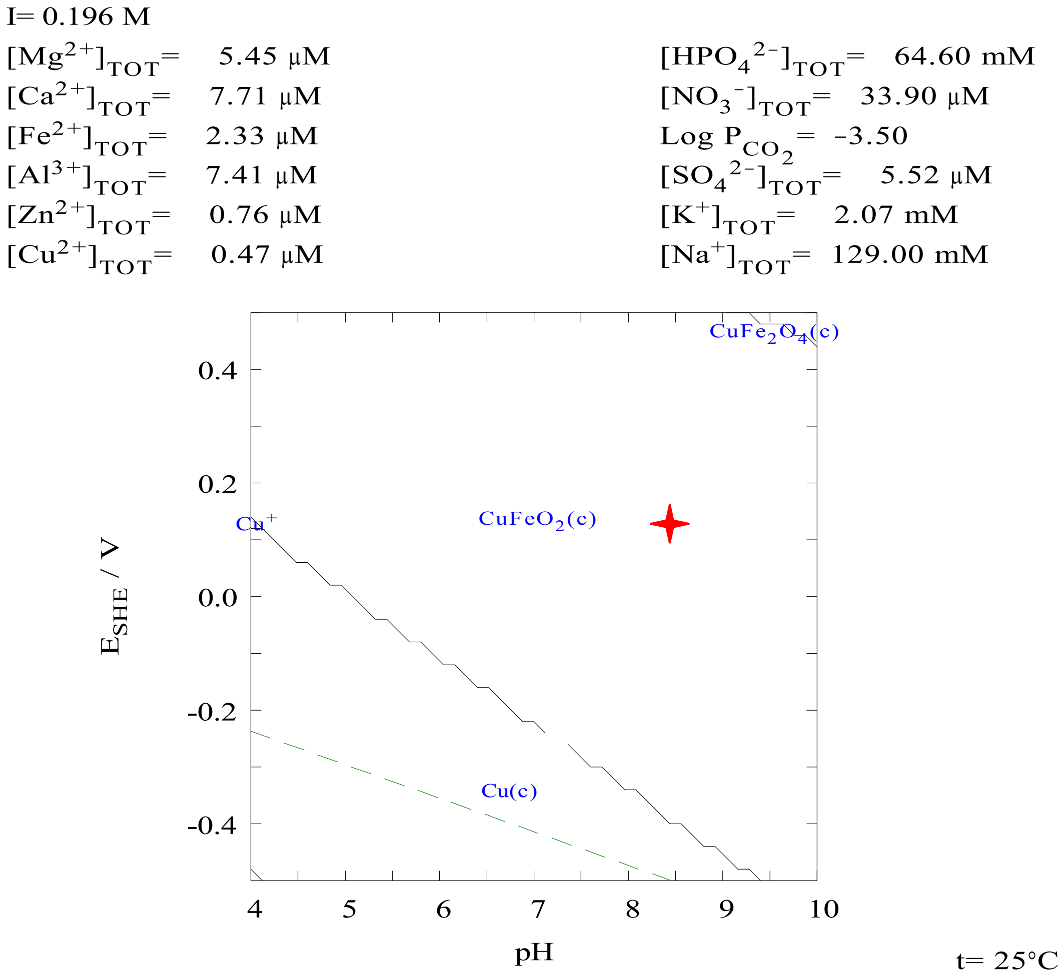


Figure C.91.Pourbaix diagram of copper for HDPE pipe section immersed into pH 8 water after three months of exposure. Study area.

Vinyl Gutter, pH 5 Water, After Three Months of Exposure

$[Na^+]_{TOT}$ = 1.27 mM
$[Mg^{2+}]_{TOT}$ = 3.91 μM
$[Ca^{2+}]_{TOT}$ = 8.01 μM
$[Fe^{2+}]_{TOT}$ = 2.15 μM
$[Cu^{2+}]_{TOT}$ = 0.47 μM
E_H = 0.21 V

I= 0.068 M
$[NO_3^-]_{TOT}$ = 1.61 μM
$[H_2PO_4^-]_{TOT}$ = 66.00 mM
Log P_{CO_2} = -3.50
$[SO_4^{2-}]_{TOT}$ = 14.10 μM
$[K^+]_{TOT}$ = 66.00 mM

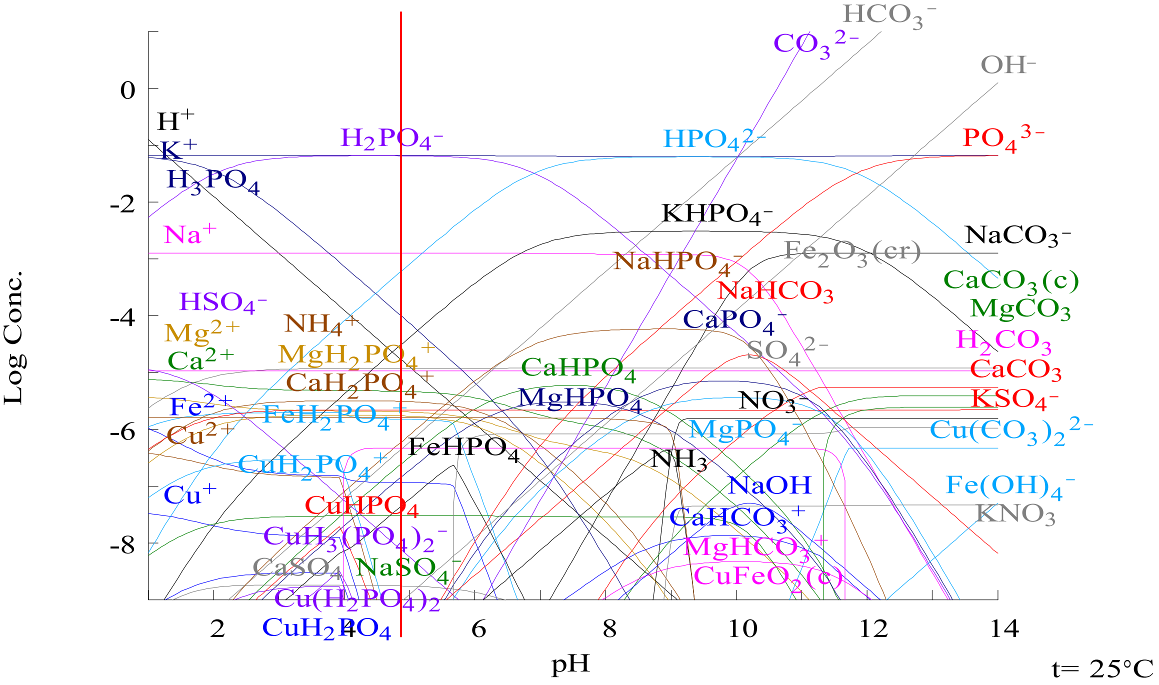


Figure C.92. Phase diagram for vinyl gutter section immersed into pH 5 water after three months of exposure.

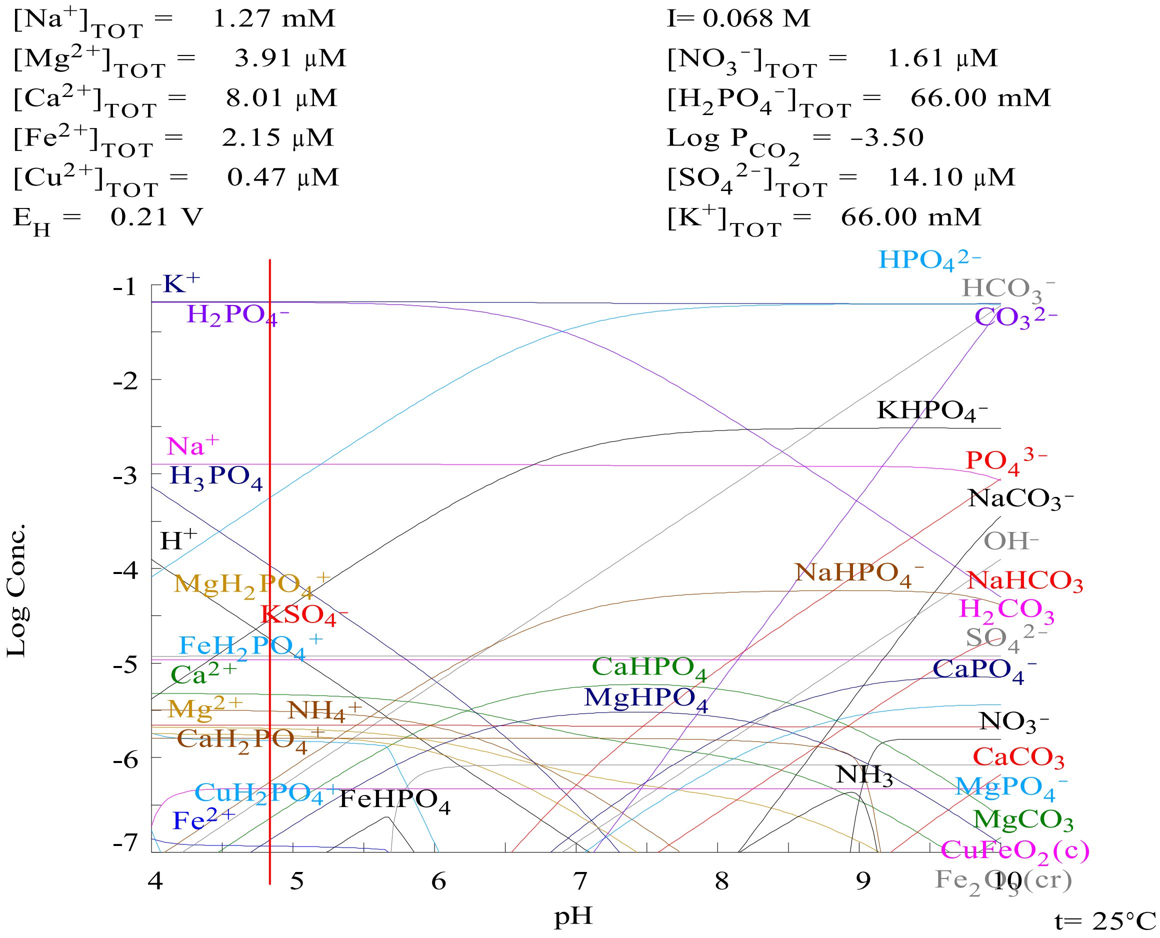


Figure C.93. Phase diagram for vinyl gutter section immersed into pH 5 water after three months of exposure. Study area.

Table C.24. The predominant species of copper. Vinyl gutter section, pH 5 water, three months exposure.

Component	Log Concentration (mol/L)	Concentration (mol/L)	Cu Concentration (mg/L as Cu)	Cumulative Percentage of Cu
$CuFeO_2$(c)	-6.33	4.72E-07	3.00E-02	99.95
$CuH_2PO_4^+$	-10.03	9.37E-11	5.96E-06	99.97
$CuHPO_4$	-10.29	5.13E-11	3.26E-06	99.98
Cu^{2+}	-10.34	4.56E-11	2.90E-06	99.99

Footnote: Cu^+ was calculated to be 2.57E-07mg/L.

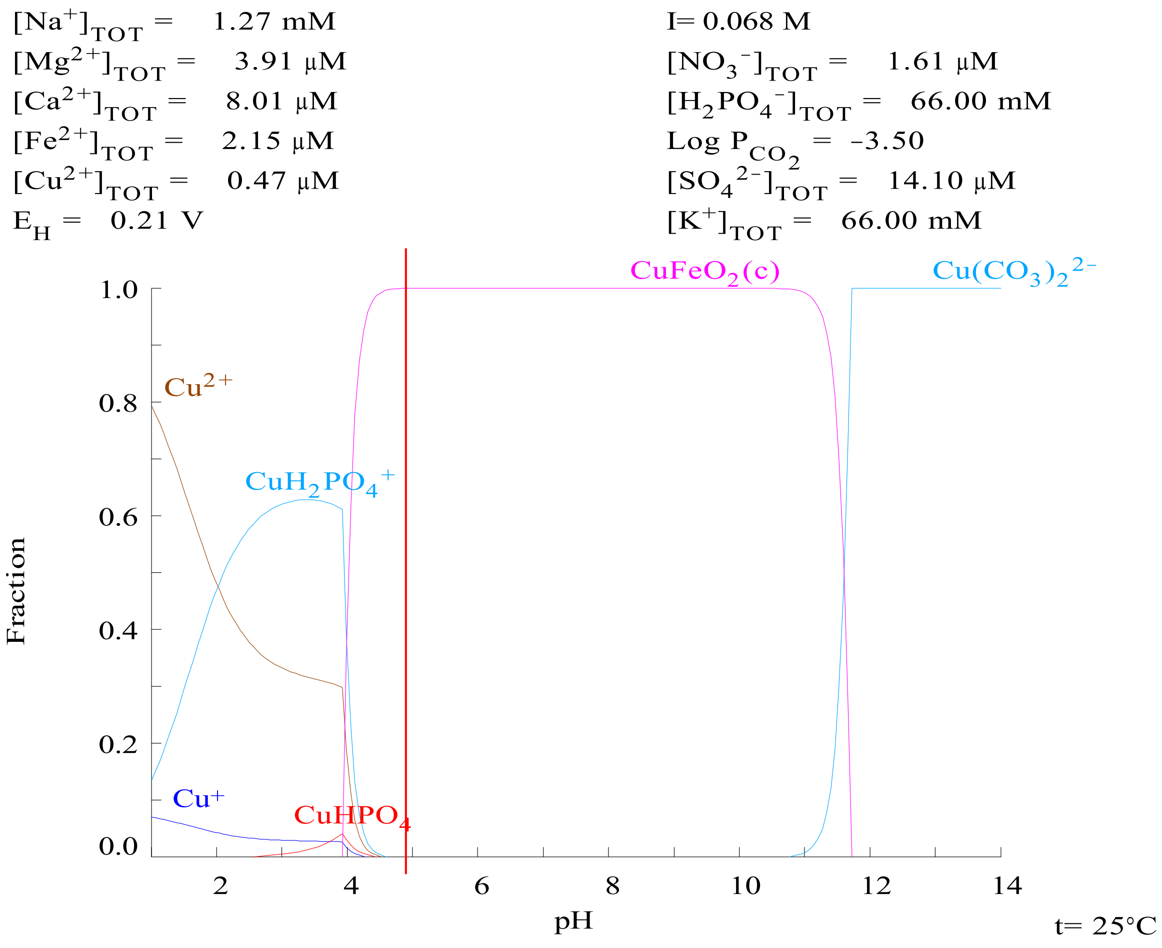


Figure C.94. Fraction diagram of copper for vinyl gutter section immersed into pH 5 water after three months of exposure.

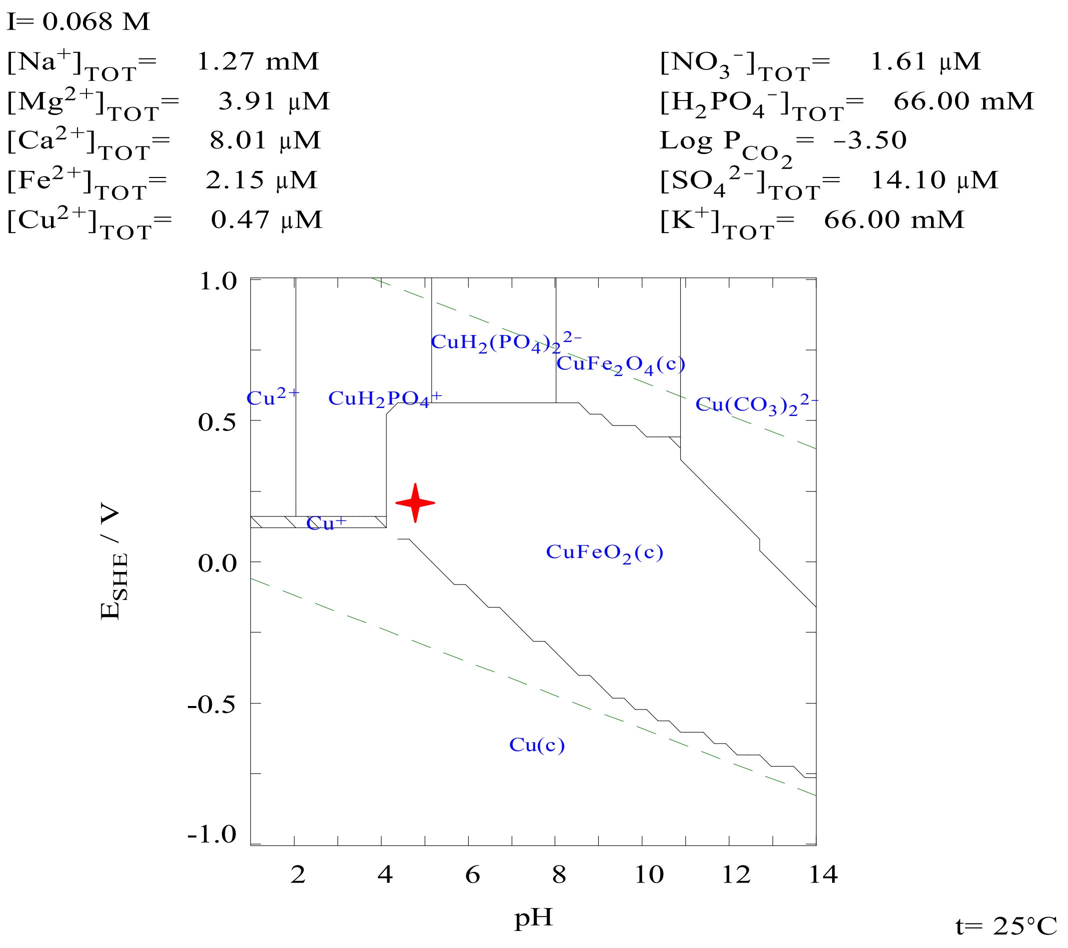


Figure C.95. Pourbaix diagram of copper for vinyl gutter section immersed into pH 5 water after three months of exposure.

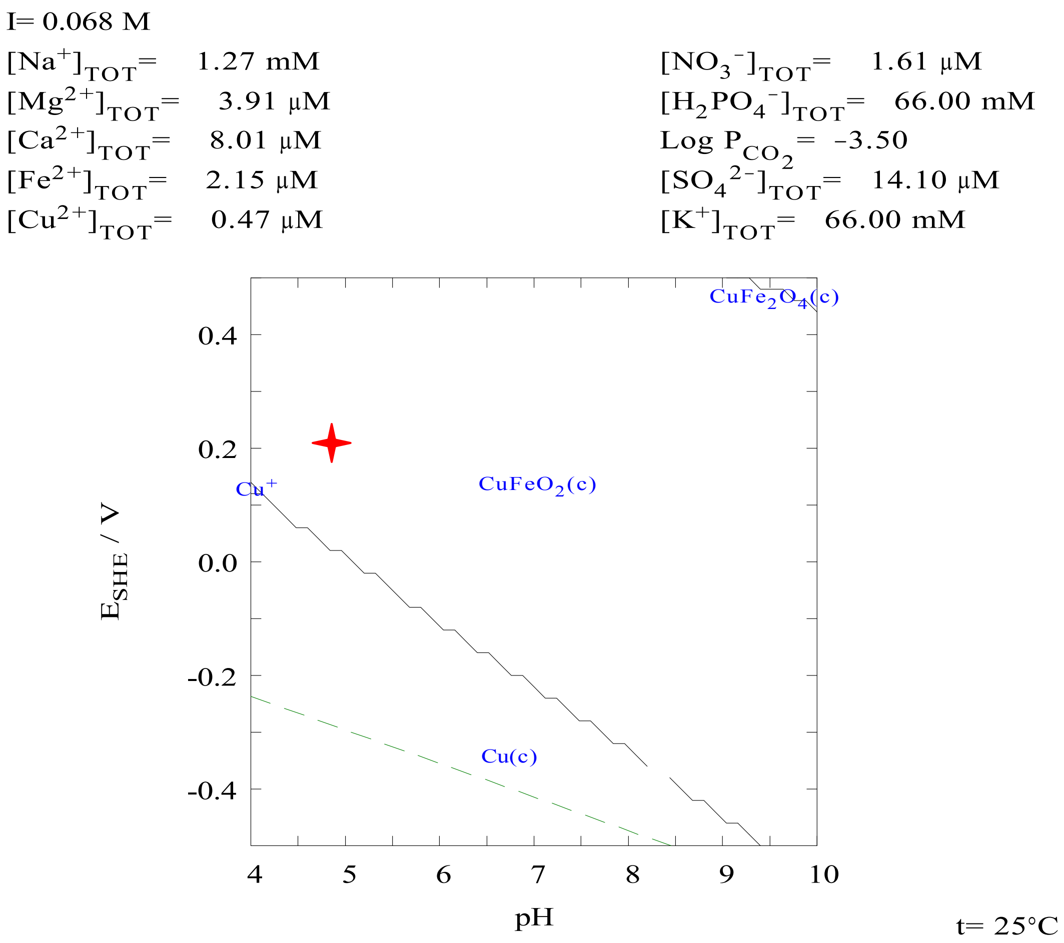


Figure C.96. Pourbaix diagram of copper for vinyl gutter section immersed into pH 5 water after three months of exposure. Study area.

Vinyl Gutter, pH 8 Water, After Three Months of Exposure

$[Mg^{2+}]_{TOT}$ = 3.91 μM
$[Ca^{2+}]_{TOT}$ = 5.01 μM
$[Fe^{2+}]_{TOT}$ = 2.69 μM
$[Al^{3+}]_{TOT}$ = 7.41 μM
$[Zn^{2+}]_{TOT}$ = 0.61 μM
$[Cu^{2+}]_{TOT}$ = 0.31 μM
E_H = 0.13 V

I= 0.196 M
$[HPO_4^{2-}]_{TOT}$ = 64.60 mM
$[NO_3^-]_{TOT}$ = 33.90 μM
Log P_{CO_2} = -3.50
$[SO_4^{2-}]_{TOT}$ = 5.21 μM
$[K^+]_{TOT}$ = 2.07 mM
$[Na^+]_{TOT}$ = 129.00 mM

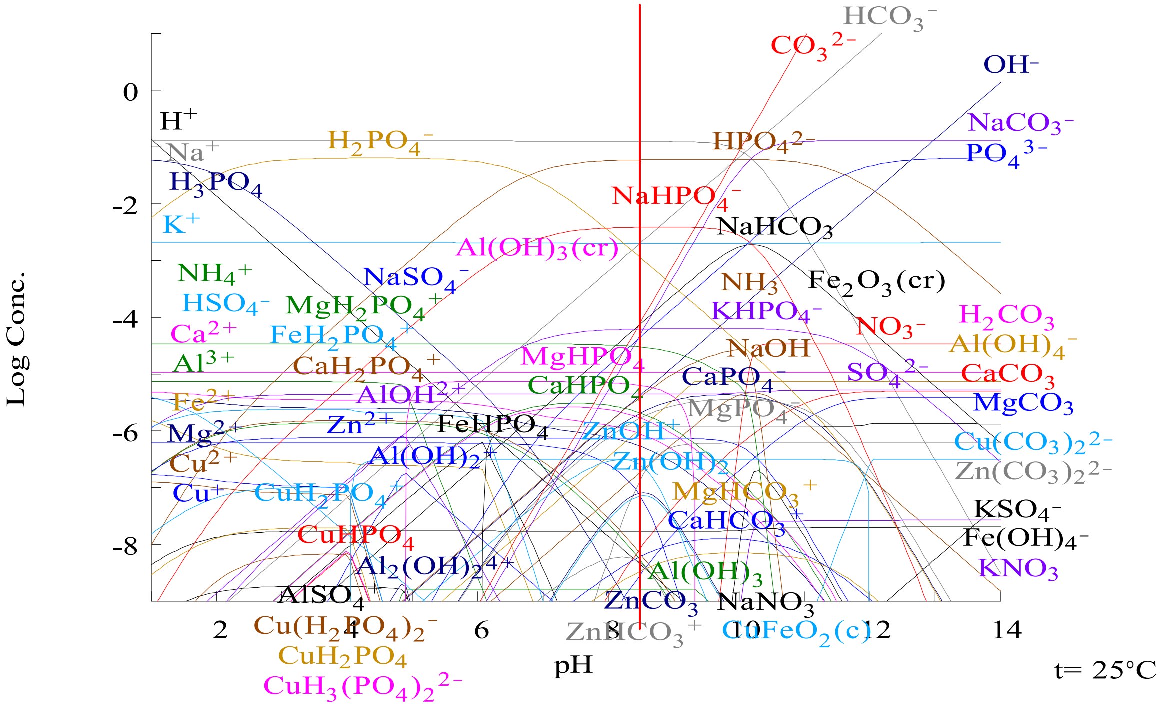


Figure C.97. Phase diagram for vinyl gutter section immersed into pH 8 water after three months of exposure.

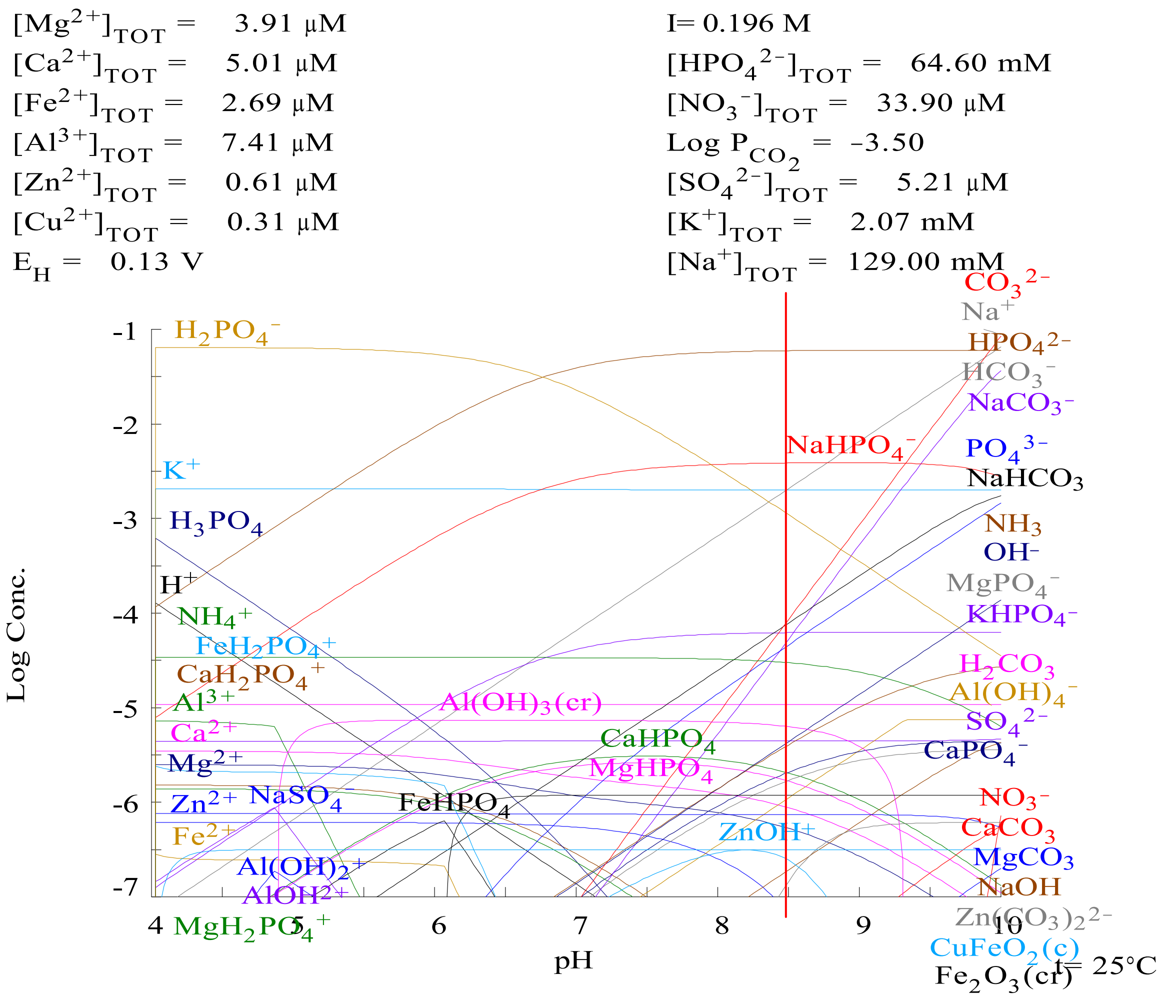


Figure C.98. Phase diagram for vinyl gutter section immersed into pH 8 water after three months of exposure. Study area.

Table C.25. The predominant species of zinc. Vinyl gutter section, pH 8 water, three months exposure.

Component	Log Concentration (mol/L)	Concentration (mol/L)	Zn Concentration (mg/L as Zn)	Cumulative Percentage of Zn
$ZnOH^+$	-6.59	2.56E-07	1.67E-02	41.78
$Zn(CO_3)_2^{2-}$	-6.90	1.27E-07	8.30E-03	62.52
$ZnCO_3$	-7.10	7.94E-08	5.20E-03	75.50
Zn^{2+}	-7.13	7.44E-08	4.87E-03	87.66
$Zn(OH)_2$	-7.15	7.06E-08	4.62E-03	99.20
$ZnHCO_3^+$	-8.31	4.87E-09	3.19E-04	99.99

Table C.26. The predominant species of copper. Vinyl gutter section, pH 8 water, three months exposure.

Component	Log Concentration (mol/L)	Concentration (mol/L)	Cu Concentration (mg/L as Cu)	Cumulative Percentage of Cu
$CuFeO_2$(c)	-6.50	3.15E-07	0.02	99.9999975
$CuH_2(PO_4)_2^{2-}$	-14.12	7.50E-15	4.77E-10	99.9999999

Footnote: Cu^+ was calculated to be 2.18E-13 mg/L; Cu^{2+} was calculated to be 1.62E-13 mg/L

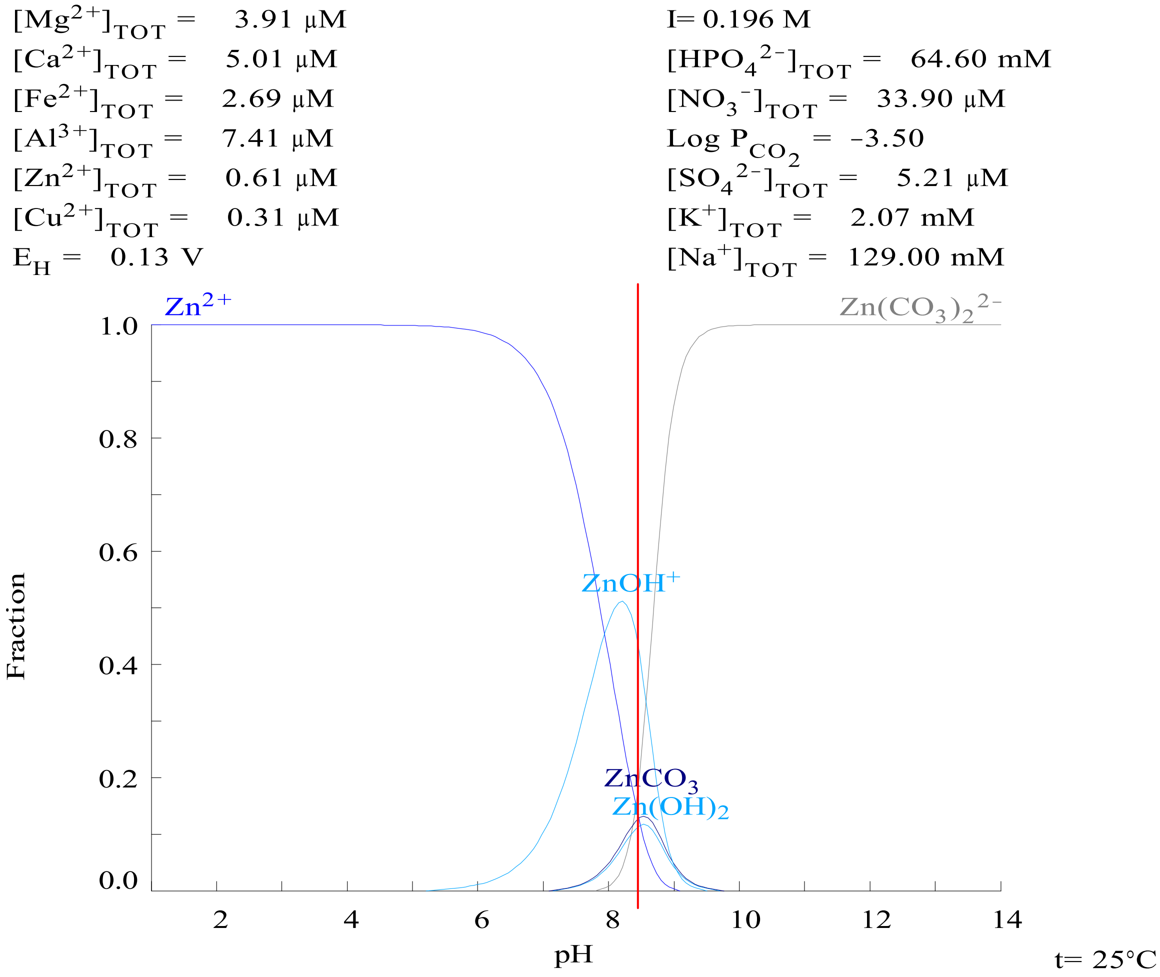


Figure C.99. Fraction diagram of zinc for vinyl gutter section immersed into pH 8 water after three months of exposure.

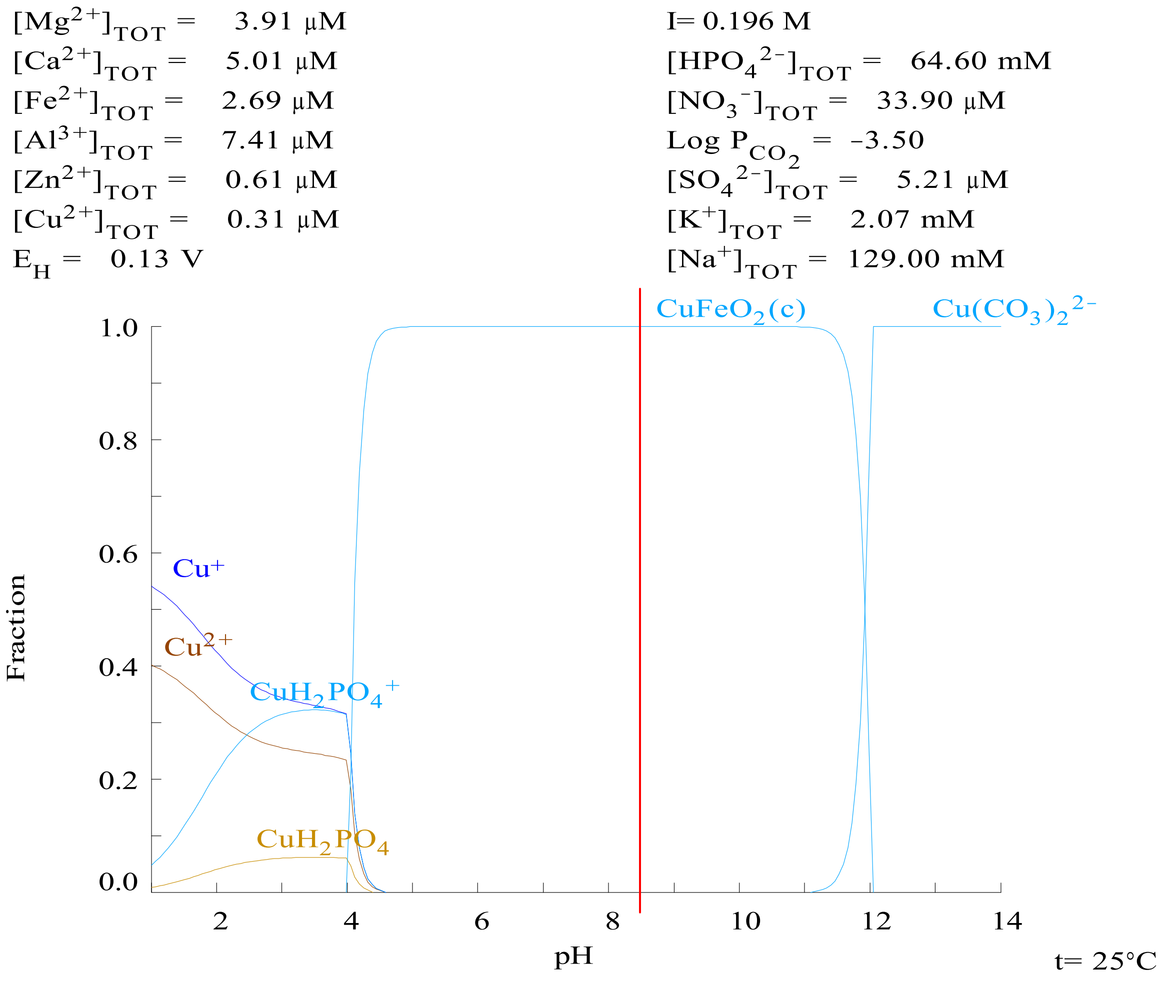


Figure C.100. Fraction diagram of copper for vinyl gutter section immersed into pH 8 water after three months of exposure.

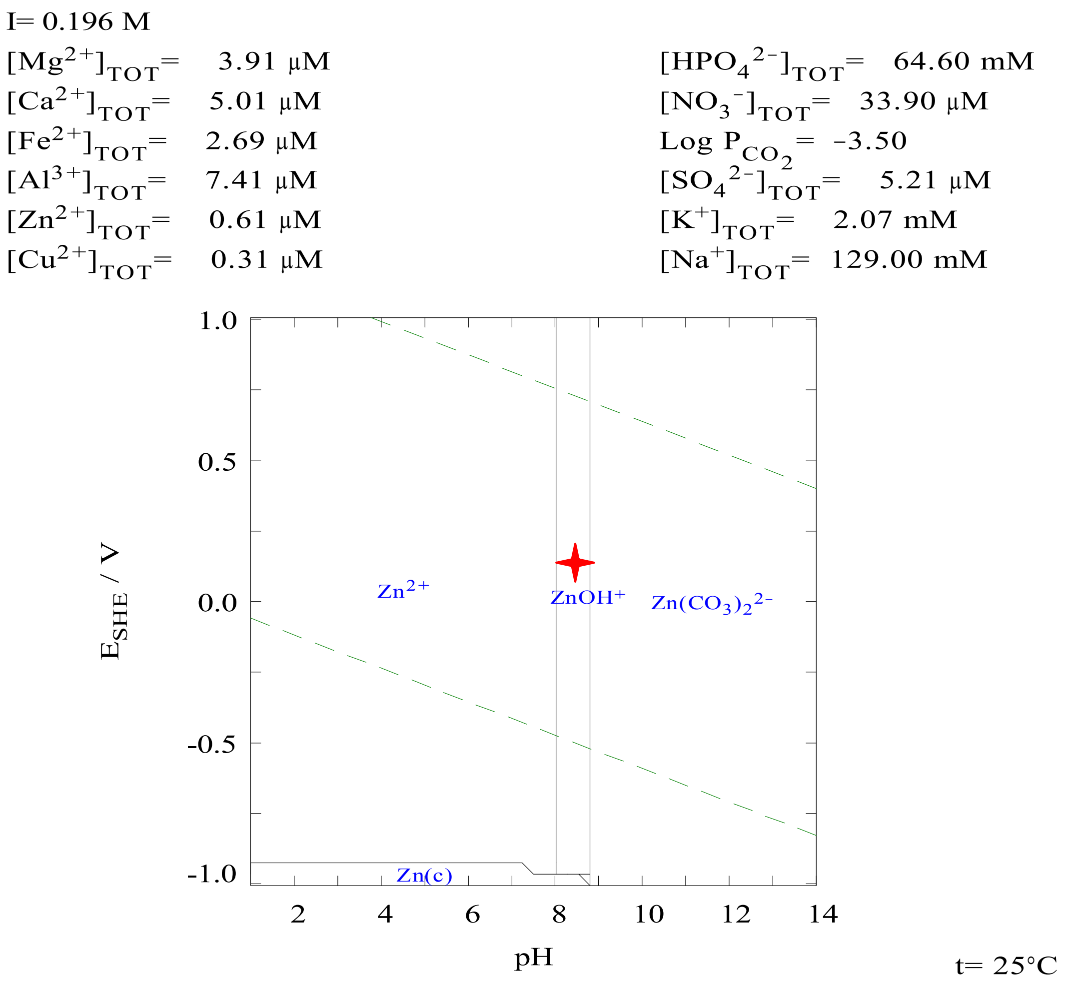


Figure C.101. Pourbaix diagram of zinc for vinyl gutter section immersed into pH 8 water after three months of exposure.

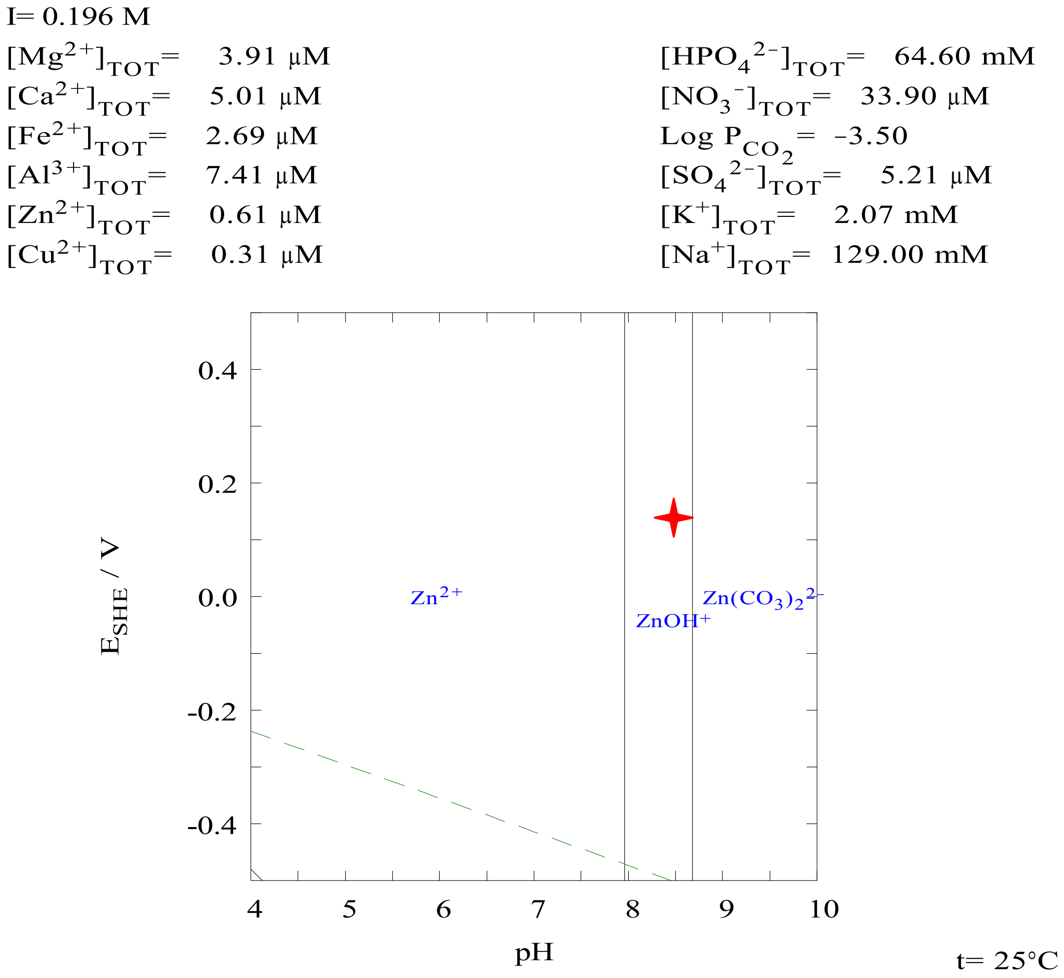


Figure C.102. Pourbaix diagram of zinc for vinyl gutter section immersed into pH 8 water after three months of exposure. Study area.

I= 0.196 M

$[Mg^{2+}]_{TOT}$= 3.91 μM
$[Ca^{2+}]_{TOT}$= 5.01 μM
$[Fe^{2+}]_{TOT}$= 2.69 μM
$[Al^{3+}]_{TOT}$= 7.41 μM
$[Zn^{2+}]_{TOT}$= 0.61 μM
$[Cu^{2+}]_{TOT}$= 0.31 μM

$[HPO_4^{2-}]_{TOT}$= 64.60 mM
$[NO_3^{-}]_{TOT}$= 33.90 μM
Log P_{CO_2}= -3.50
$[SO_4^{2-}]_{TOT}$= 5.21 μM
$[K^{+}]_{TOT}$= 2.07 mM
$[Na^{+}]_{TOT}$= 129.00 mM

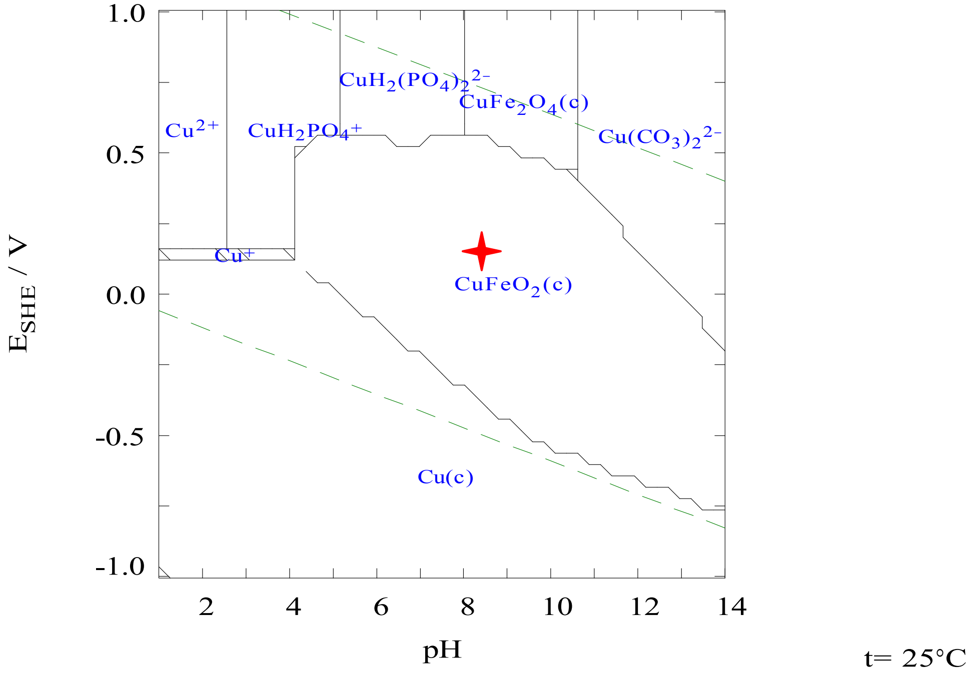


Figure C.103. Pourbaix diagram of copper for vinyl gutter section immersed into pH 8 water after three months of exposure.

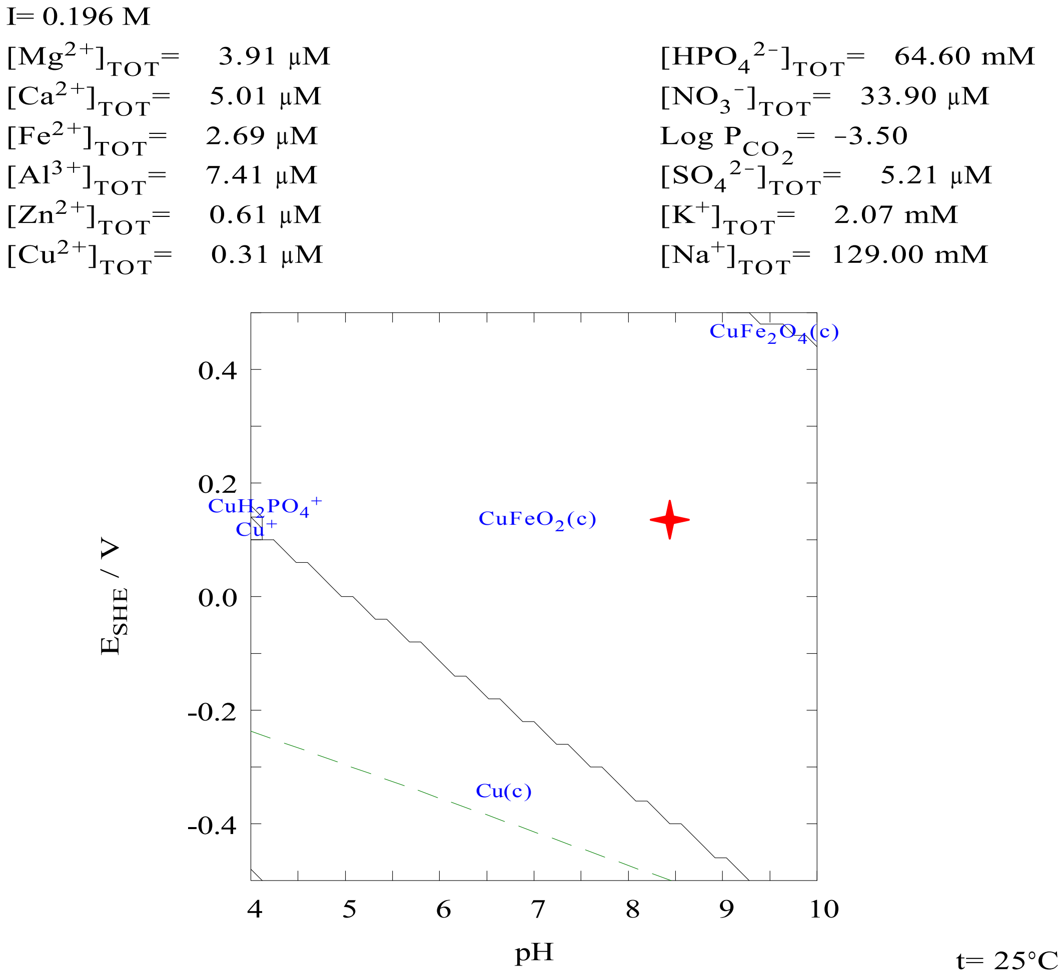


Figure C.104. Pourbaix diagram of copper for vinyl gutter section immersed into pH 8 water after three months of exposure. Study area.

Aluminum Gutter, pH 5 Water, After Three Months of Exposure

$[Mg^{2+}]_{TOT}$ = 5.81 μM
$[Ca^{2+}]_{TOT}$ = 5.01 μM
$[Fe^{2+}]_{TOT}$ = 2.15 μM
$[Al^{3+}]_{TOT}$ = 11.10 μM
$[Zn^{2+}]_{TOT}$ = 0.31 μM
$[Cu^{2+}]_{TOT}$ = 0.47 μM
E_H = 0.20 V

I= 0.068 M
$[H_2PO_4^-]_{TOT}$ = 66.00 mM
$[NO_3^-]_{TOT}$ = 1.61 μM
Log P_{CO_2} = -3.50
$[SO_4^{2-}]_{TOT}$ = 19.80 μM
$[K^+]_{TOT}$ = 66.00 mM
$[Na^+]_{TOT}$ = 1.27 mM

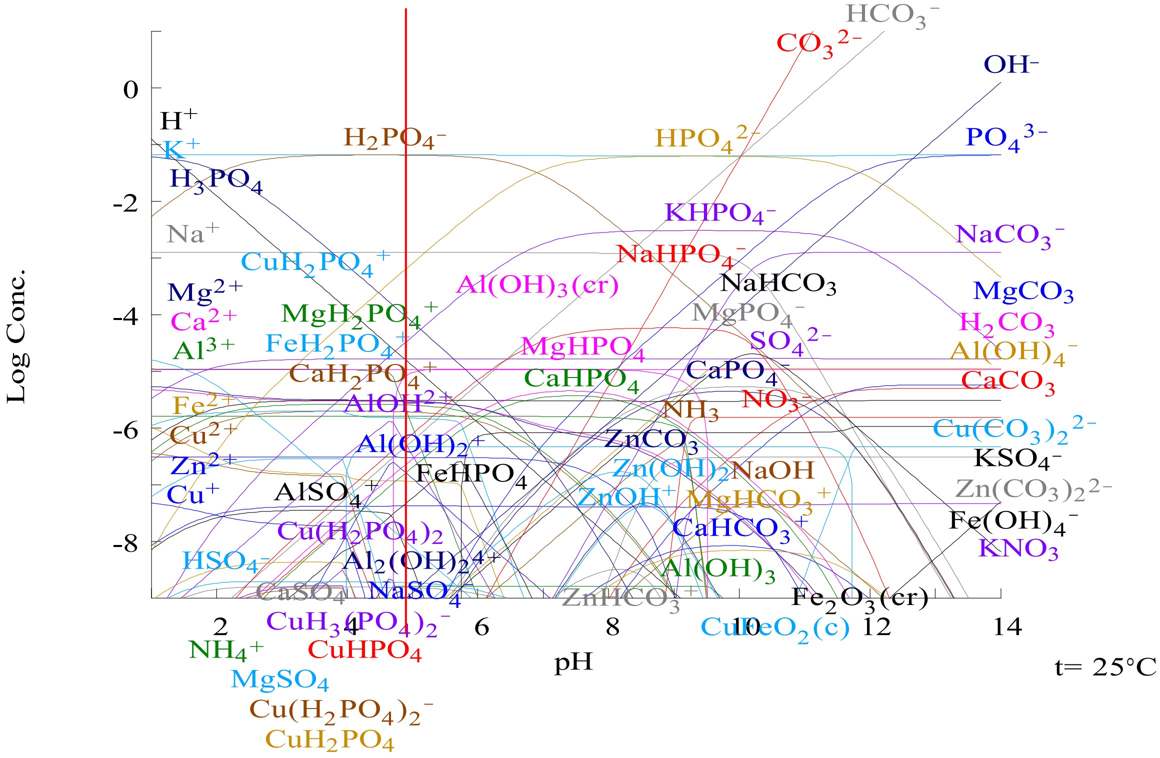


Figure C.105. Phase diagram for Aluminum gutter section immersed into pH 5 water after three months of exposure.

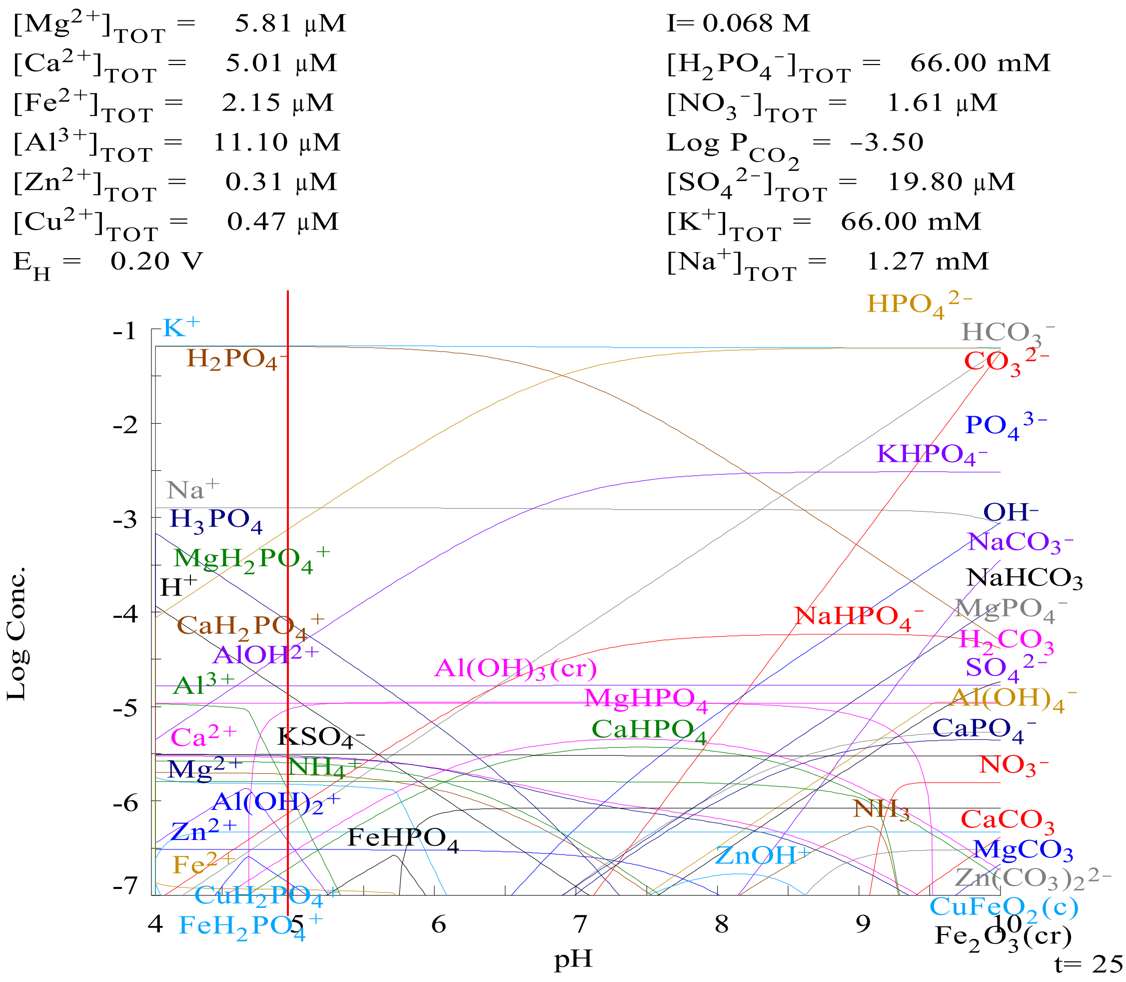


Figure C.106. Phase diagram for Aluminum gutter section immersed into pH 5 water after three months of exposure. Study area.

Table C.27. The predominant species of zinc. Aluminum gutter section, pH 5 water, three months exposure.

Component	Log Concentration (mol/L)	Concentration (mol/L)	Zn Concentration (mg/L as Zn)	Cumulative Percentage of Zn
Zn^{2+}	-6.52	3.05E-07	1.998E-02	99.83
$ZnOH^+$	-9.48	3.29E-10	2.16E-05	99.94

Table C.28. The predominant species of copper. Aluminum gutter section, pH 5 water, three months exposure.

Component	Log Concentration (mol/L)	Concentration (mol/L)	Cu Concentration (mg/L as Cu)	Cumulative Percentage of Cu
$CuFeO_2(c)$	-6.33	4.72E-07	2.999E-02	99.95
$CuH_2PO_4^+$	-10.03	9.37E-11	5.96E-06	99.97

Footnote: Cu^+ was calculated to be 3.79E-07 mg/L; Cu^{2+} was calculated to be 2.90E-06 mg/L

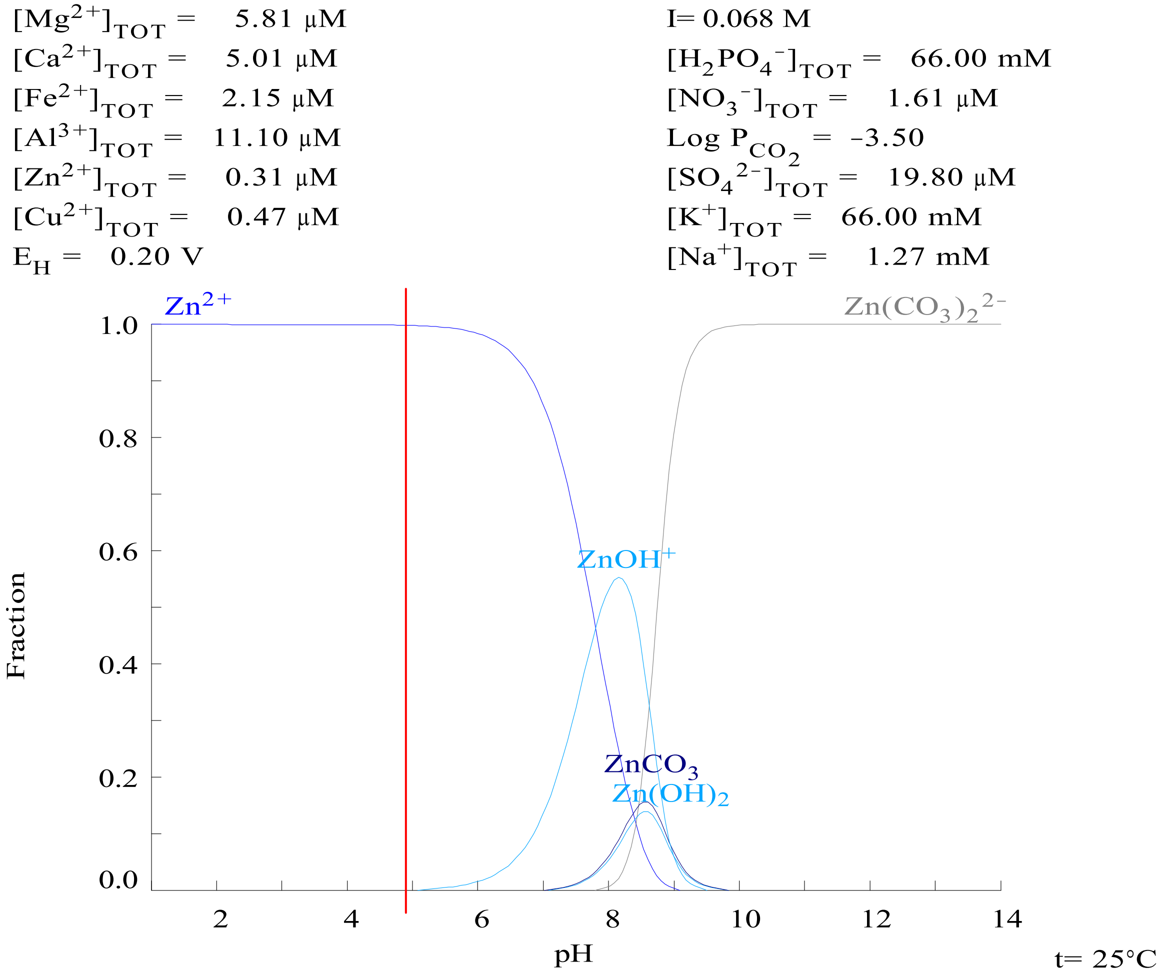


Figure C.107. Fraction diagram of zinc for Aluminum gutter section immersed into pH 5 water after three months of exposure.

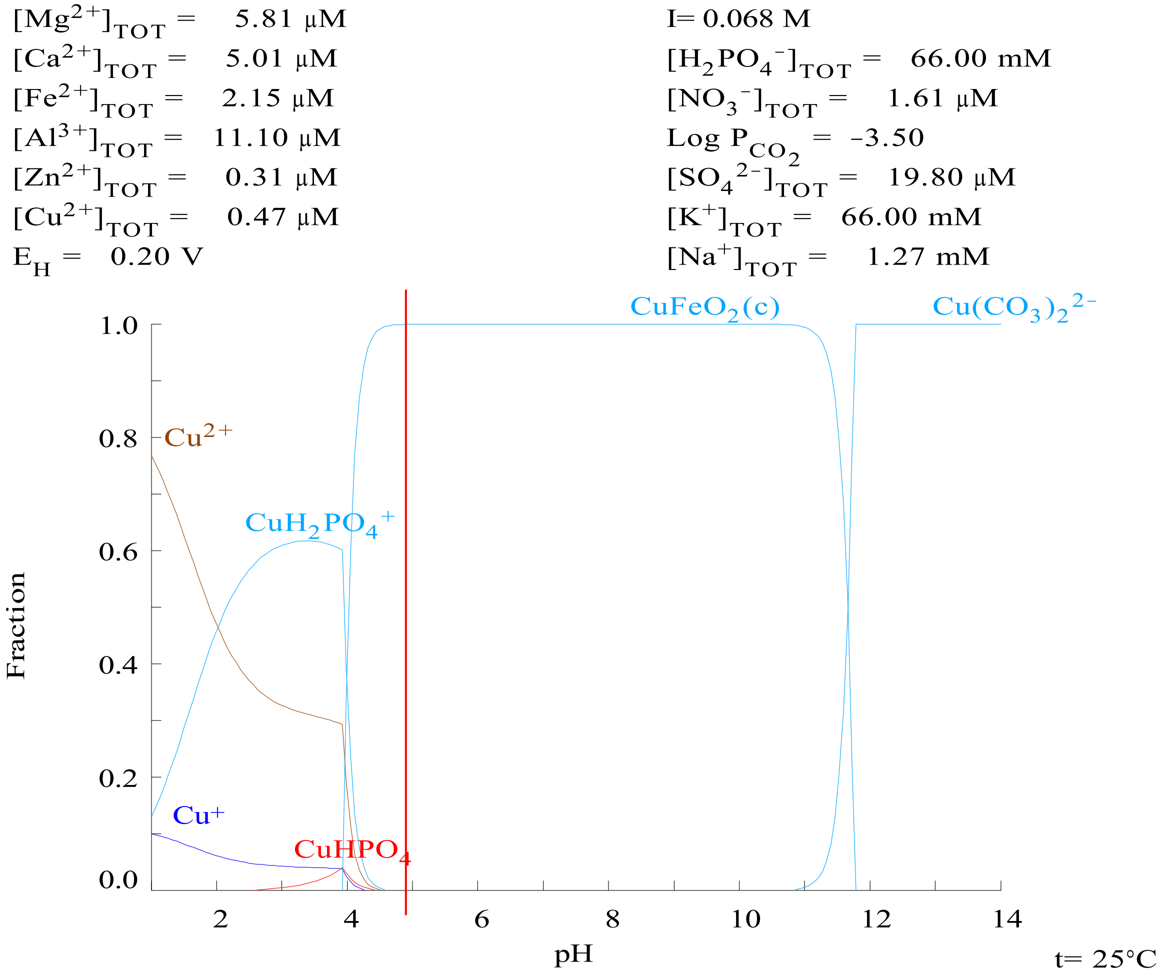


Figure C.108. Fraction diagram of copper for Aluminum gutter section immersed into pH 5 water after three months of exposure.

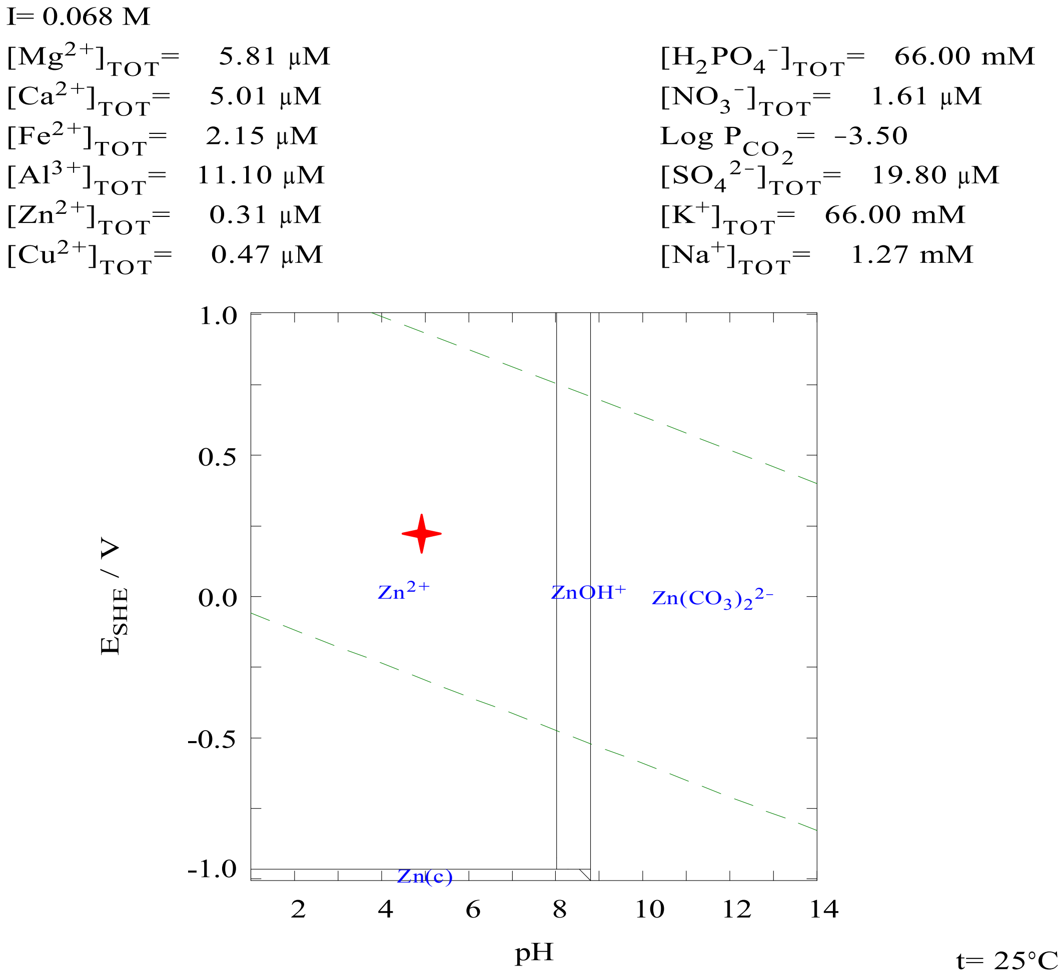


Figure C.109. Pourbaix diagram of zinc for Aluminum gutter section immersed into pH 5 water after three months of exposure.

I= 0.068 M

$[Mg^{2+}]_{TOT}$= 5.81 μM
$[Ca^{2+}]_{TOT}$= 5.01 μM
$[Fe^{2+}]_{TOT}$= 2.15 μM
$[Al^{3+}]_{TOT}$= 11.10 μM
$[Zn^{2+}]_{TOT}$= 0.31 μM
$[Cu^{2+}]_{TOT}$= 0.47 μM

$[H_2PO_4^{-}]_{TOT}$= 66.00 mM
$[NO_3^{-}]_{TOT}$= 1.61 μM
Log P_{CO_2}= -3.50
$[SO_4^{2-}]_{TOT}$= 19.80 μM
$[K^{+}]_{TOT}$= 66.00 mM
$[Na^{+}]_{TOT}$= 1.27 mM

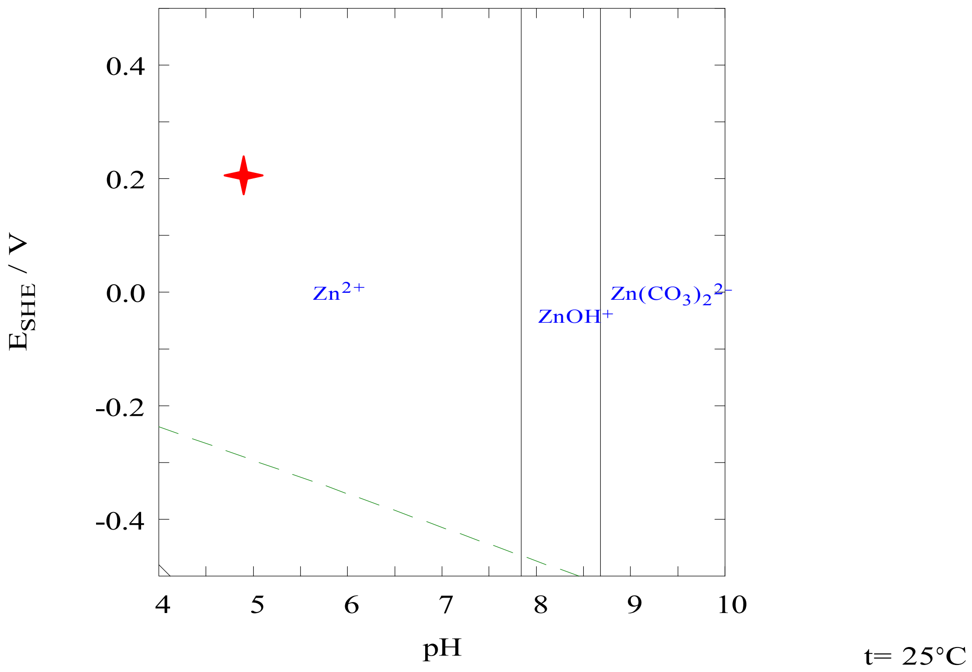


Figure C.110. Pourbaix diagram of zinc for Aluminum gutter section immersed into pH 5 water after three months of exposure. Study area.

I= 0.068 M
$[Mg^{2+}]_{TOT}$= 5.81 μM
$[Ca^{2+}]_{TOT}$= 5.01 μM
$[Fe^{2+}]_{TOT}$= 2.15 μM
$[Al^{3+}]_{TOT}$= 11.10 μM
$[Zn^{2+}]_{TOT}$= 0.31 μM
$[Cu^{2+}]_{TOT}$= 0.47 μM

$[H_2PO_4^{-}]_{TOT}$= 66.00 mM
$[NO_3^{-}]_{TOT}$= 1.61 μM
Log P_{CO_2}= -3.50
$[SO_4^{2-}]_{TOT}$= 19.80 μM
$[K^{+}]_{TOT}$= 66.00 mM
$[Na^{+}]_{TOT}$= 1.27 mM

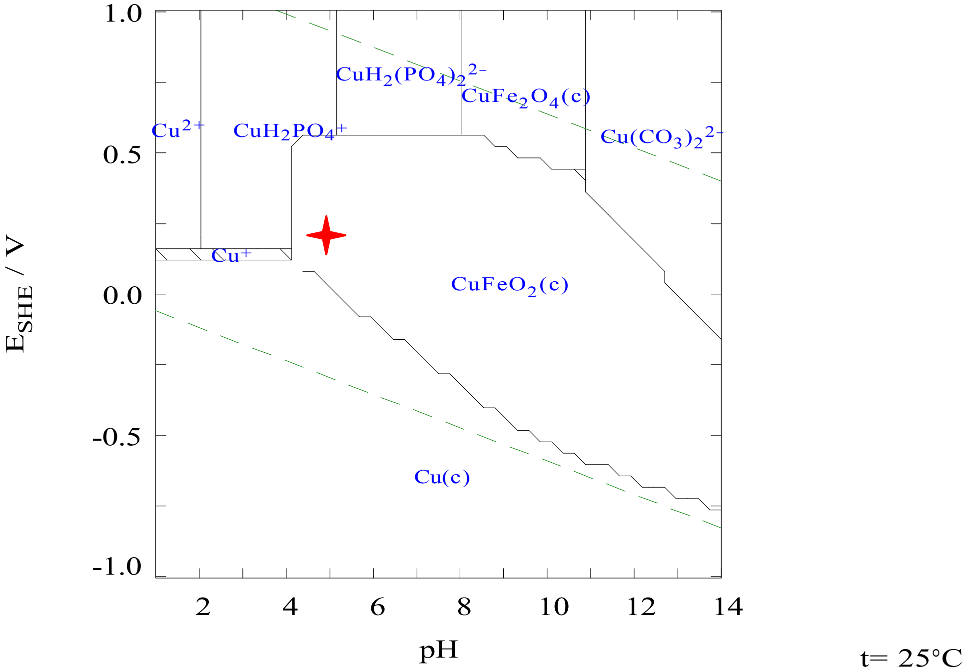


Figure C.111. Pourbaix diagram of copper for Aluminum gutter section immersed into pH 5 water after three months of exposure.

I= 0.068 M

$[Mg^{2+}]_{TOT}$= 5.81 μM
$[Ca^{2+}]_{TOT}$= 5.01 μM
$[Fe^{2+}]_{TOT}$= 2.15 μM
$[Al^{3+}]_{TOT}$= 11.10 μM
$[Zn^{2+}]_{TOT}$= 0.31 μM
$[Cu^{2+}]_{TOT}$= 0.47 μM

$[H_2PO_4^-]_{TOT}$= 66.00 mM
$[NO_3^-]_{TOT}$= 1.61 μM
Log P_{CO_2}= -3.50
$[SO_4^{2-}]_{TOT}$= 19.80 μM
$[K^+]_{TOT}$= 66.00 mM
$[Na^+]_{TOT}$= 1.27 mM

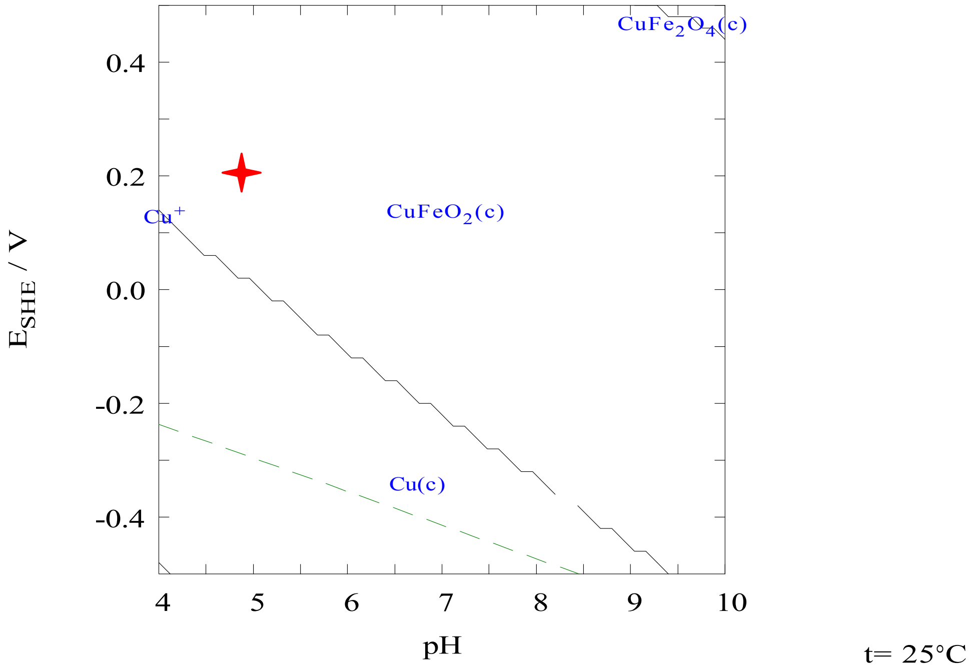


Figure C.112. Pourbaix diagram of copper for Aluminum gutter section immersed into pH 5 water after three months of exposure. Study area.

Aluminum Gutter, pH 8 Water, After Three Months of Exposure

$[Mg^{2+}]_{TOT}$ = 2.85 μM
$[Ca^{2+}]_{TOT}$ = 0.10 μM
$[Fe^{2+}]_{TOT}$ = 2.33 μM
$[Al^{3+}]_{TOT}$ = 14.80 μM
$[Zn^{2+}]_{TOT}$ = 3.21 μM
$[Cu^{2+}]_{TOT}$ = 0.47 μM
E_H = 0.14 V

I= 0.196 M
$[HPO_4^{2-}]_{TOT}$ = 64.60 mM
$[NO_3^-]_{TOT}$ = 30.60 μM
Log P_{CO_2} = -3.50
$[SO_4^{2-}]_{TOT}$ = 7.91 μM
$[K^+]_{TOT}$ = 2.07 mM
$[Na^+]_{TOT}$ = 129.00 mM

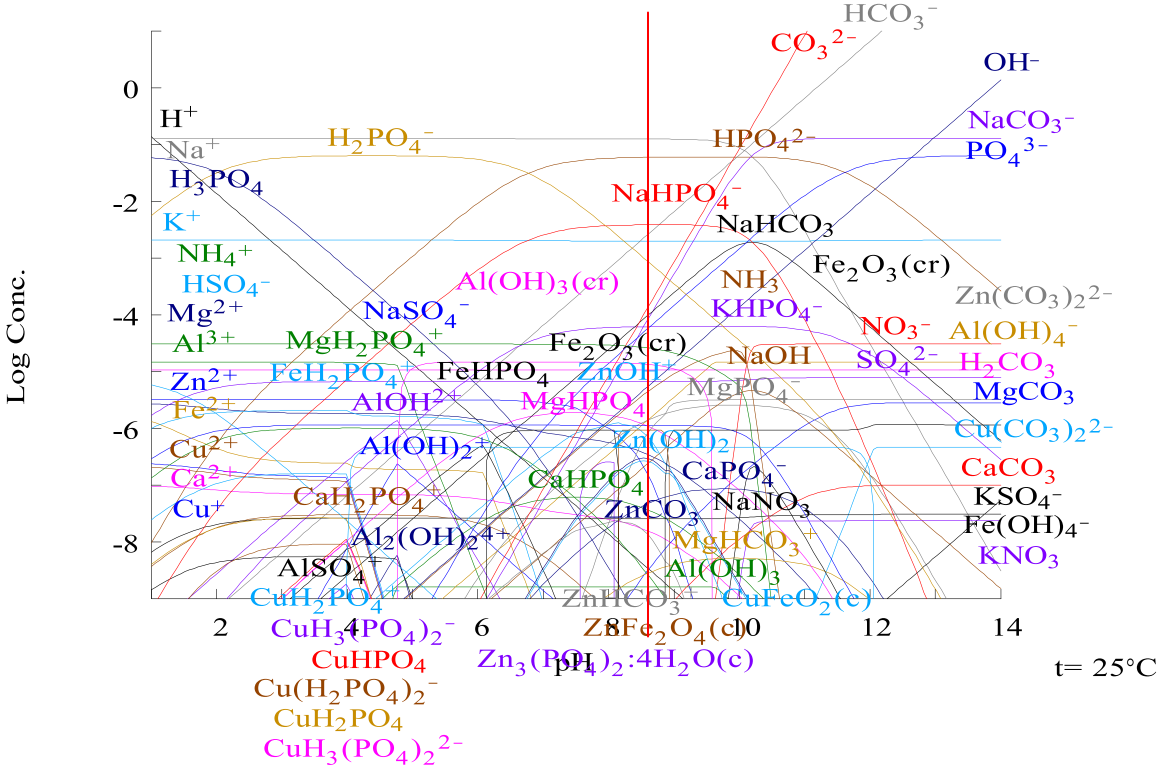


Figure C.113. Phase diagram for Aluminum gutter section immersed into pH 8 water after three months of exposure.

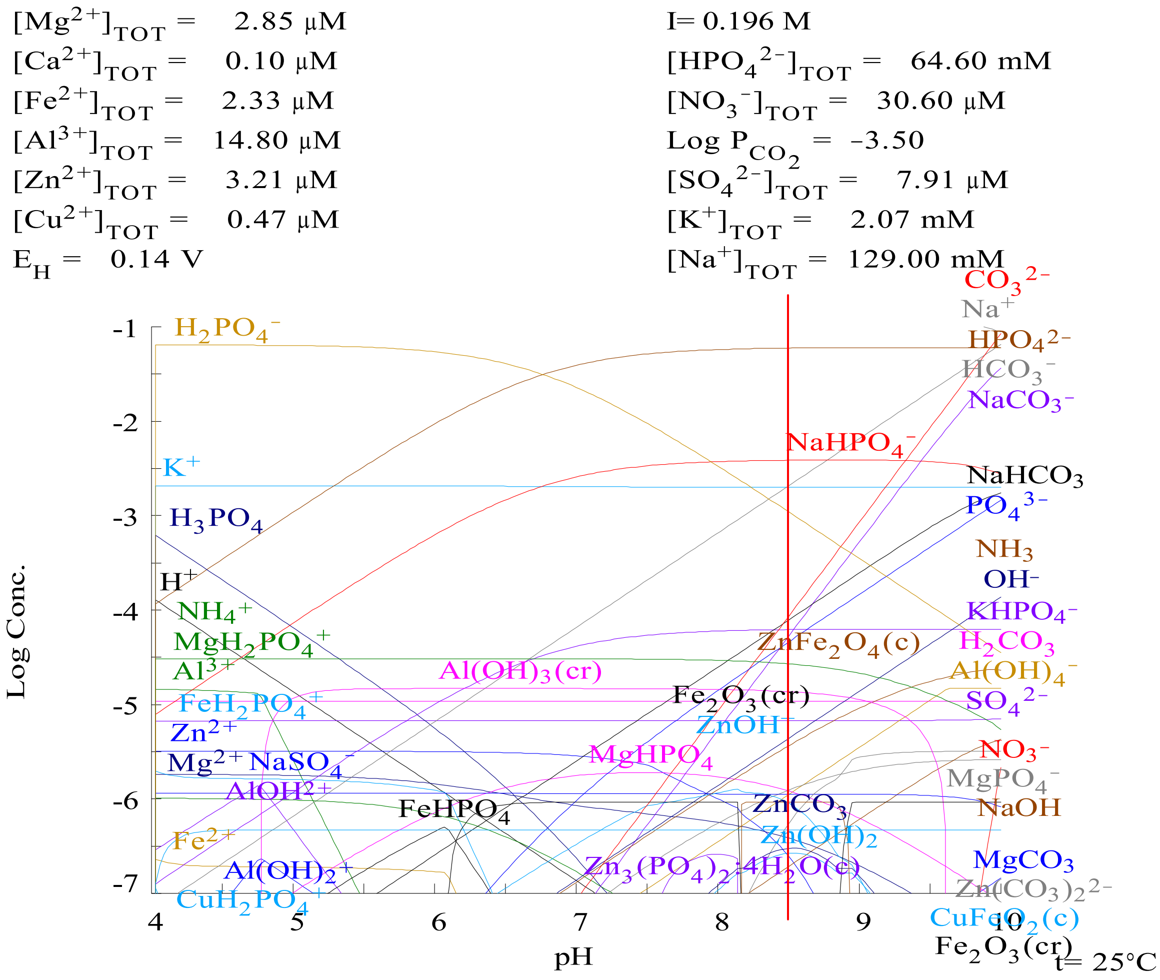


Figure C.114. Phase diagram for Aluminum gutter section immersed into pH 8 water after three months of exposure. Study area.

Table C.29. The predominant species of zinc. Aluminum gutter section, pH 8 water, three months exposure.

Component	Log Concentration (mol/L)	Concentration (mol/L)	Zn Concentration (mg/L as Zn)	Cumulative Percentage of Zn
$ZnOH^+$	-6.02	9.53E-07	6.23E-02	29.69
$ZnFe_2O_4$(c)	-6.03	9.29E-07	6.08E-02	58.63
$Zn(CO_3)_2^{2-}$	-6.32	4.73E-07	3.10E-02	73.37
$ZnCO_3$	-6.53	2.96E-07	1.94E-02	82.59
Zn^{2+}	-6.56	2.77E-07	1.81E-02	91.23
$Zn(OH)_2$	-6.58	2.63E-07	1.72E-02	99.43
$ZnHCO_3^+$	-7.74	1.82E-08	1.19E-03	99.99

Table C.30. The predominant species of copper. Aluminum gutter section, pH 8 water, three months exposure.

Component	Log Concentration (mol/L)	Concentration (mol/L)	Cu Concentration (mg/L as Cu)	Cumulative Percentage of Cu
$CuFeO_2$(c)	-6.33	4.72E-07	0.02999	99.9999976
$CuH_2(PO_4)_2^{2-}$	-6.33	1.11E-14	7.07E-10	99.9999999

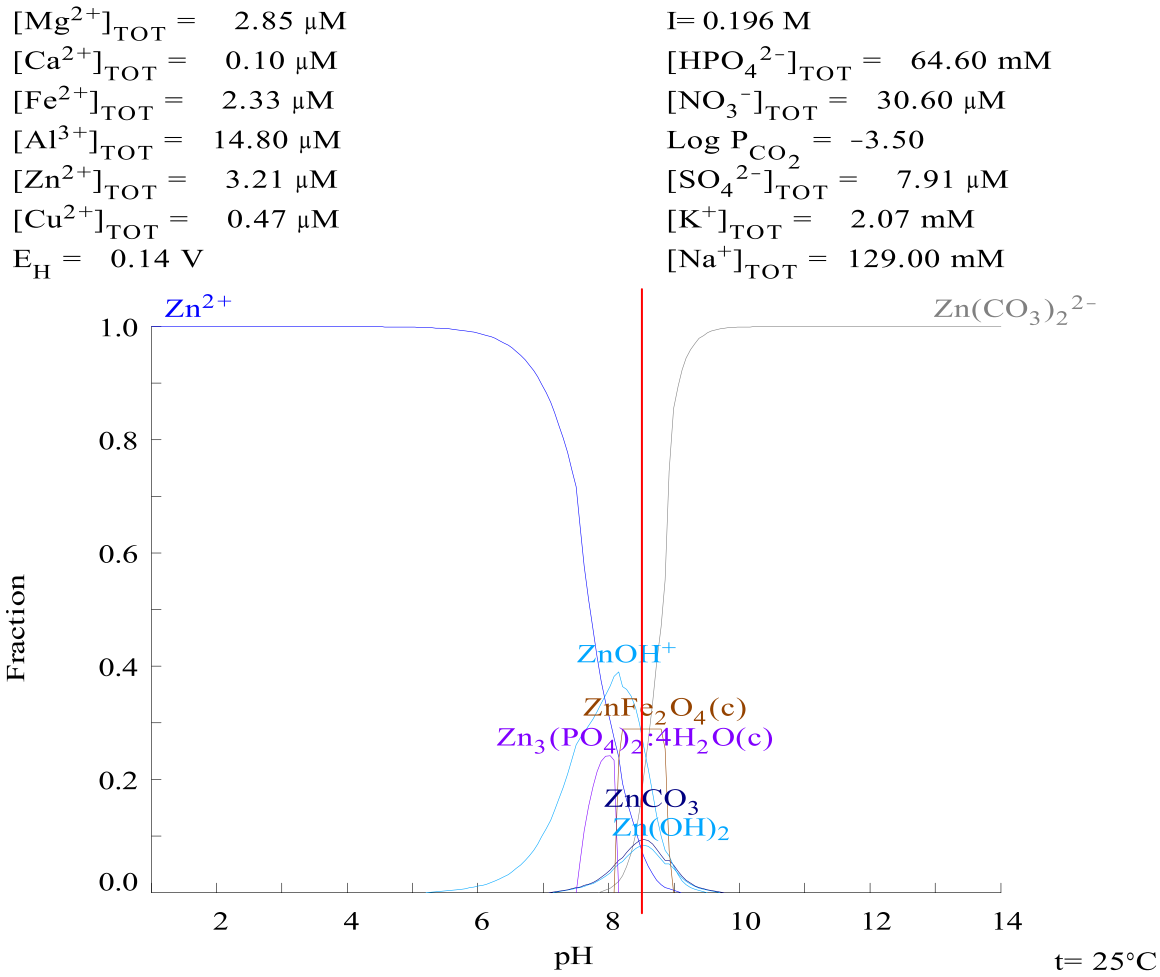


Figure C.115. Fraction diagram of zinc for Aluminum gutter section immersed into pH 8 water after three months of exposure.

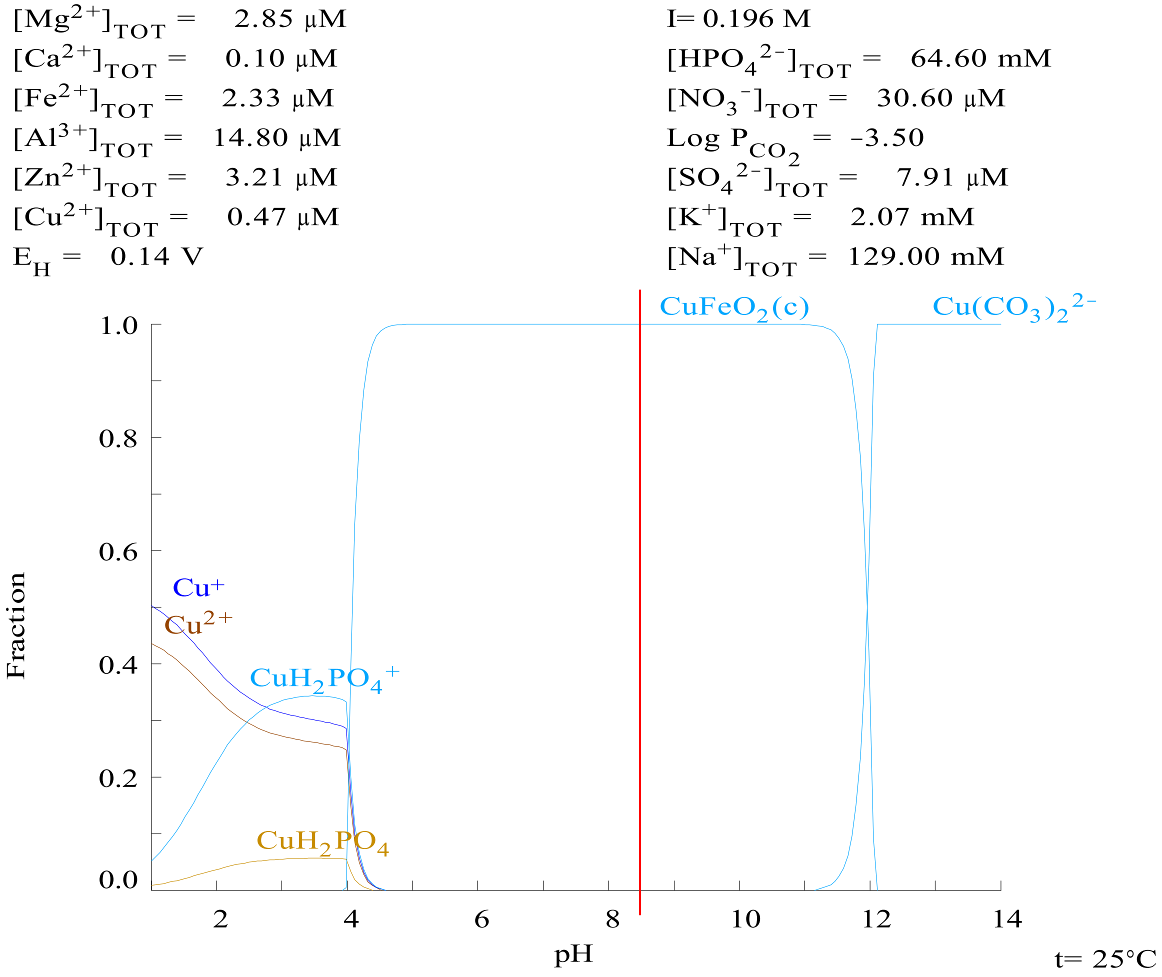


Figure C.116. Fraction diagram of copper for aluminum gutter section immersed into pH 8 water after three months of exposure.

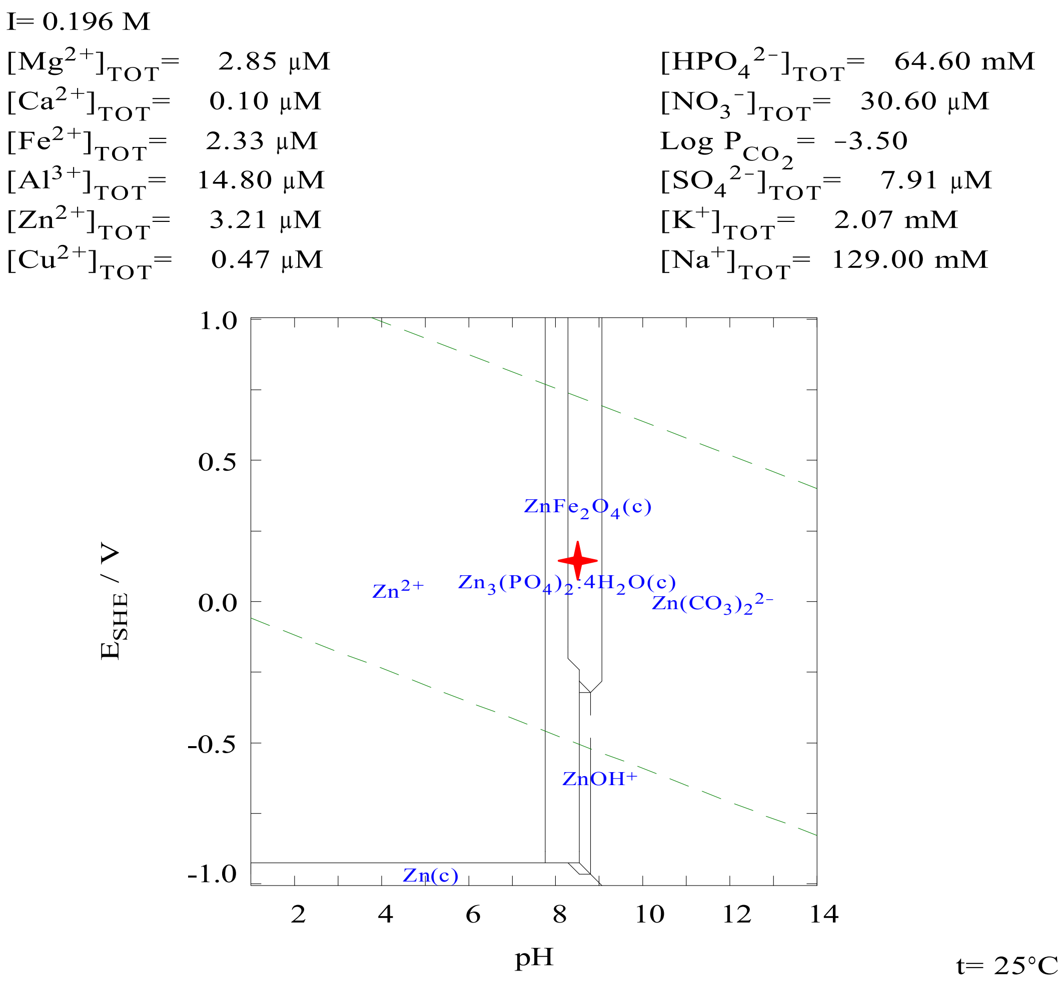


Figure C.117. Pourbaix diagram of zinc for aluminum gutter section immersed into pH 8 water after three months of exposure.

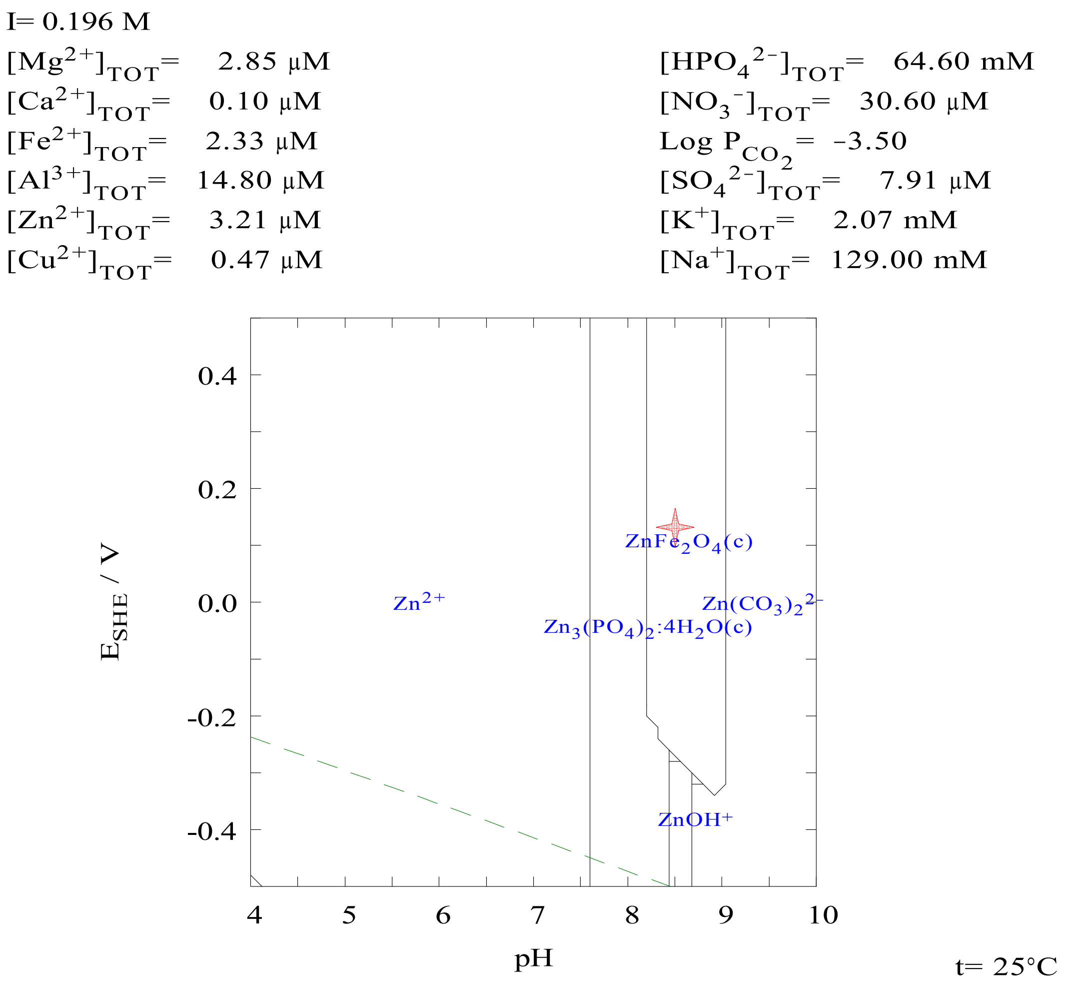


Figure C.118. Pourbaix diagram of zinc for aluminum gutter section immersed into pH 8 water after three months of exposure. Study area.

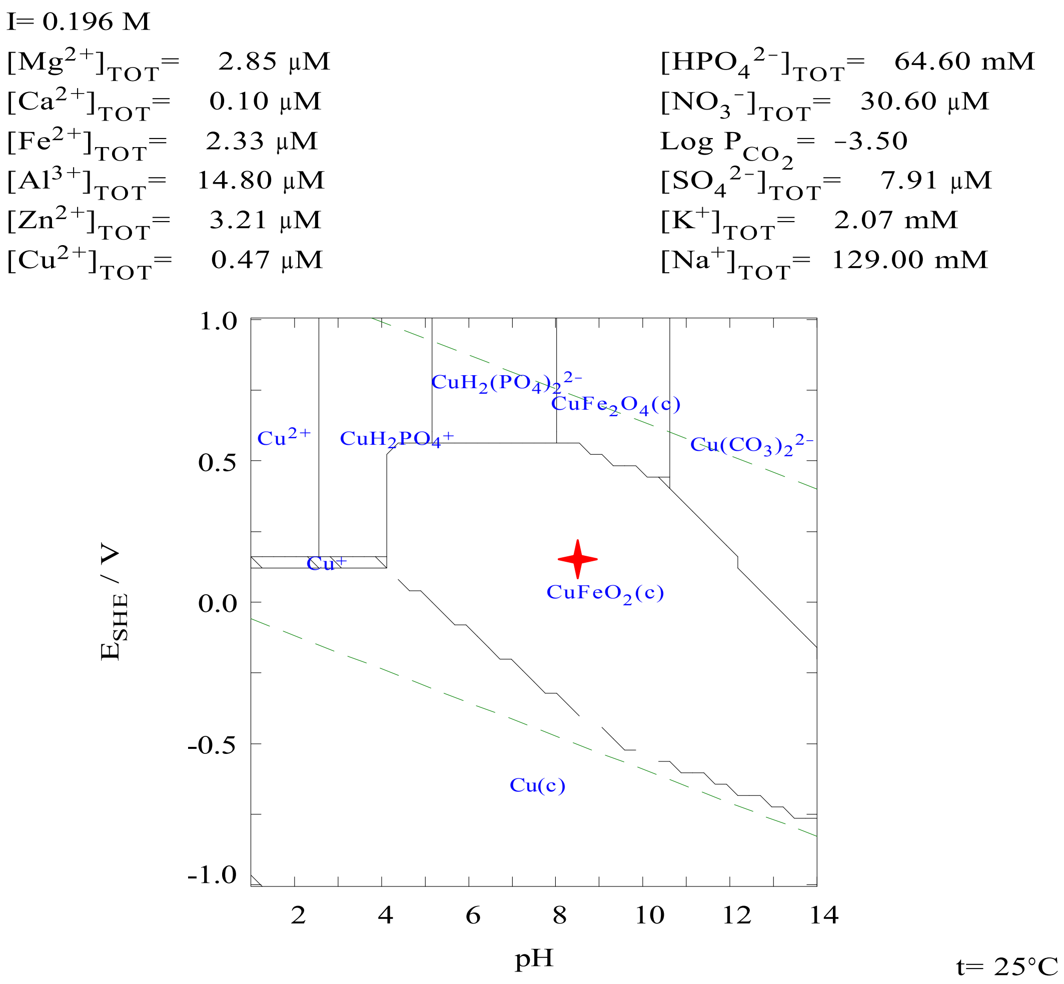


Figure C.119. Pourbaix diagram of copper for Aluminum gutter section immersed into pH 8 water after three months of exposure.

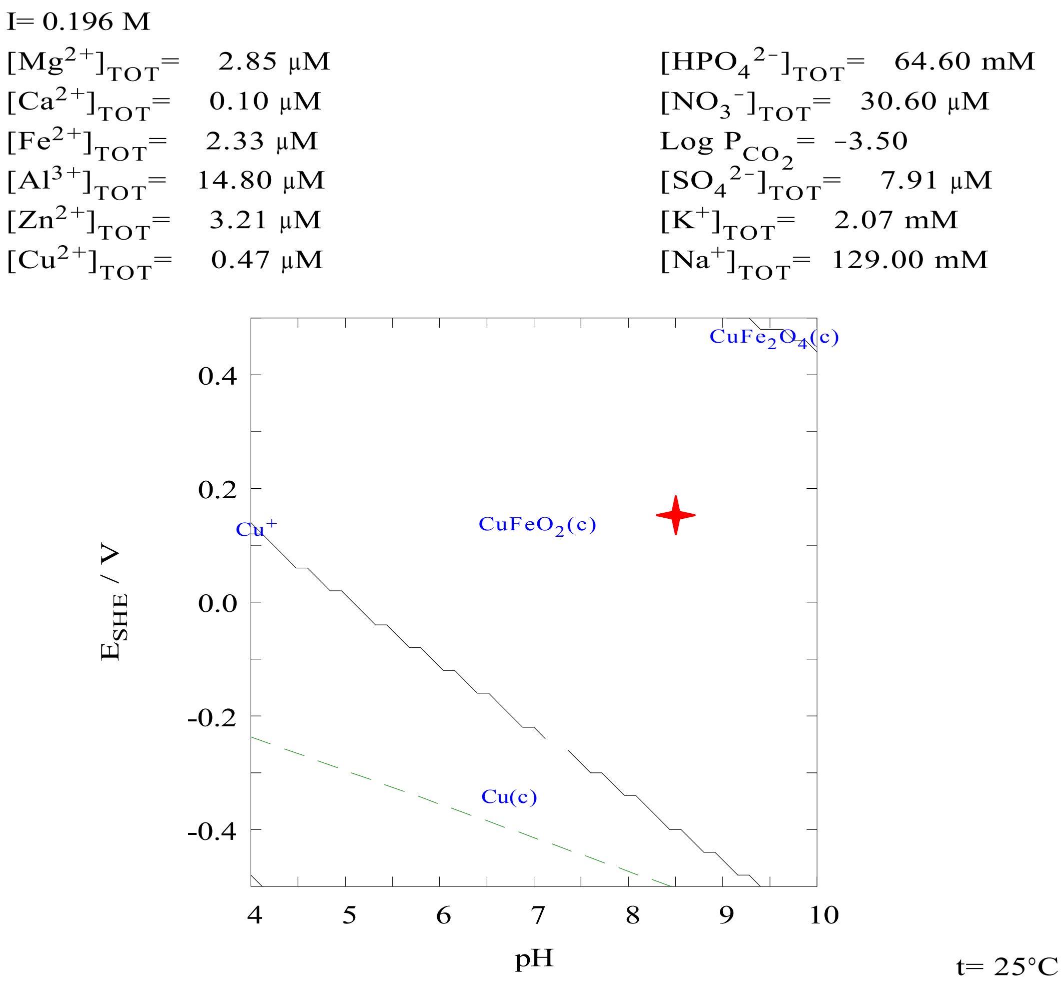


Figure C.120. Pourbaix diagram of copper for Aluminum gutter section immersed into pH 8 water after three months of exposure. Study area.

Steel Pipe, pH 8 Water, Time Zero

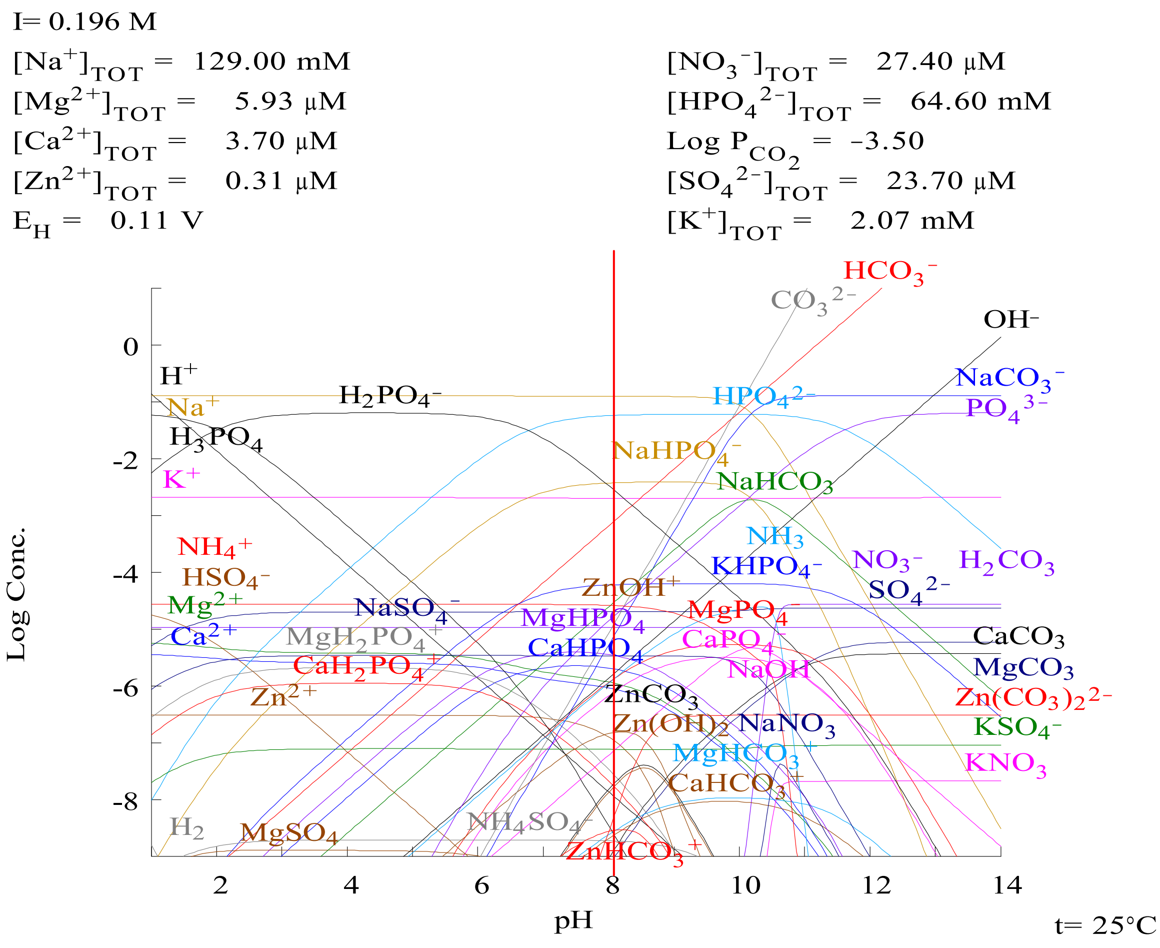


Figure C.121. Phase diagram for the container of steel pipe section at time zero in pH 8 water.

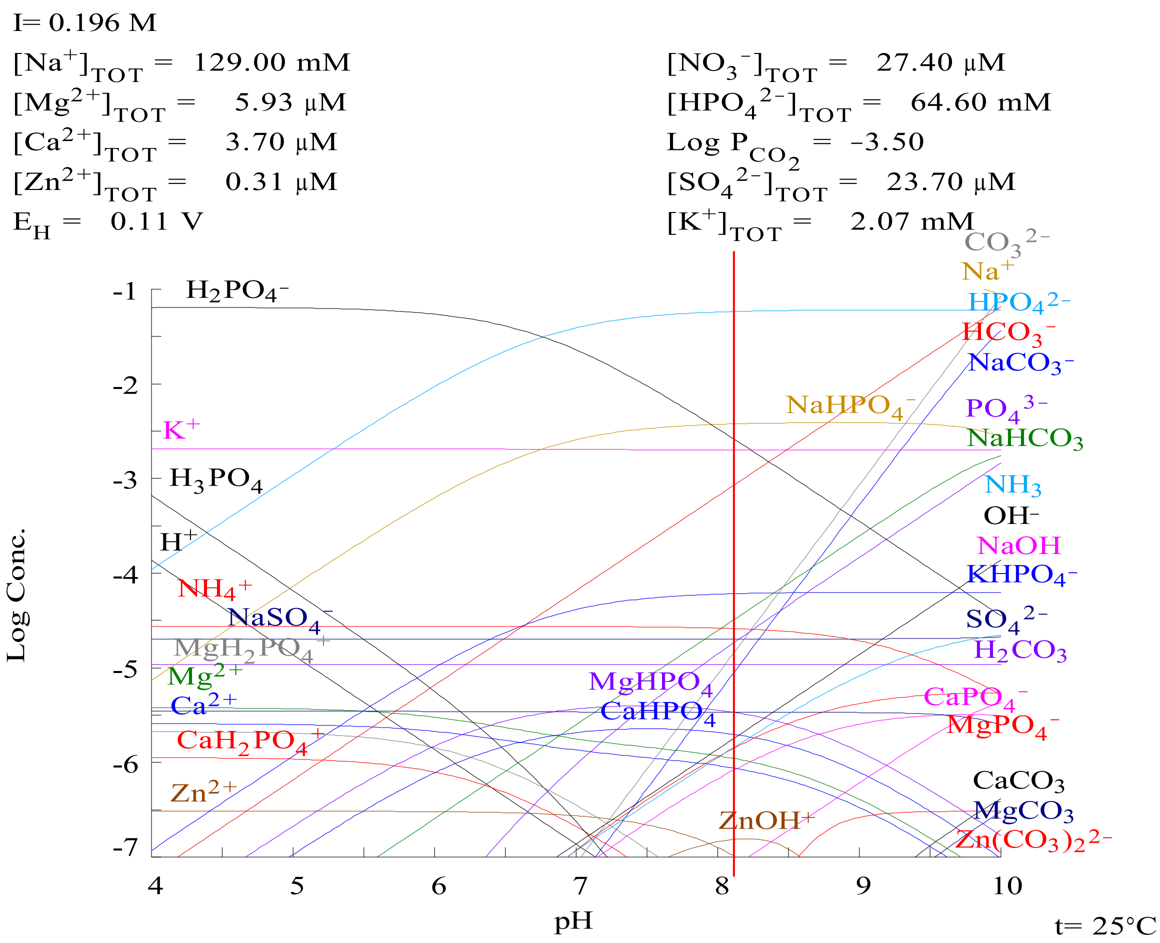


Figure C.122. Phase diagram for the container of steel pipe section at time zero in pH 8 water. Study area.

Table C.31. The predominant species of zinc. Container for steel pipe section, pH 8 water, time zero.

Component	Log Concentration (mol/L)	Concentration (mol/L)	Zn Concentration (mg/L as Zn)	Cumulative Percentage of Zn
$ZnOH^+$	-6.81	1.56E-07	1.02E-02	50.90
Zn^{2+}	-7.02	9.58E-08	6.27E-03	82.21
$ZnCO_3$	-7.64	2.29E-08	1.50E-03	89.69
$Zn(OH)_2$	-7.69	2.04E-08	1.33E-03	96.34
$Zn(CO_3)_2^{2-}$	-8.09	8.19E-09	5.36E-04	99.02
$ZnHCO_3^+$	-8.53	2.97E-09	1.94E-04	99.99

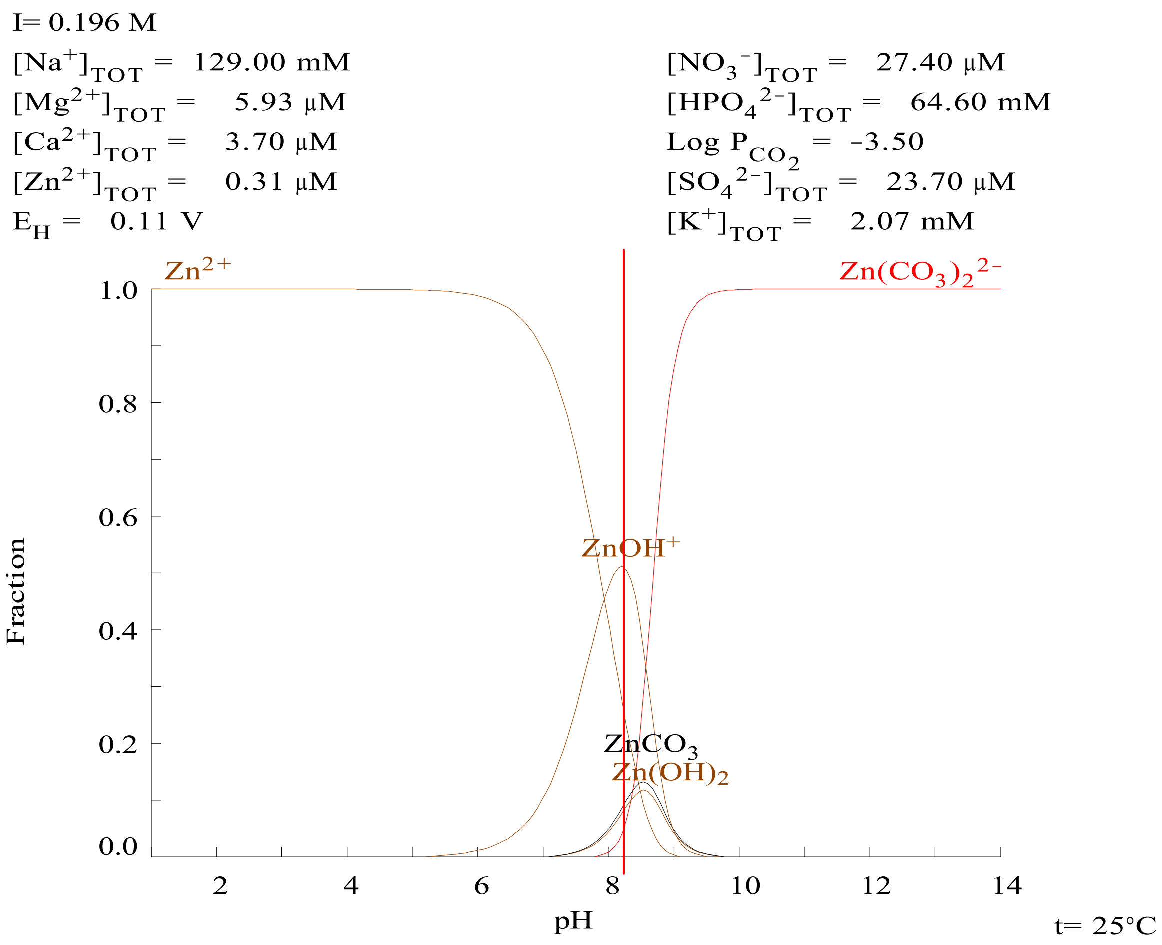


Figure C.123. Fraction diagram of zinc for the container of steel pipe section at time zero in pH 8 water.

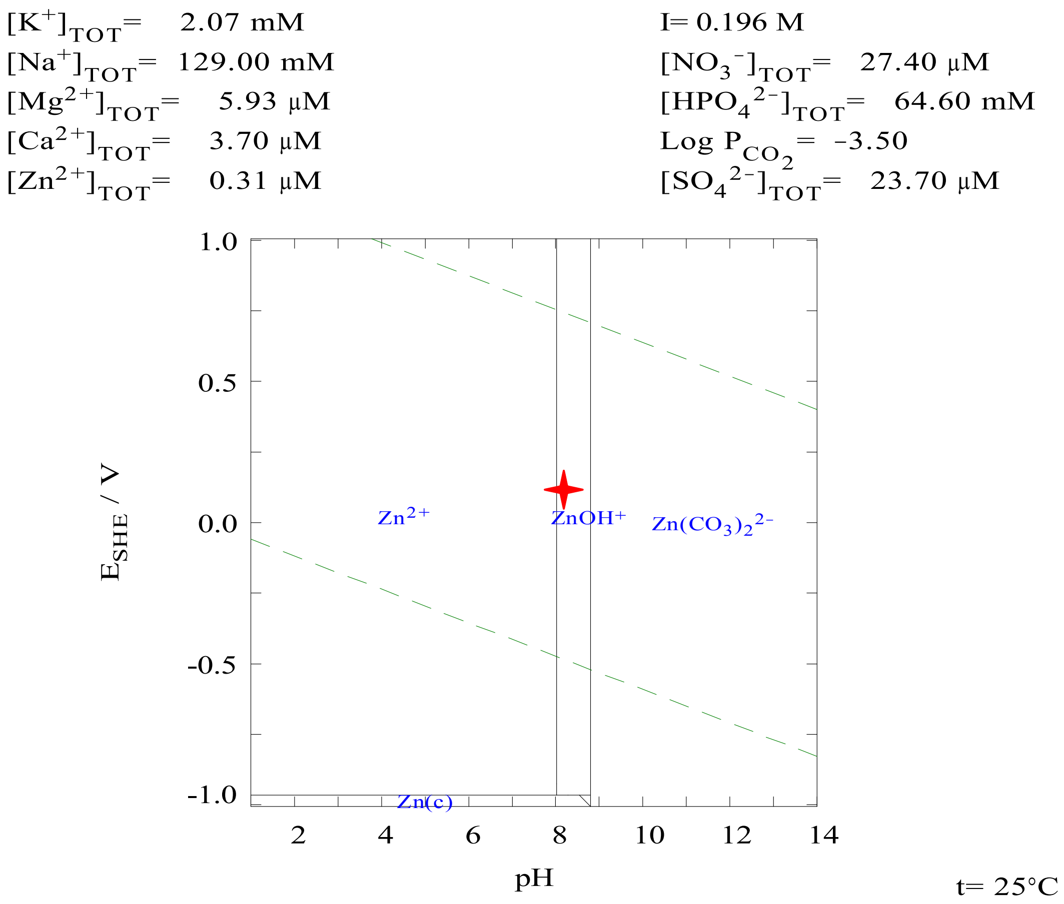


Figure C.124. Pourbaix diagram of zinc for the container of steel pipe section at time zero in pH 8 water.

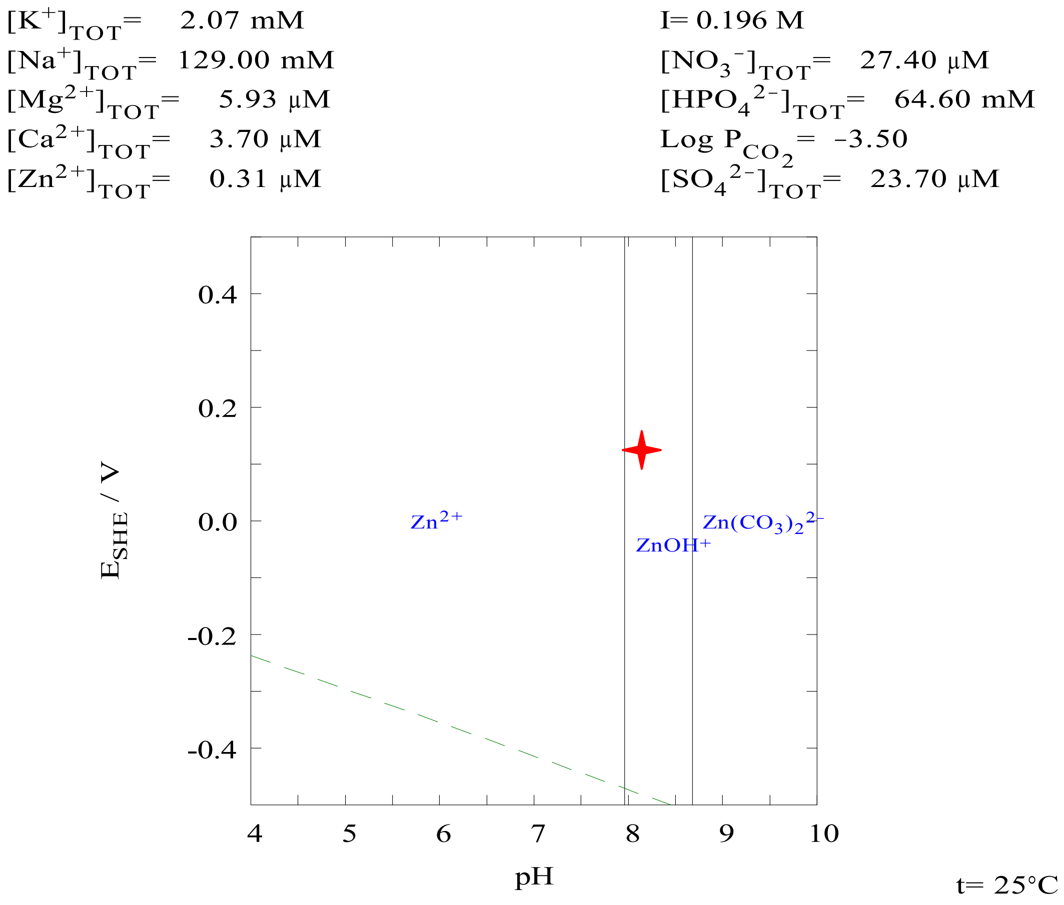


Figure C.125. Pourbaix diagram of zinc for the container of steel pipe section at time zero in pH 8 water. Study area.

Steel Gutter, pH 8 Water, Time Zero

I= 0.196 M

$[Na^+]_{TOT}$ = 129.00 mM

$[Mg^{2+}]_{TOT}$ = 5.93 µM

$[Ca^{2+}]_{TOT}$ = 4.71 µM

$[Zn^{2+}]_{TOT}$ = 0.31 µM

E_H = 0.12 V

$[NO_3^-]_{TOT}$ = 22.60 µM

$[HPO_4^{2-}]_{TOT}$ = 64.60 mM

Log P_{CO_2} = -3.50

$[SO_4^{2-}]_{TOT}$ = 7.18 µM

$[K^+]_{TOT}$ = 2.07 mM

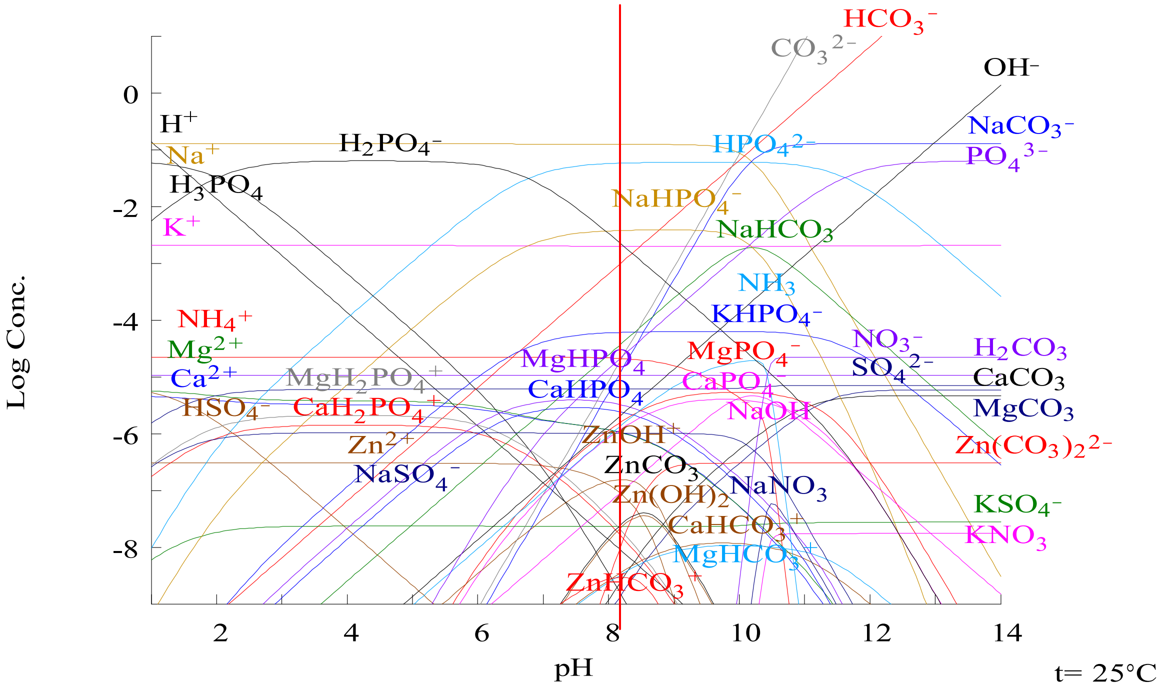


Figure C.126. Phase diagram for the container of steel gutter section at time zero in pH 8 water.

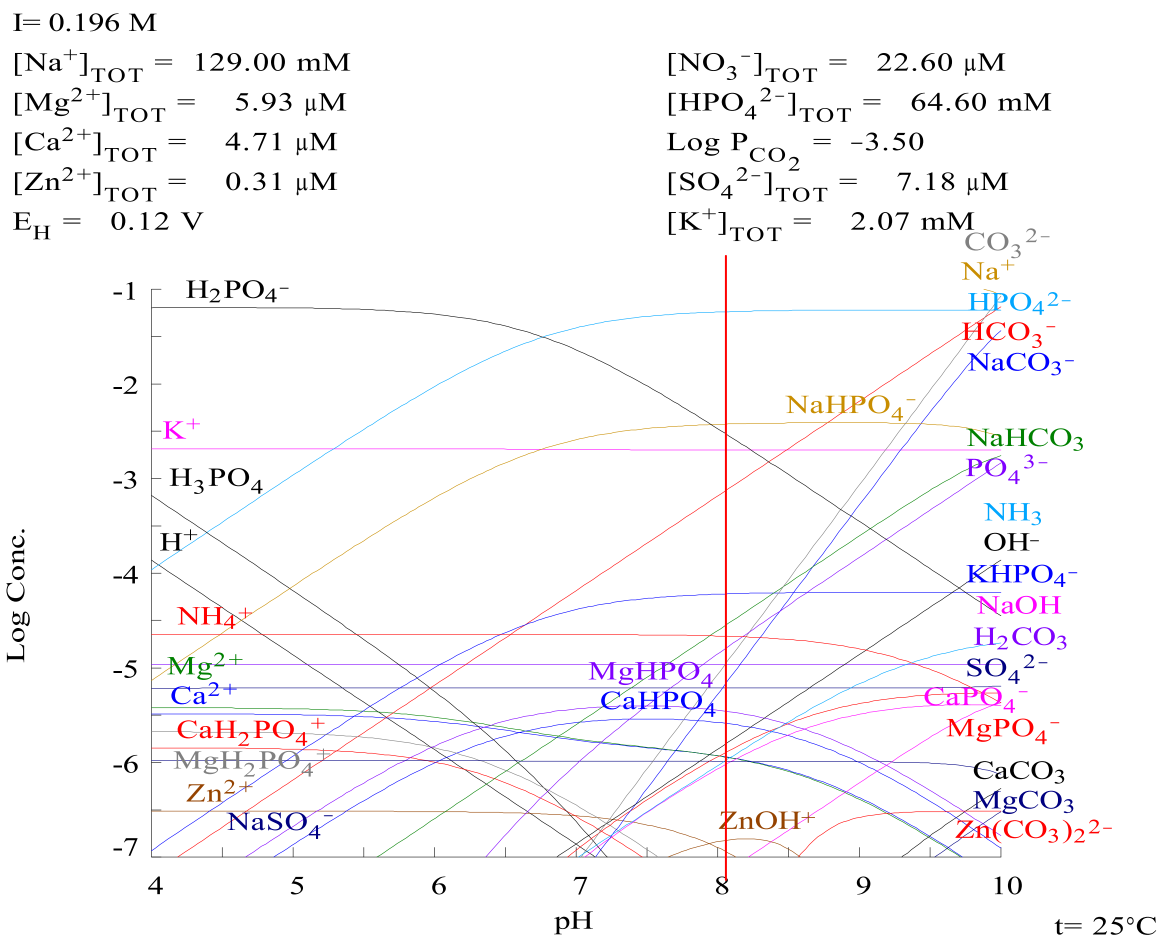


Figure C.127. Phase diagram for the container of steel gutter section at time zero in pH 8 water. Study area.

Table C.32. The predominant species of zinc. Container for steel gutter section, pH 8 water, time zero.

Component	Log Concentration (mol/L)	Concentration (mol/L)	Zn Concentration (mg/L as Zn)	Cumulative Percentage of Zn
$ZnOH^+$	-6.81	1.57E-07	1.02E-02	51.19
Zn^{2+}	-7.08	8.30E-08	5.43E-03	78.29
$ZnCO_3$	-7.57	2.67E-08	1.75E-03	87.03
$Zn(OH)_2$	-7.62	2.38E-08	1.56E-03	94.80
$Zn(CO_3)_2^{2-}$	-7.89	1.29E-08	8.44E-04	99.02
$ZnHCO_3^+$	-8.53	2.98E-09	1.95E-04	99.99

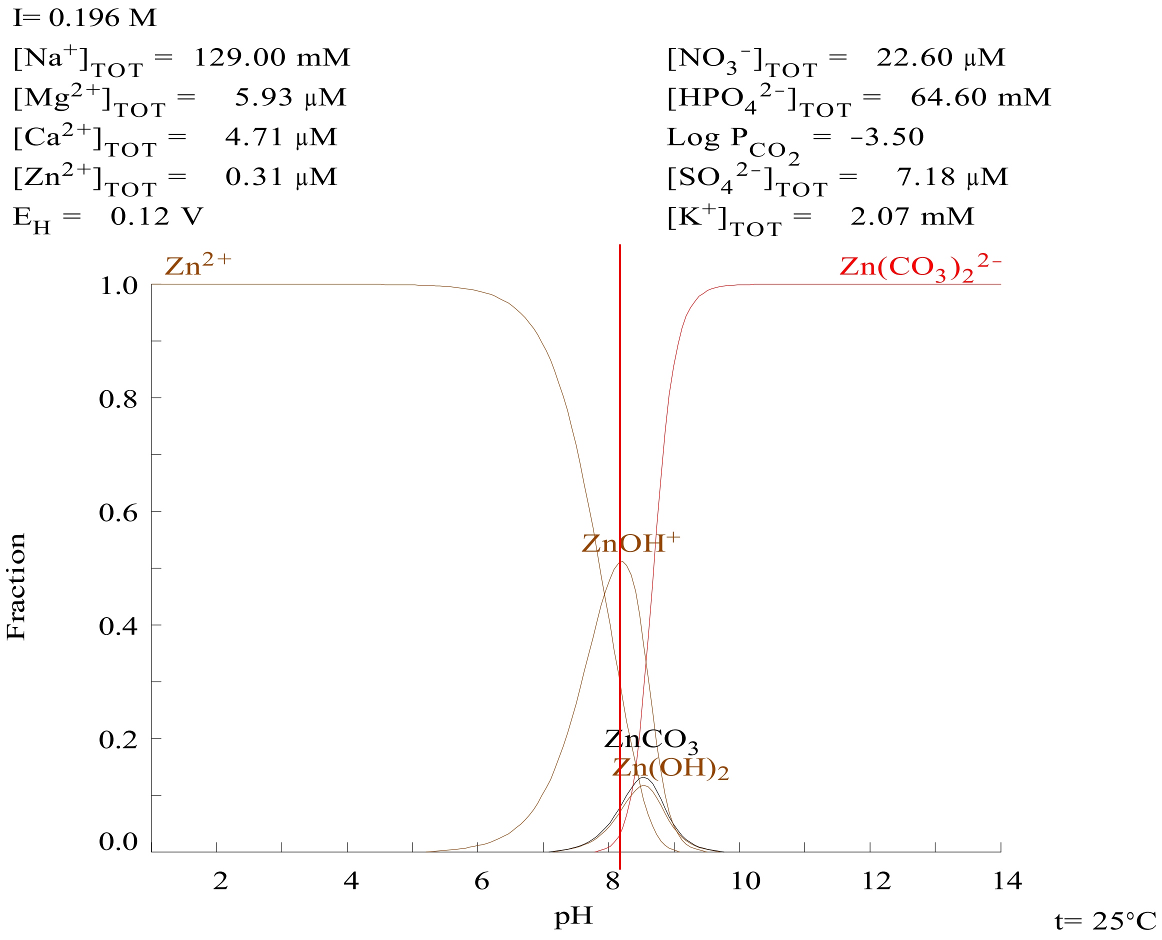


Figure C.128. Fraction diagram of zinc for the container of steel gutter section at time zero in pH 8 water.

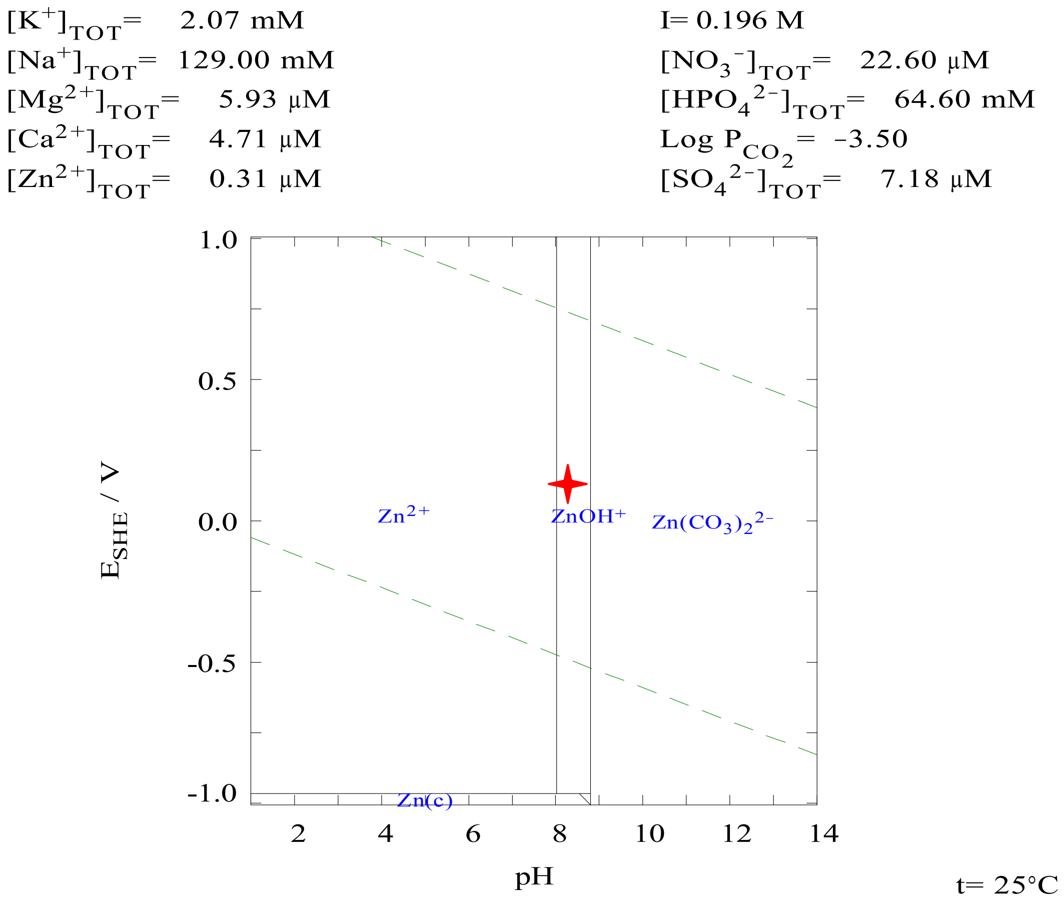


Figure C.129. Pourbaix diagram of zinc for the container of steel gutter section at time zero in pH 8 water.

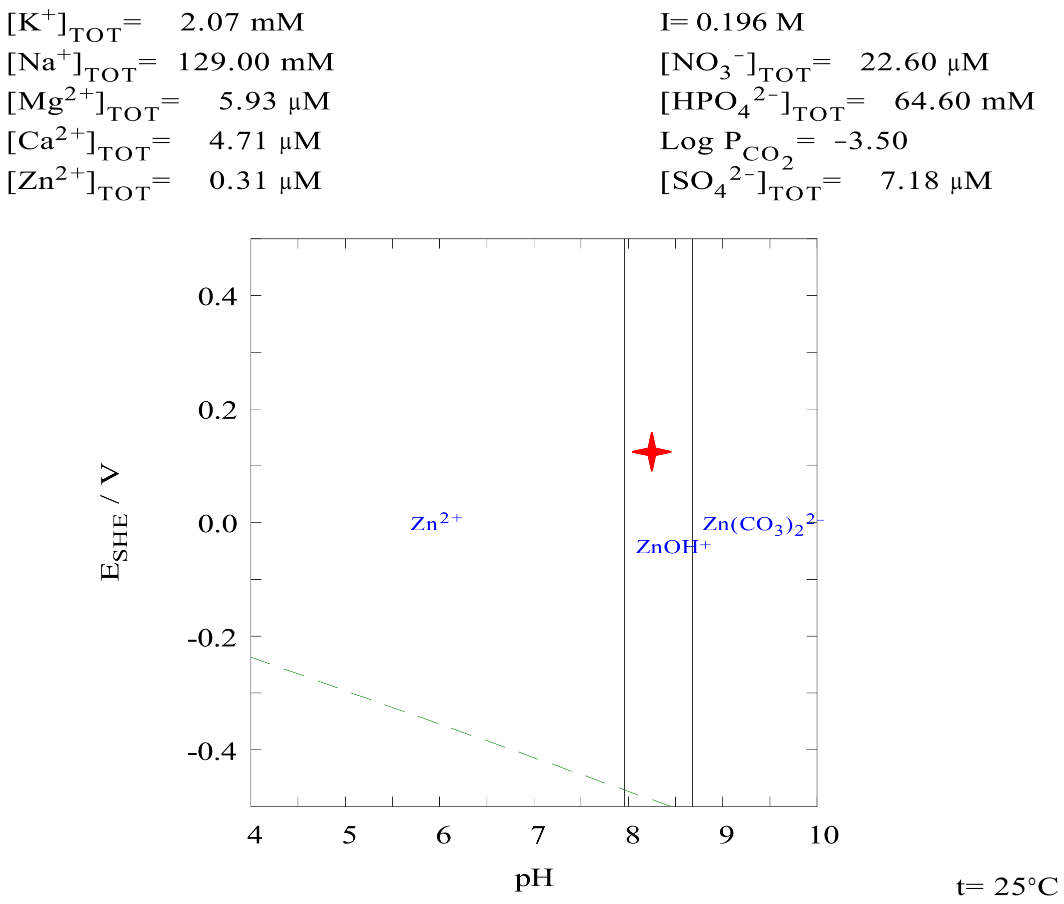


Figure C.130. Pourbaix diagram of zinc for the container of steel gutter section at time zero in pH 8 water. Study area.

Copper Gutter, pH 8 Water, Time Zero

I= 0.196 M

$[Na^+]_{TOT}$ = 129.00 mM

$[Mg^{2+}]_{TOT}$ = 3.91 µM

$[Ca^{2+}]_{TOT}$ = 1.50 µM

$[Zn^{2+}]_{TOT}$ = 0.31 µM

E_H = 0.16 V

$[NO_3^-]_{TOT}$ = 96.80 µM

$[HPO_4^{2-}]_{TOT}$ = 64.60 mM

Log P_{CO_2} = -3.50

$[SO_4^{2-}]_{TOT}$ = 24.80 µM

$[K^+]_{TOT}$ = 2.07 mM

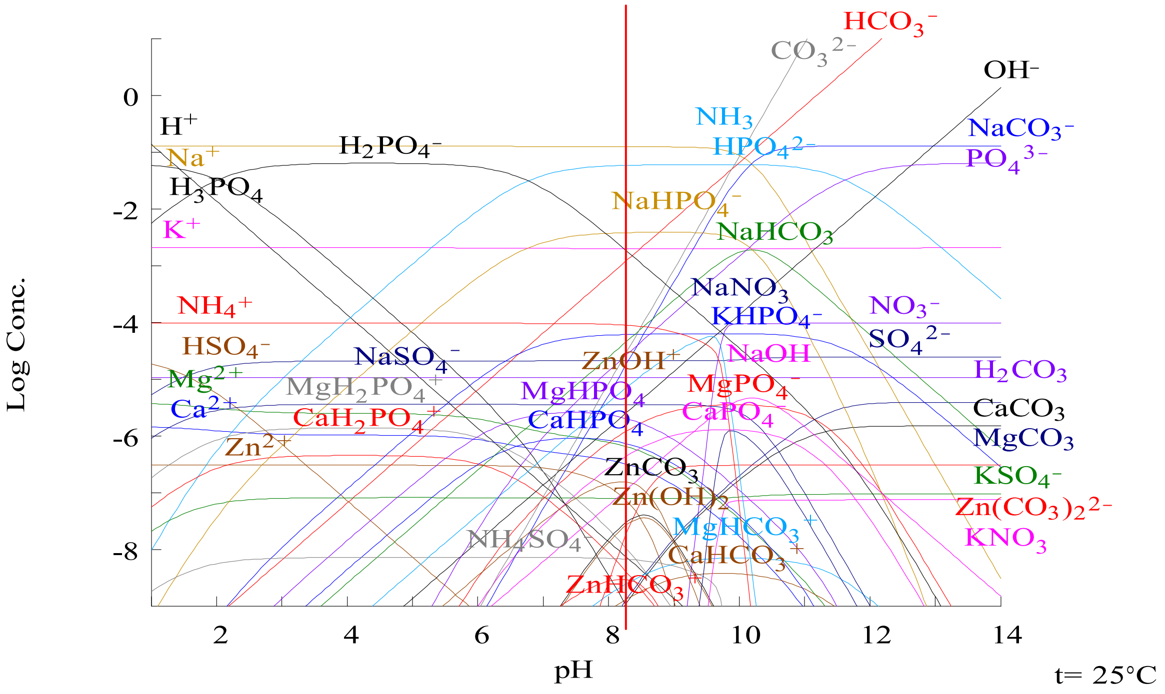


Figure C.131. Phase diagram for the container of copper gutter section at time zero in pH 8 water.

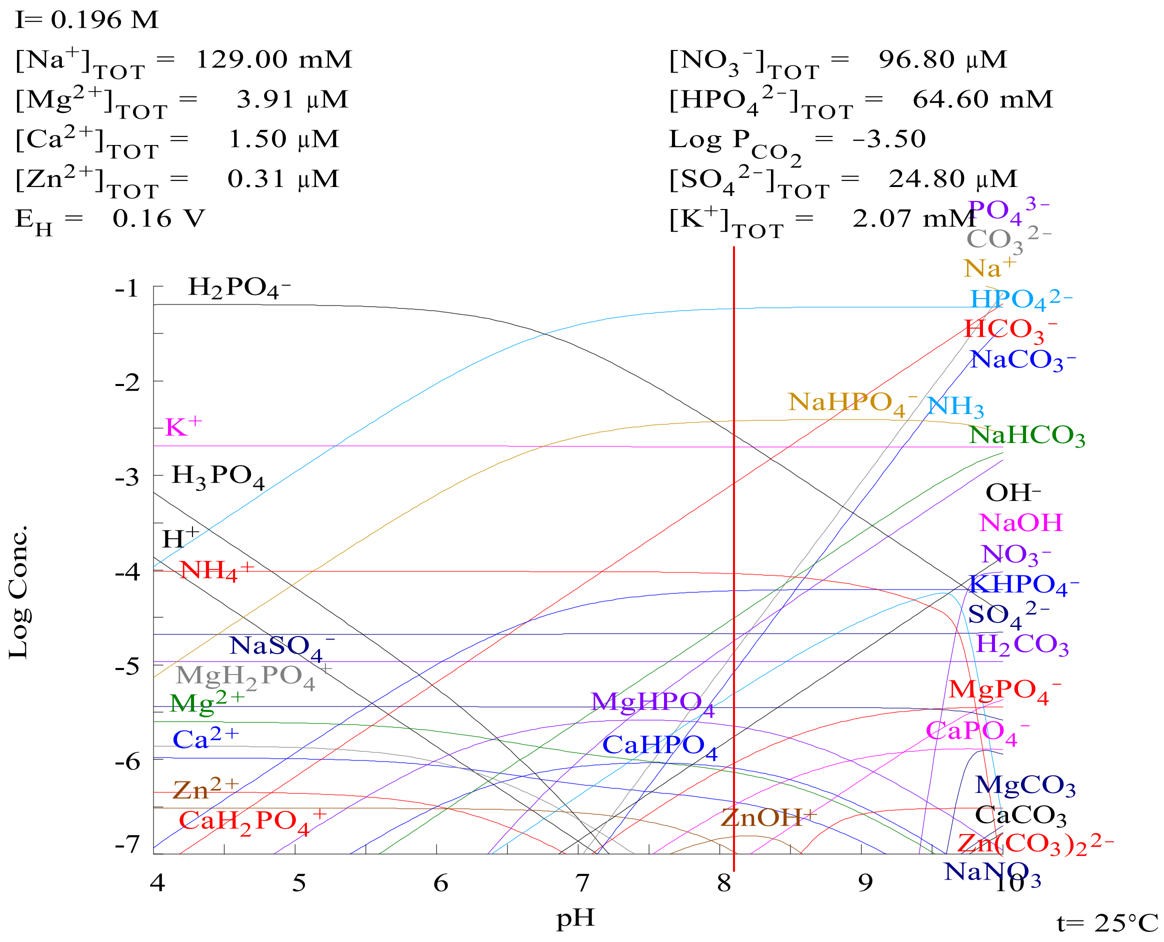


Figure C.132. Phase diagram for the container of copper gutter section at time zero in pH 8 water. Study area.

Table C.33. The predominant species of zinc. Container for copper gutter section, pH 8 water, time zero.

Component	Log Concentration (mol/L)	Concentration (mol/L)	Zn Concentration (mg/L as Zn)	Cumulative Percentage of Zn
$ZnOH^+$	-6.81	1.57E-07	1.02E-02	51.18
Zn^{2+}	-7.08	8.30E-08	5.43E-03	78.29
$ZnCO_3$	-7.57	2.67E-08	1.75E-03	87.03
$Zn(OH)_2$	-7.62	2.38E-08	1.56E-03	94.79
$Zn(CO_3)_2^{2-}$	-7.89	1.29E-08	8.44E-04	99.01
$ZnHCO_3^+$	-8.53	2.98E-09	1.95E-04	99.99

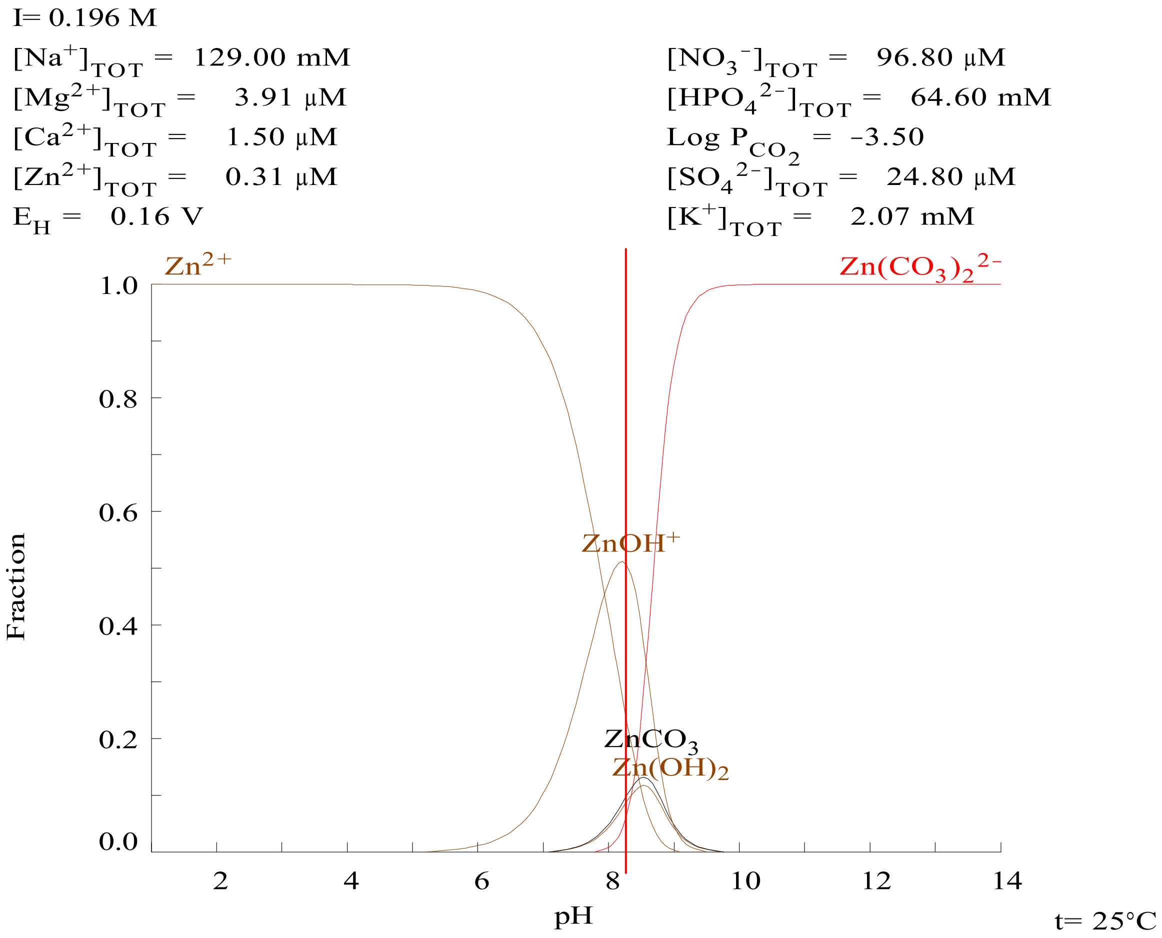


Figure C.133. Fraction diagram of zinc for the container of copper gutter section at time zero in pH 8 water.

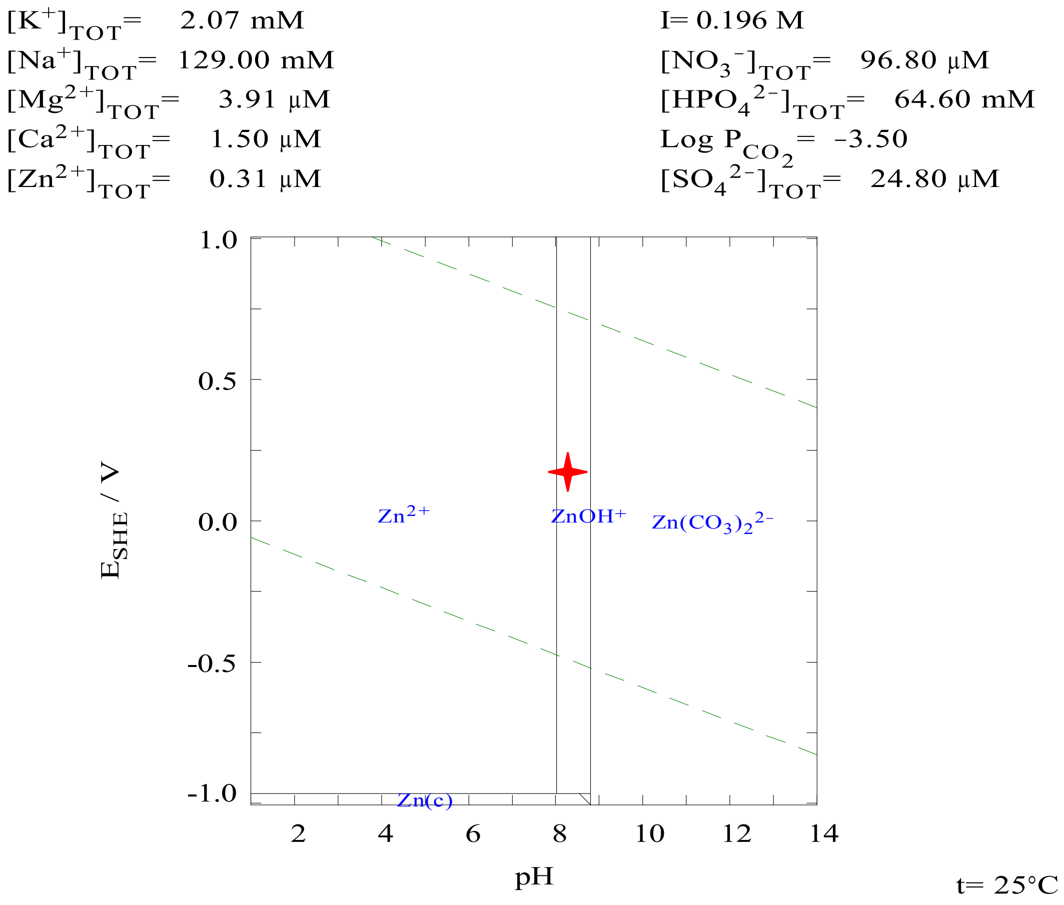


Figure C.134. Pourbaix diagram of zinc for the container of copper gutter section at time zero in pH 8 water.

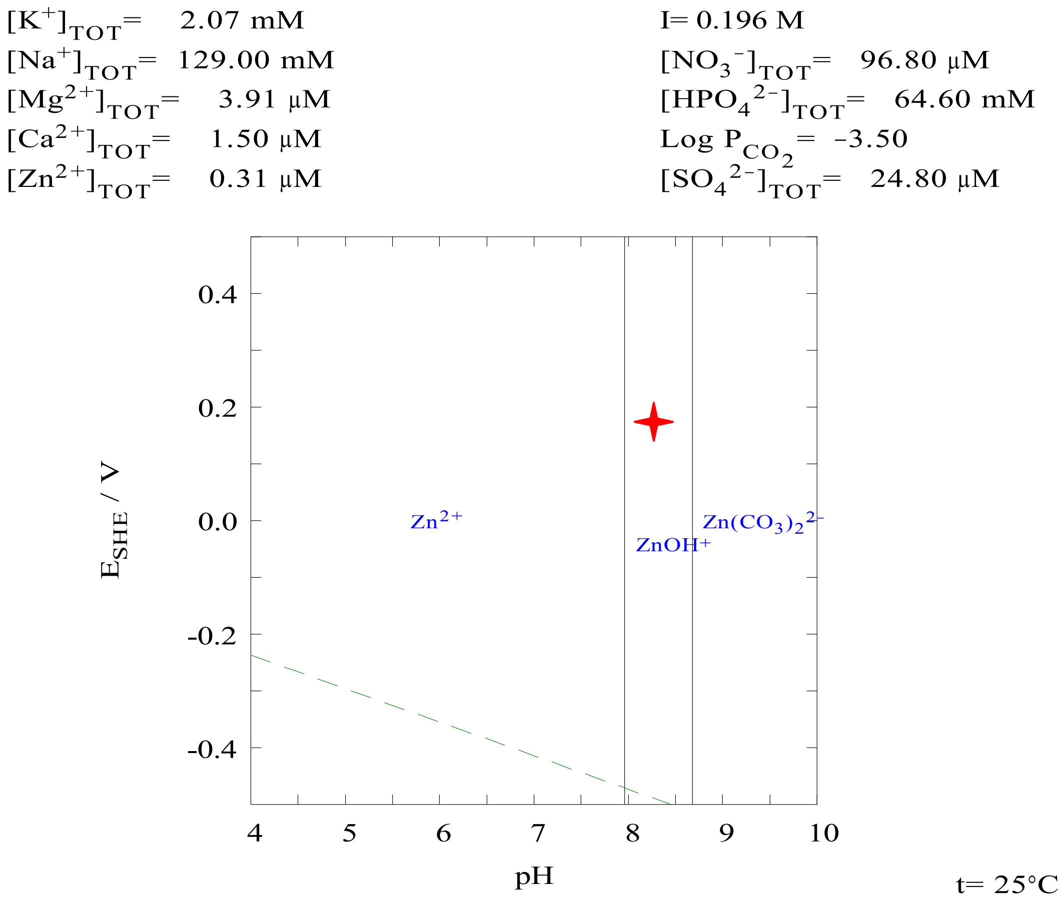


Figure C.135. Pourbaix diagram of zinc for the container of copper gutter section at time zero in pH 8 water. Study area.

PVC Pipe, pH 5 Water, Time Zero

$[Na^+]_{TOT}$ = 1.27 mM
$[Mg^{2+}]_{TOT}$ = 37.90 µM
$[Ca^{2+}]_{TOT}$ = 0.61 mM
$[Zn^{2+}]_{TOT}$ = 3.82 µM
$[Cu^{2+}]_{TOT}$ = 1.42 µM
E_H = 0.22 V

I= 0.070 M
$[H_2PO_4^-]_{TOT}$ = 66.00 mM
$[NO_3^-]_{TOT}$ = 4.84 µM
Log P_{CO_2} = -3.50
$[SO_4^{2-}]_{TOT}$ = 0.15 mM
$[K^+]_{TOT}$ = 66.00 mM

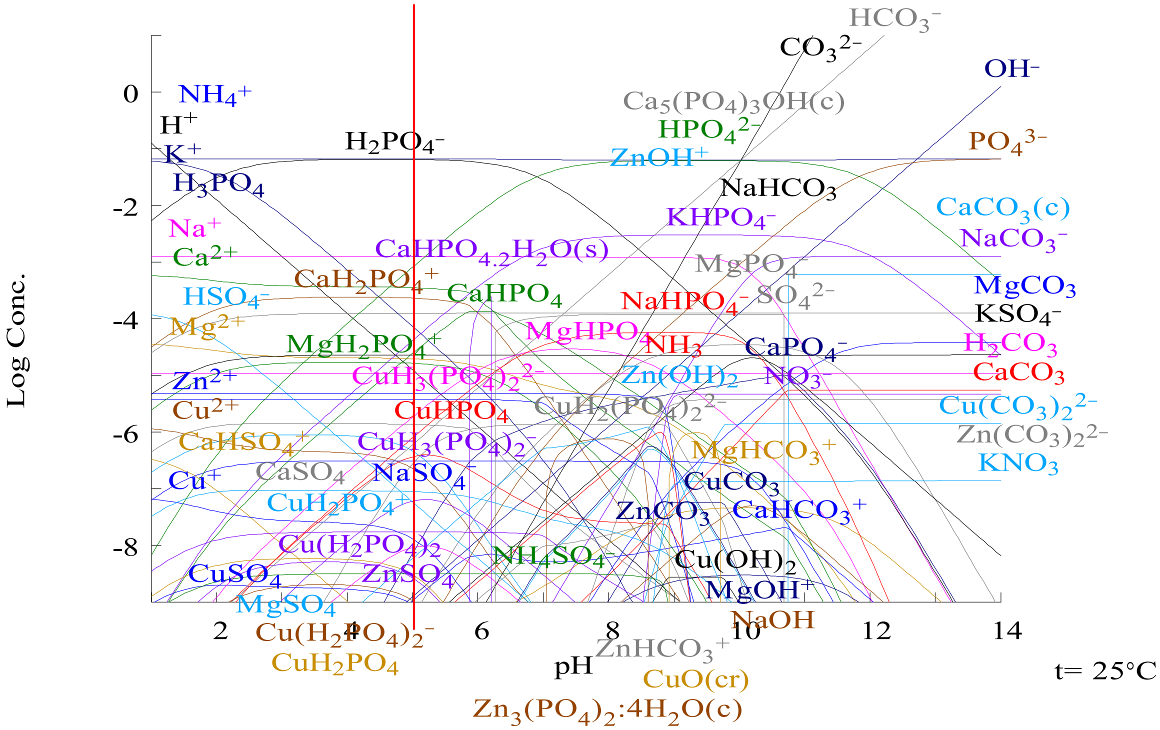


Figure C.136. Phase diagram for the container of PVC pipe section at time zero in pH 5 water.

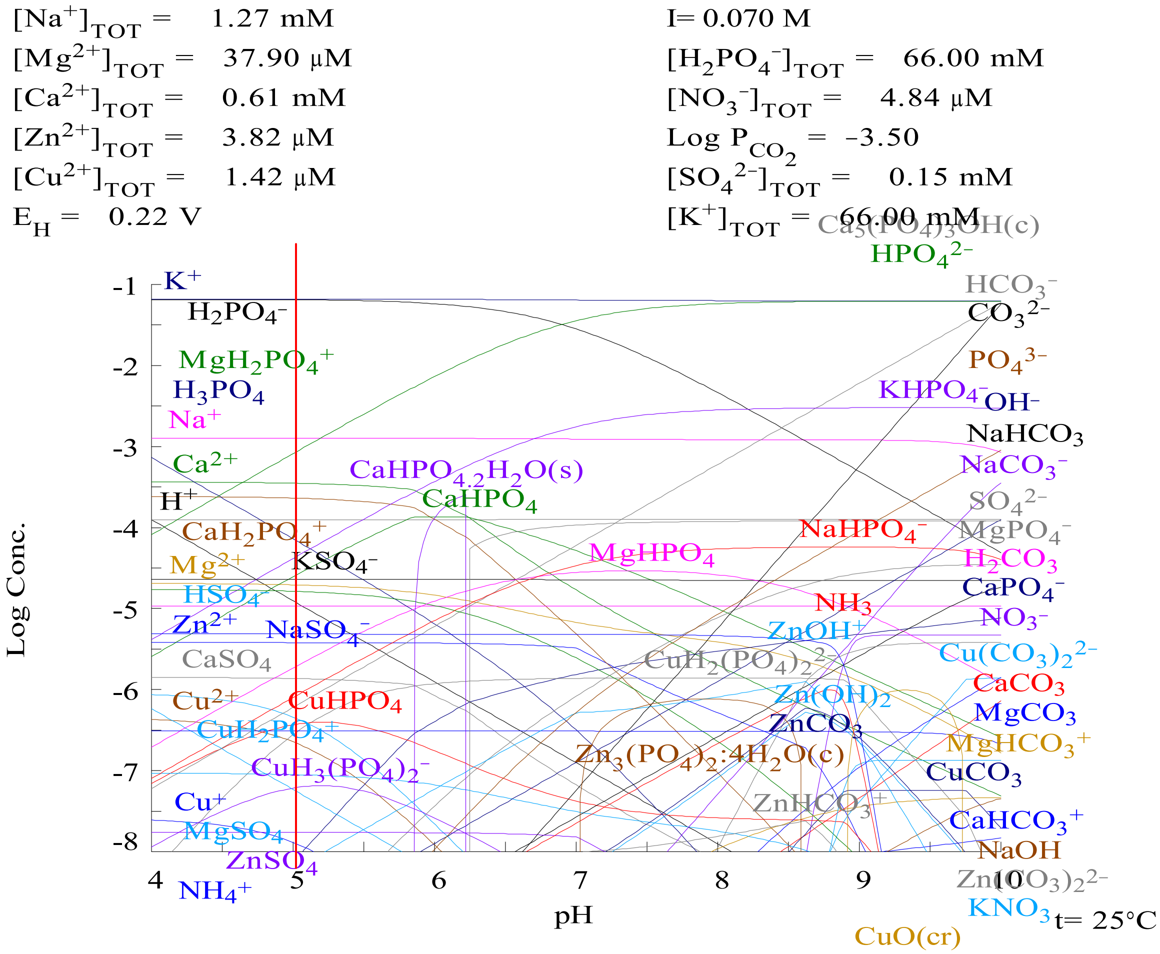


Figure C.137. Phase diagram for the container of PVC pipe section at time zero in pH 5 water. Study area.

Table C.34. The predominant species of zinc. Container for PVC pipe section, pH 5 water, time zero.

Component	Log Concentration (mol/L)	Concentration (mol/L)	Zn Concentration (mg/L as Zn)	Cumulative Percentage of Zn
Zn^{2+}	-5.42	3.80E-06	2.48E-01	99.38
$ZnSO_4$	-7.76	1.73E-08	1.13E-03	99.83
$ZnOH^+$	-8.20	6.37E-09	4.16E-04	99.996

Table C.35. The predominant species of copper. Container for PVC pipe section, pH 5 water, time zero.

Component	Log Concentration (mol/L)	Concentration (mol/L)	Cu Concentration (mg/L as Cu)	Cumulative Percentage of Cu
$CuH_2PO_4^+$	-6.36	4.38E-07	2.78E-02	30.81
$CuHPO_4$	-6.43	3.75E-07	2.38E-02	57.20
$CuH_2(PO_4)_2^{2-}$	-6.52	3.00E-07	1.91E-02	78.31
Cu^{2+}	-6.66	2.17E-07	1.38E-02	93.59
$CuH_3(PO_4)_2^-$	-7.21	6.19E-08	3.93E-03	97.94
Cu^+	-7.91	1.24E-08	7.90E-04	98.82
$CuH_3(PO_4)_2^{2-}$	-8.03	9.34E-09	5.94E-04	99.48
CuH_2PO_4	-8.54	2.87E-09	1.82E-04	99.68
$Cu(H_2PO_4)_2$	-8.60	2.54E-09	1.61E-04	99.86
$Cu(H_2PO_4)_2^-$	-9.00	1.01E-09	6.43E-05	99.93

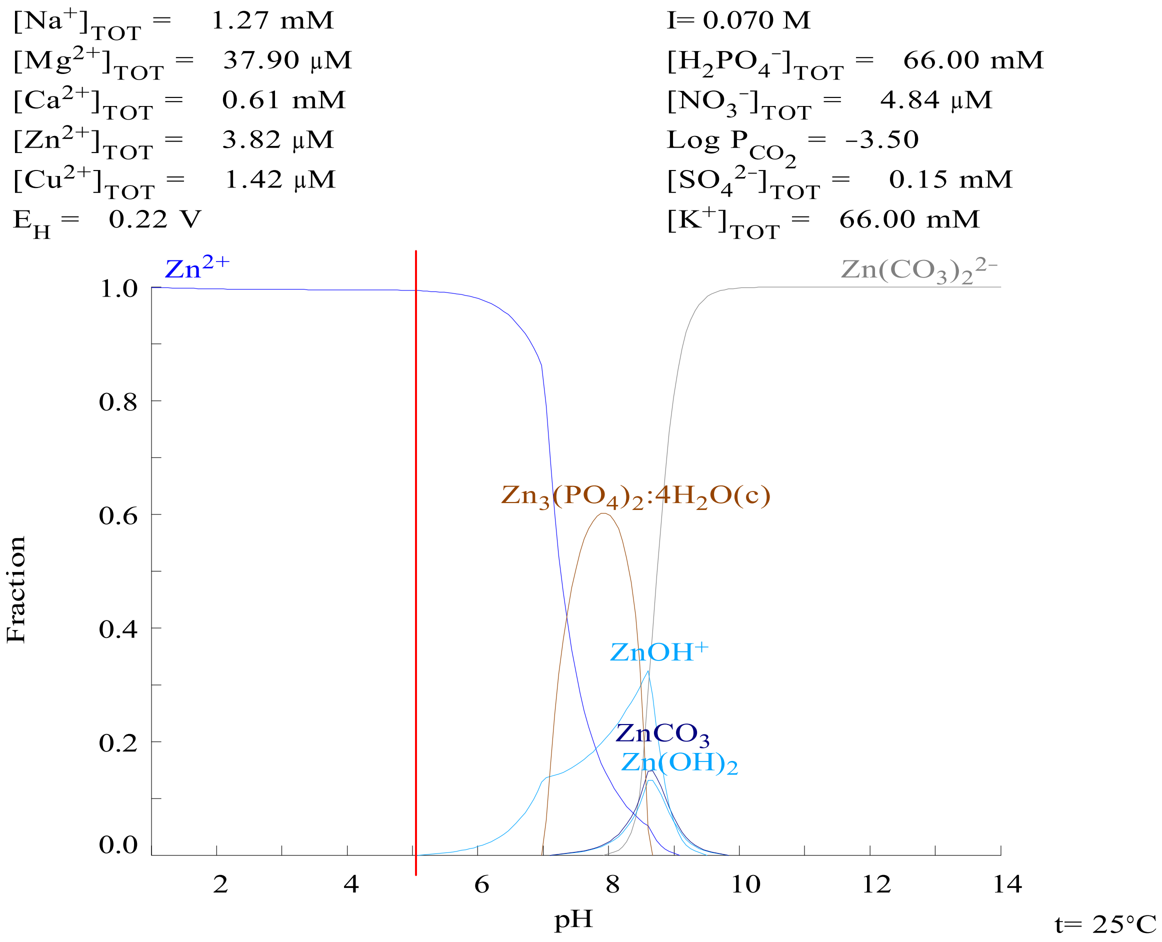


Figure C.138. Fraction diagram of zinc for the container of PVC pipe section at time zero in pH 5 water.

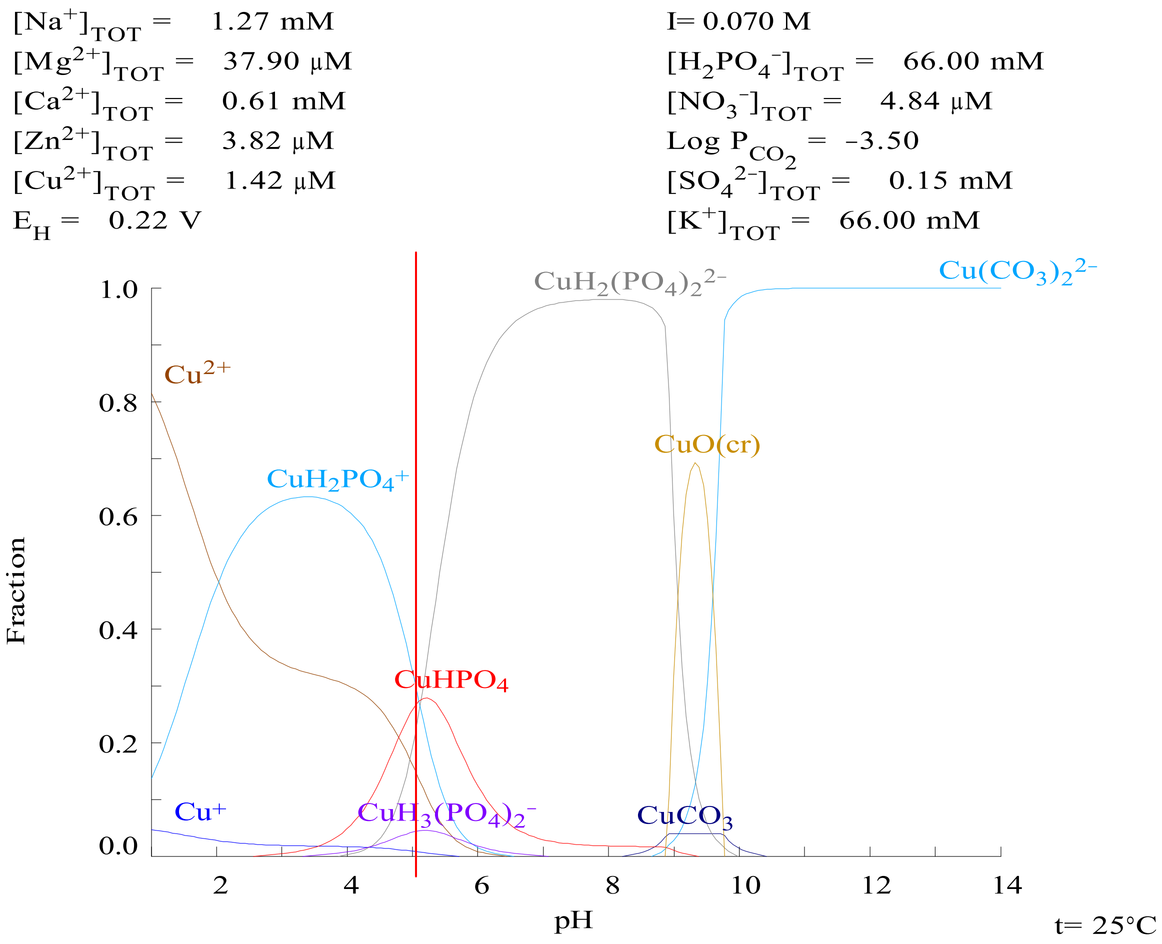


Figure C.139. Fraction diagram of copper for the container of PVC pipe section at time zero in pH 5 water.

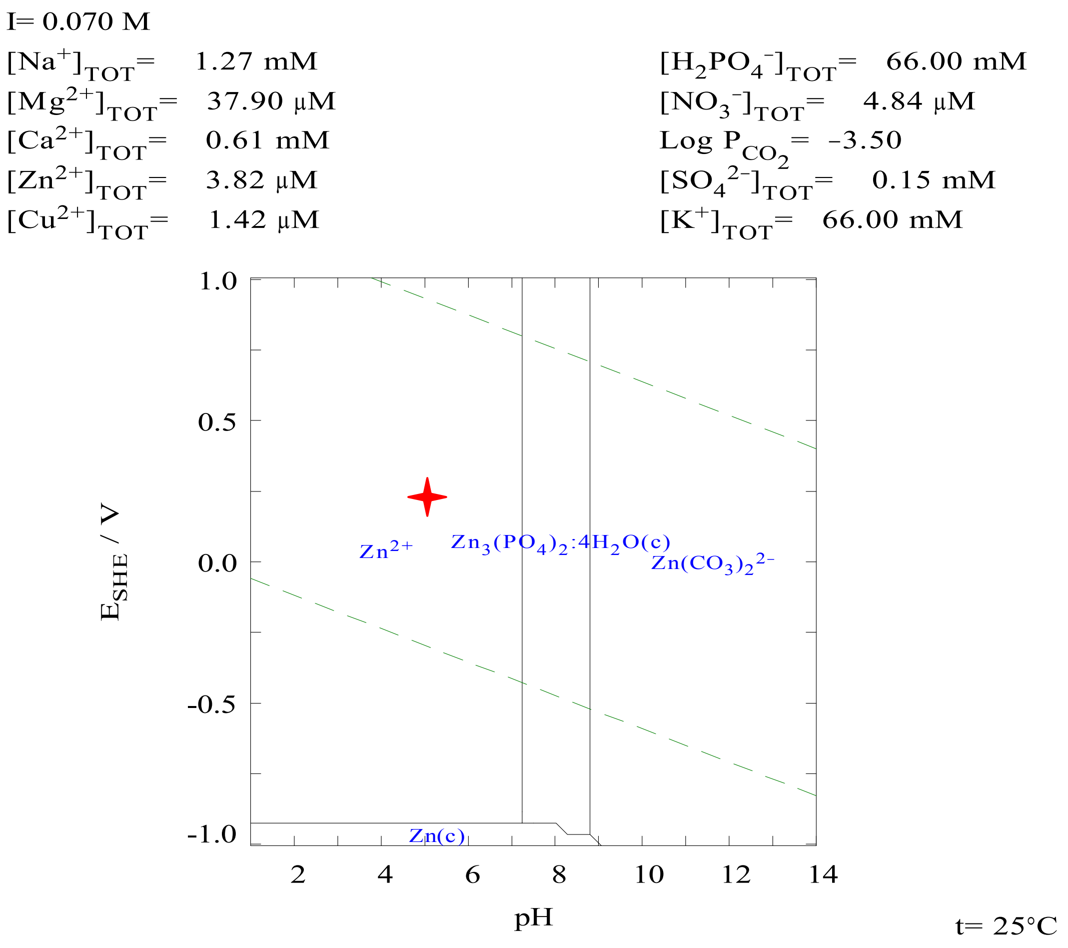


Figure C.140. Pourbaix diagram of zinc for the container of PVC pipe section at time zero in pH 5 water.

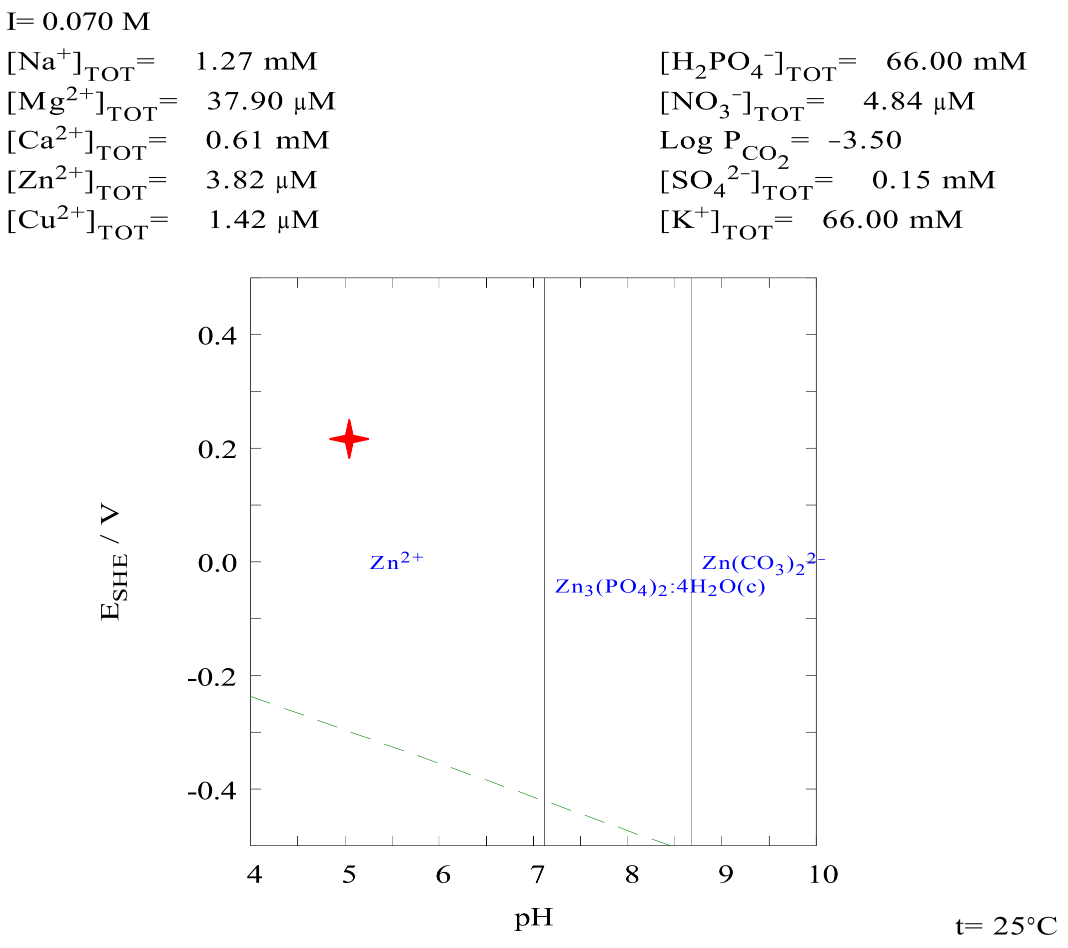


Figure C.141. Pourbaix diagram of zinc for the container of PVC pipe section at time zero in pH 5 water. Study area.

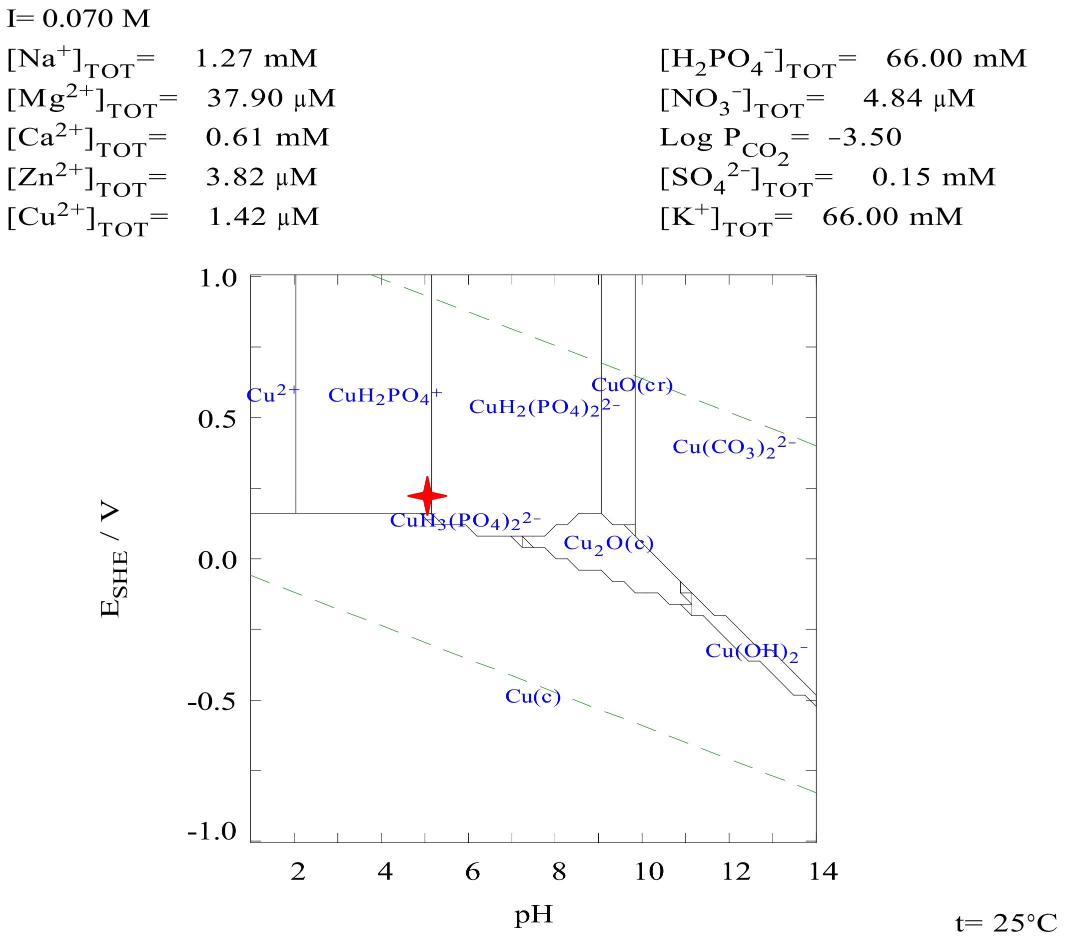


Figure C.142. Pourbaixdiagram of copper for the container of PVC pipe section at time zero in pH 5 water.

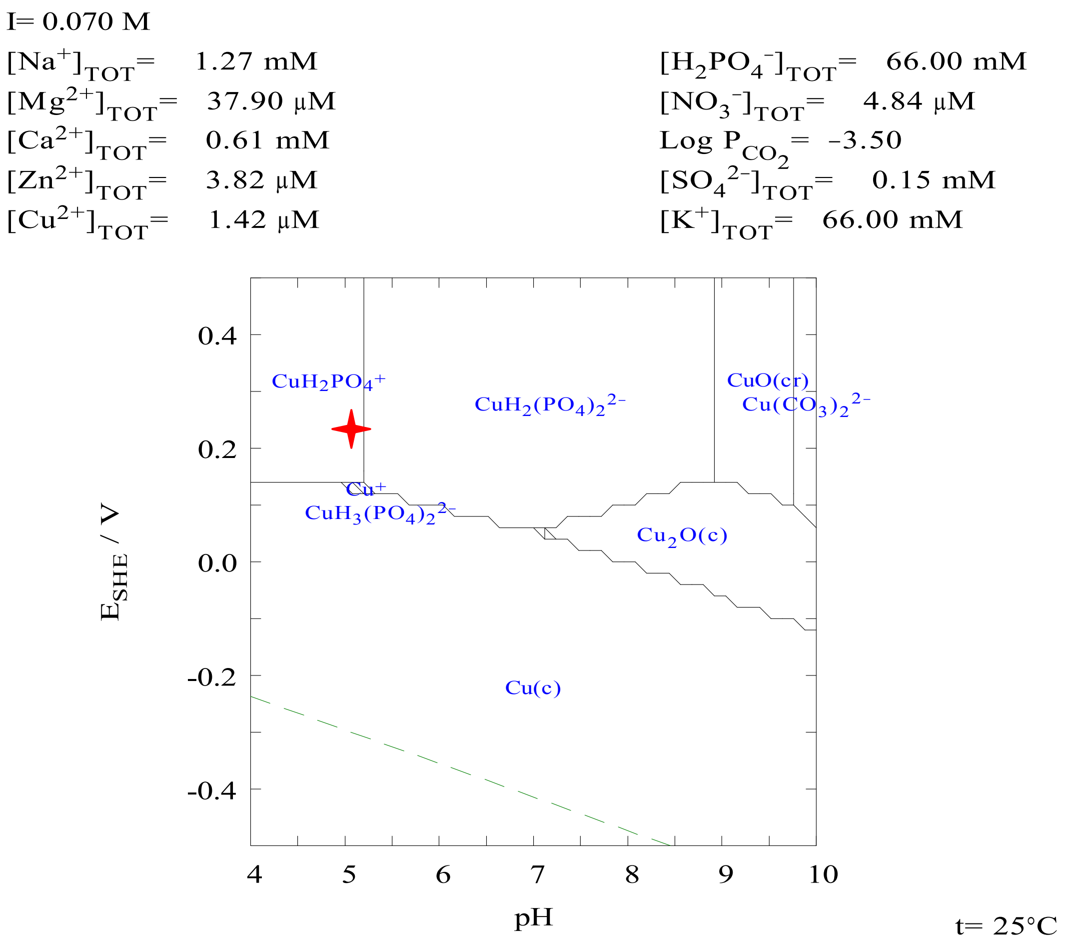


Figure C.143. Pourbaix diagram of copper for the container of PVC pipe section at time zero in pH 5 water. Study area.

PVC Pipe, pH 8 Water, Time Zero

$[Na^+]_{TOT}$ = 129.00 mM
$[Mg^{2+}]_{TOT}$ = 27.40 µM
$[Ca^{2+}]_{TOT}$ = 47.00 µM
$[Zn^{2+}]_{TOT}$ = 2.60 µM
$[Cu^{2+}]_{TOT}$ = 1.42 µM
E_H = 0.13 V

I= 0.196 M
$[HPO_4^{2-}]_{TOT}$ = 64.60 mM
$[NO_3^-]_{TOT}$ = 27.40 µM
Log P_{CO_2} = -3.50
$[SO_4^{2-}]_{TOT}$ = 0.17 mM
$[K^+]_{TOT}$ = 2.07 mM

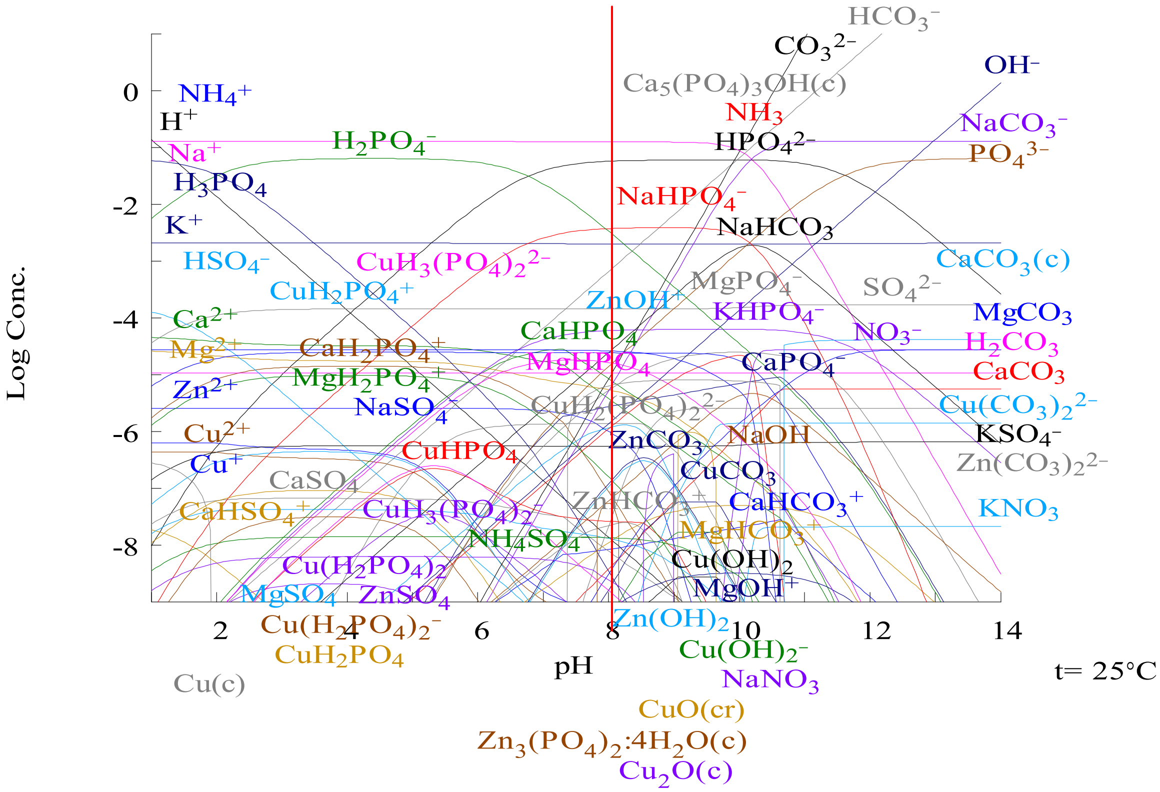


Figure C.144. Phase diagram for the container of PVC pipe section at time zero in pH 8 water.

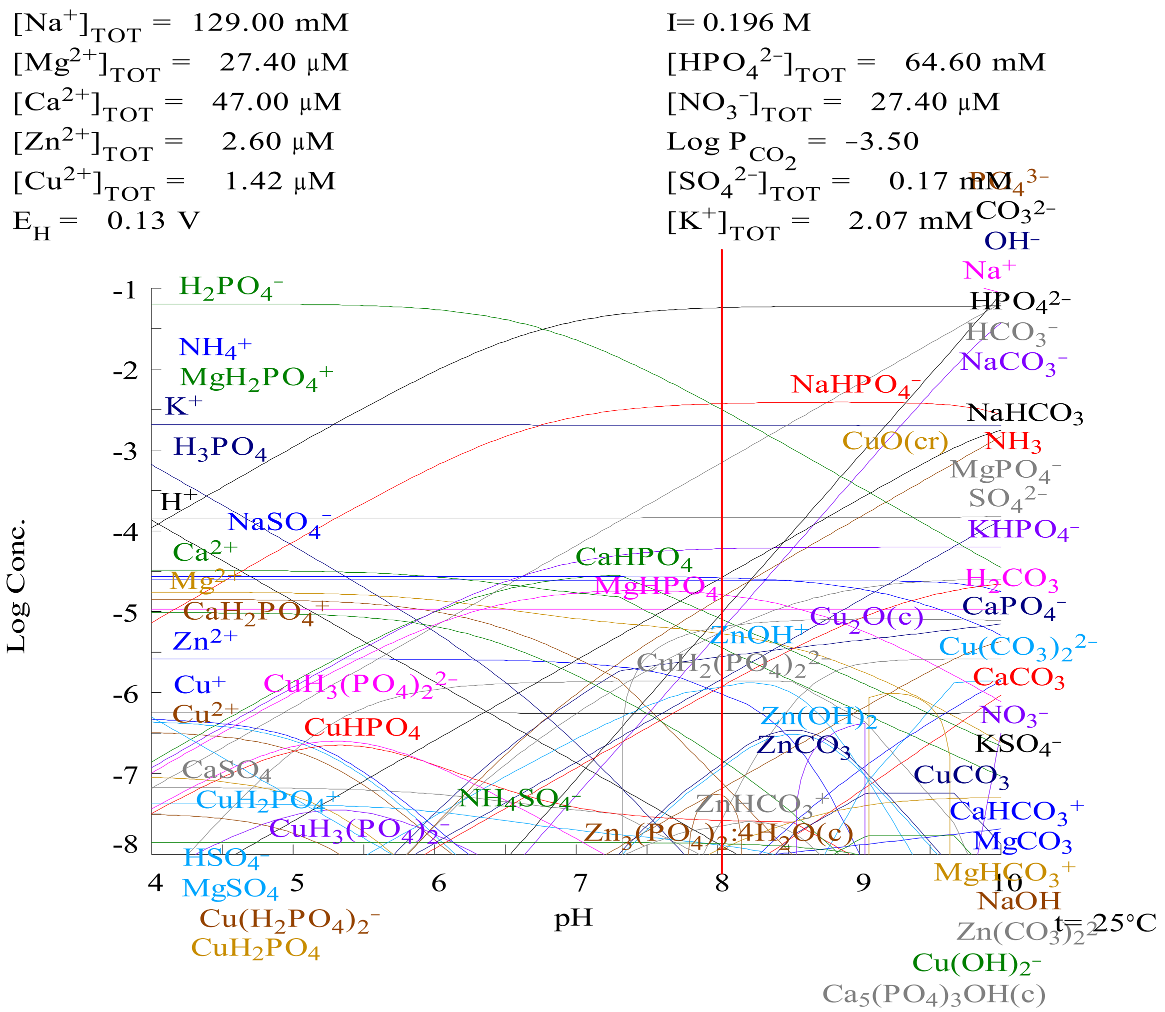


Figure C.145. Phase diagram for the container of PVC pipe section at time zero in pH 8 water. Study area.

Table C.36. The predominant species of zinc. Container for PVC pipe section, pH 8 water, time zero.

Component	Log Concentration (mol/L)	Concentration (mol/L)	Zn Concentration (mg/L as Zn)	Cumulative Percentage of Zn
$ZnOH^+$	-5.91	1.23E-06	8.02E-02	47.17
Zn^{2+}	-6.06	8.76E-07	5.73E-02	80.87
$ZnCO_3$	-6.81	1.55E-07	1.02E-02	86.84
$Zn(OH)_2$	-6.86	1.38E-07	9.03E-03	92.15
$Zn_3(PO_4)_2{:}4H_2O(c)$	-7.34	4.58E-08	8.99E-03	97.43
$Zn(CO_3)_2^{2-}$	-7.39	4.12E-08	2.69E-03	99.02
$ZnHCO_3^+$	-7.63	2.34E-08	1.53E-03	99.92

Table C.37. The predominant species of copper. Container for PVC pipe section, pH 8 water, time zero.

Component	Log Concentration (mol/L)	Concentration (mol/L)	Cu Concentration (mg/L as Cu)	Cumulative Percentage of Cu
$CuH_2(PO_4)_2^{2-}$	-5.86	1.39E-06	8.82E-02	97.72
$CuHPO_4$	-7.58	2.61E-08	1.66E-03	99.56
$CuCO_3$	-8.62	2.37E-09	1.51E-04	99.72
$CuH_3(PO_4)_2^{2-}$	-8.88	1.32E-09	8.36E-05	99.82
Cu^+	-9.14	7.25E-10	4.60E-05	99.87
$Cu(OH)_2^-$	-9.15	7.08E-10	4.50E-05	99.92

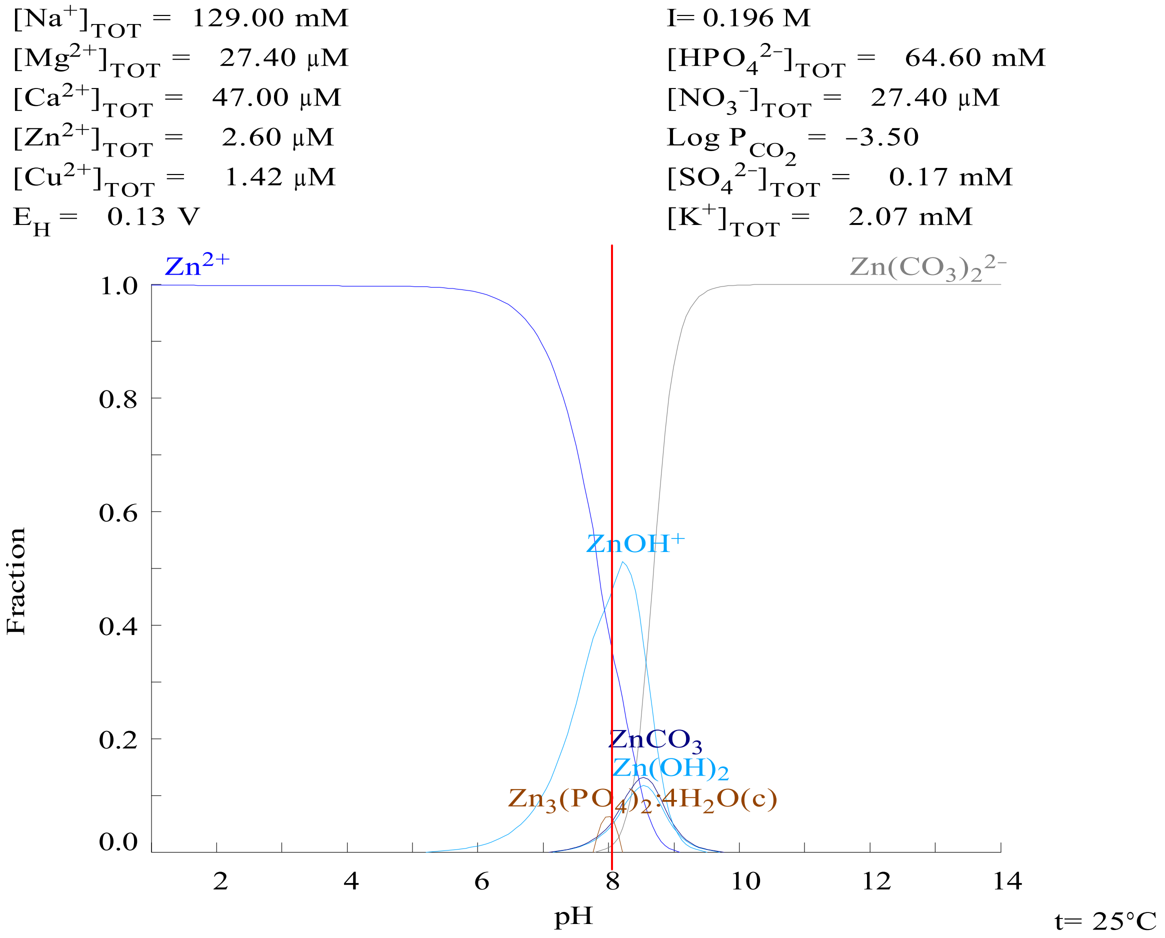


Figure C.146. Fraction diagram of zinc for the container of PVC pipe section at time zero in pH 8 water.

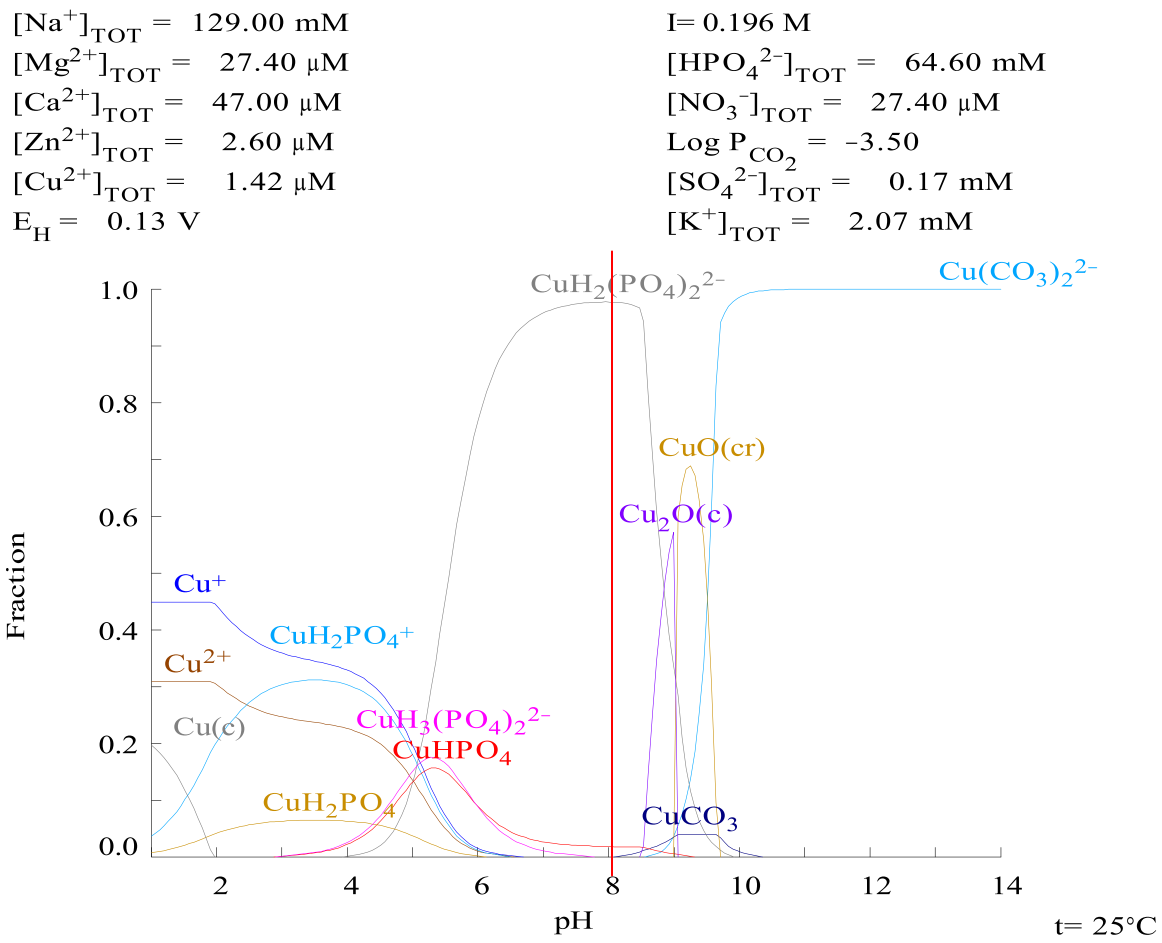


Figure C.147. Fraction diagram of copper for the container of PVC pipe section at time zero in pH 8 water.

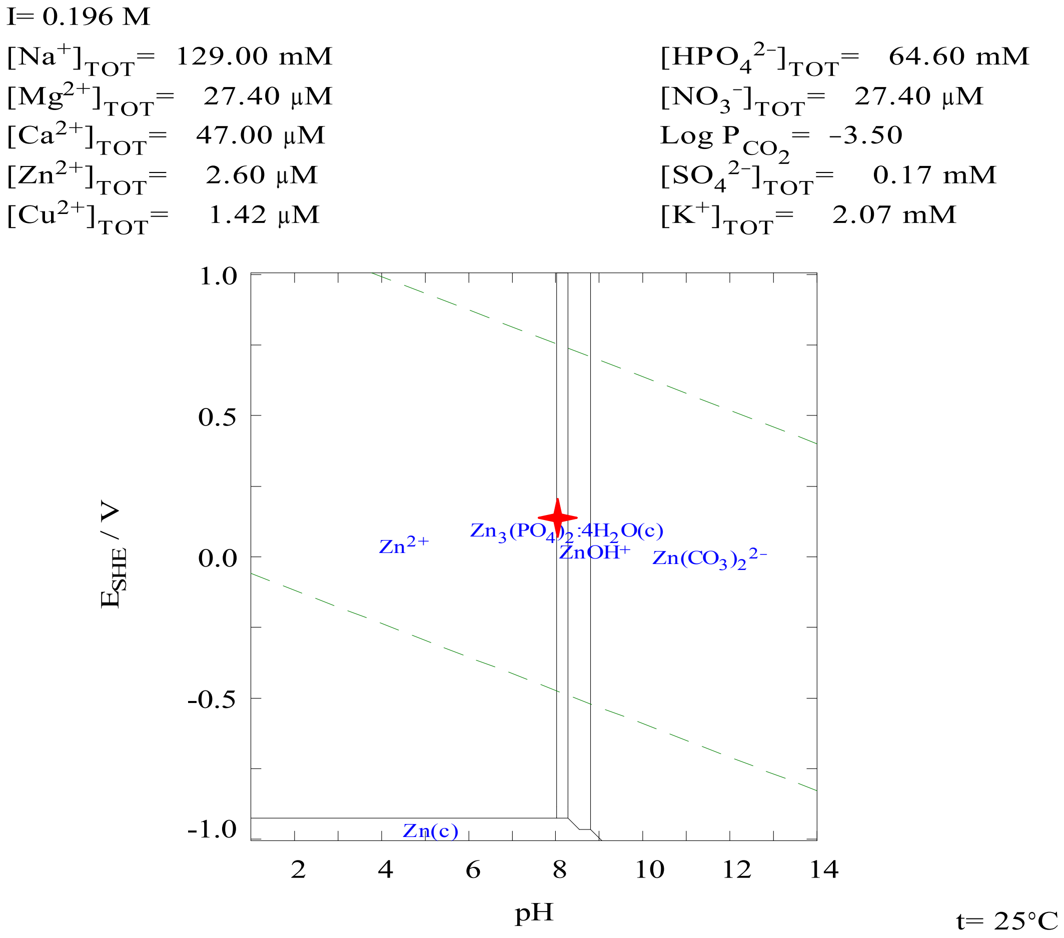


Figure C.148. Pourbaix diagram of zinc for the container of PVC pipe section at time zero in pH 8 water.

I= 0.196 M

$[\mathrm{Na^+}]_{\mathrm{TOT}}$= 129.00 mM

$[\mathrm{Mg^{2+}}]_{\mathrm{TOT}}$= 27.40 μM

$[\mathrm{Ca^{2+}}]_{\mathrm{TOT}}$= 47.00 μM

$[\mathrm{Zn^{2+}}]_{\mathrm{TOT}}$= 2.60 μM

$[\mathrm{Cu^{2+}}]_{\mathrm{TOT}}$= 1.42 μM

$[\mathrm{HPO_4^{2-}}]_{\mathrm{TOT}}$= 64.60 mM

$[\mathrm{NO_3^-}]_{\mathrm{TOT}}$= 27.40 μM

Log $P_{\mathrm{CO_2}}$= -3.50

$[\mathrm{SO_4^{2-}}]_{\mathrm{TOT}}$= 0.17 mM

$[\mathrm{K^+}]_{\mathrm{TOT}}$= 2.07 mM

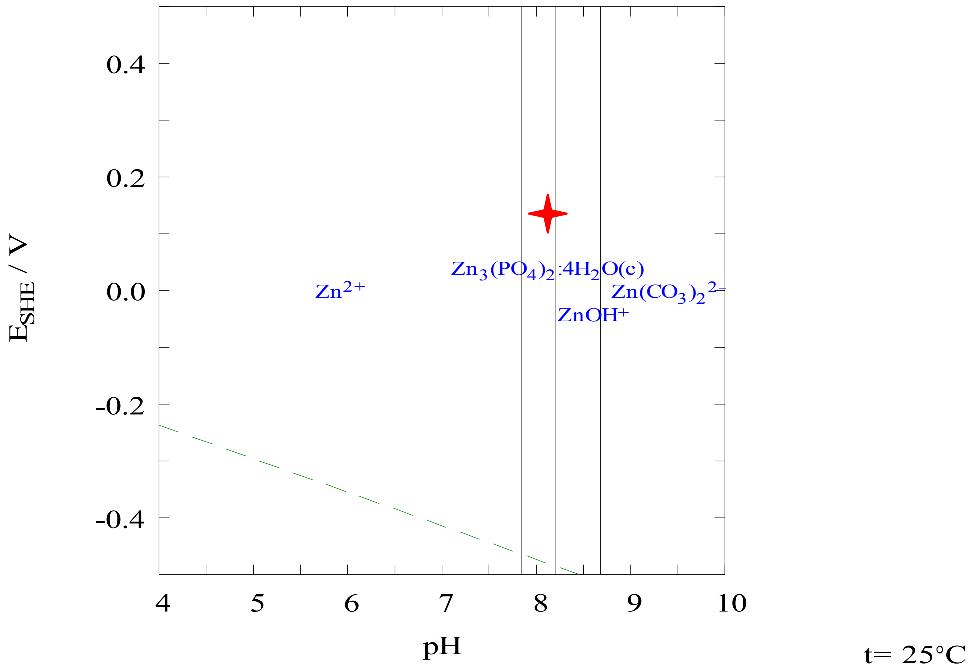


Figure C.149. Pourbaix diagram of zinc for the container of PVC pipe section at time zero in pH 8 water. Study area.

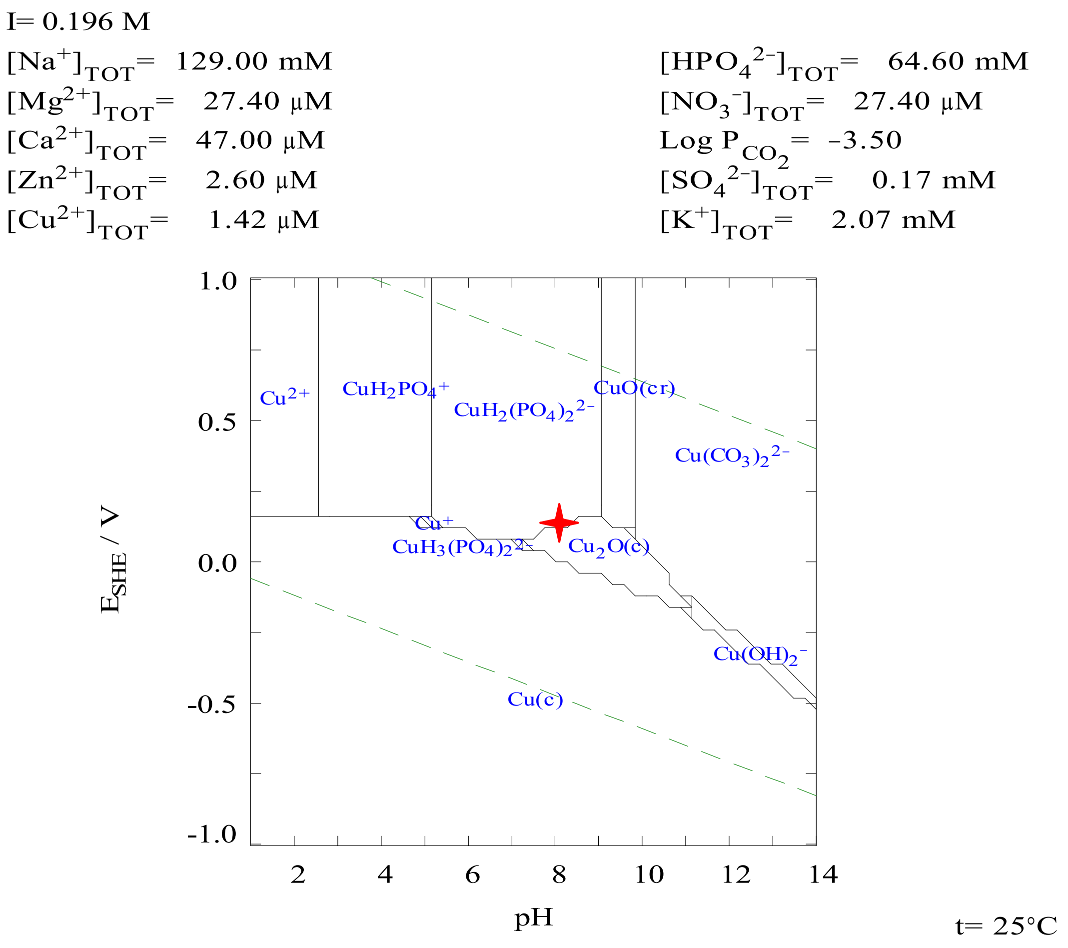


Figure C.150. Pourbaix diagram of copper for the container of PVC pipe section at time zero in pH 8 water.

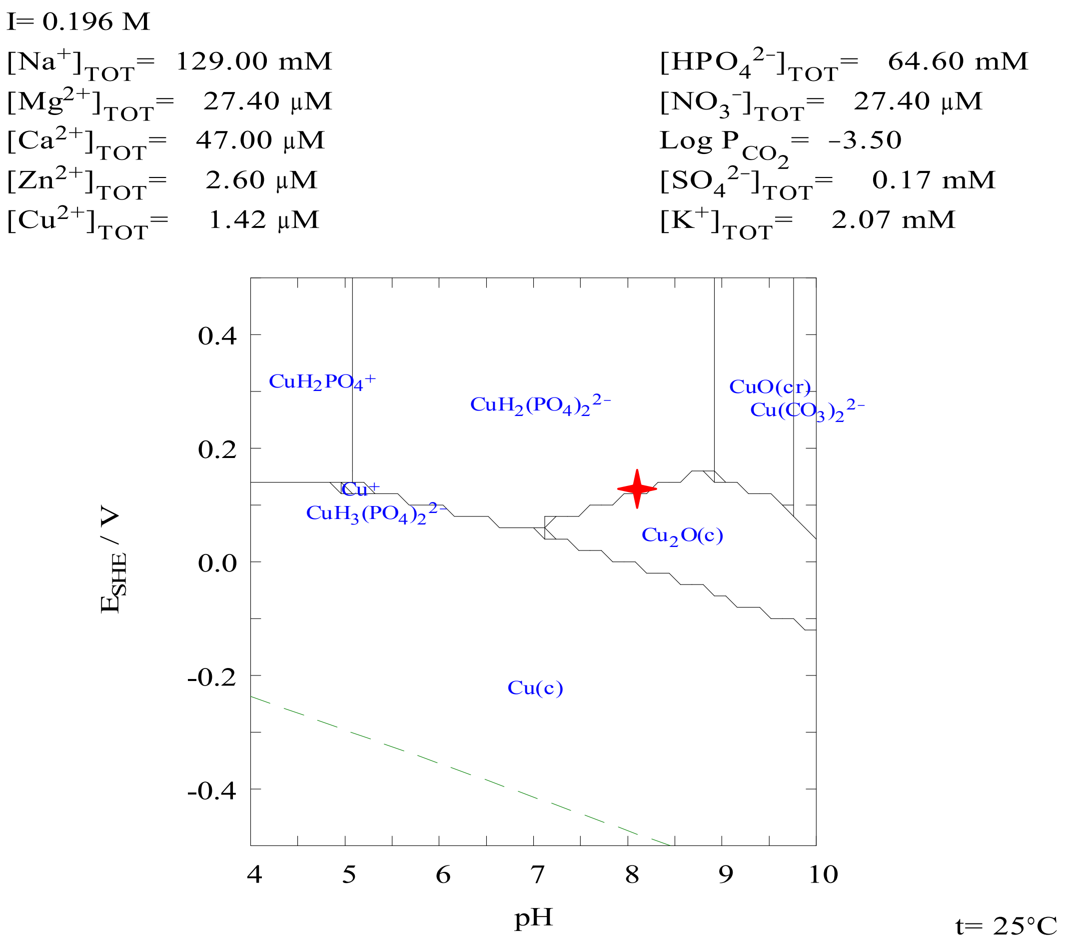


Figure C.151. Pourbaix diagram of copper for the container of PVC pipe section at time zero in pH 8 water. Study area.

HDPE Pipe, pH 8 Water, Time Zero

I= 0.196 M

$[Na^+]_{TOT}$ = 129.00 mM

$[Mg^{2+}]_{TOT}$ = 5.45 μM

$[Ca^{2+}]_{TOT}$ = 7.71 μM

$[Zn^{2+}]_{TOT}$ = 0.46 μM

E_H = 0.13 V

$[NO_3^-]_{TOT}$ = 22.60 μM

$[HPO_4^{2-}]_{TOT}$ = 64.60 mM

Log P_{CO_2} = -3.50

$[SO_4^{2-}]_{TOT}$ = 5.52 μM

$[K^+]_{TOT}$ = 2.07 mM

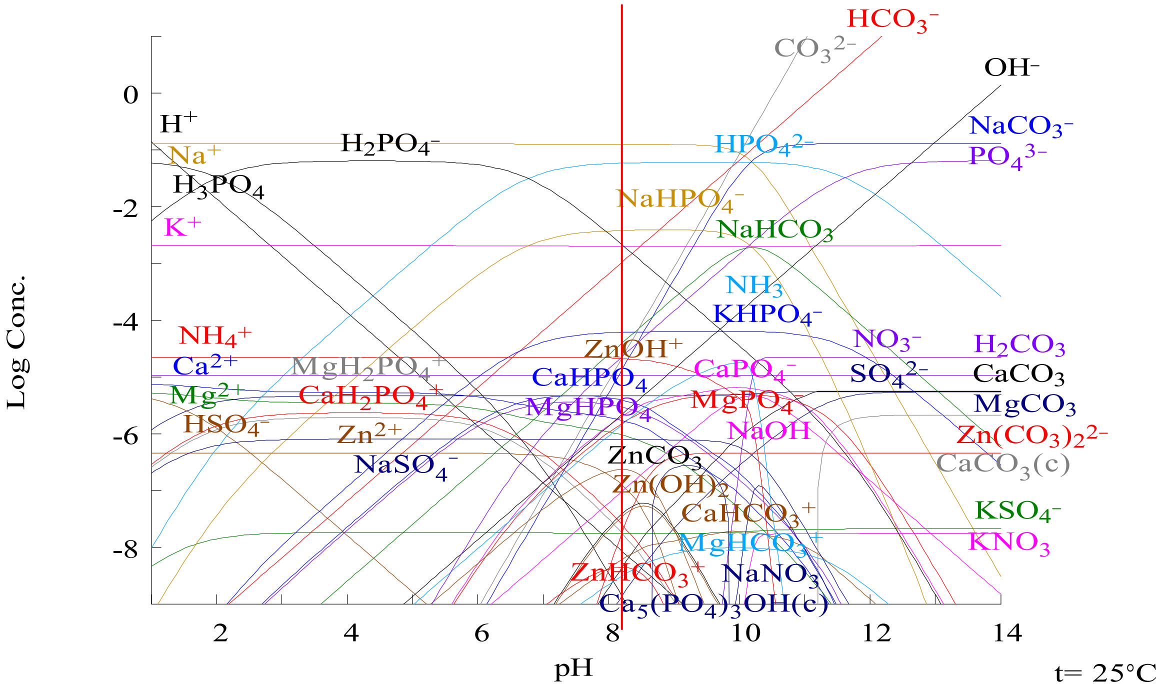


Figure C.152. Phase diagram for the container of HDPE pipe section at time zero in pH 8 water.

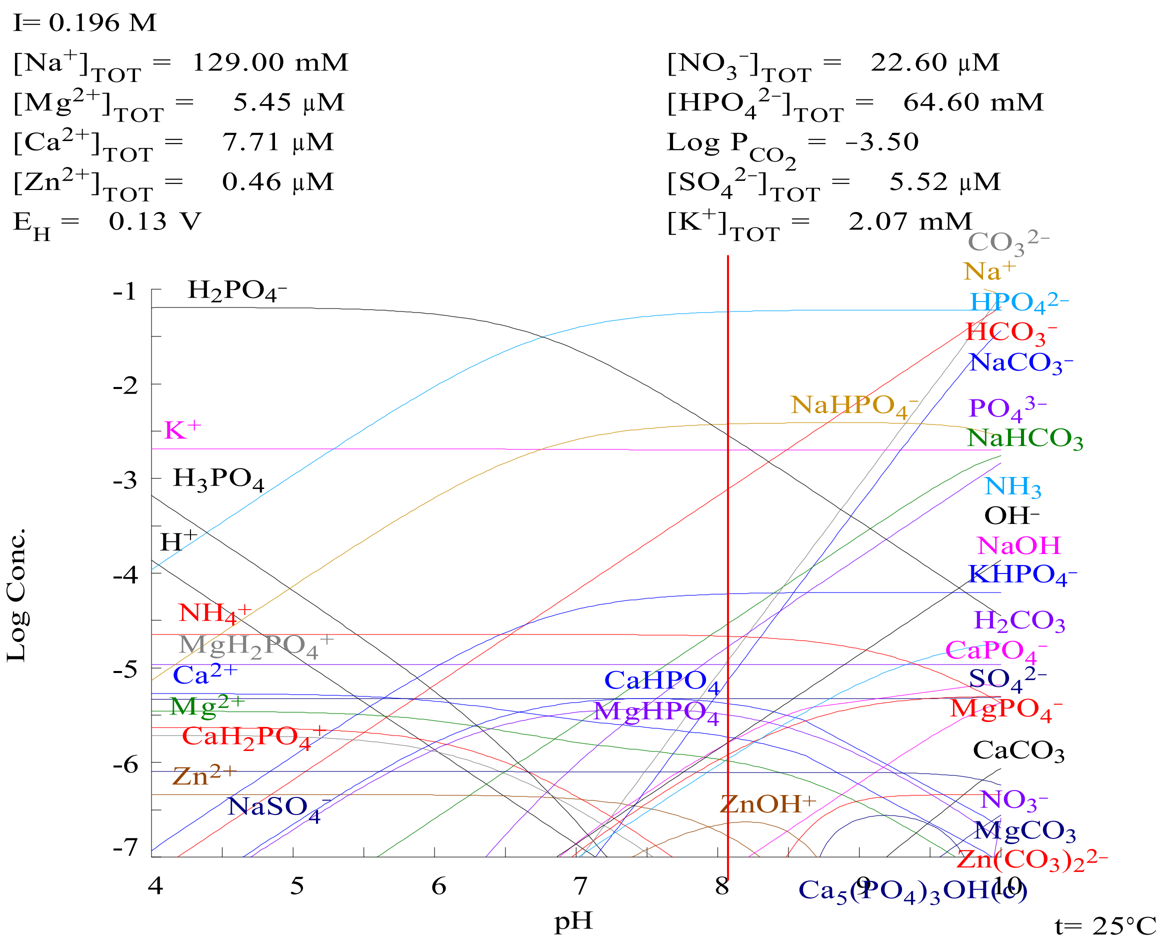


Figure C.153. Phase diagram for the container of HDPE pipe section at time zero in pH 8 water. Study area.

Table C.38. The predominant species of zinc. Container for HDPE pipe section, pH 8 water, time zero.

Component	Log Concentration (mol/L)	Concentration (mol/L)	Zn Concentration (mg/L as Zn)	Cumulative Percentage of Zn
$ZnOH^+$	-6.63	2.34E-07	1.53E-02	50.90
Zn^{2+}	-6.84	1.44E-07	9.40E-03	82.21
$ZnCO_3$	-7.46	3.43E-08	2.25E-03	89.70
$Zn(OH)_2$	-7.52	3.05E-08	2.00E-03	96.35
$Zn(CO_3)_2^{2-}$	-7.91	1.23E-08	8.04E-04	99.03
$ZnHCO_3^+$	-8.35	4.45E-09	2.91E-04	99.996

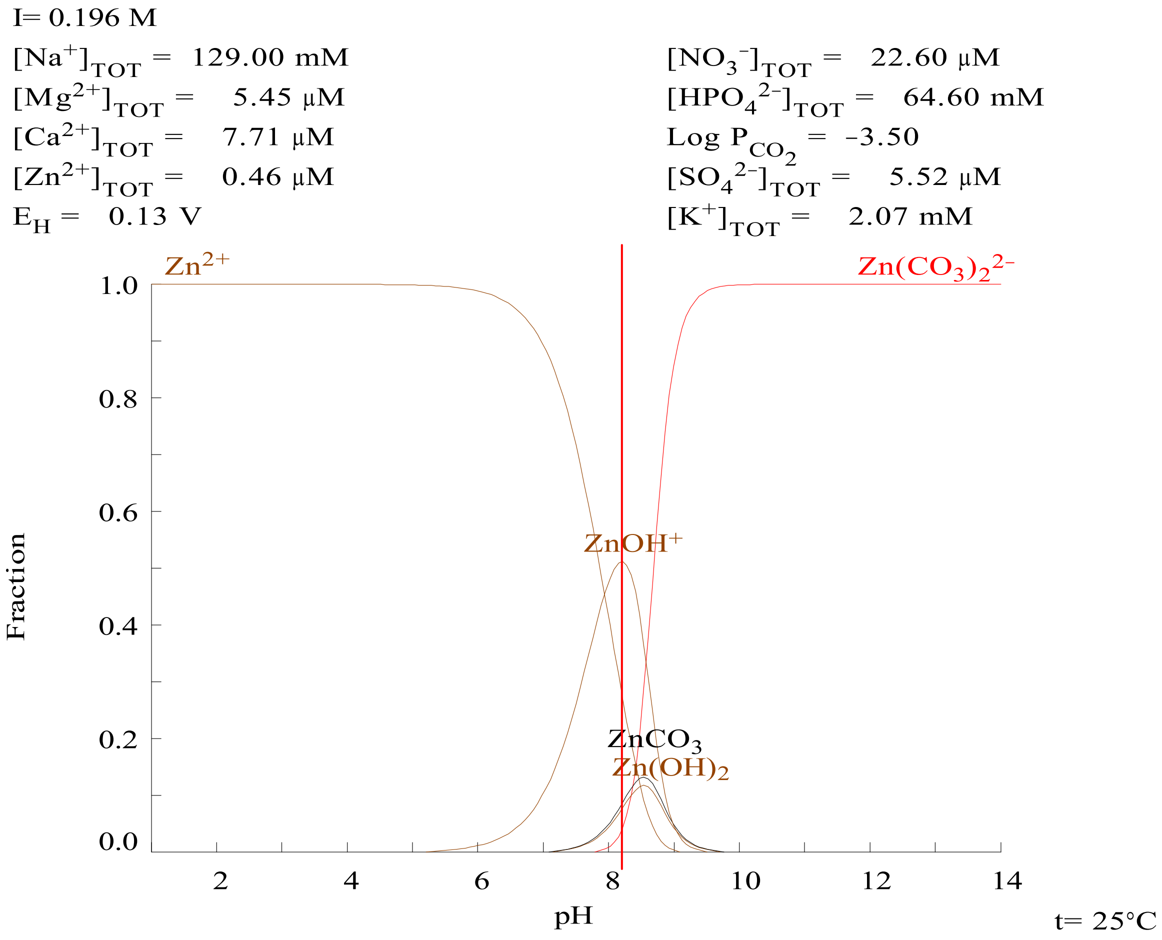


Figure C.154. Fraction diagram of zinc for the container of HDPE pipe section at time zero in pH 8 water.

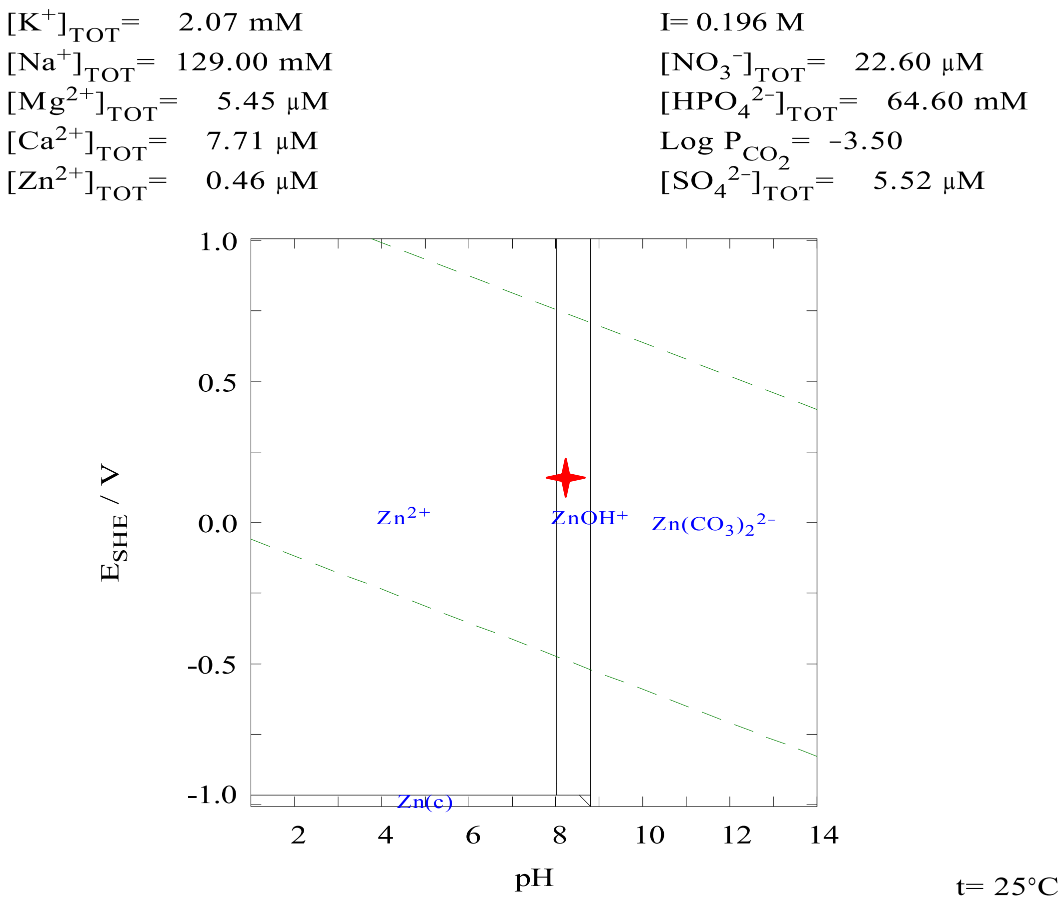


Figure C.155. Pourbaix diagram of zinc for the container of HDPE pipe section at time zero in pH 8 water.

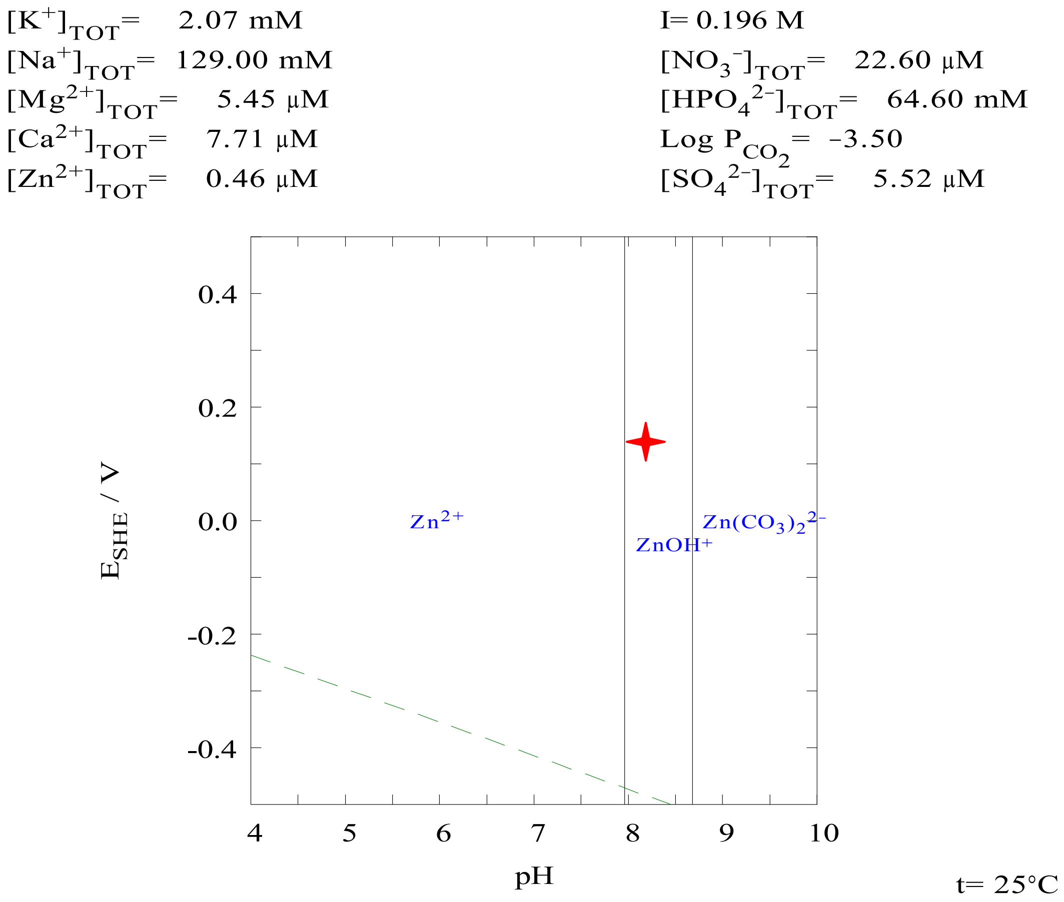


Figure C.156. Pourbaix diagram of zinc for the container of HDPE pipe section at time zero in pH 8 water. Study area.

Steel Pipe, pH 5 Water, After One Day of Exposure

$[Na^+]_{TOT}$ = 1.27 mM
$[Mg^{2+}]_{TOT}$ = 16.10 μM
$[Ca^{2+}]_{TOT}$ = 10.50 μM
$[Zn^{2+}]_{TOT}$ = 0.16 mM
E_H = 0.17 V

I= 0.068 M
$[H_2PO_4^-]_{TOT}$ = 66.00 mM
Log P_{CO_2} = -3.50
$[SO_4^{2-}]_{TOT}$ = 53.20 μM
$[K^+]_{TOT}$ = 66.00 mM

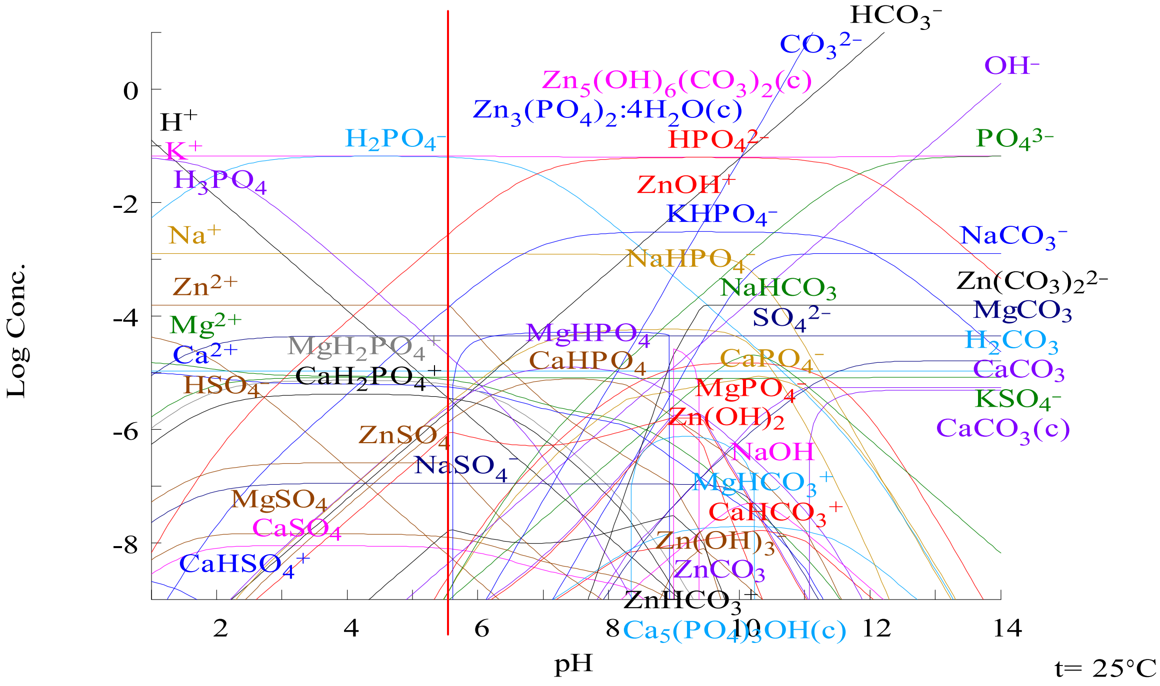


Figure C.157. Phase diagram for steel pipe section immersed into pH 5 water after one day of exposure.

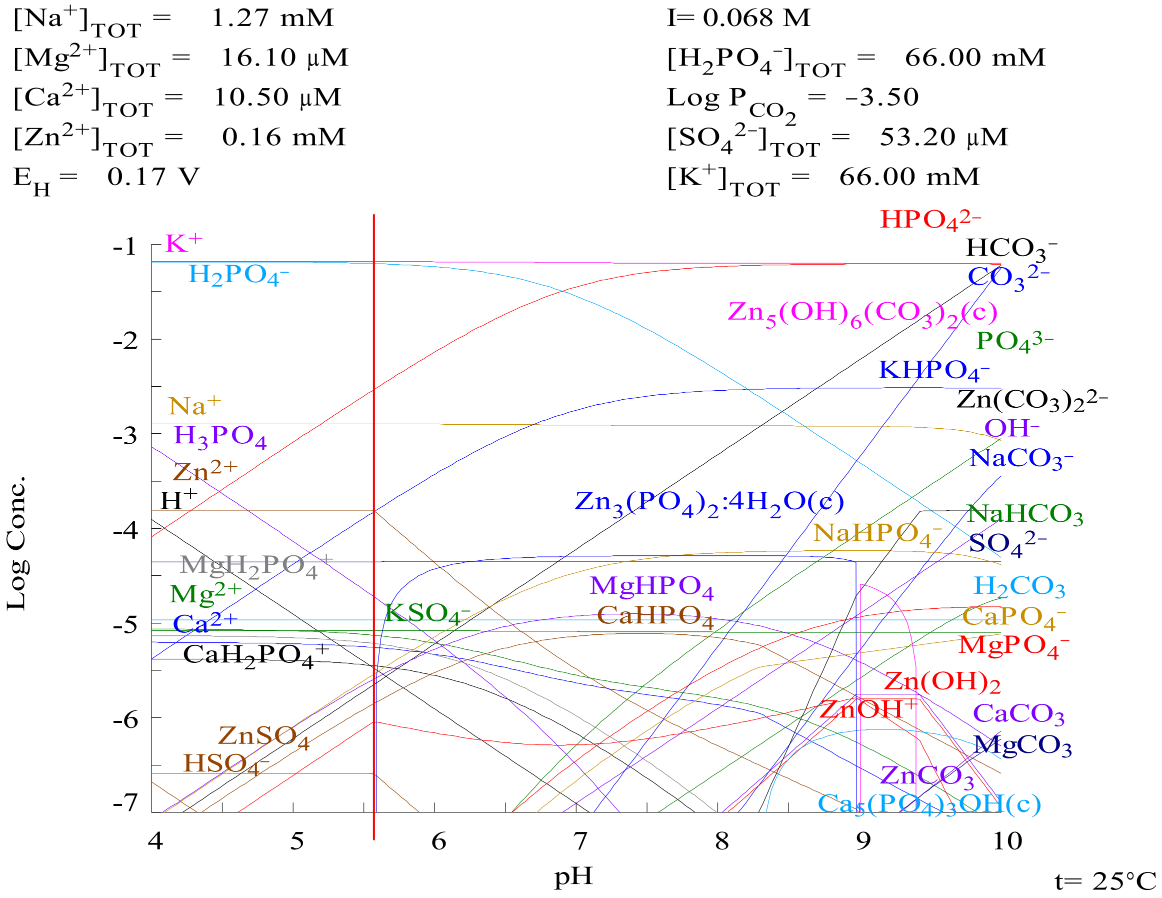


Figure C.158. Phase diagram for steel pipe section immersed into pH 5 water after one day of exposure. Study area.

Table C.39. The predominant species of zinc. Steel pipe section, pH 5 water, one day exposure.

Component	Log Concentration (mol/L)	Concentration (mol/L)	Zn Concentration (mg/L as Zn)	Cumulative Percentage of Zn
Zn^{2+}	-3.81	1.55E-04	10.13	99.27
$ZnOH^+$	-6.06	8.67E-07	5.67E-02	99.82
$ZnSO_4$	-6.59	2.58E-07	1.69E-02	99.99

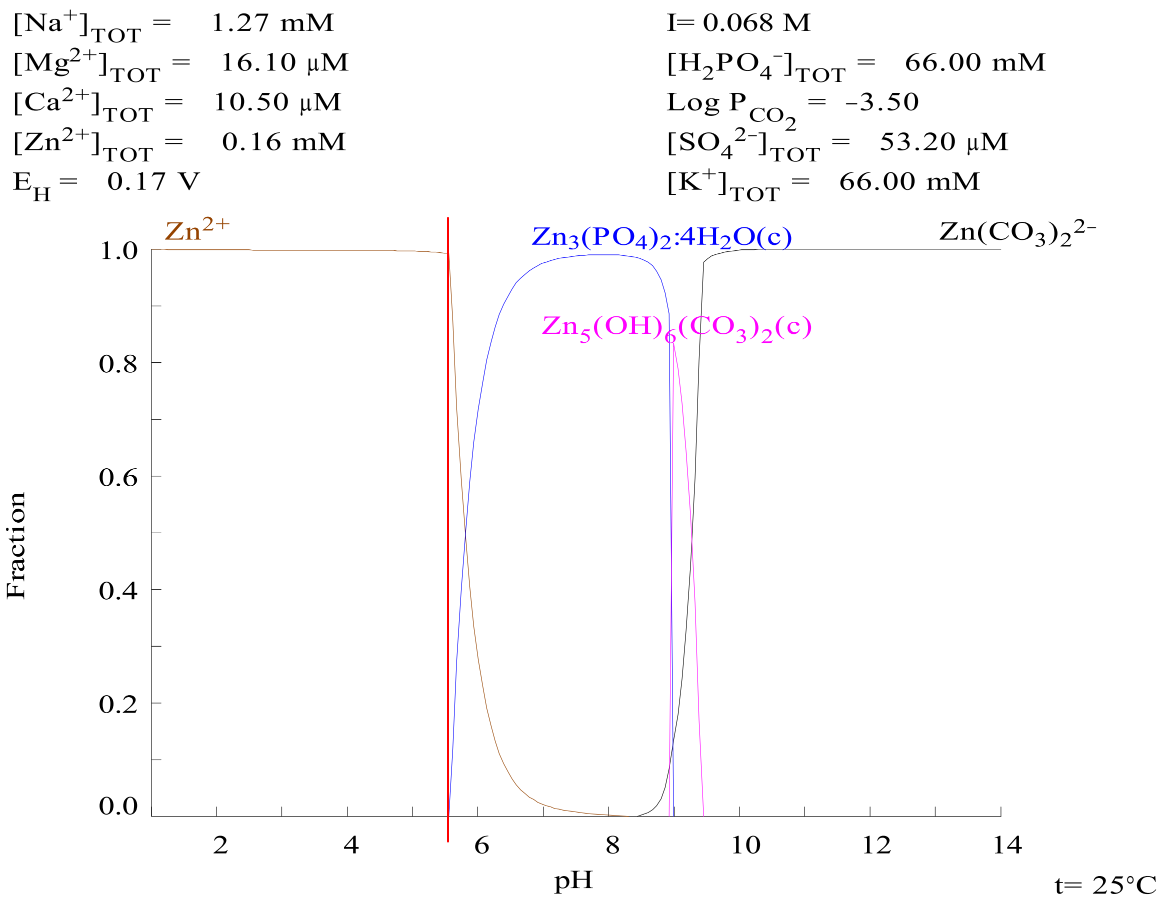


Figure C.159. Fraction diagram of zinc for steel pipe section immersed into pH 5 water after one day of exposure.

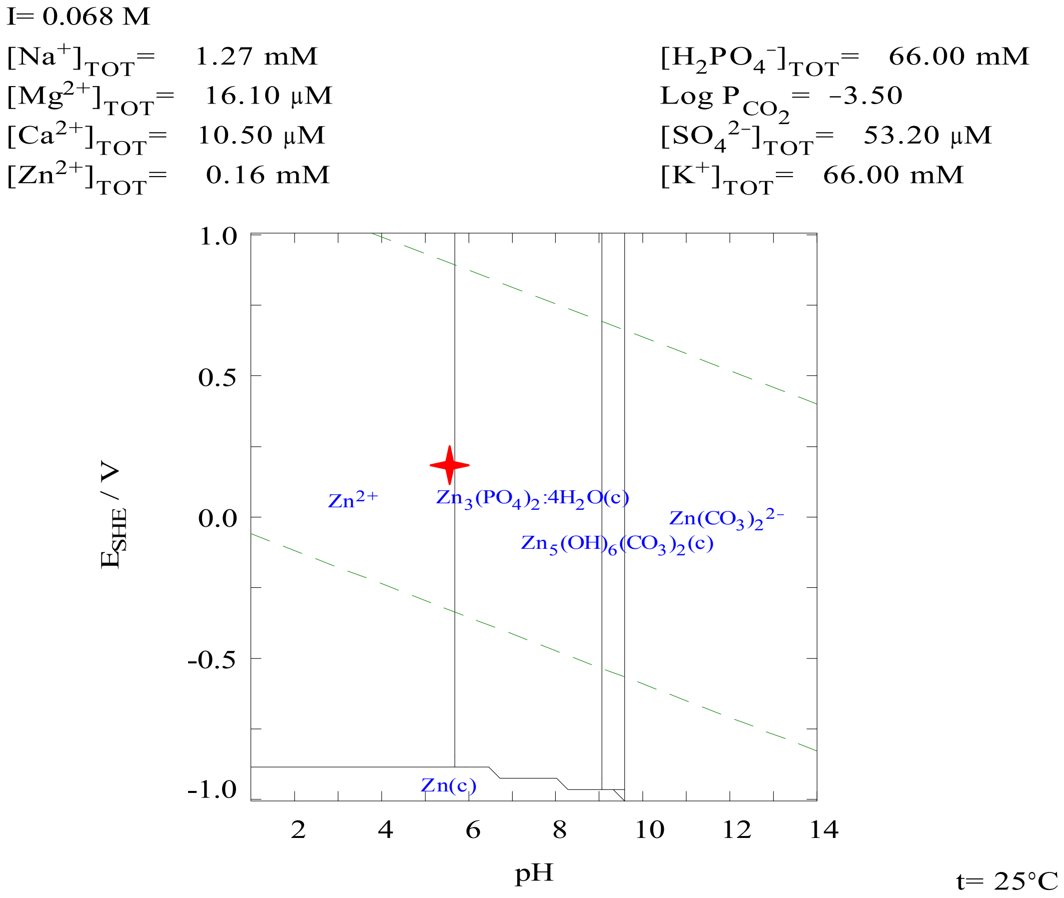


Figure C.160. Pourbaix diagram of zinc for steel pipe section immersed into pH 5 water after one day of exposure.

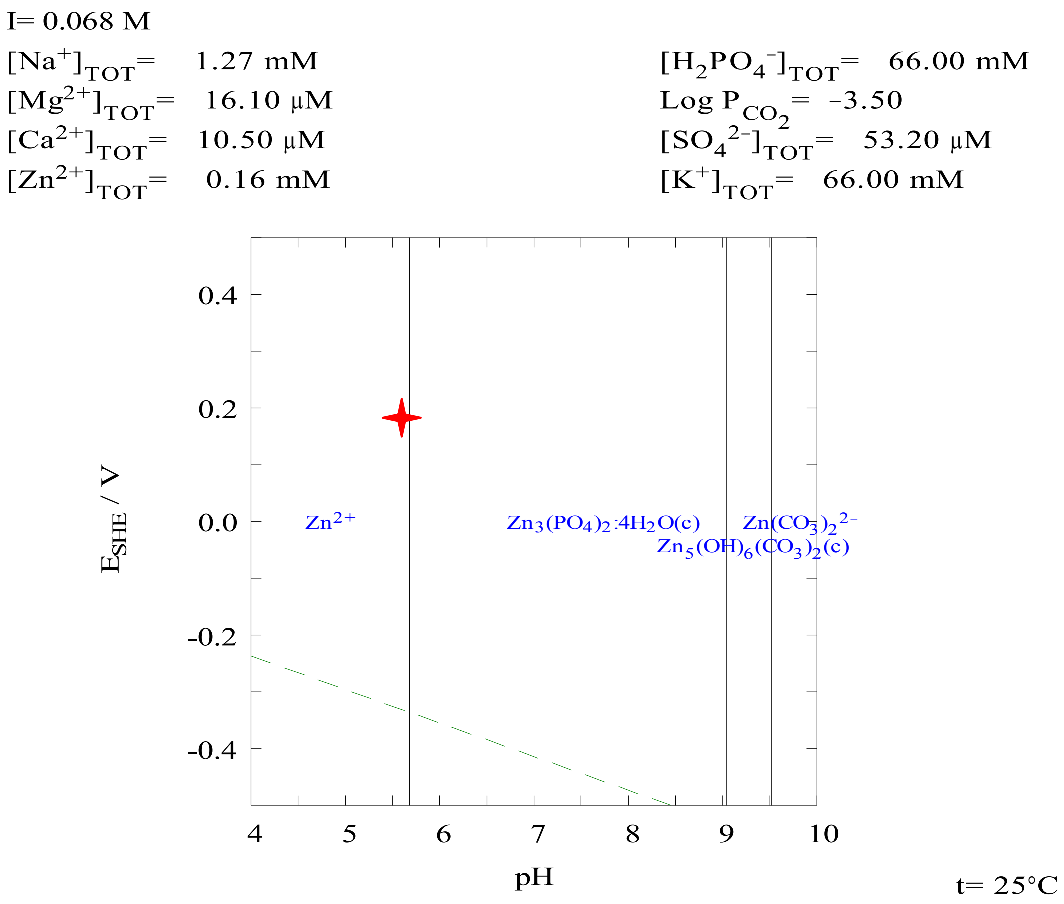


Figure C.161. Pourbaix diagram of zinc for steel pipe section immersed into pH 5 water after one day of exposure. Study area.

Steel Pipe, pH 8 Water, After One Day of Exposure

I= 0.196 M

$[Na^+]_{TOT}$ = 129.00 mM

$[Mg^{2+}]_{TOT}$ = 5.93 μM

$[Ca^{2+}]_{TOT}$ = 3.70 μM

$[Zn^{2+}]_{TOT}$ = 15.50 μM

E_H = 0.11 V

$[HPO_4^{2-}]_{TOT}$ = 64.60 mM

$[NO_3^-]_{TOT}$ = 25.80 μM

Log P_{CO_2} = -3.50

$[SO_4^{2-}]_{TOT}$ = 23.70 μM

$[K^+]_{TOT}$ = 2.07 mM

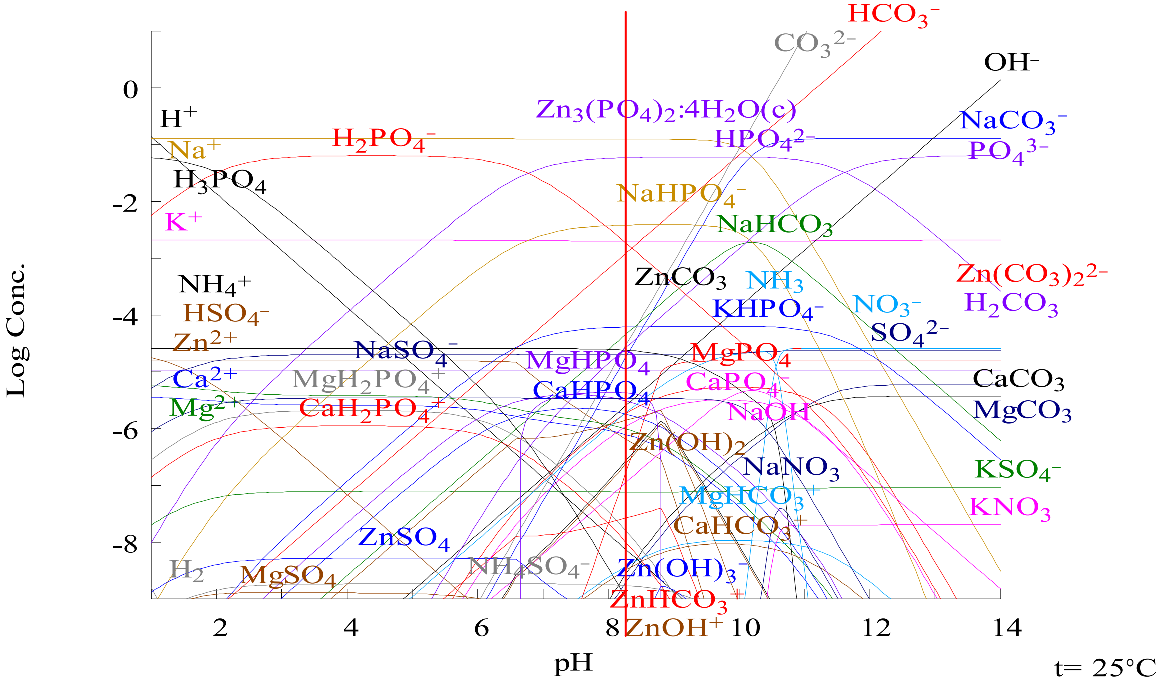


Figure C.162. Phase diagram for steel pipe section immersed into pH 8 water after one day of exposure.

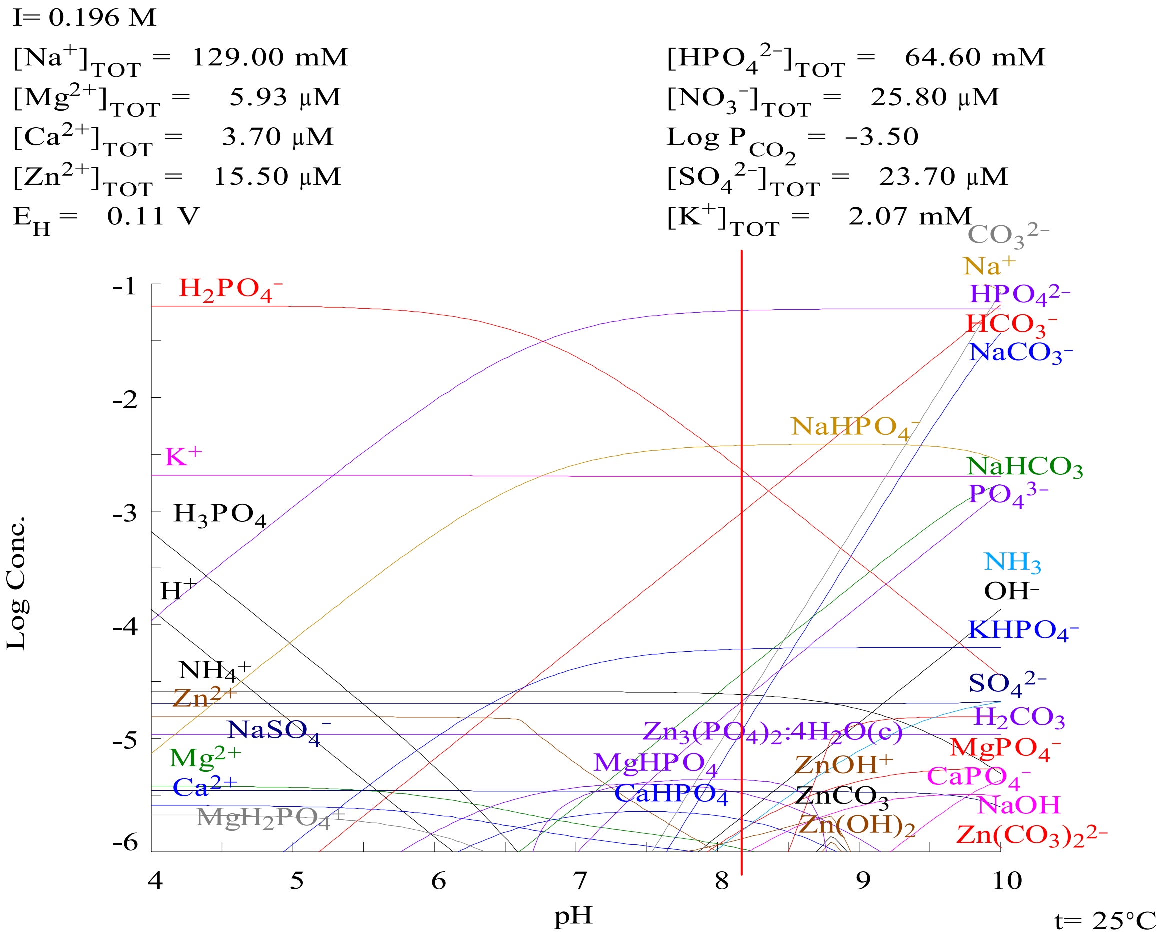


Figure C.163. Phase diagram for steel pipe section immersed into pH 8 water after one day of exposure. Study area.

Table C.40. The predominant species of zinc. Steel pipe section, pH 8 water, one day exposure.

Component	Log Concentration (mol/L)	Concentration (mol/L)	Zn Concentration (mg/L as Zn)	Cumulative Percentage of Zn
$Zn_3(PO_4)_2$:$4H_2O$(c)	-5.37	4.29E-06	8.42E-01	83.05
$ZnOH^+$	-5.87	1.34E-06	8.79E-02	91.73
Zn^{2+}	-6.15	7.12E-07	4.66E-02	96.32
$ZnCO_3$	-6.64	2.30E-07	1.50E-02	97.80
$Zn(OH)_2$	-6.69	2.04E-07	1.33E-02	99.12
$Zn(CO_3)_2^{2-}$	-6.96	1.11E-07	7.25E-03	99.83
$ZnHCO_3^+$	-7.59	2.56E-08	1.68E-03	99.998

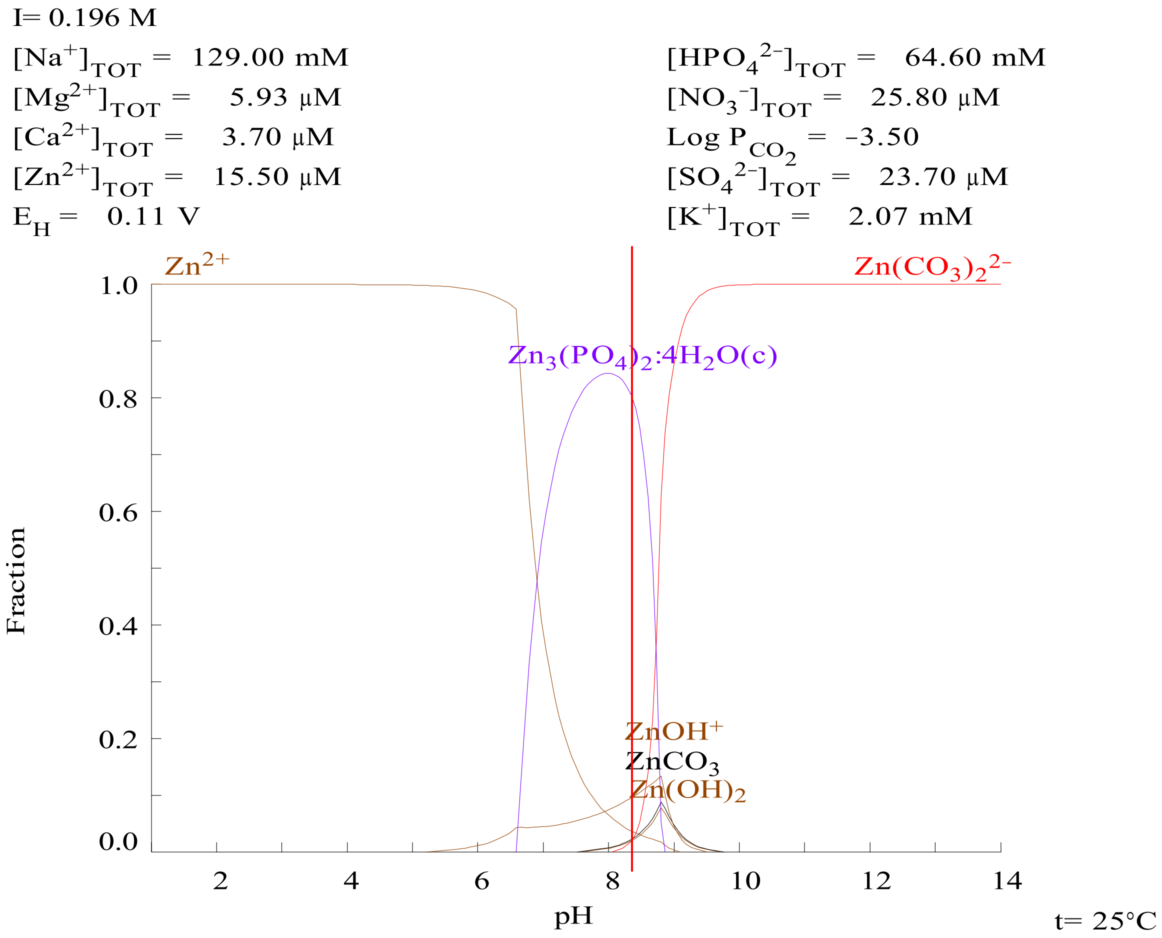


Figure C.164. Fraction diagram of zinc for steel pipe section immersed into pH 8 water after one day of exposure.

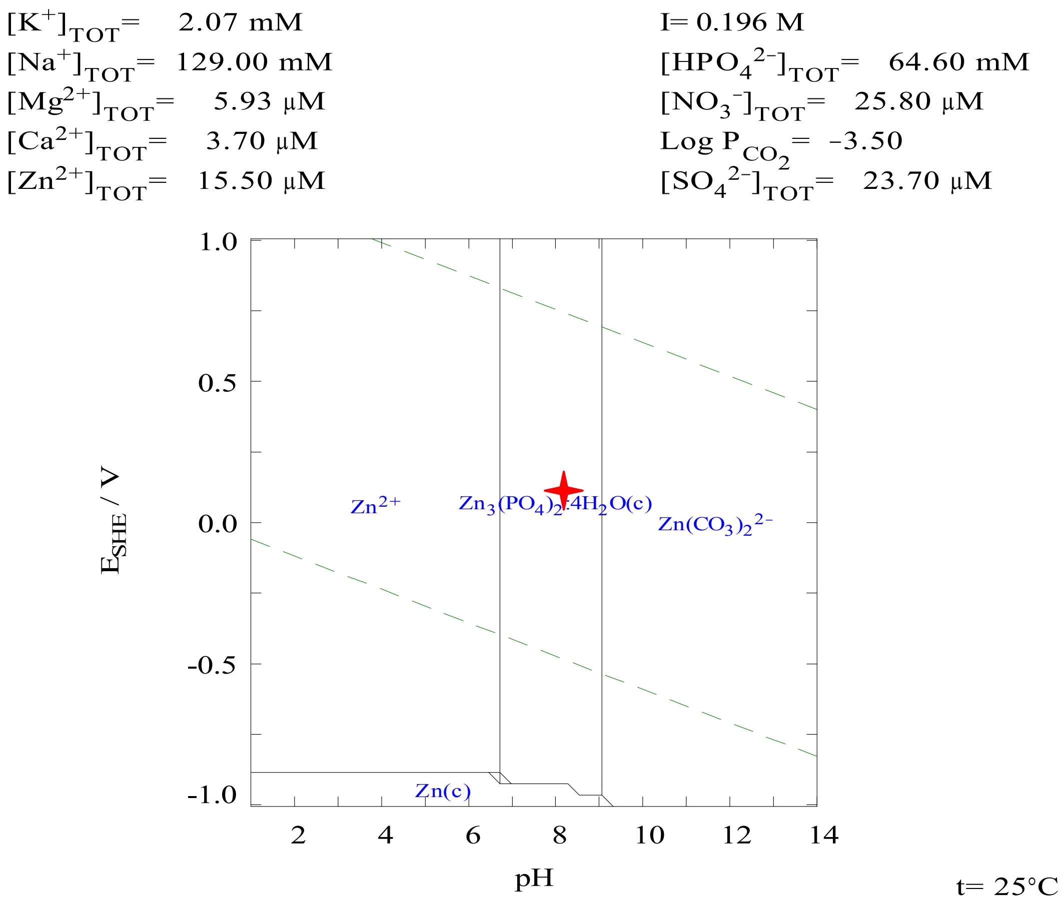


Figure C.165. Pourbaix diagram of zinc for steel pipe section immersed into pH 8 water after one day of exposure.

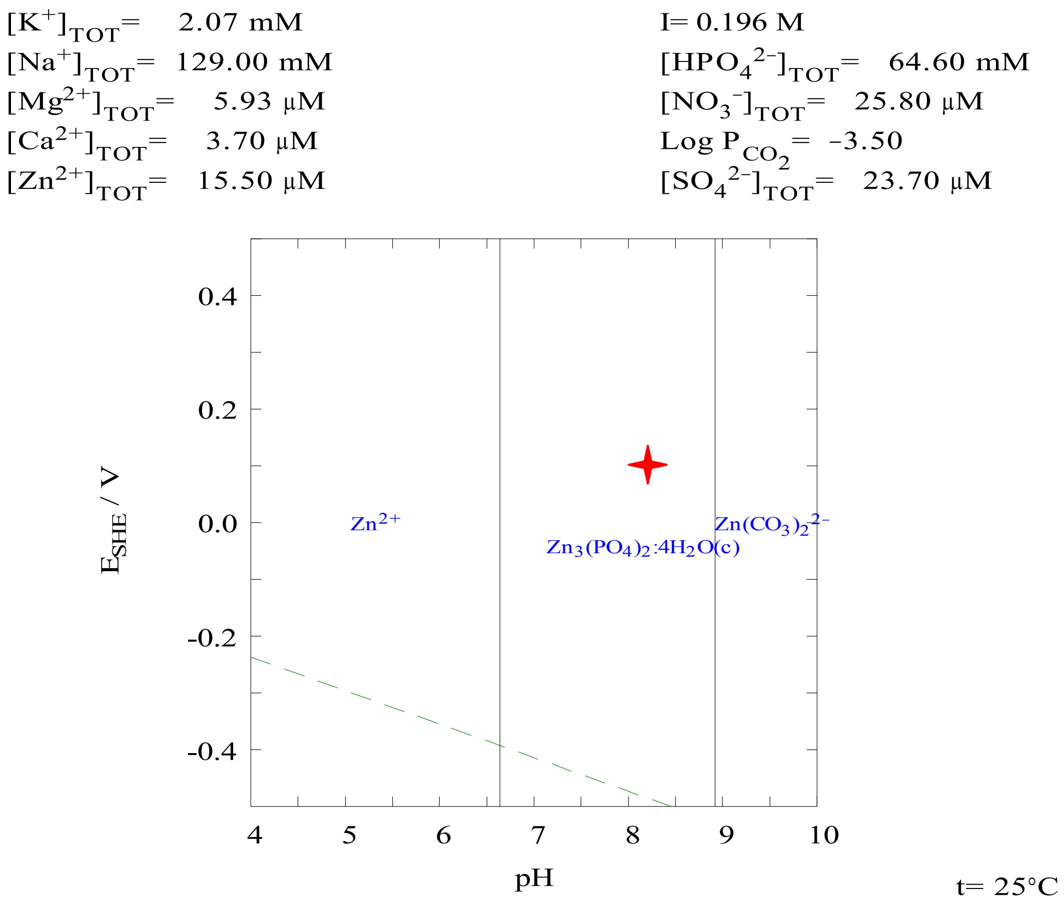


Figure C.166. Pourbaix diagram of zinc for steel pipe section immersed into pH 8 water after one day of exposure.

Steel Gutter, pH 5 Water, After One Day of Exposure

$[Na^+]_{TOT}$ = 1.27 mM
$[Mg^{2+}]_{TOT}$ = 4.39 µM
$[Ca^{2+}]_{TOT}$ = 10.50 µM
$[Zn^{2+}]_{TOT}$ = 0.22 mM
E_H = 0.19 V

I= 0.068 M
$[H_2PO_4^-]_{TOT}$ = 66.00 mM
Log P_{CO_2} = -3.50
$[SO_4^{2-}]_{TOT}$ = 21.00 µM
$[K^+]_{TOT}$ = 66.00 mM

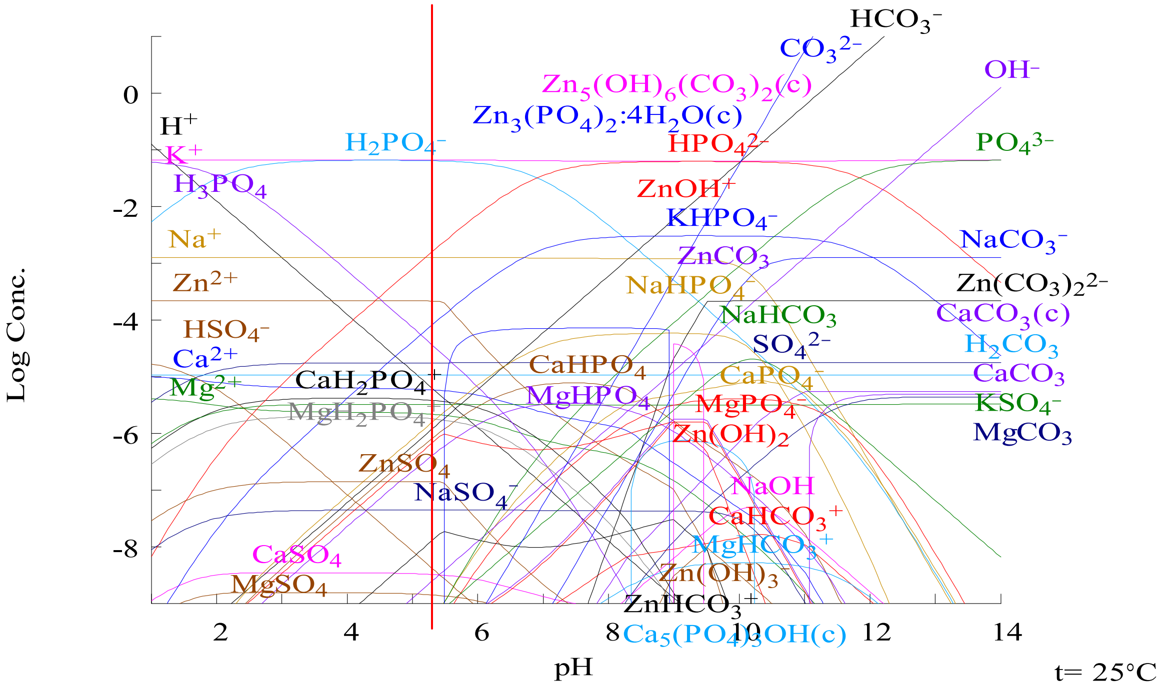


Figure C.167. Phase diagram for steel gutter section immersed into pH 5 water after one day of exposure.

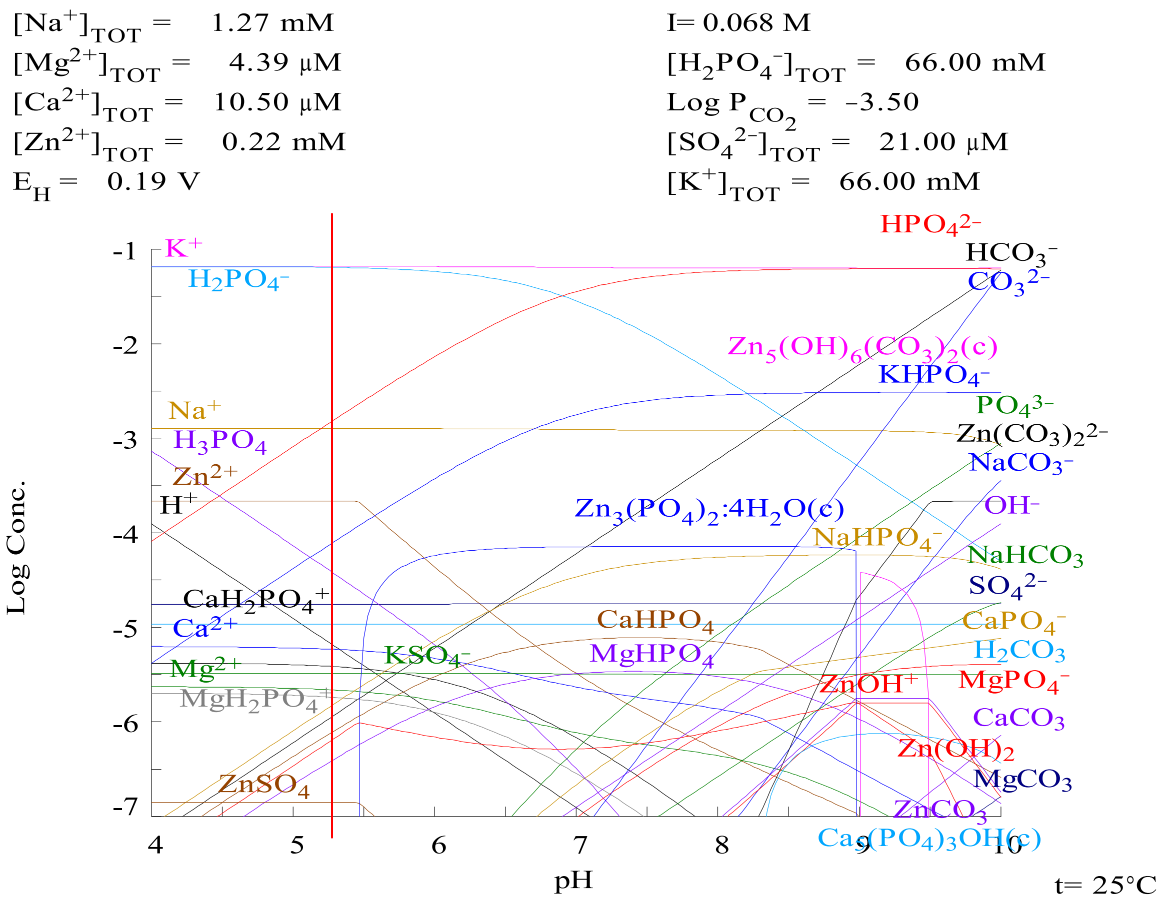


Figure C.168. Phase diagram for steel gutter section immersed into pH 5 water after one day of exposure. Study area.

Table C.41. The predominant species of zinc. Steel gutter section, pH 5 water, one day exposure.

Component	Log Concentration (mol/L)	Concentration (mol/L)	Zn Concentration (mg/L as Zn)	Cumulative Percentage of Zn
Zn $^{2+}$	-3.67	2.16E-04	14.14	99.62
ZnOH$^+$	-6.18	6.65E-07	4.35E-02	99.93

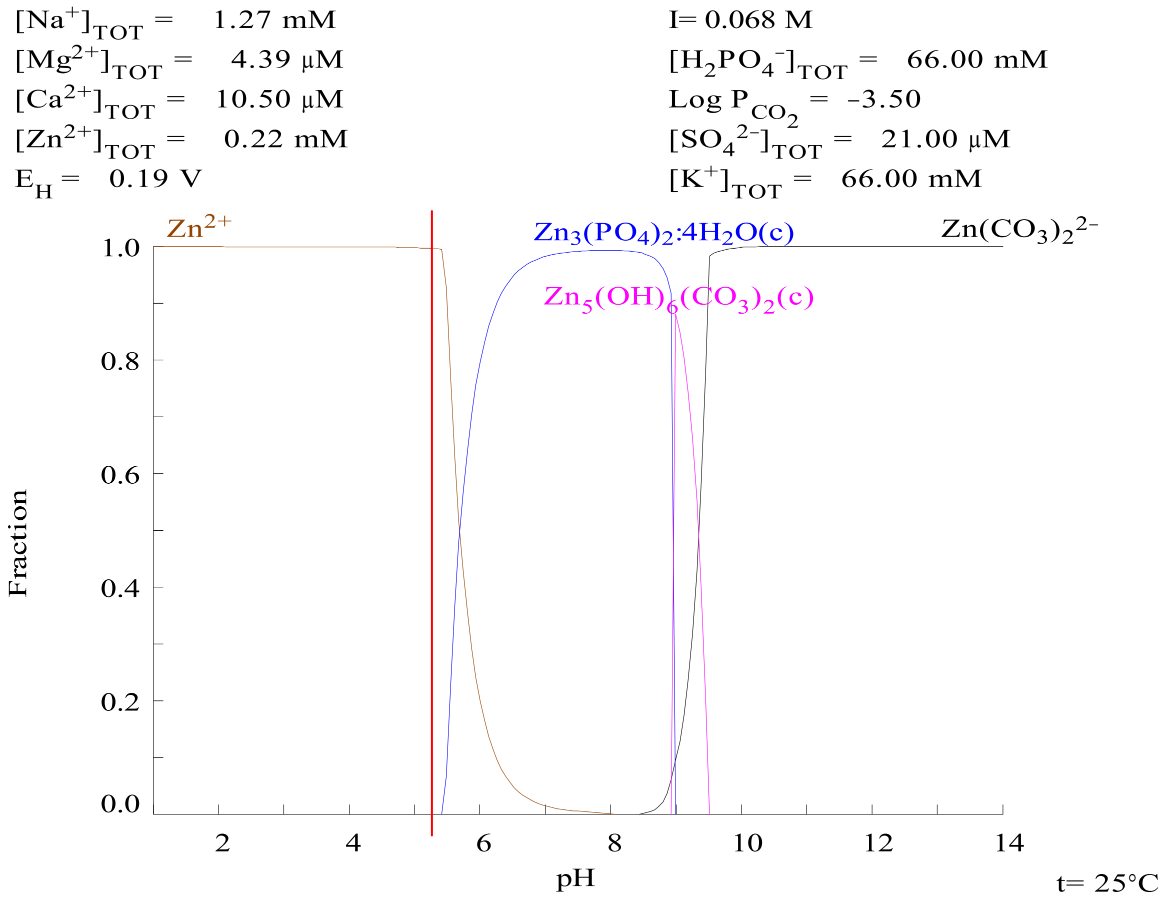


Figure C.169. Fraction diagram of zinc for steel gutter section immersed into pH 5 water after one day of exposure.

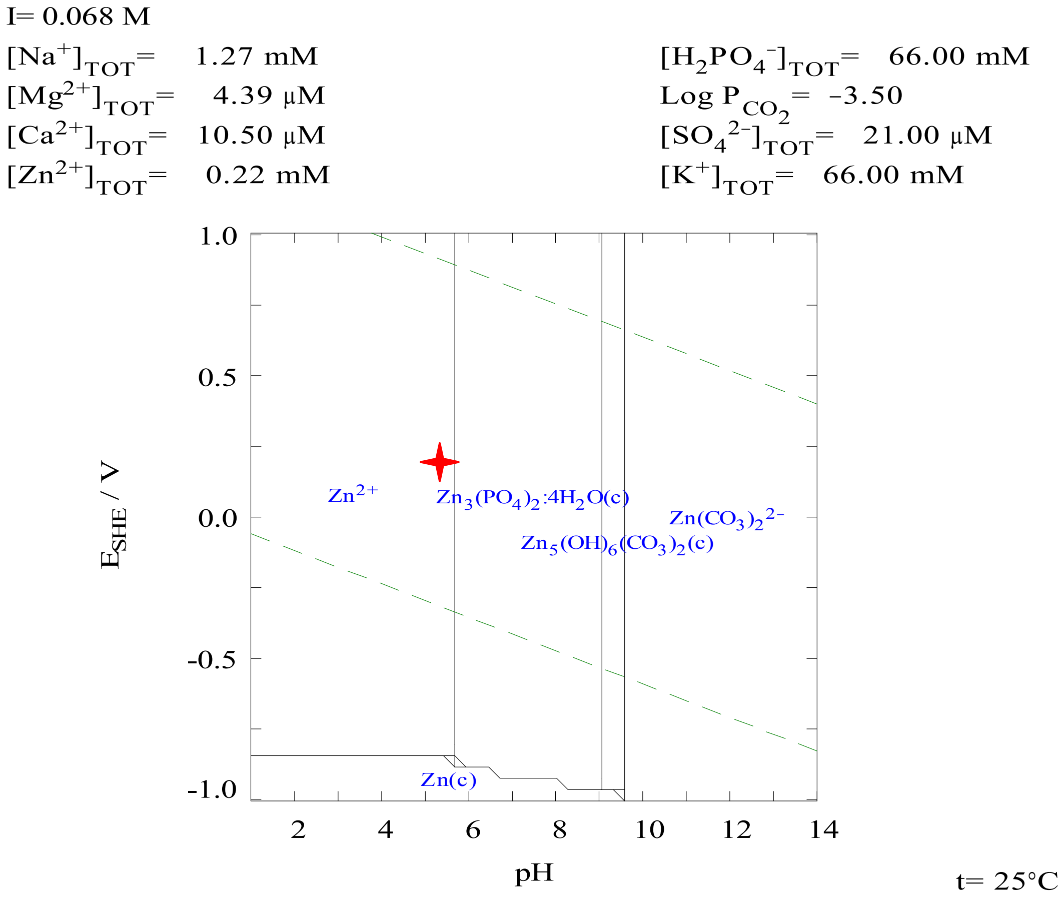


Figure C.170. Pourbaix diagram of zinc for steel gutter section immersed into pH 5 water after one day of exposure.

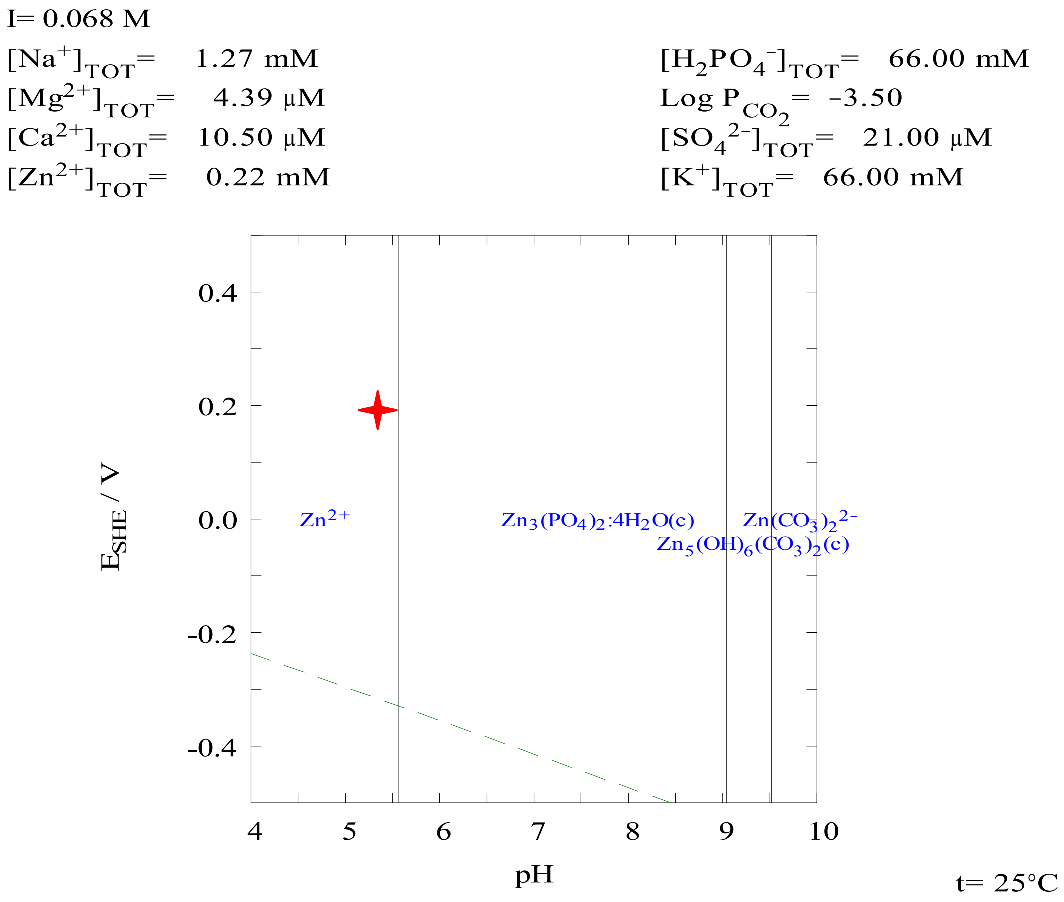


Figure C.171. Pourbaix diagram of zinc for steel gutter section immersed into pH 5 water after one day of exposure. Study area.

Steel Gutter, pH 8 Water, After One Day of Exposure

$[Na^+]_{TOT}$ = 129.00 mM
$[Mg^{2+}]_{TOT}$ = 5.93 µM
$[Ca^{2+}]_{TOT}$ = 4.71 µM
$[Zn^{2+}]_{TOT}$ = 32.00 µM
$[Pb^{2+}]_{TOT}$ = 38.60 nM
E_H = 0.12 V

I= 0.196 M
$[HPO_4{}^{2-}]_{TOT}$ = 64.60 mM
$[NO_3{}^-]_{TOT}$ = 32.30 µM
Log P_{CO_2} = -3.50
$[SO_4{}^{2-}]_{TOT}$ = 7.18 µM
$[K^+]_{TOT}$ = 2.07 mM

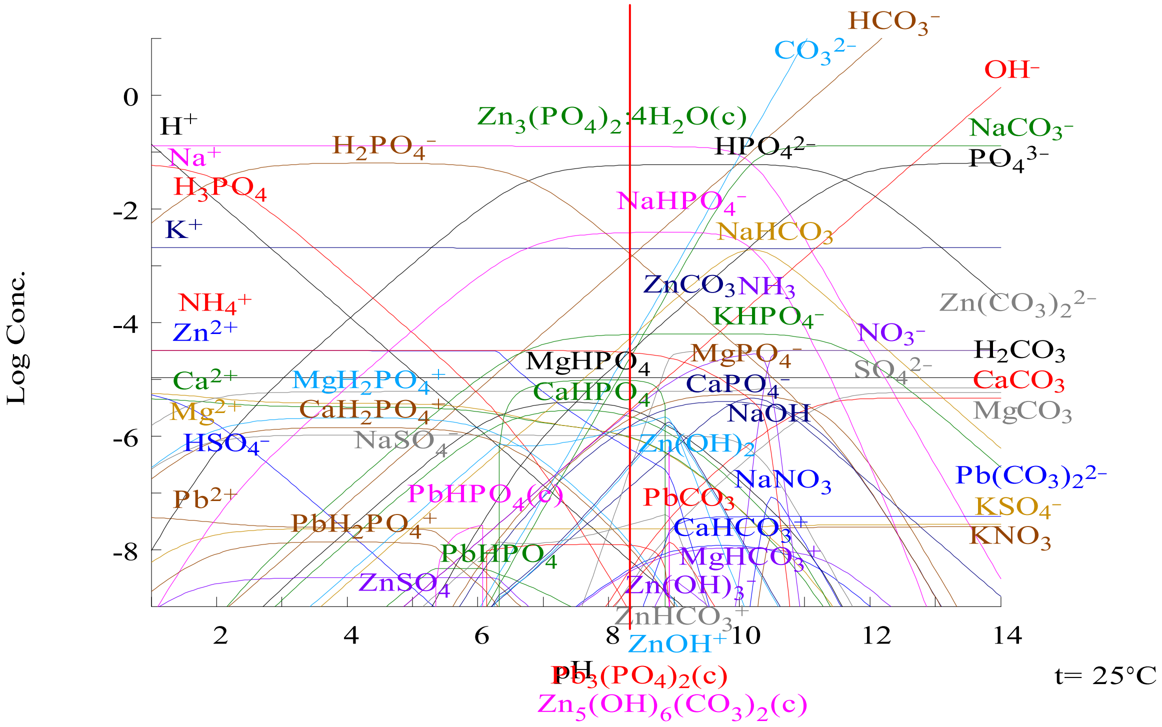


Figure C.172. Phase diagram for steel gutter section immersed into pH 8 water after one day of exposure.

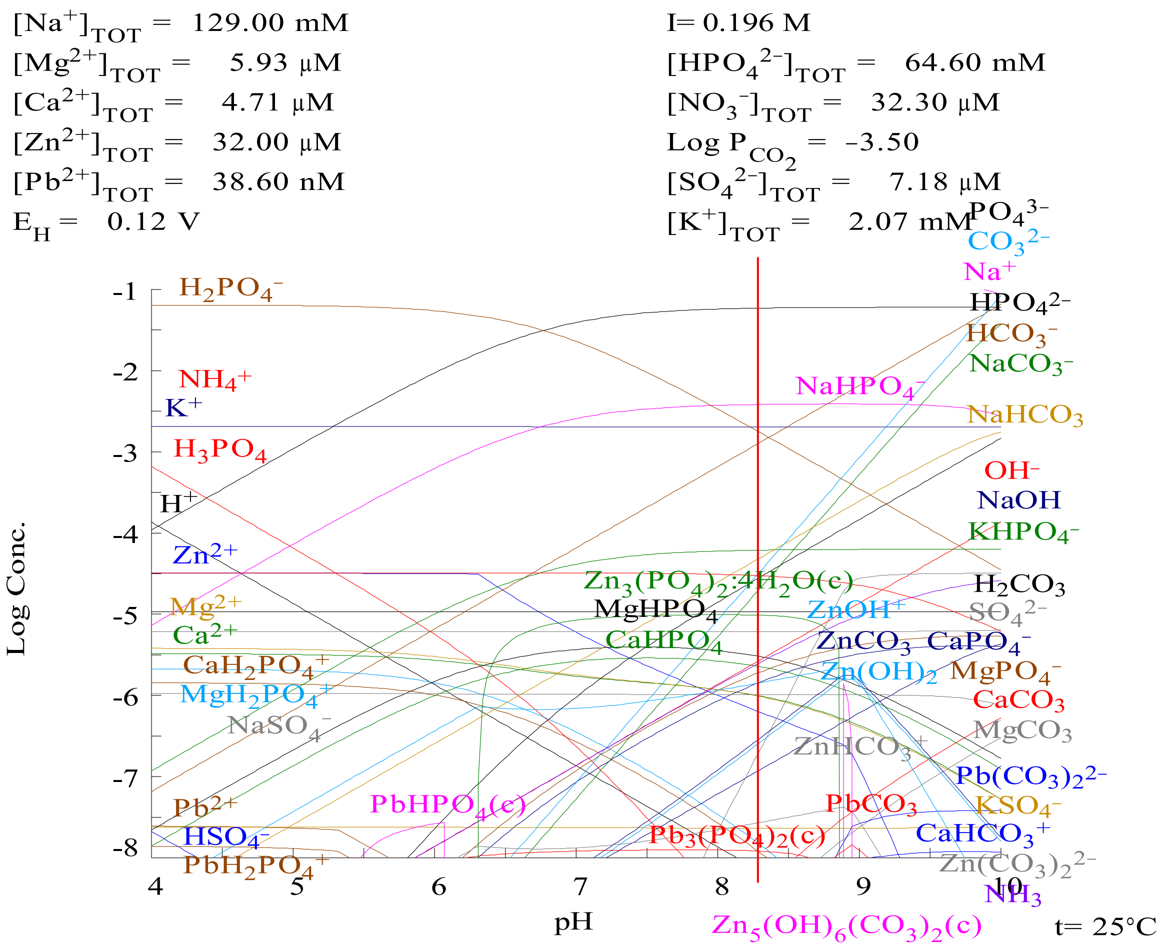


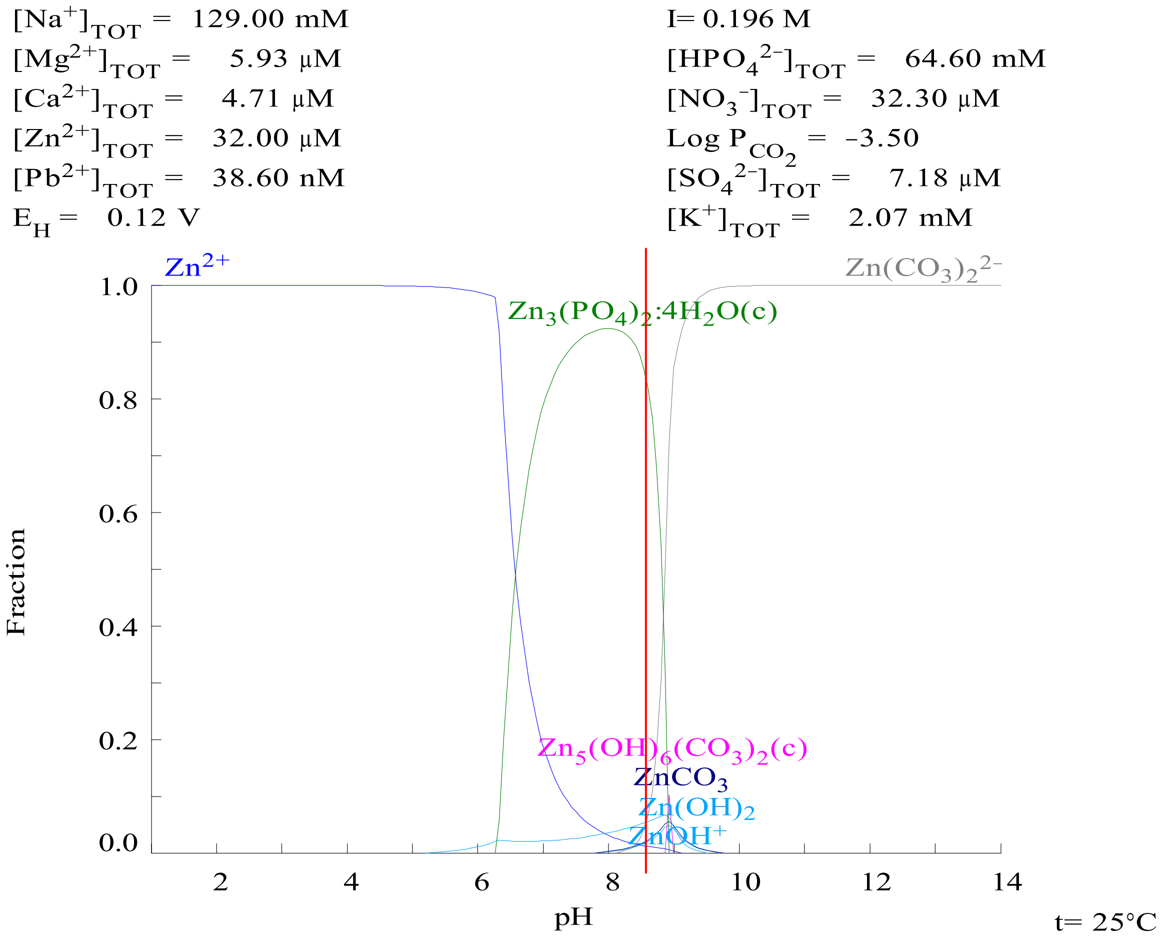
Figure C.173. Phase diagram for steel gutter section immersed into pH 8 water after one day of exposure. Study area.

Table C.42. The predominant species of zinc. Steel gutter section, pH 8 water, one day exposure.

Component	Log Concentration (mol/L)	Concentration (mol/L)	Zn Concentration (mg/L as Zn)	Cumulative Percentage of Zn
$Zn_3(PO_4)_2$:$4H_2O$(c)	-5.02	9.66E-06	1.90	90.54
$ZnOH^+$	-5.83	1.48E-06	9.66E-02	95.16
Zn^{2+}	-6.24	5.80E-07	3.79E-02	96.97
$ZnCO_3$	-6.47	3.40E-07	2.23E-02	98.03
$Zn(OH)_2$	-6.52	3.03E-07	1.98E-02	98.98
$Zn(CO_3)_2^{2-}$	-6.52	2.99E-07	1.96E-02	99.91

Table C.43. The predominant species of lead. Steel gutter section, pH 8 water, one day exposure.

Component	Log Concentration (mol/L)	Concentration (mol/L)	Pb Concentration (mg/L as Pb)	Cumulative Percentage of Pb
$Pb_3(PO_4)_2(c)$	-7.92	1.19E-08	7.42E-03	92.40
$PbCO_3$	-8.64	2.31E-09	4.80E-04	98.37
$PbHPO_4$	-9.59	2.57E-10	5.32E-05	99.03
$Pb(CO_3)_2^{2-}$	-9.62	2.39E-10	4.95E-05	99.65
$PbOH^+$	-10.15	7.12E-11	1.47E-05	99.83
Pb^{2+}	-10.34	4.53E-11	9.39E-06	99.95



$[Na^+]_{TOT}$ = 129.00 mM
$[Mg^{2+}]_{TOT}$ = 5.93 µM
$[Ca^{2+}]_{TOT}$ = 4.71 µM
$[Zn^{2+}]_{TOT}$ = 32.00 µM
$[Pb^{2+}]_{TOT}$ = 38.60 nM
E_H = 0.12 V

I= 0.196 M
$[HPO_4^{2-}]_{TOT}$ = 64.60 mM
$[NO_3^-]_{TOT}$ = 32.30 µM
Log P_{CO_2} = -3.50
$[SO_4^{2-}]_{TOT}$ = 7.18 µM
$[K^+]_{TOT}$ = 2.07 mM

Figure 174. Fraction diagram of zinc for steel gutter section immersed into pH 8 water after one day of exposure.

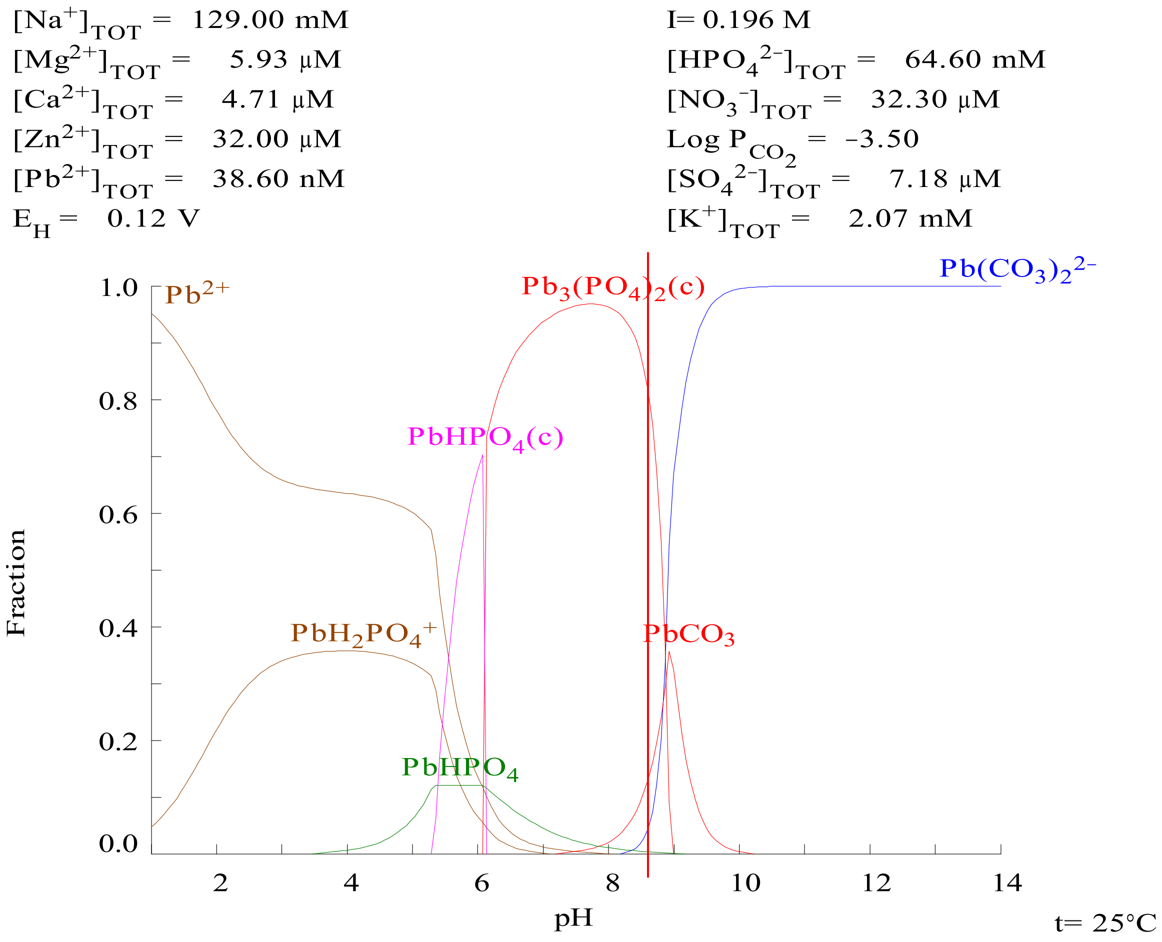


Figure C.175. Fraction diagram of lead for steel gutter section immersed into pH 8 water after one day of exposure.

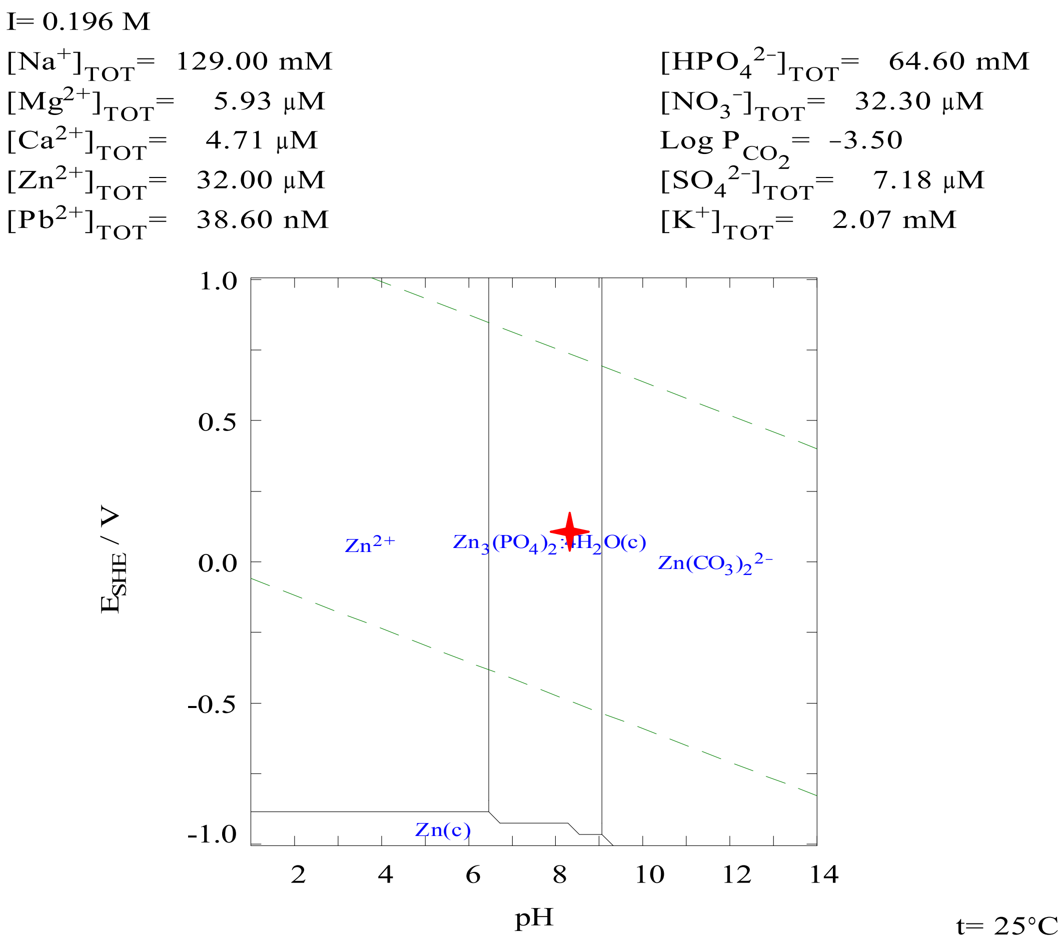


Figure C.176. Pourbaix diagram of zinc for steel gutter section immersed into pH 8 water after one day of exposure.

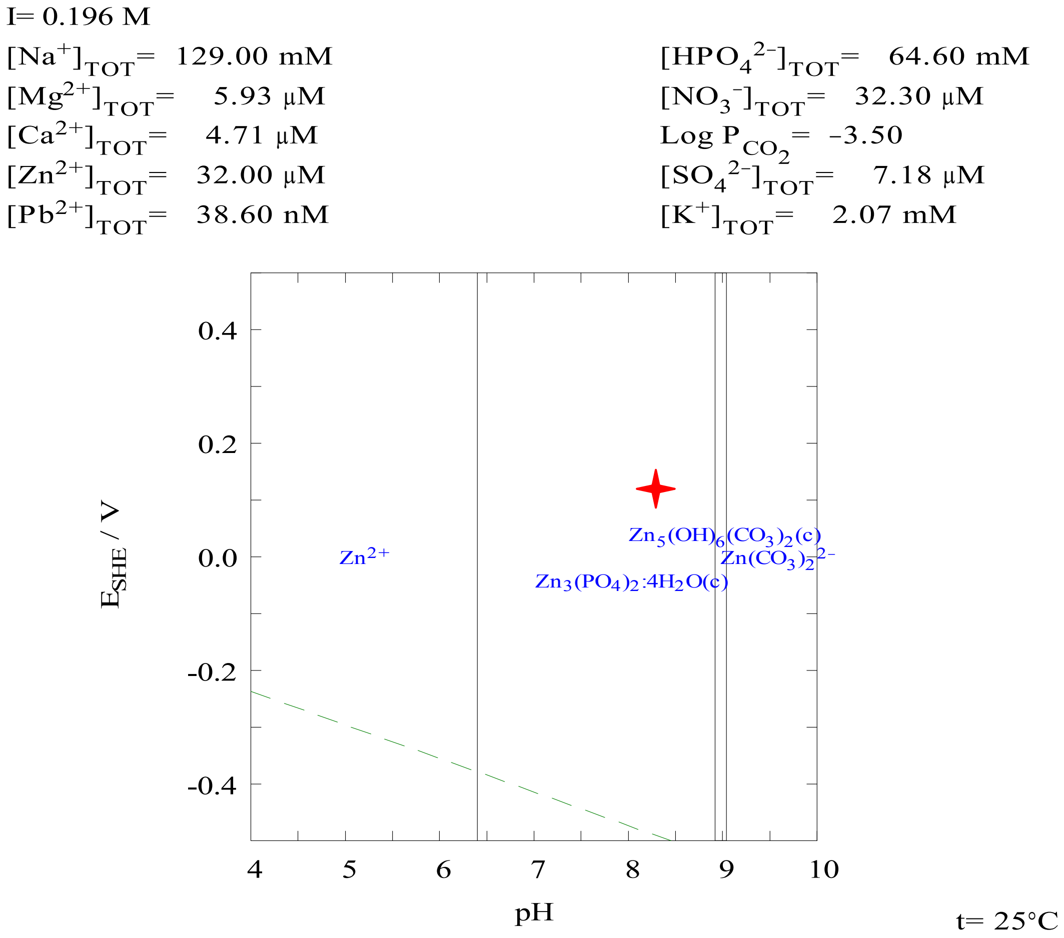


Figure C.177. Pourbaix diagram of zinc for steel gutter section immersed into pH 8 water after one day of exposure. Study area.

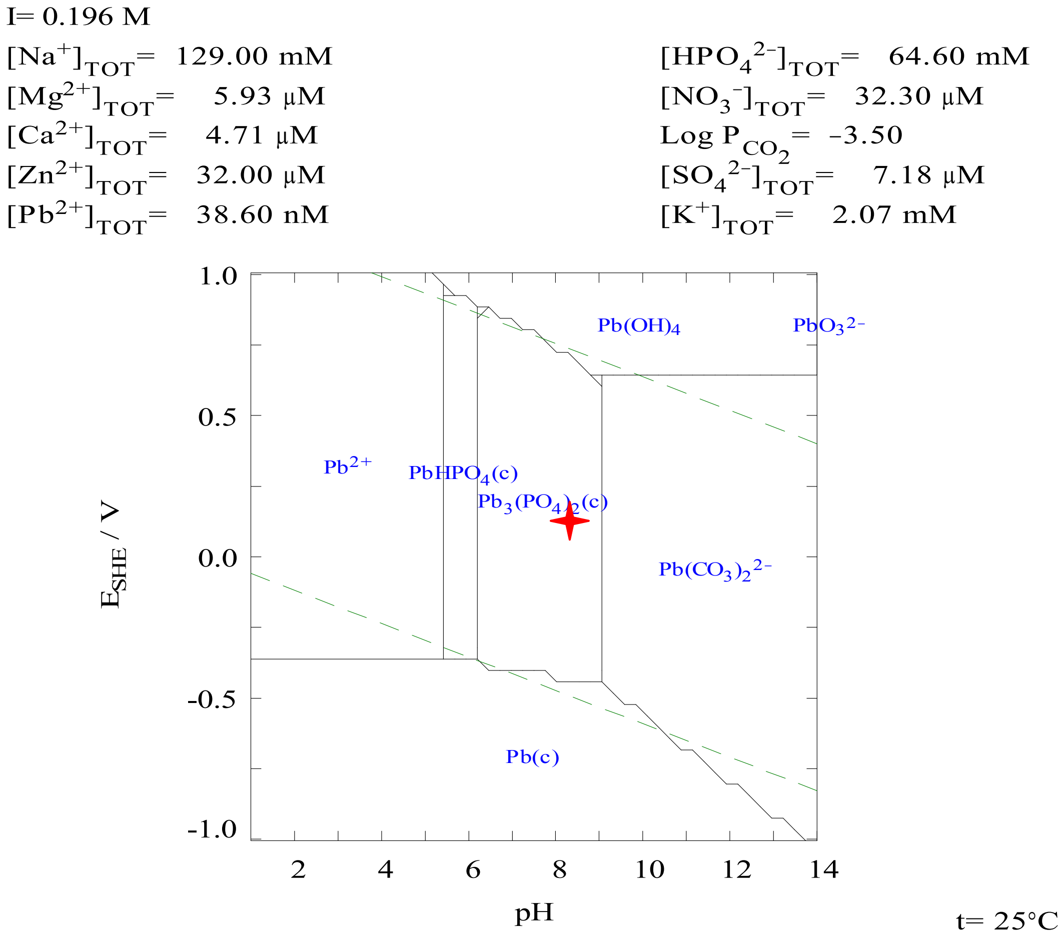


Figure C.178. Pourbaix diagram of lead for steel gutter section immersed into pH 8 water after one day of exposure.

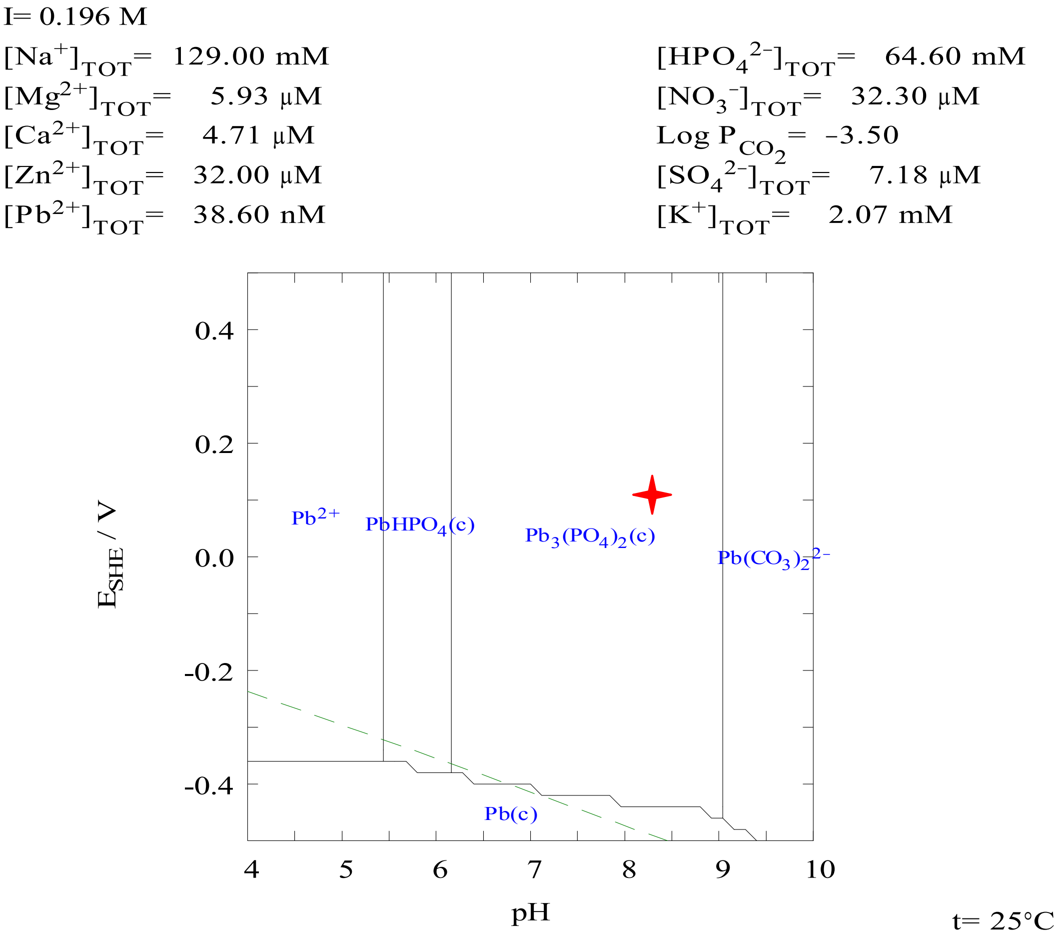


Figure C.179. Pourbaix diagram of lead for steel gutter section immersed into pH 8 water after one day of exposure. Study area.

PVC Pipe, pH 5 Water, After One Day of Exposure

$[Na^+]_{TOT}$ = 1.27 mM
$[Mg^{2+}]_{TOT}$ = 37.90 µM
$[Ca^{2+}]_{TOT}$ = 0.61 mM
$[Zn^{2+}]_{TOT}$ = 3.37 µM
$[Cu^{2+}]_{TOT}$ = 1.26 µM
E_H = 0.22 V

I= 0.070 M
$[H_2PO_4^-]_{TOT}$ = 66.00 mM
$[NO_3^-]_{TOT}$ = 16.10 µM
Log P_{CO_2} = -3.50
$[SO_4^{2-}]_{TOT}$ = 0.15 mM
$[K^+]_{TOT}$ = 66.00 mM

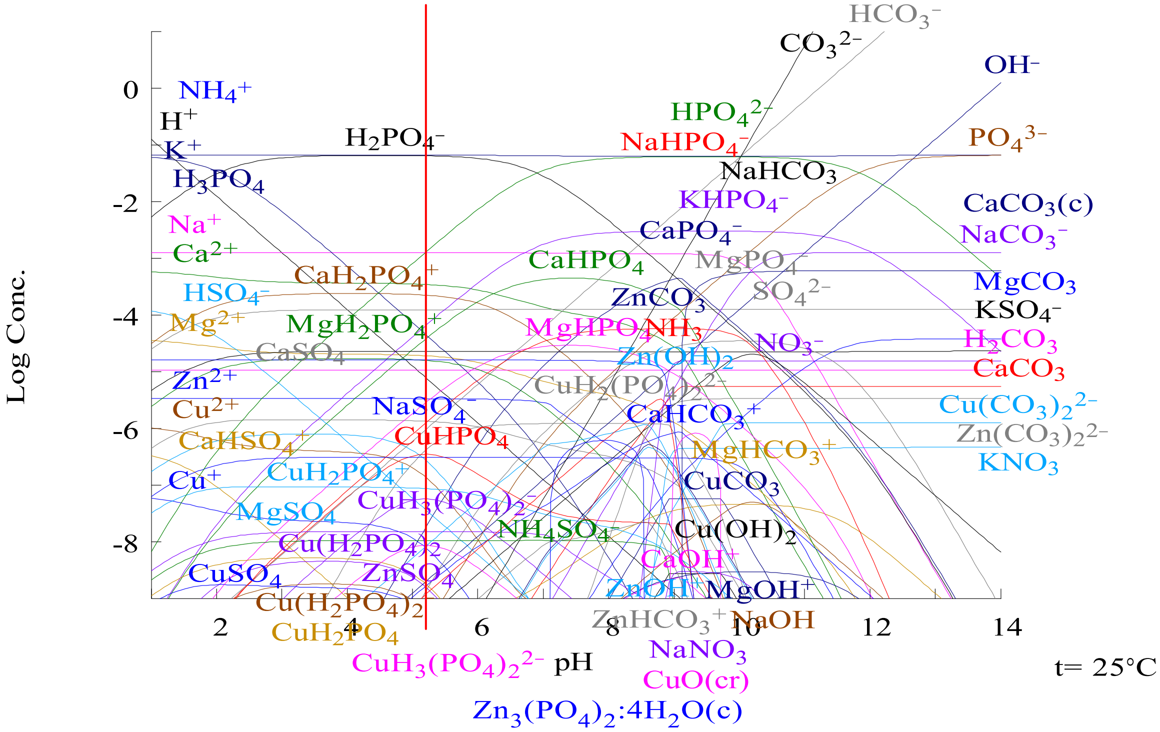


Figure C.180. Phase diagram for PVC pipe section immersed into pH 5 water after one day of exposure.

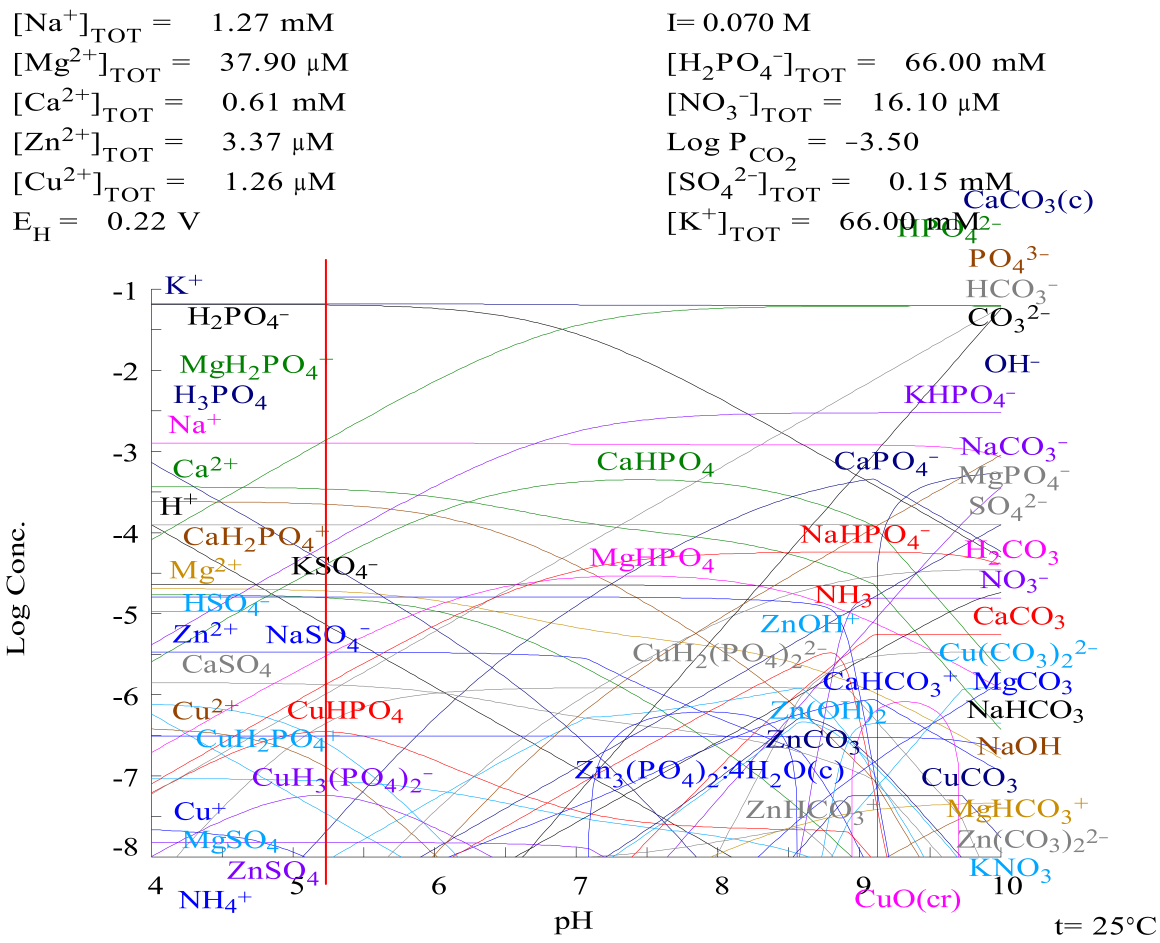


Figure C.181. Phase diagram for PVC pipe section immersed into pH 5 water after one day of exposure. Study area.

Table C.44. The predominant species of zinc. PVC pipe section, pH 5 water, one day exposure.

Component	Log Concentration (mol/L)	Concentration (mol/L)	Zn Concentration (mg/L as Zn)	Cumulative Percentage of Zn
Zn^{2+}	-5.48	3.35E-06	2.19E-01	99.28
$ZnSO_4$	-7.82	1.52E-08	9.96E-04	99.73
$ZnOH^+$	-8.06	8.79E-09	5.75E-04	99.99

Table C.45. The predominant species of copper. PVC pipe section, pH 5 water, one day exposure.

Component	Log Concentration (mol/L)	Concentration (mol/L)	Cu Concentration (mg/L as Cu)	Cumulative Percentage of Cu
$CuH_2(PO_4)_2^{2-}$	-6.36	4.37E-07	2.78E-02	34.71
$CuHPO_4$	-6.45	3.52E-07	2.23E-02	62.61
$CuH_2PO_4^+$	-6.58	2.62E-07	1.67E-02	83.40
Cu^{2+}	-6.88	1.31E-07	8.32E-03	93.79
$CuH_3(PO_4)_2^-$	-7.24	5.76E-08	3.66E-03	98.36
$CuH_3(PO_4)_2^{2-}$	-8.06	8.70E-09	5.53E-04	99.05
Cu^+	-8.13	7.50E-09	4.76E-04	99.64
CuH_2PO_4	-8.77	1.72E-09	1.09E-04	99.78
$Cu(H_2PO_4)_2$	-8.82	1.51E-09	9.57E-05	99.90
$Cu(H_2PO_4)_2^-$	-9.22	6.01E-10	3.82E-05	99.95

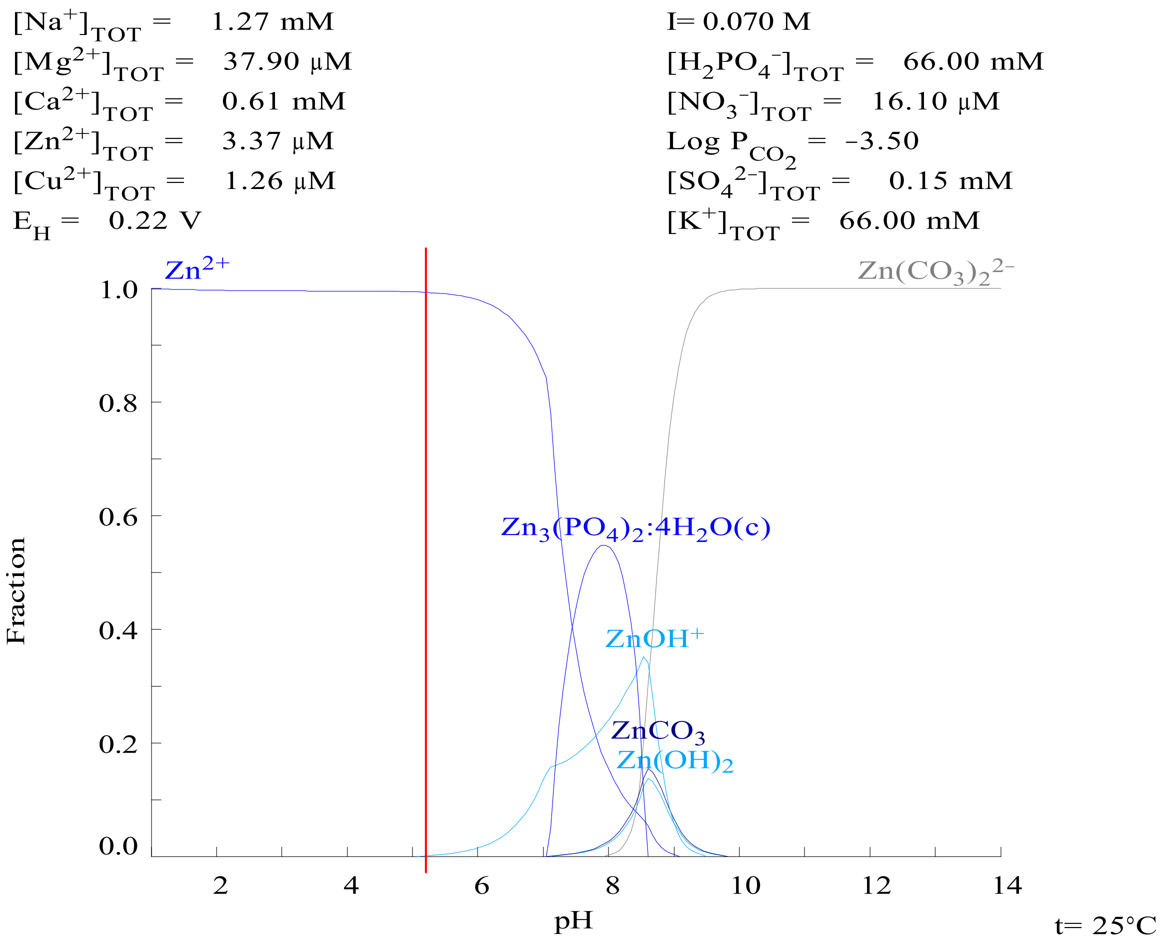


Figure C.182. Fraction diagram of zinc for PVC pipe section immersed into pH 5 water after one day of exposure.

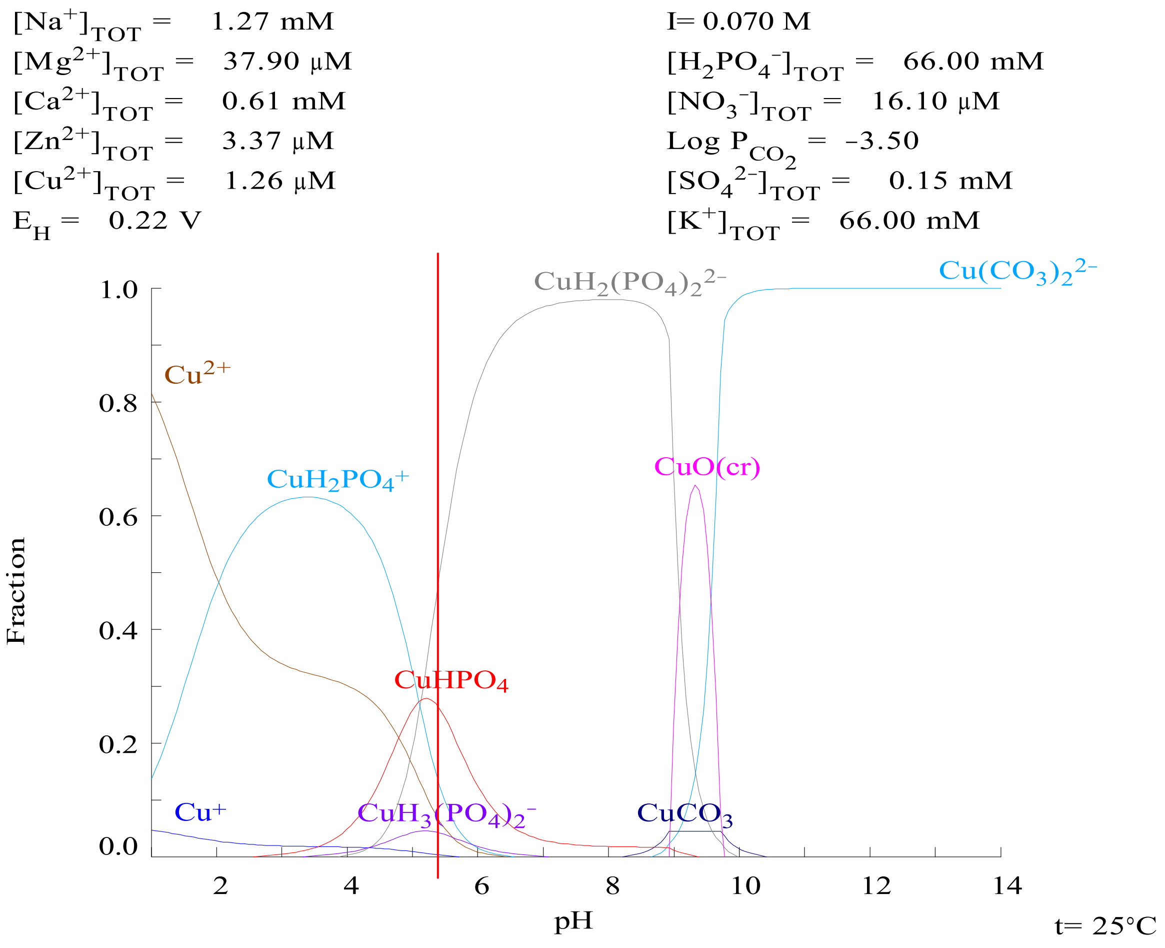


Figure C.183. Fraction diagram of copper for PVC pipe section immersed into pH 5 water after one day of exposure.

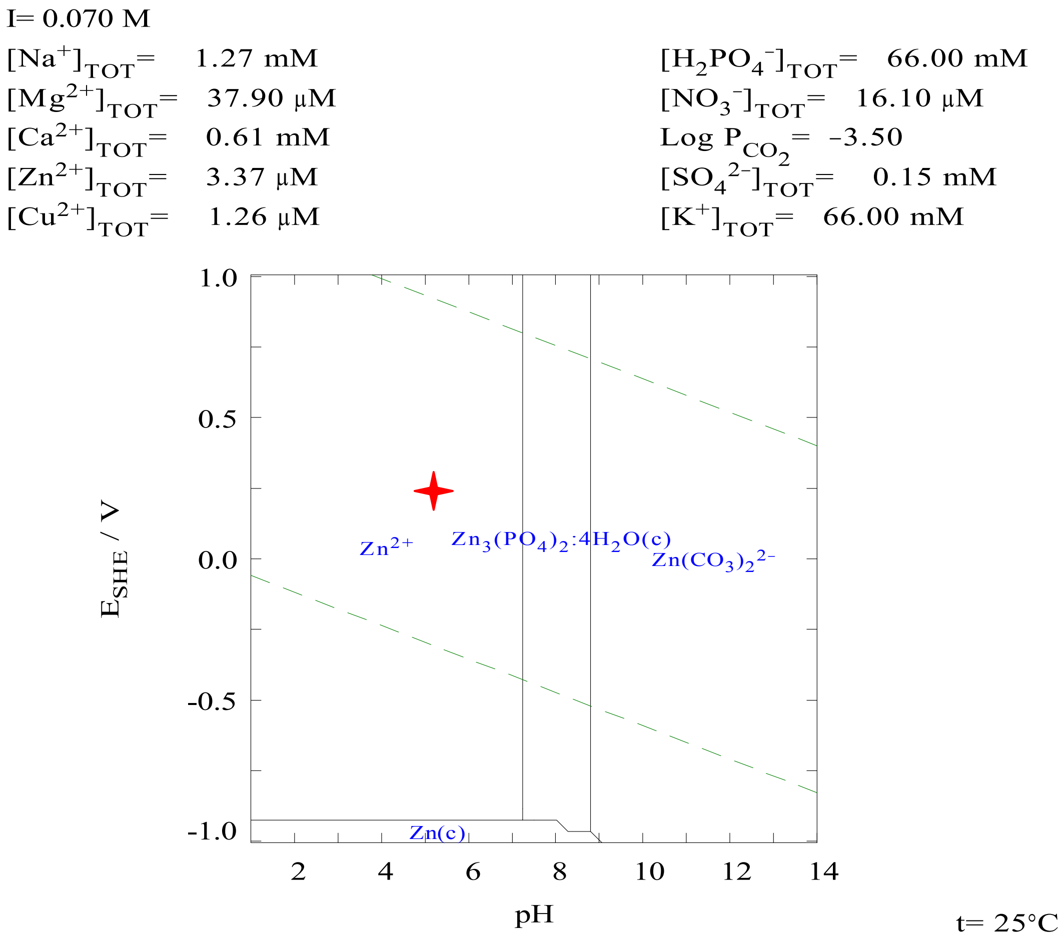


Figure C.184. Pourbaix diagram of zinc for PVC pipe section immersed into pH 5 water after one day of exposure.

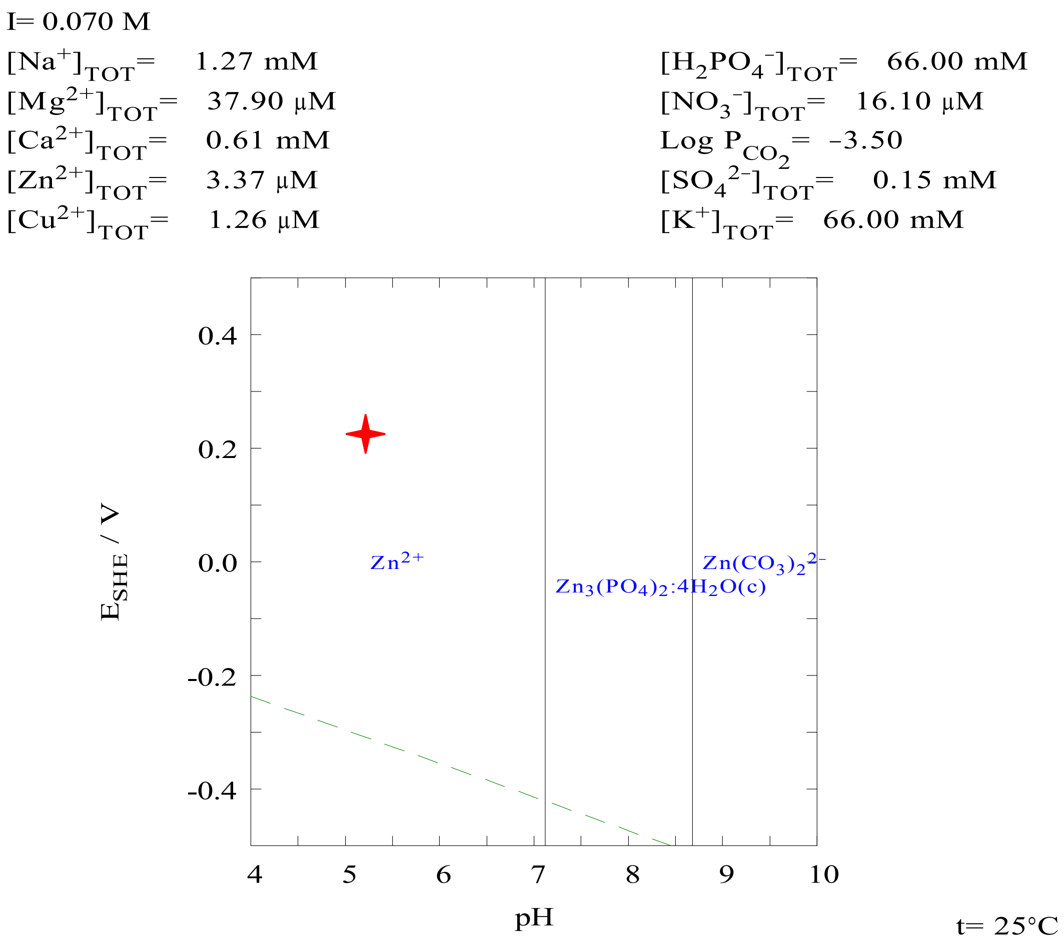


Figure C.185. Pourbaix diagram of zinc for PVC pipe section immersed into pH 5 water after one day of exposure. Study area.

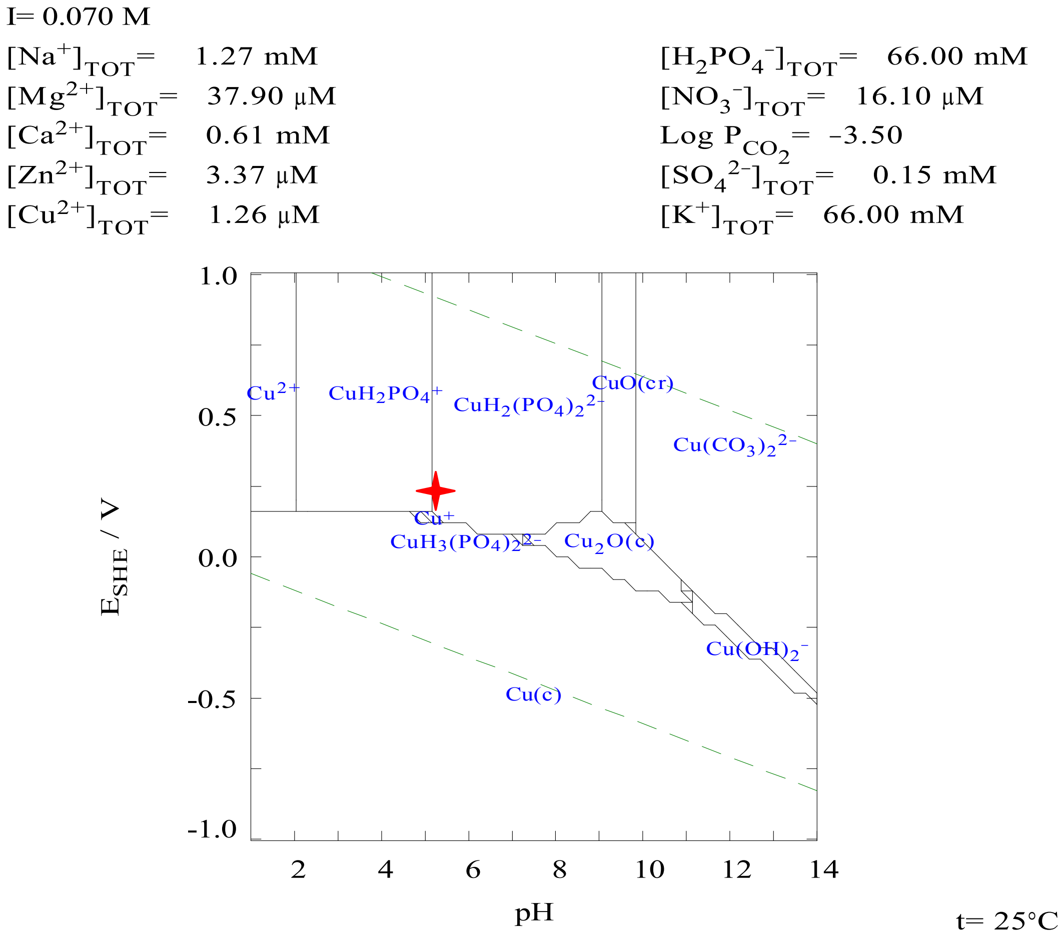


Figure C.186. Pourbaix diagram of copper for PVC pipe section immersed into pH 5 water after one day of exposure.

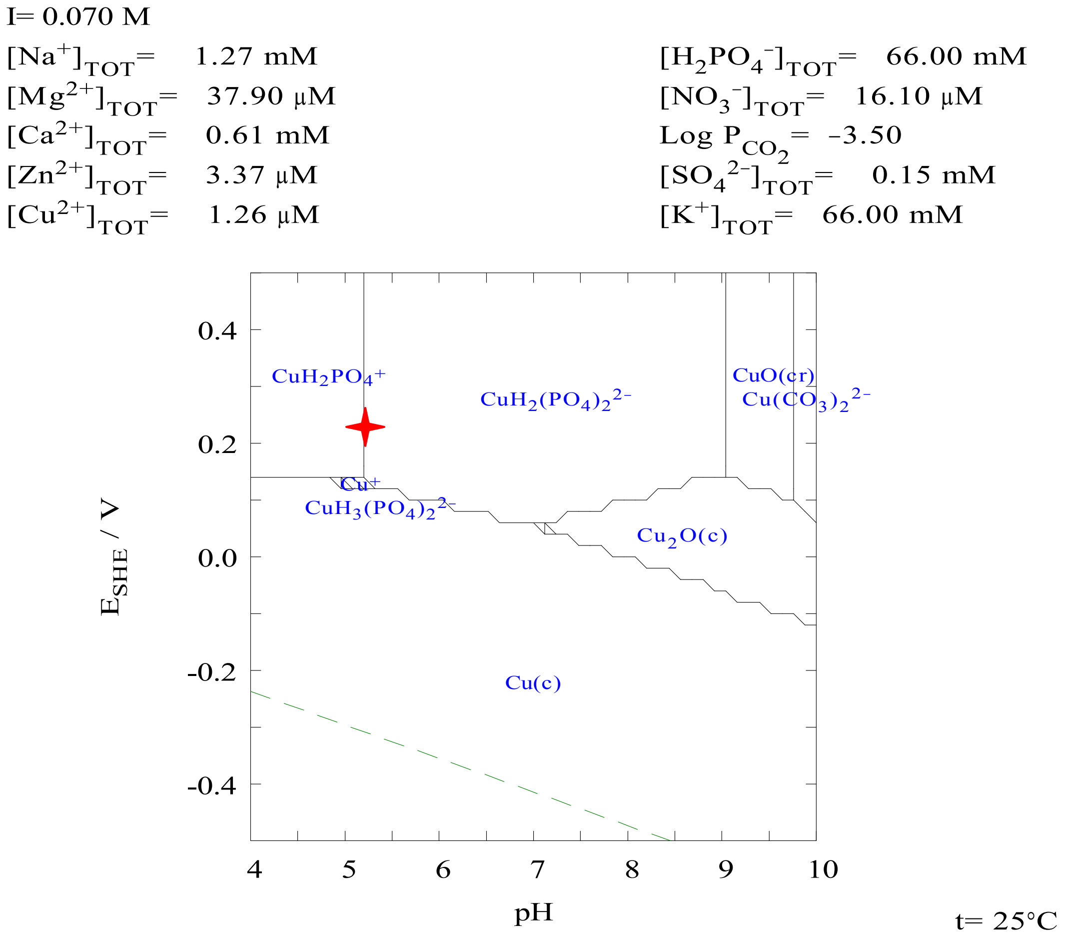


Figure C.187. Pourbaix diagram of copper for PVC pipe section immersed into pH 5 water after one day of exposure. Study area.

PVC Pipe, pH 8 Water, After One Day of Exposure

$[Na^+]_{TOT}$ = 129.00 mM
$[Mg^{2+}]_{TOT}$ = 27.40 µM
$[Ca^{2+}]_{TOT}$ = 47.00 µM
$[Zn^{2+}]_{TOT}$ = 2.45 µM
$[Cu^{2+}]_{TOT}$ = 1.26 µM
E_H = 0.13 V

I= 0.196 M
$[HPO_4^{2-}]_{TOT}$ = 64.60 mM
$[NO_3^-]_{TOT}$ = 30.60 µM
Log P_{CO_2} = -3.50
$[SO_4^{2-}]_{TOT}$ = 0.17 mM
$[K^+]_{TOT}$ = 2.07 mM

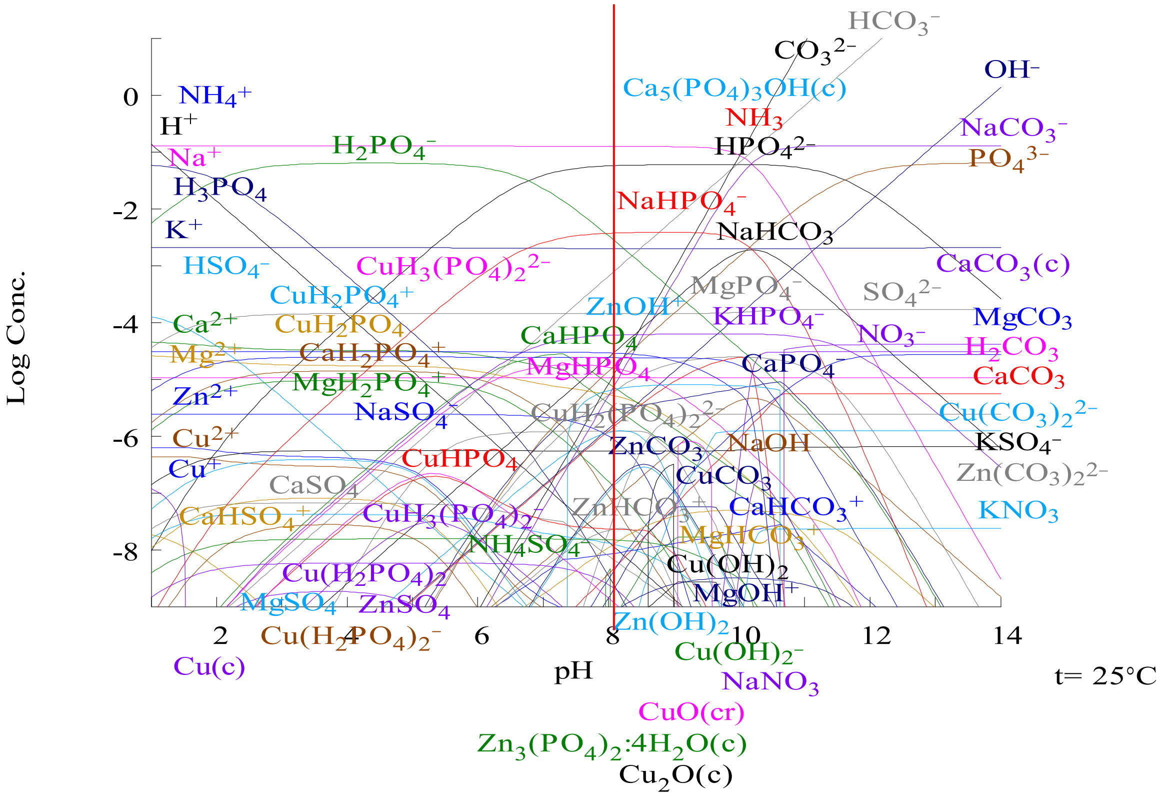


Figure C.188. Phase diagram for PVC pipe section immersed into pH 8 water after one day of exposure.

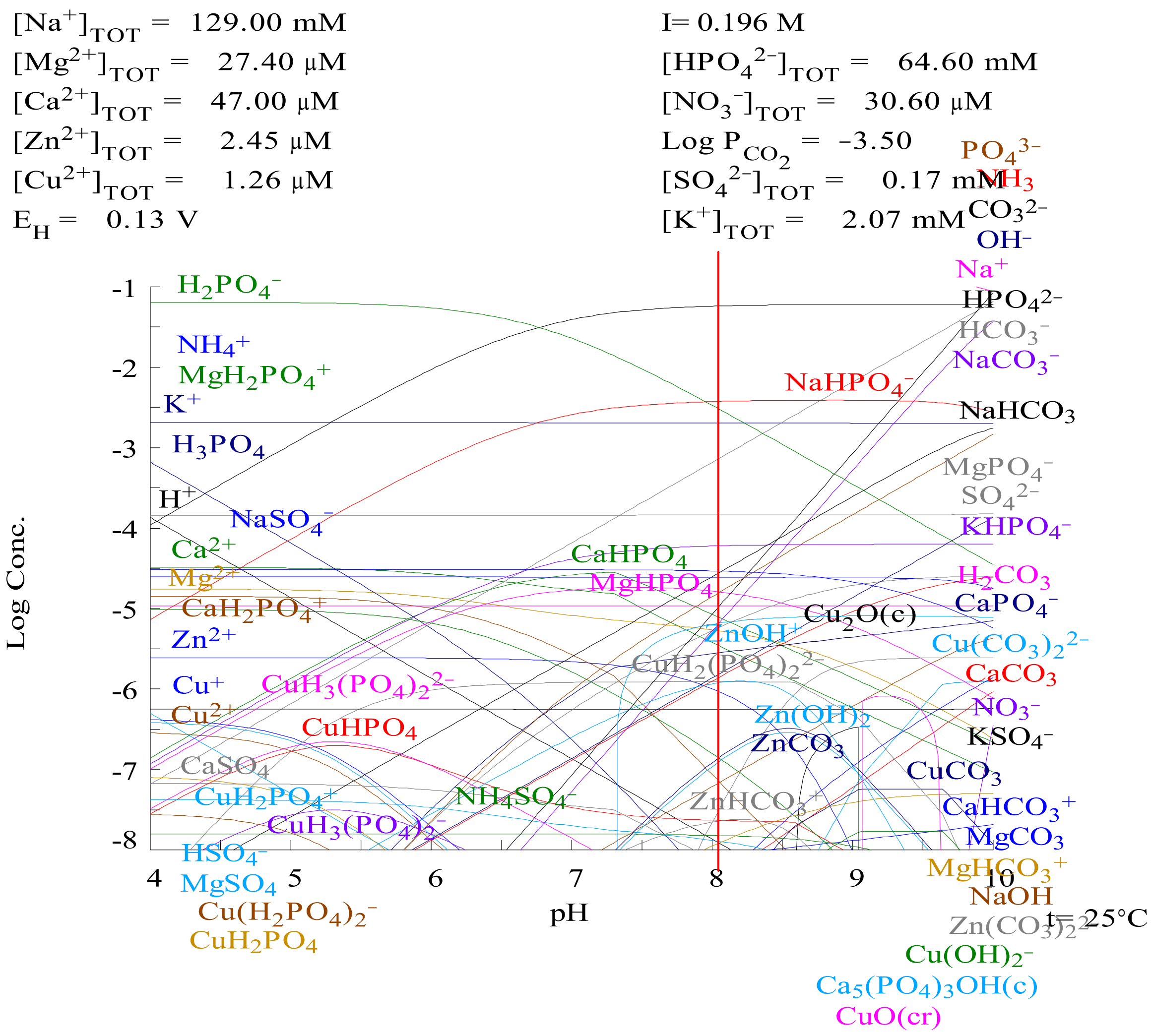


Figure C.189. Phase diagram for PVC pipe section immersed into pH 8 water after one day of exposure. Study area.

Table C.46. The predominant species of zinc. PVC pipe section, pH 8 water, one day exposure.

Component	Log Concentration (mol/L)	Concentration (mol/L)	Zn Concentration (mg/L as Zn)	Cumulative Percentage of Zn
$ZnOH^+$	-5.90	1.25E-06	8.15E-02	50.87
Zn^{2+}	-6.12	7.67E-07	5.01E-02	82.15
ZnCO3	-6.74	1.83E-07	1.20E-02	89.63
$Zn(OH)_2$	-6.79	1.63E-07	1.07E-02	96.28
$Zn(CO_3)_2^{2-}$	-7.18	6.55E-08	4.29E-03	98.95
$ZnHCO_3^+$	-7.62	2.37E-08	1.55E-03	99.92

Table C.47. The predominant species of copper. PVC pipe section, pH 8 water, one day exposure.

Component	Log Concentration (mol/L)	Concentration (mol/L)	Cu Concentration (mg/L as Cu)	Cumulative Percentage of Cu
$CuH_2(PO_4)_2^{2-}$	-5.91	1.23E-06	7.82E-02	97.67
$CuHPO_4$	-7.64	2.30E-08	1.46E-03	99.49
$CuCO_3$	-8.55	2.81E-09	1.78E-04	99.72
$CuH_3(PO_4)_2^{2-}$	-9.00	1.00E-09	6.38E-05	99.80
$Cu(OH)_2^-$	-9.08	8.37E-10	5.32E-05	99.86
Cu^+	-9.20	6.35E-10	4.04E-05	99.91
Cu^{2+}	-9.36	4.37E-10	2.77E-05	99.95

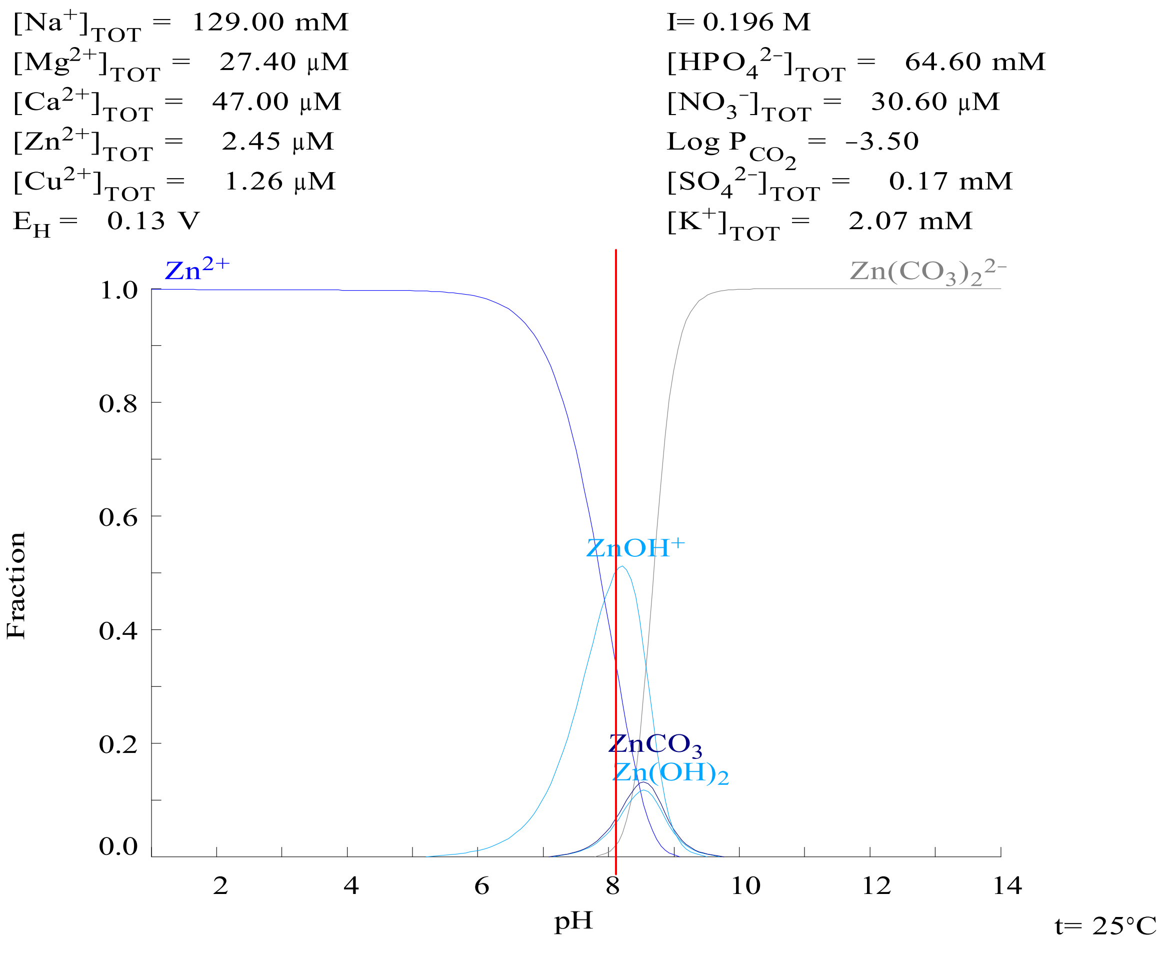


Figure C.190. Fraction diagram of zinc for PVC pipe section immersed into pH 8 water after one day of exposure.

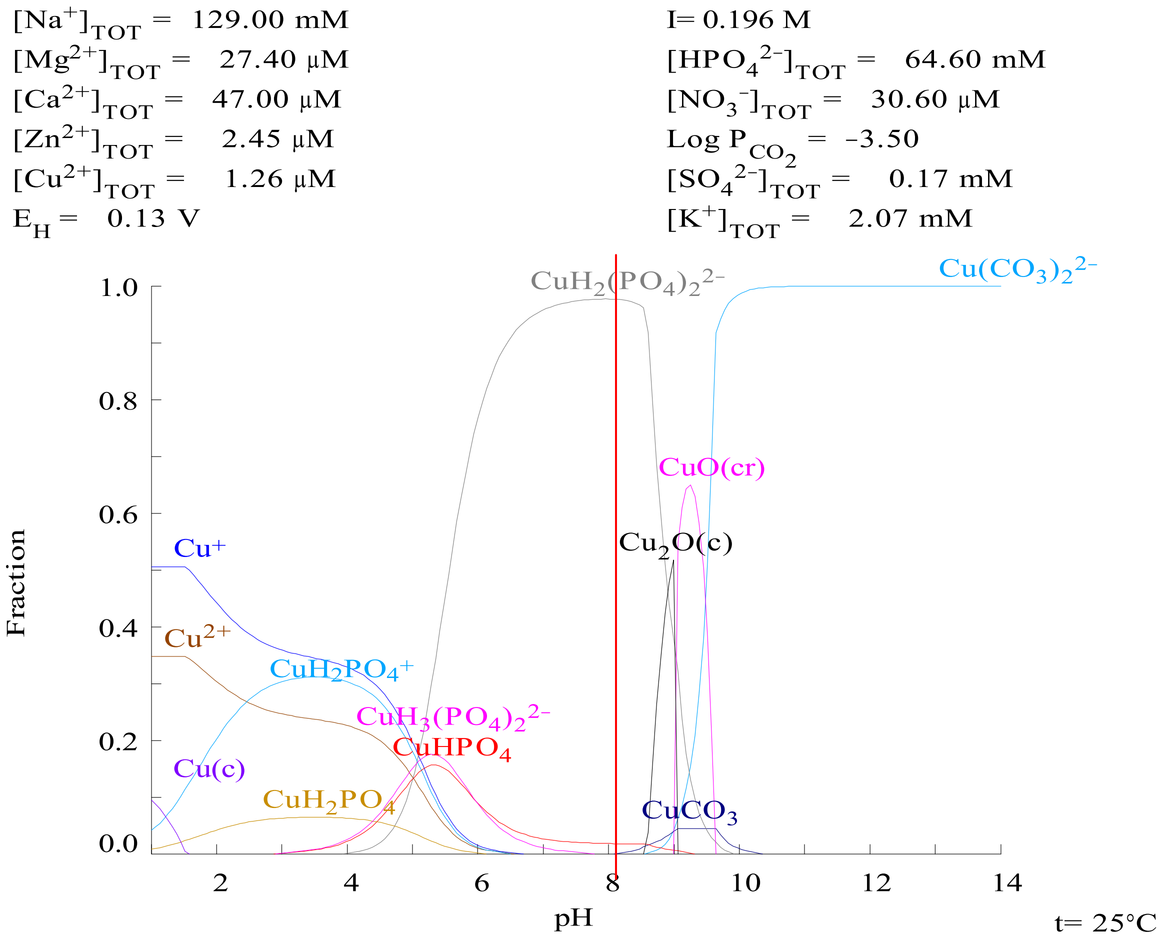


Figure C.191. Fraction diagram of copper for PVC pipe section immersed into pH 8 water after one day of exposure.

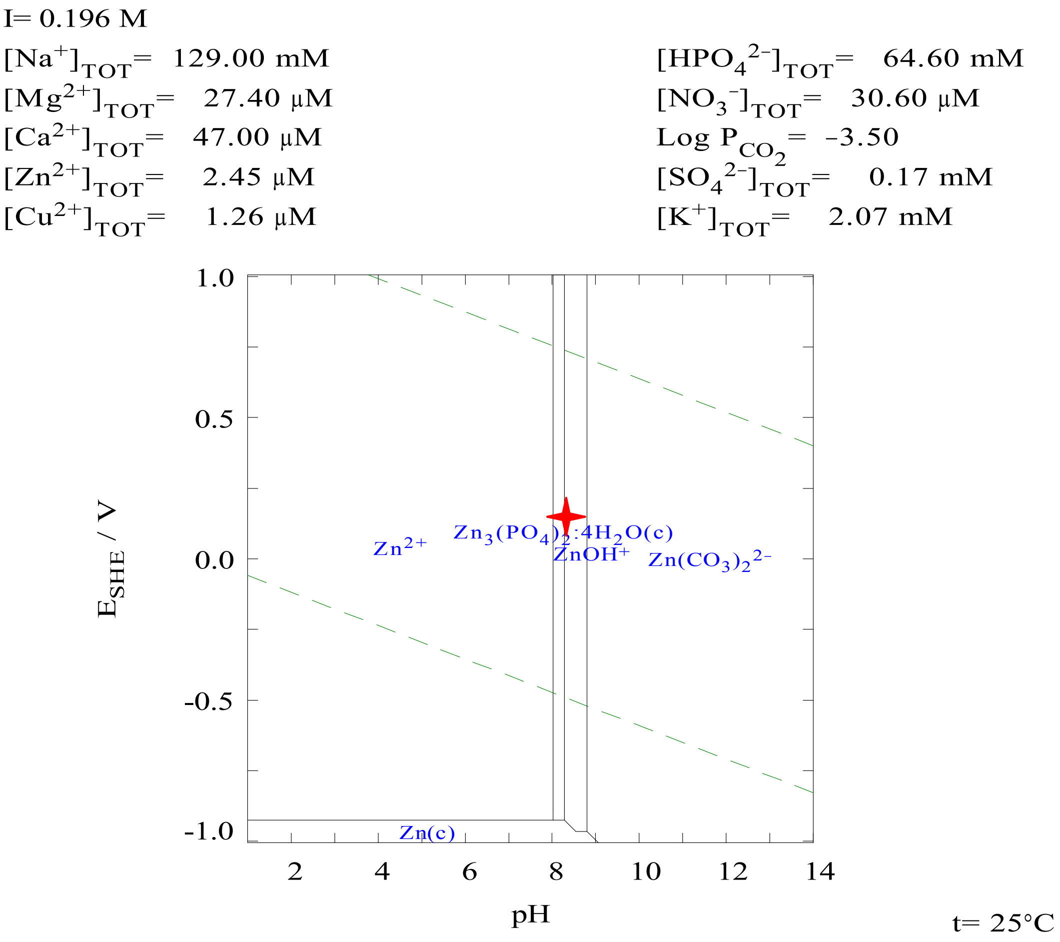


Figure C.192. Pourbaix diagram of zinc for PVC pipe section immersed into pH 8 water after one day of exposure.

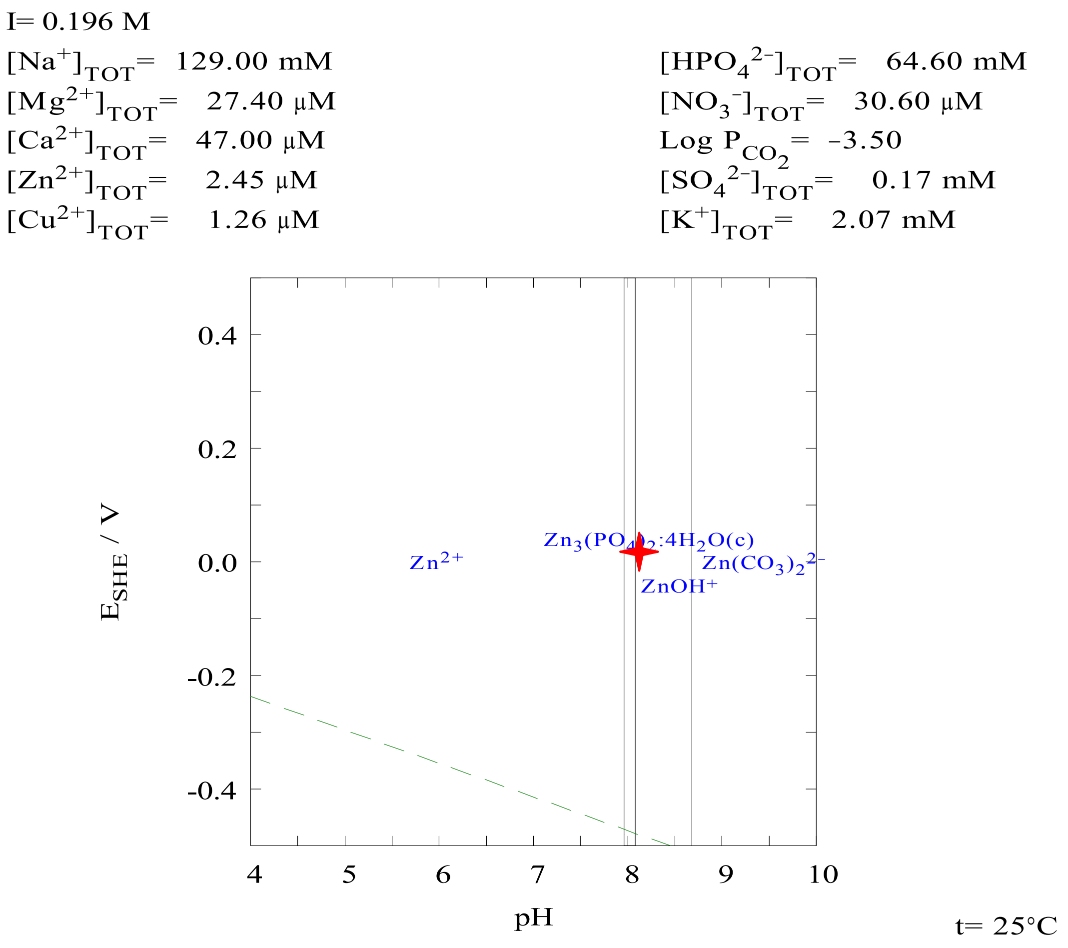


Figure C.193. Pourbaix diagram of zinc for PVC pipe section immersed into pH 8 water after one day of exposure. Study area.

I= 0.196 M

$[Na^{+}]_{TOT}$= 129.00 mM
$[Mg^{2+}]_{TOT}$= 27.40 μM
$[Ca^{2+}]_{TOT}$= 47.00 μM
$[Zn^{2+}]_{TOT}$= 2.45 μM
$[Cu^{2+}]_{TOT}$= 1.26 μM

$[HPO_4^{2-}]_{TOT}$= 64.60 mM
$[NO_3^{-}]_{TOT}$= 30.60 μM
Log P_{CO_2}= -3.50
$[SO_4^{2-}]_{TOT}$= 0.17 mM
$[K^{+}]_{TOT}$= 2.07 mM

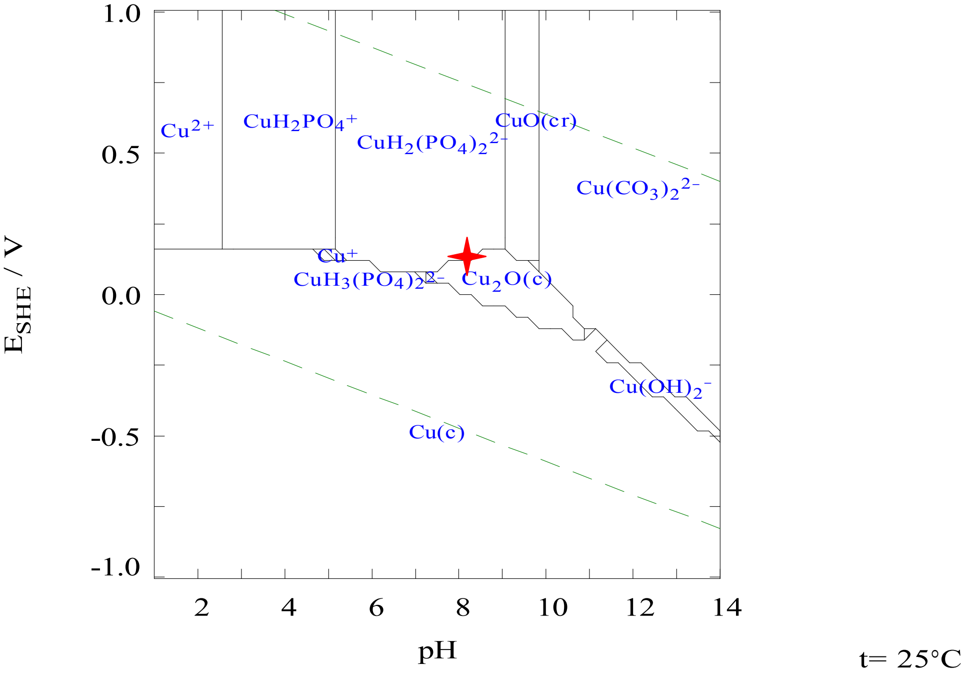


Figure C.194. Pourbaix diagram of copper for PVC pipe section immersed into pH 8 water after one day of exposure.

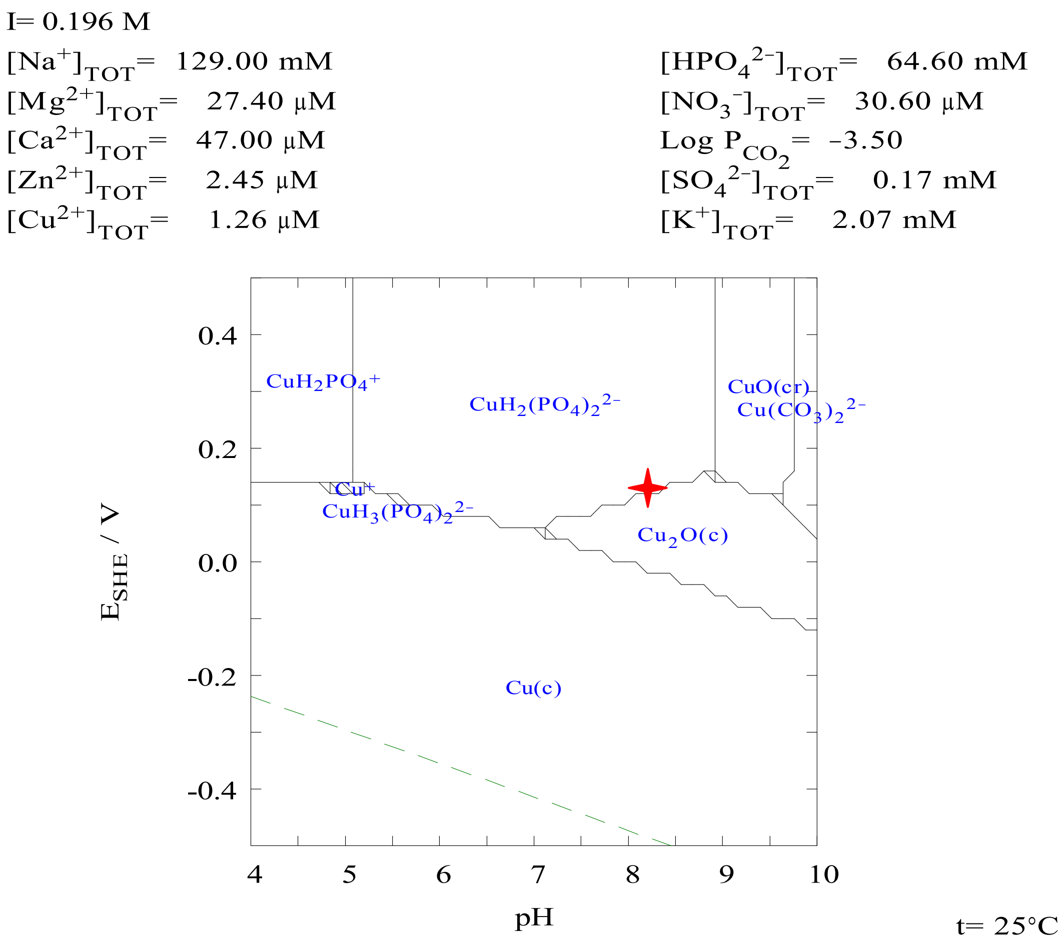
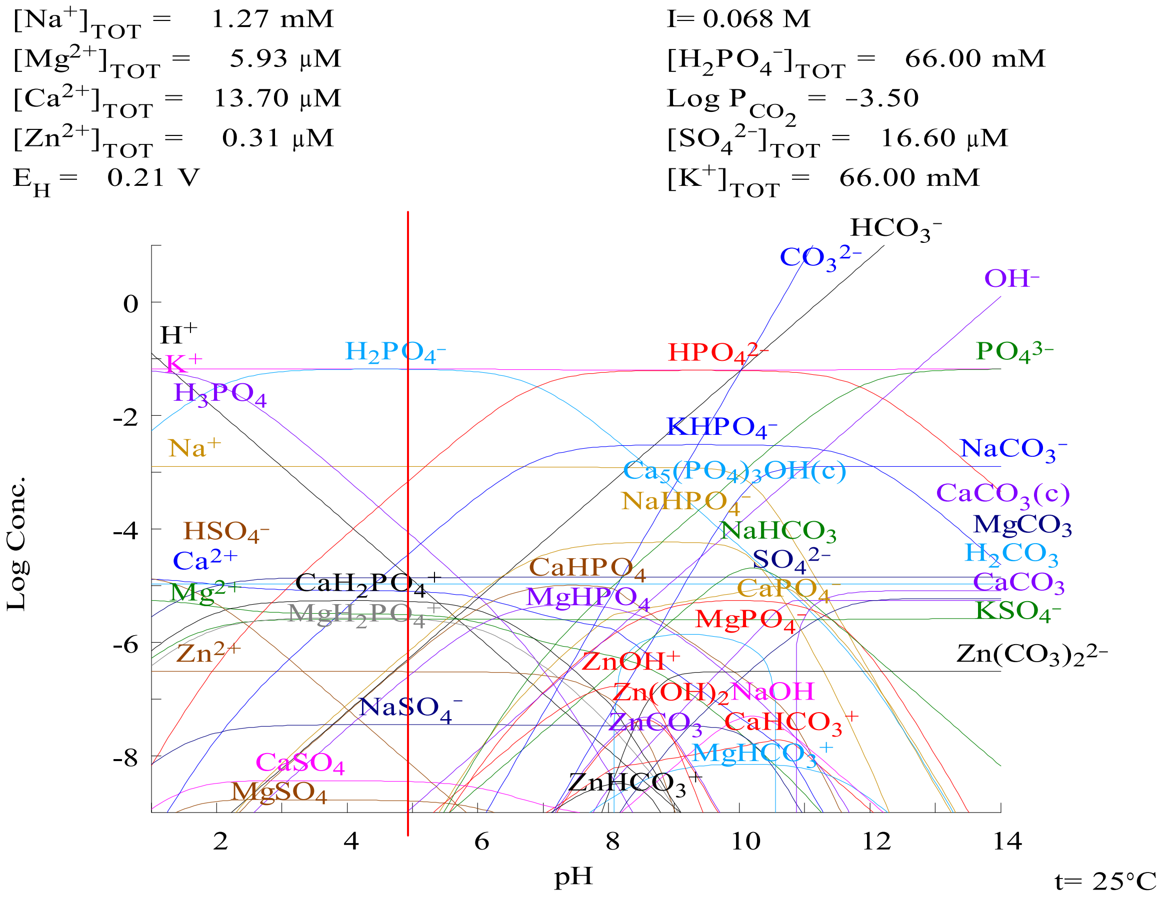


Figure C.195. Pourbaix diagram of copper for PVC pipe section immersed into pH 8 water after one day of exposure. Study area.

HDPE Pipe, pH 5 Water, After One Day of Exposure



$[Na^+]_{TOT}$ = 1.27 mM

$[Mg^{2+}]_{TOT}$ = 5.93 µM

$[Ca^{2+}]_{TOT}$ = 13.70 µM

$[Zn^{2+}]_{TOT}$ = 0.31 µM

E_H = 0.21 V

I= 0.068 M

$[H_2PO_4^-]_{TOT}$ = 66.00 mM

Log P_{CO_2} = -3.50

$[SO_4^{2-}]_{TOT}$ = 16.60 µM

$[K^+]_{TOT}$ = 66.00 mM

Figure C.196. Phase diagram for HDPE pipe section immersed into pH 5 water after one day of exposure.

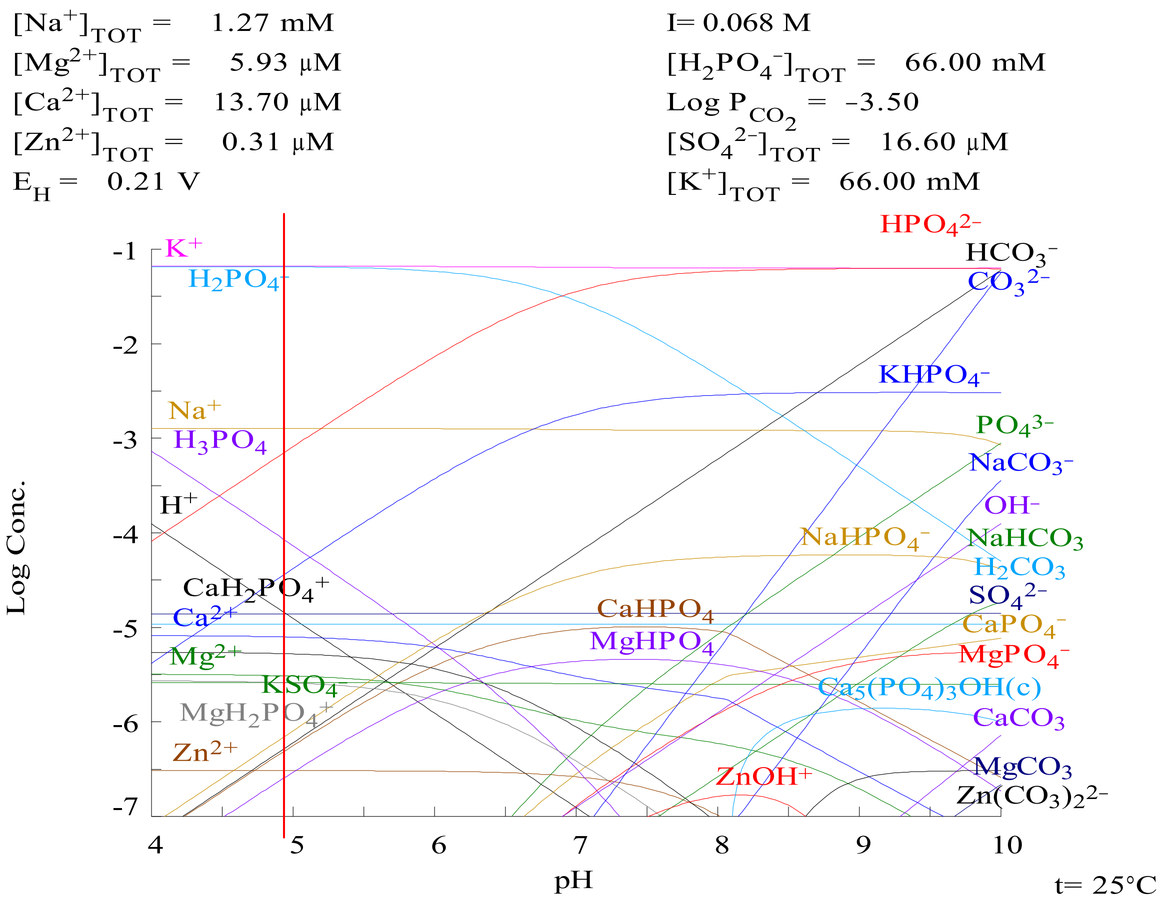


Figure C.197. Phase diagram for HDPE pipe section immersed into pH 5 water after one day of exposure. Study area.

Table C.48. The predominant species of zinc. HDPE pipe section, pH 5 water, one day exposure.

Component	Log Concentration (mol/L)	Concentration (mol/L)	Zn Concentration (mg/L as Zn)	Cumulative Percentage of Zn
Zn^{2+}	-6.52	3.05E-07	2.00E-02	99.82
$ZnOH^{+}$	-9.42	3.83E-10	2.50E-05	99.95

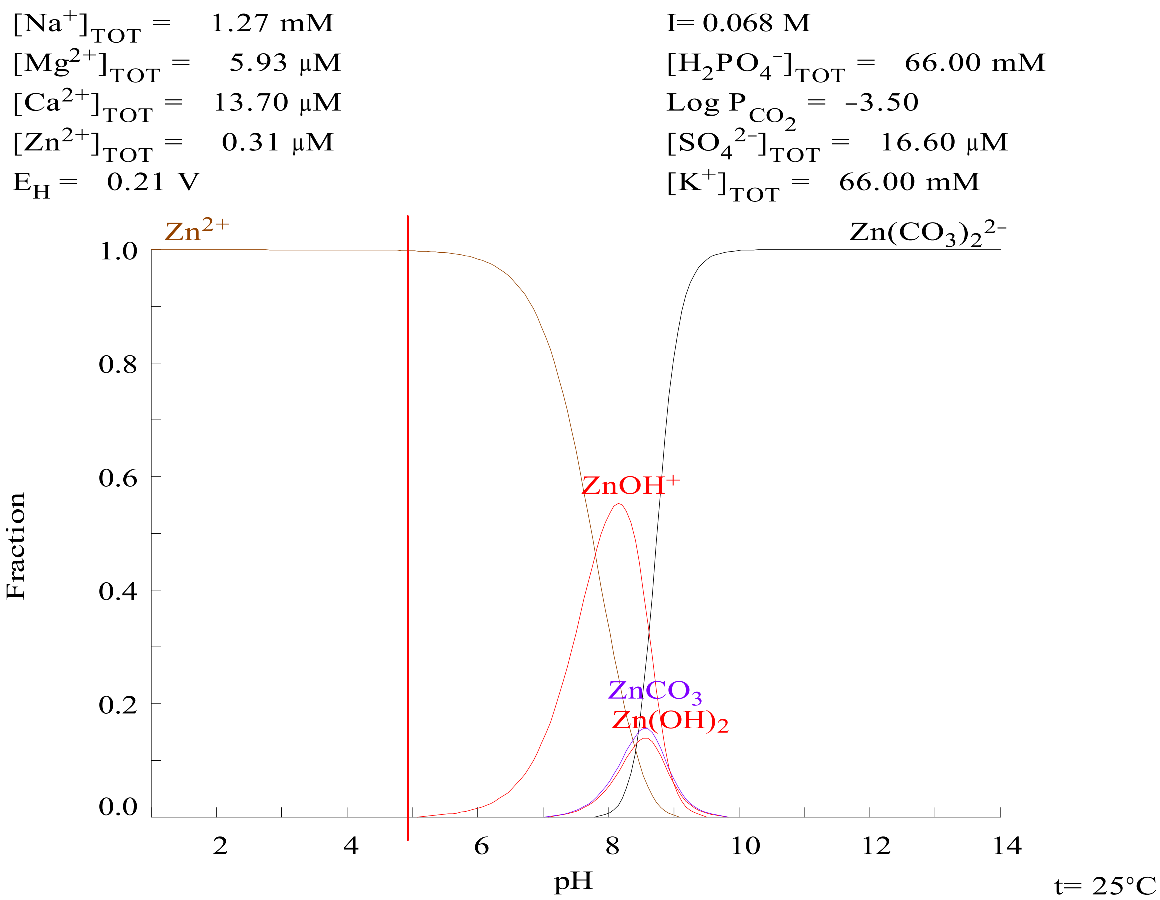


Figure C.198. Fraction diagram of zinc for HDPE pipe section immersed into pH 5 water after one day of exposure.

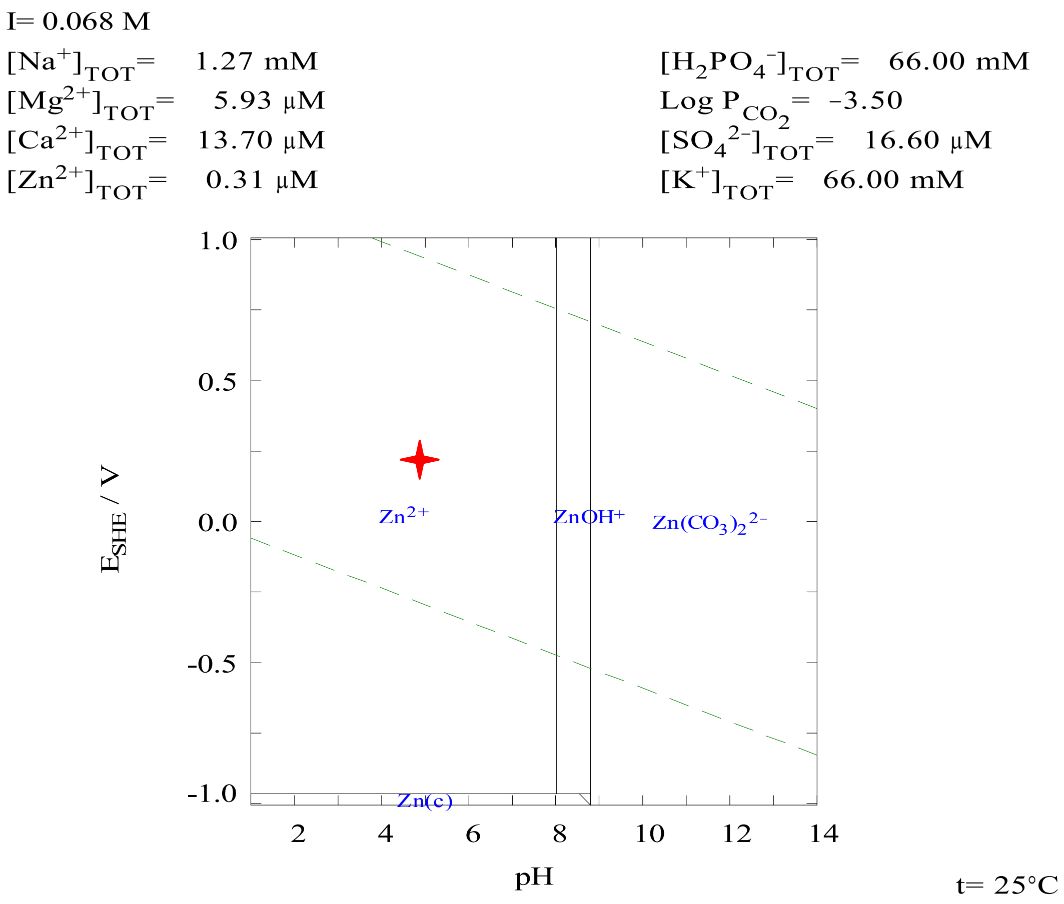


Figure C.199. Pourbaix diagram of zinc for HDPE pipe section immersed into pH 5 water after one day of exposure.

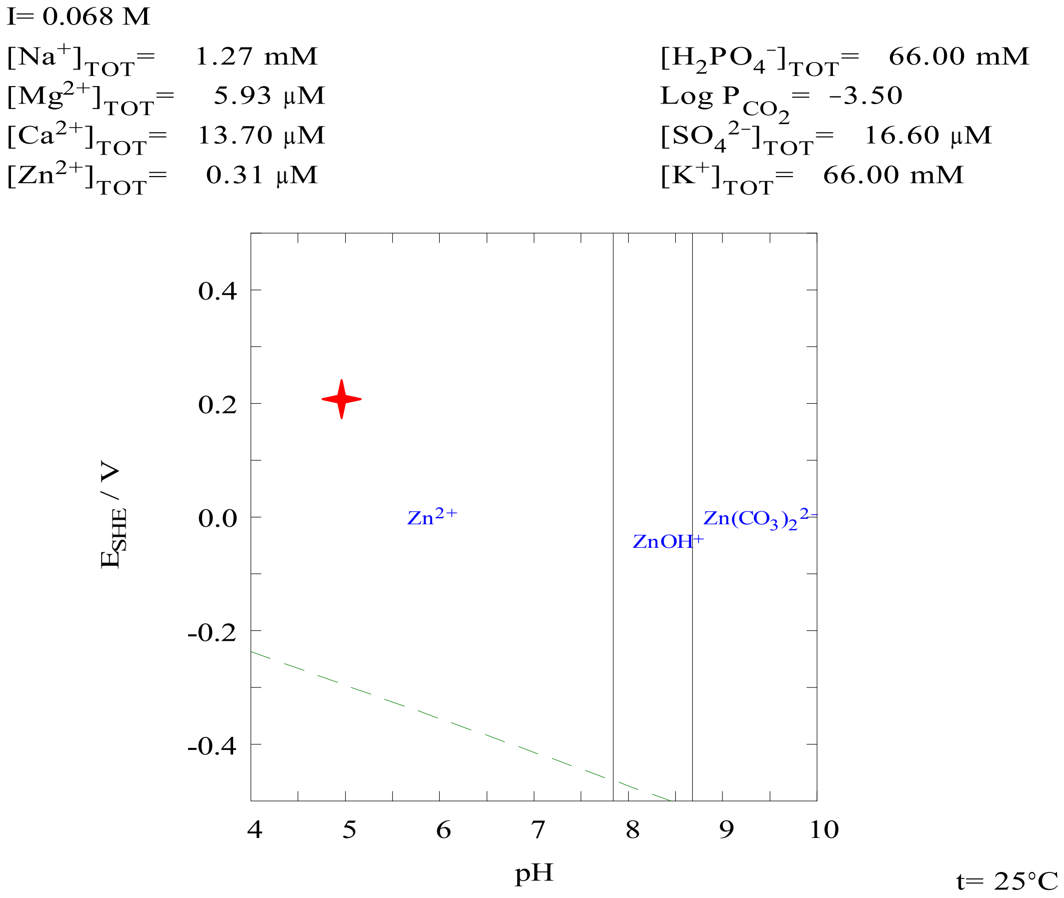


Figure C.200. Pourbaix diagram of zinc for HDPE pipe section immersed into pH 5 water after one day of exposure. Study area.

HDPE Pipe, pH 8 Water, After One Day of Exposure

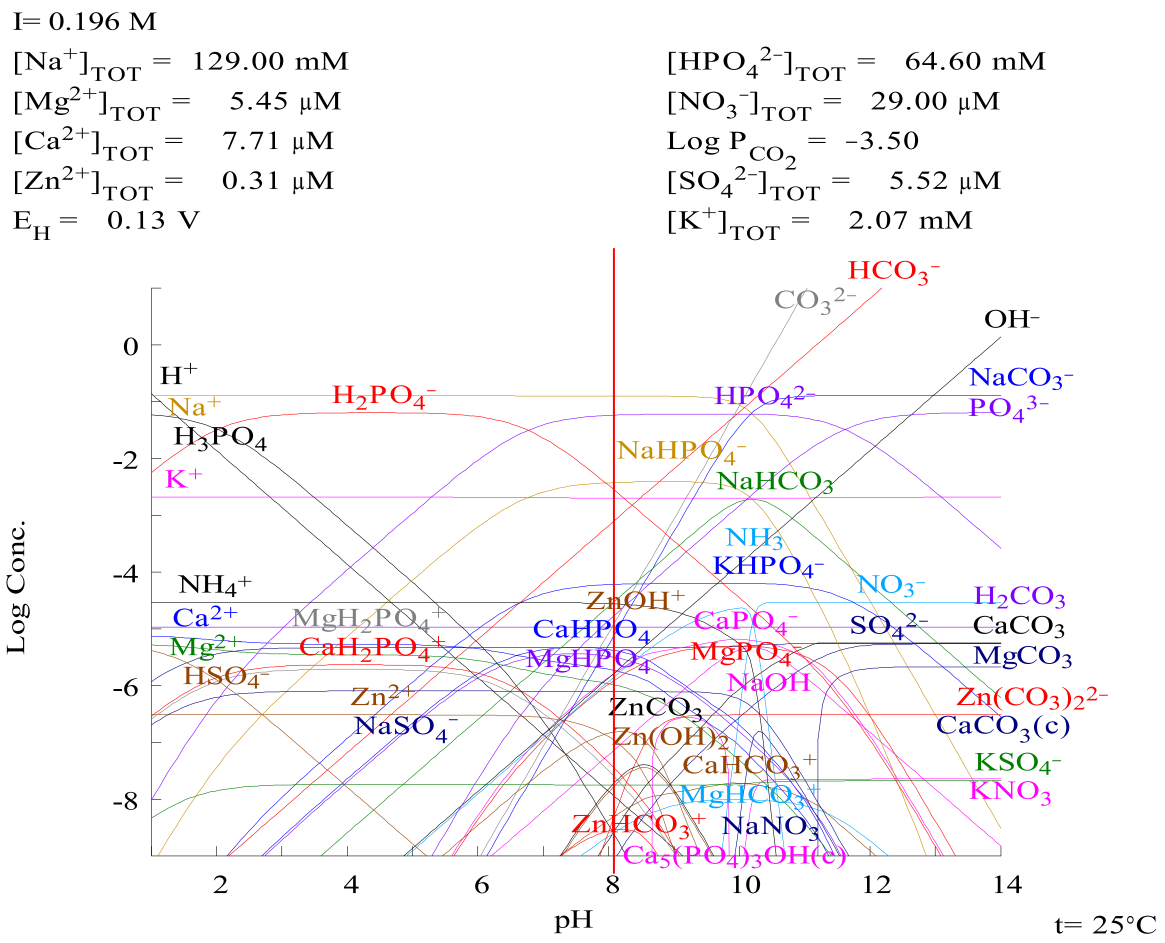


Figure C.201. Phase diagram for HDPE pipe section immersed into pH 8 water after one day of exposure.

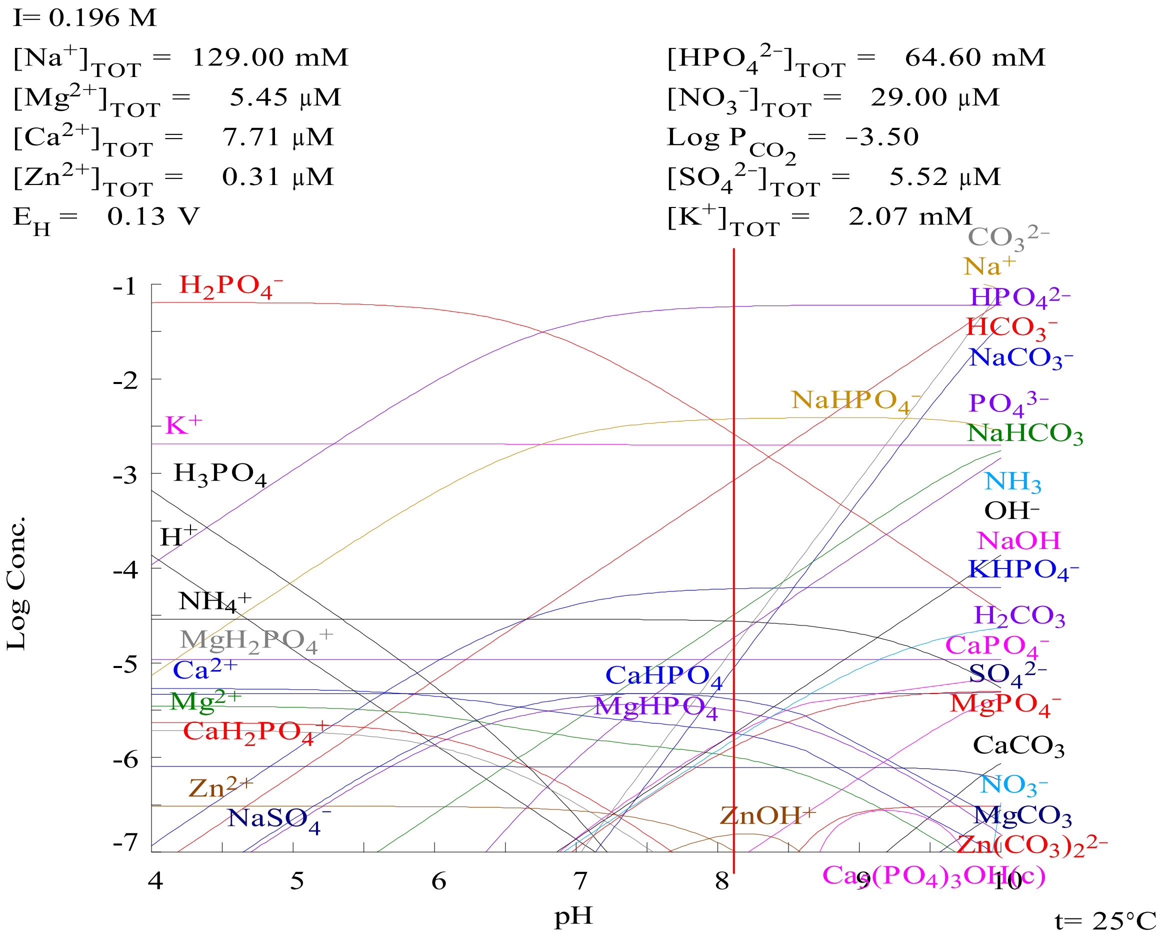


Figure C.202. Phase diagram for HDPE pipe section immersed into pH 8 water after one day of exposure. Study area.

Table C.49. The predominant species of zinc. HDPE pipe section, pH 8 water, one day exposure.

Component	Log Concentration (mol/L)	Concentration (mol/L)	Zn Concentration (mg/L as Zn)	Cumulative Percentage of Zn
Zn^{2+}	-6.52	3.05E-07	1.998E-02	99.82
$ZnOH^+$	-9.29	5.08E-10	3.32E-05	99.99

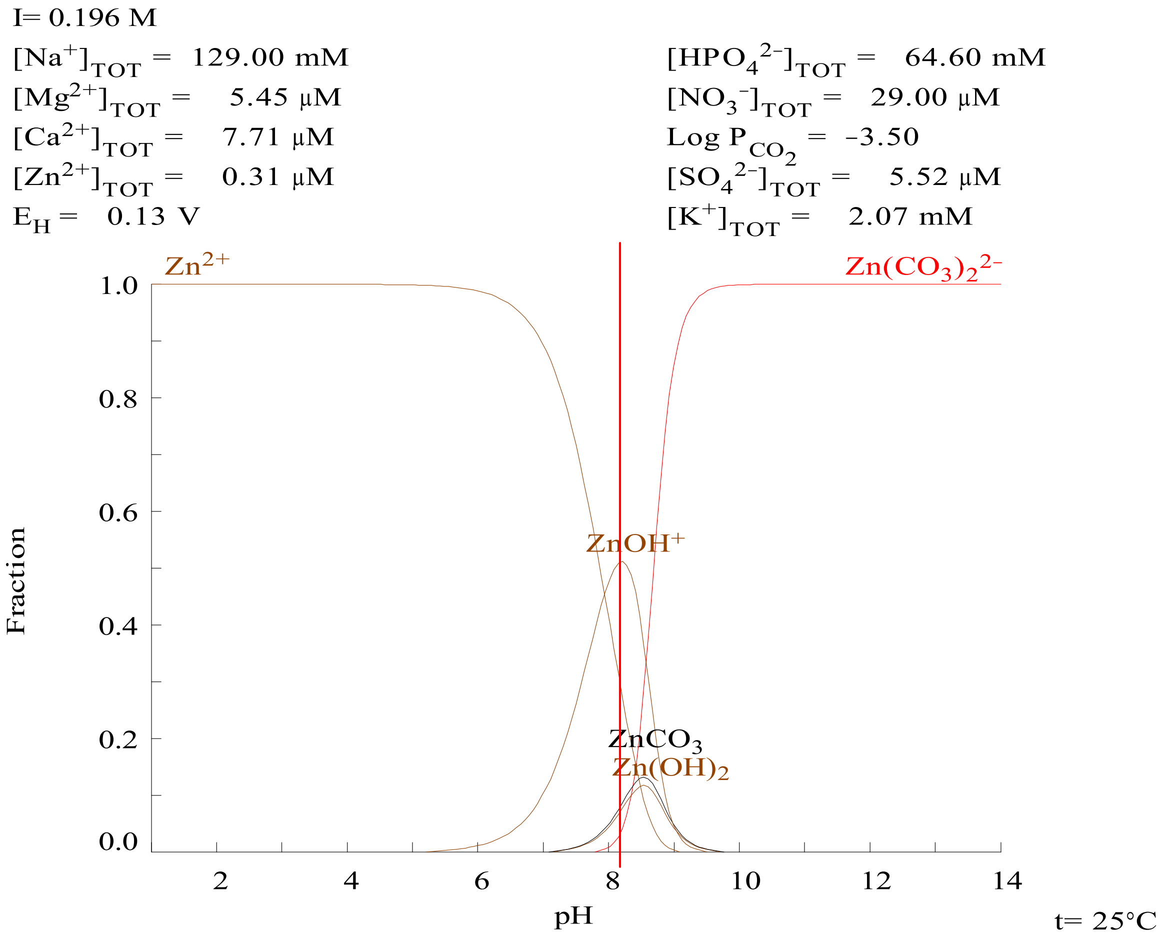


Figure C.203. Fraction diagram of zinc for HDPE pipe section immersed into pH 8 water after one day of exposure.

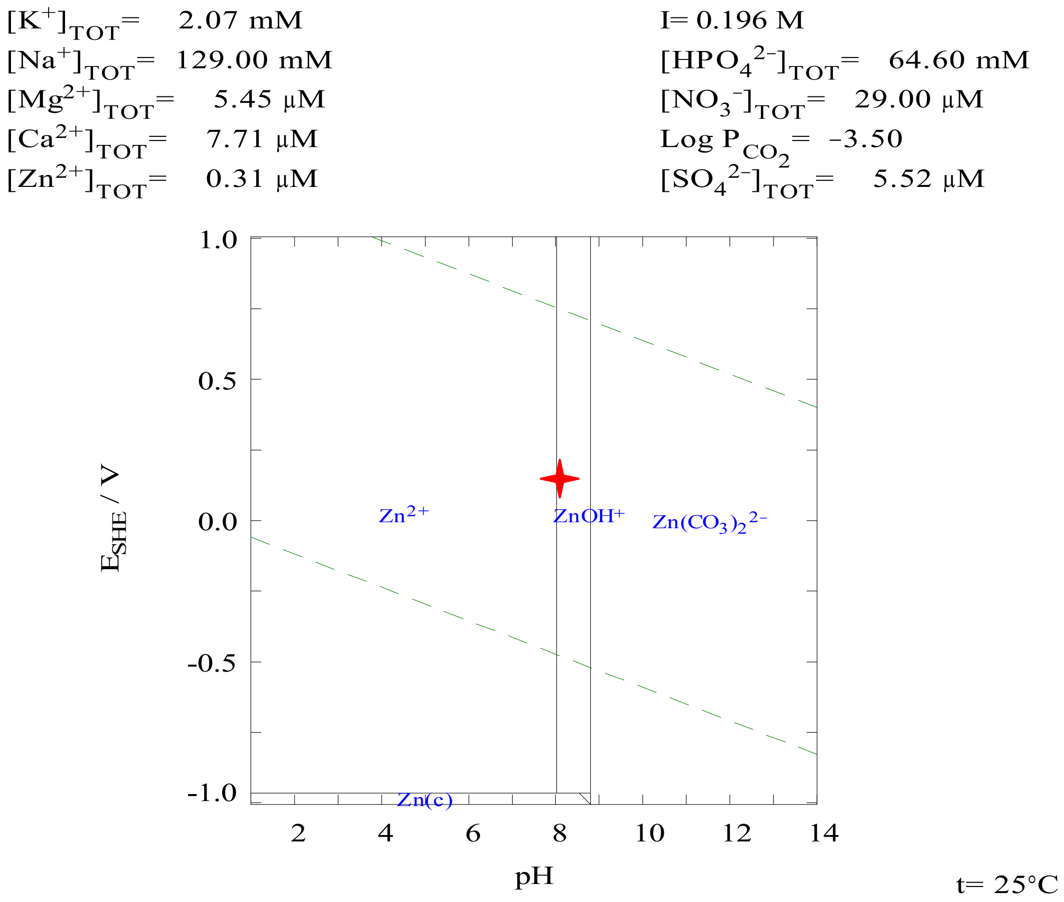


Figure C.204. Pourbaix diagram of zinc for HDPE pipe section immersed into pH 8 water after one day of exposure.

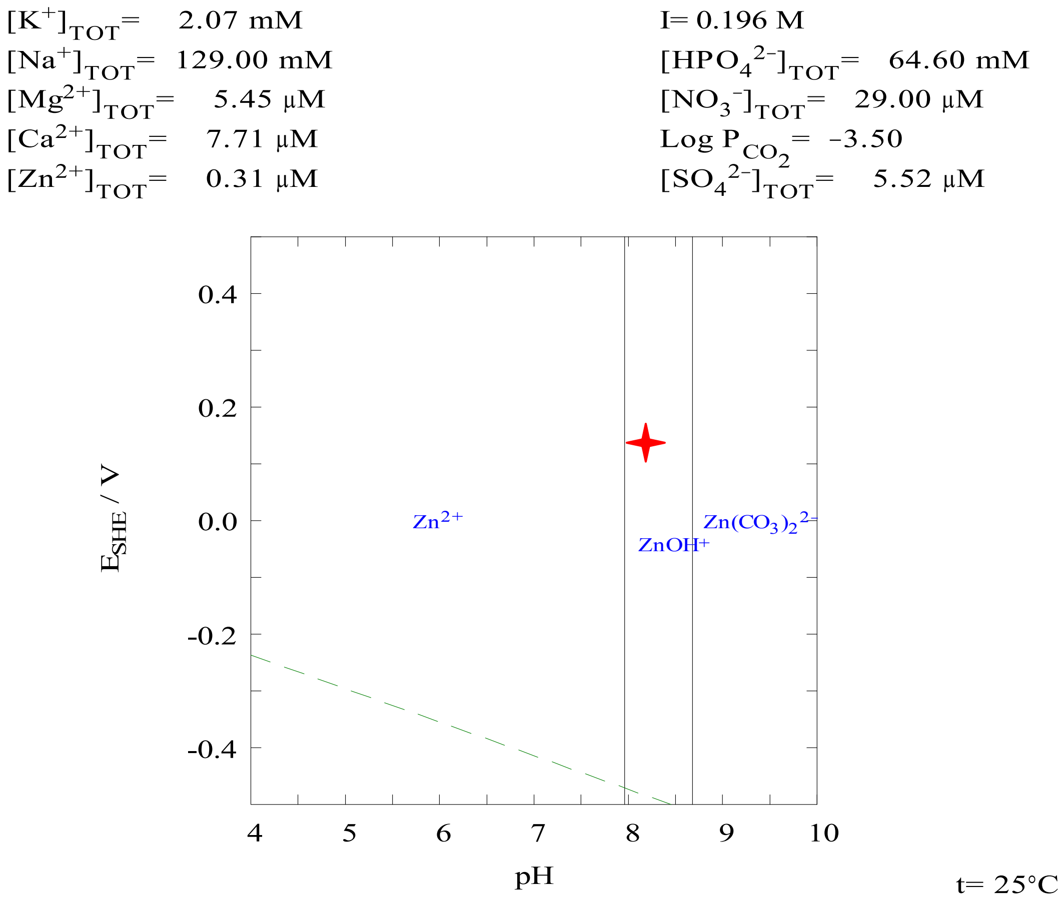


Figure C.205. Pourbaix diagram of zinc for HDPE pipe section immersed into pH 8 water after one day of exposure. Study area.

Aluminum Gutter, pH 8 Water, After One Day of Exposure

I= 0.196 M

$[Na^+]_{TOT}$ = 129.00 mM

$[Mg^{2+}]_{TOT}$ = 2.85 µM

$[Ca^{2+}]_{TOT}$ = 0.10 µM

$[Zn^{2+}]_{TOT}$ = 0.31 µM

E_H = 0.14 V

$[HPO_4^{2-}]_{TOT}$ = 64.60 mM

$[NO_3^-]_{TOT}$ = 32.30 µM

Log P_{CO_2} = -3.50

$[SO_4^{2-}]_{TOT}$ = 7.91 µM

$[K^+]_{TOT}$ = 2.07 mM

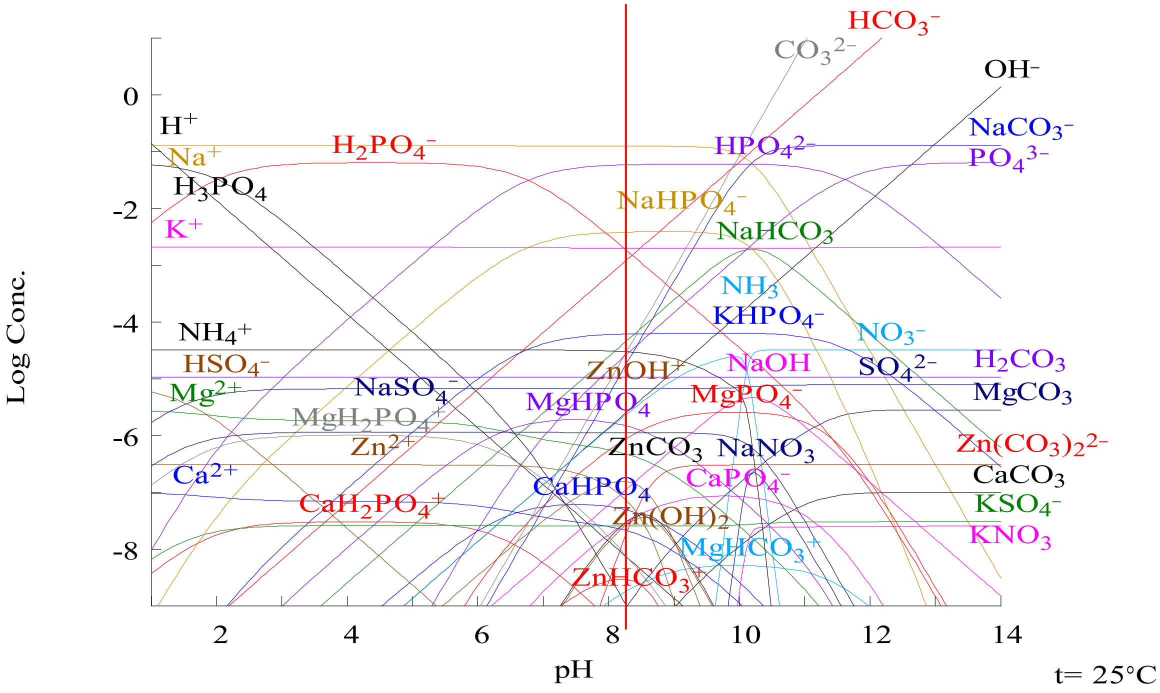


Figure C.206. Phase diagram for Aluminum gutter section immersed into pH 8 water after one day of exposure.

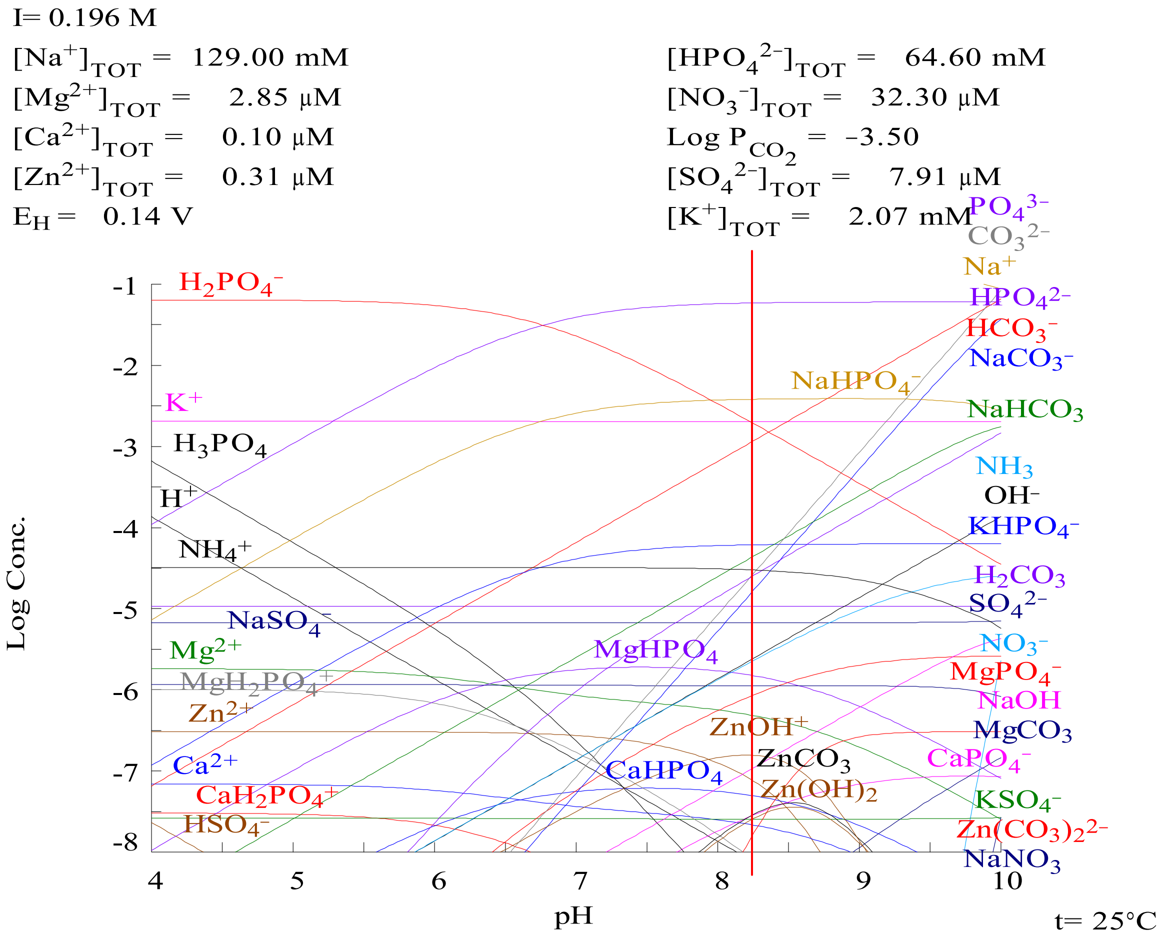


Figure C.207. Phase diagram for aluminum gutter section immersed into pH 8 water after one day of exposure. Study area.

Table C.50. The predominant species of zinc. Aluminum gutter section, pH 8 water, one day exposure.

Component	Log Concentration (mol/L)	Concentration (mol/L)	Zn Concentration (mg/L as Zn)	Cumulative Percentage of Zn
$ZnOH^+$	-6.81	1.57E-07	1.02E-02	51.19
Zn^{2+}	-7.08	8.30E-08	5.43E-03	78.29
$ZnCO_3$	-7.57	2.67E-08	1.75E-03	87.03
$Zn(OH)_2$	-7.62	2.38E-08	1.56E-03	94.80
$Zn(CO_3)_2^{2-}$	-7.89	1.29E-08	8.44E-04	99.02
$ZnHCO_3^+$	-8.53	2.98E-09	1.95E-04	99.99

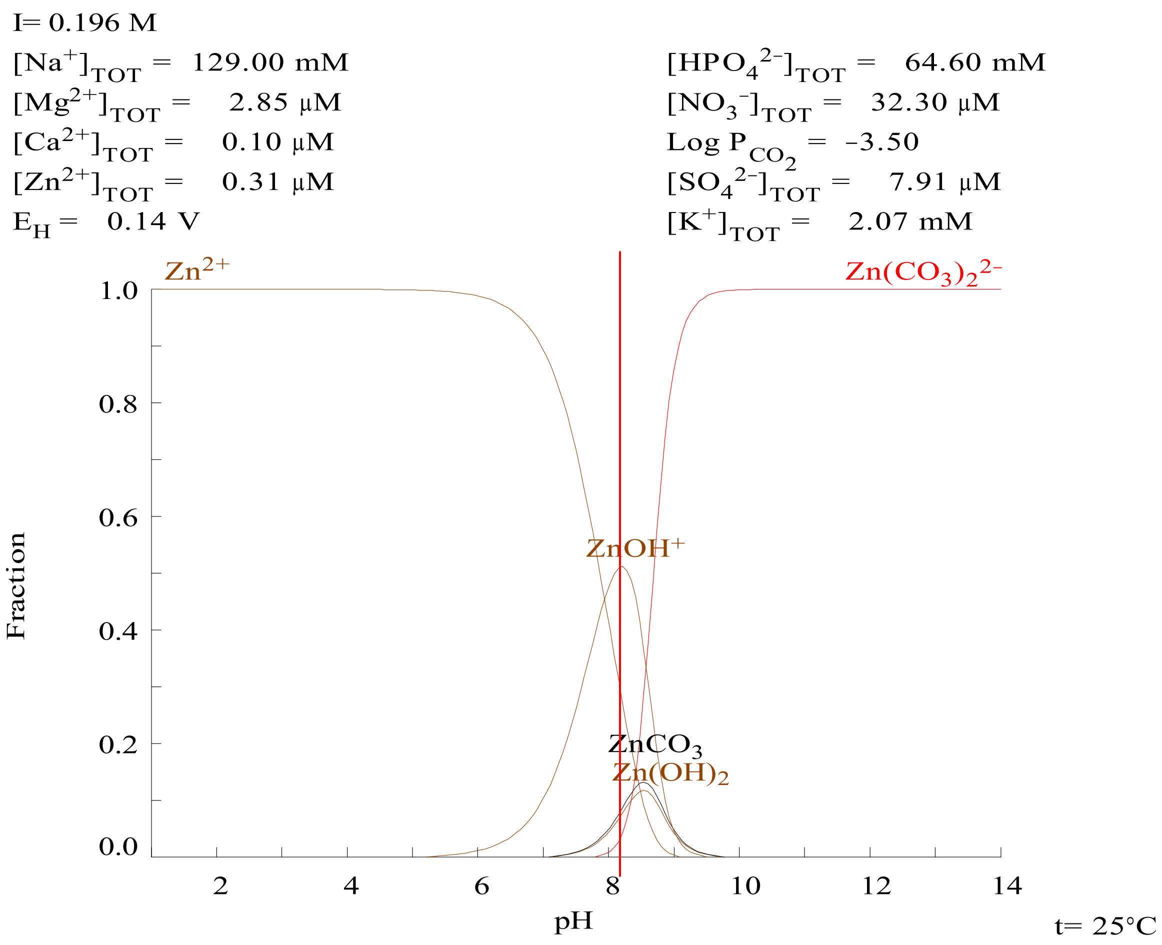


Figure C.208. Fraction diagram of zinc for aluminum gutter section immersed into pH 8 water after one day of exposure.

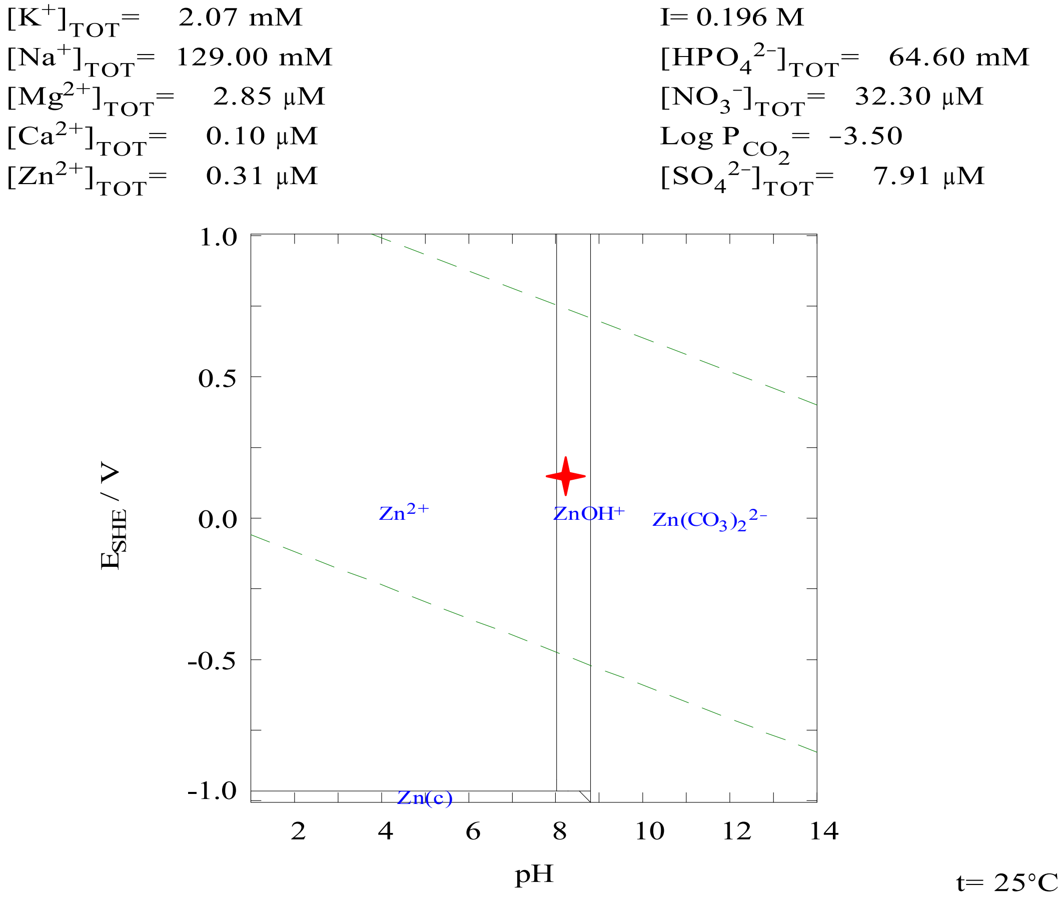


Figure C.209. Pourbaix diagram of zinc for aluminum gutter section immersed into pH 8 water after one day of exposure.

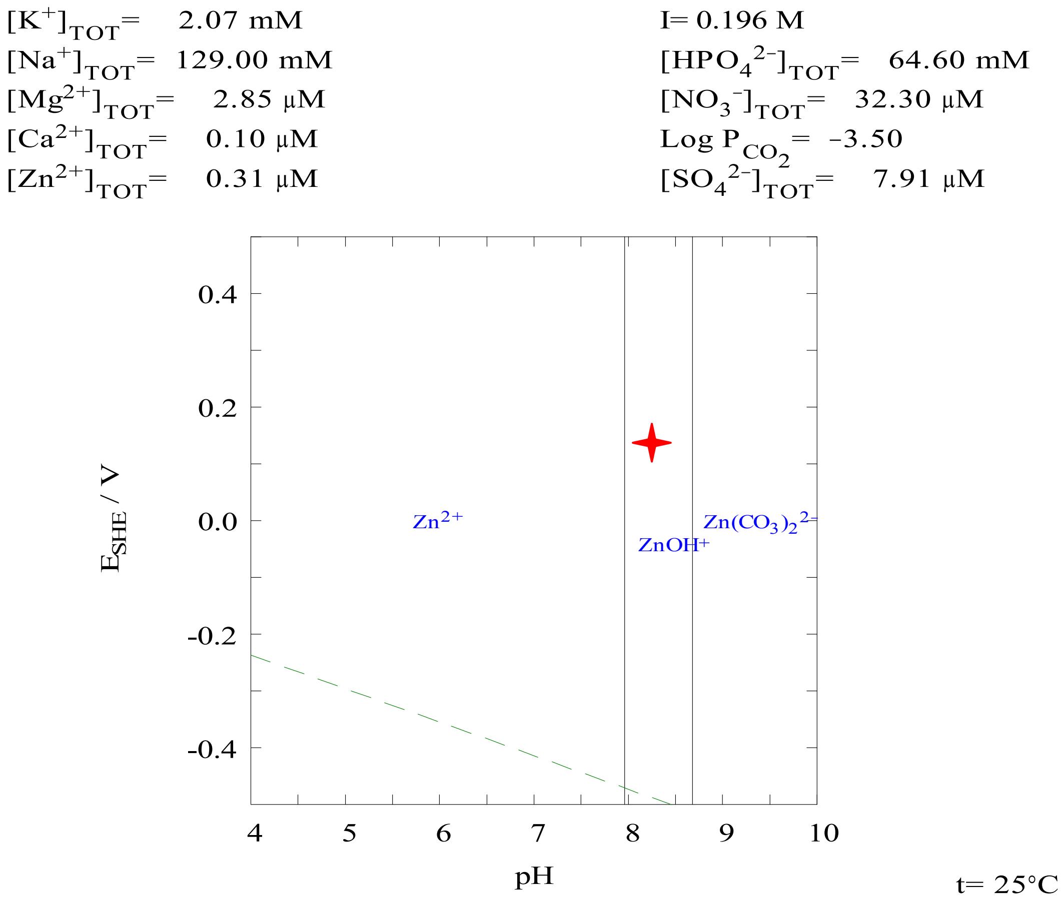


Figure C.210. Pourbaix diagram of zinc for aluminum gutter section immersed into pH 8 water after one day of exposure. Study area.

Copper Gutter, pH 5 Water, After One Day of Exposure

$[Na^+]_{TOT}$ = 1.27 mM
$[Mg^{2+}]_{TOT}$ = 5.22 μM
$[Ca^{2+}]_{TOT}$ = 0.10 μM
$[Zn^{2+}]_{TOT}$ = 0.61 μM
$[Cu^{2+}]_{TOT}$ = 0.11 mM
E_H = 0.25 V

I= 0.068 M
$[H_2PO_4^-]_{TOT}$ = 66.00 mM
$[NO_3^-]_{TOT}$ = 1.61 μM
Log P_{CO_2} = -3.50
$[SO_4^{2-}]_{TOT}$ = 27.60 μM
$[K^+]_{TOT}$ = 66.00 mM

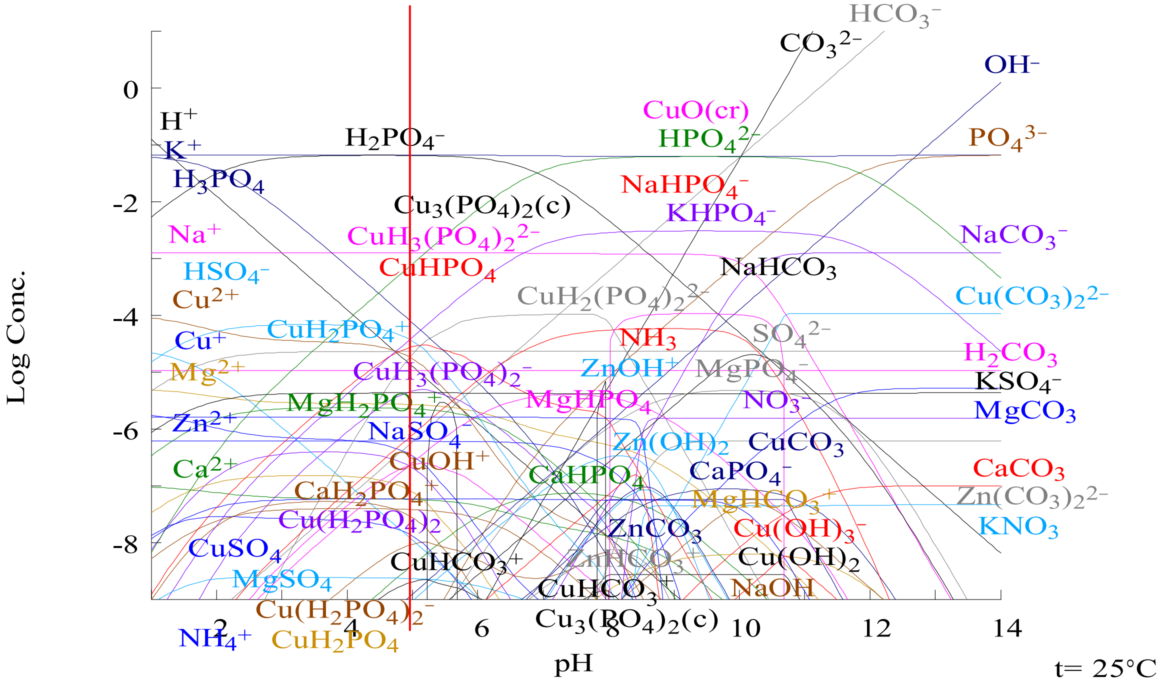


Figure C.211. Phase diagram for copper gutter section immersed into pH 5 water after one day of exposure.

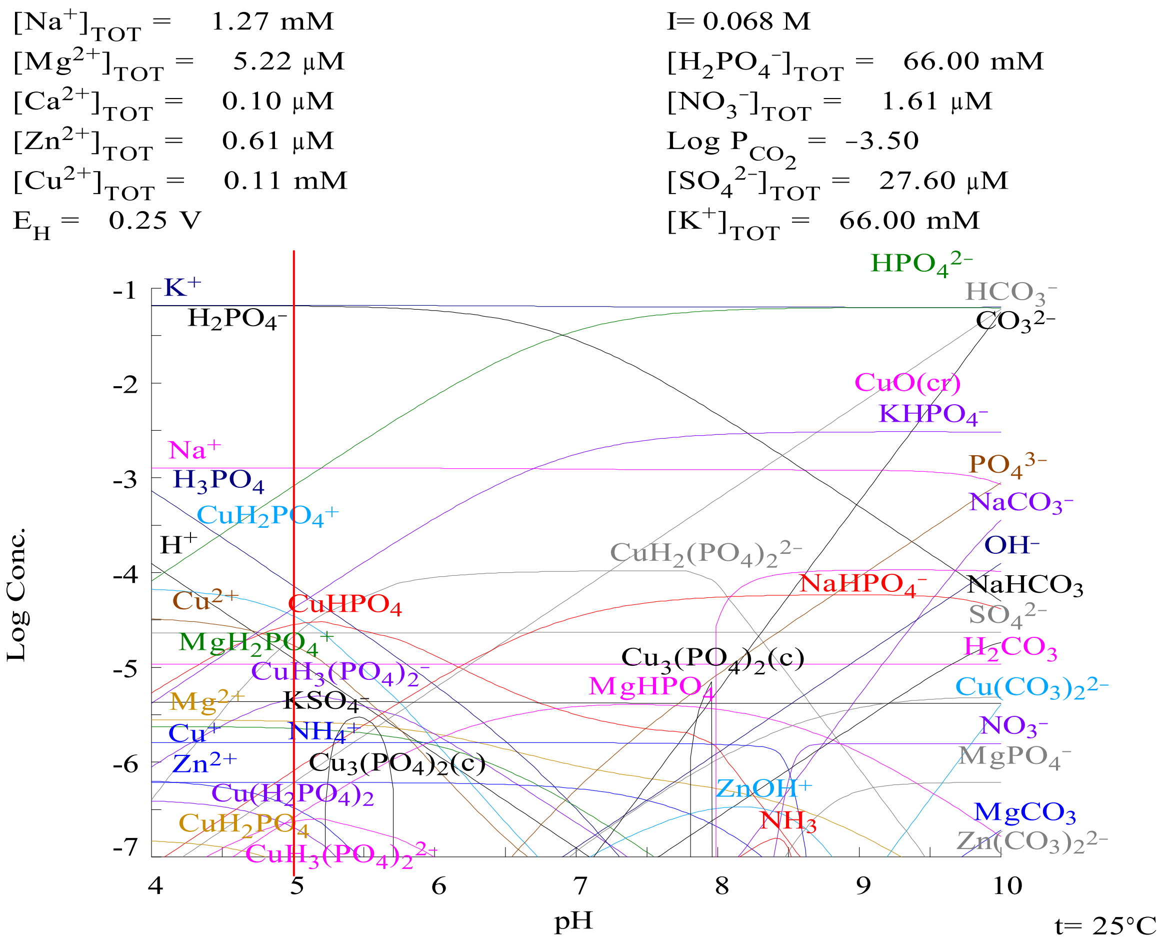


Figure C.212. Phase diagram for copper gutter section immersed into pH 5 water after one day of exposure. Study area.

Table C.51. The predominant species of zinc. Copper gutter section, pH 5 water, one day exposure.

Component	Log Concentration (mol/L)	Concentration (mol/L)	Zn Concentration (mg/L as Zn)	Cumulative Percentage of Zn
Zn^{2+}	-6.21	6.10E-07	3.99E-02	99.74
$ZnOH^+$	-8.99	1.03E-09	6.75E-05	99.91

Table C.52. The predominant species of copper. Copper gutter section, pH 5 water, one day exposure.

Component	Log Concentration (mol/L)	Concentration (mol/L)	Cu Concentration (mg/L as Cu)	Cumulative Percentage of Cu
CuH_2PO4^+	-4.48	3.34E-05	2.13	31.26
$CuHPO_4$	-4.54	2.87E-05	1.82	58.09
$CuH_2(PO_4)_2^{2-}$	-4.64	2.28E-05	1.45	79.44
Cu^{2+}	-4.79	1.64E-05	1.04	94.74
$CuH_3(PO_4)_2^-$	-5.32	4.75E-06	3.02E-01	99.18
Cu^+	-6.50	3.18E-07	2.02E-02	99.48
$CuH_3(PO_4)_2^{2-}$	-6.62	2.39E-07	1.52E-02	99.70
$Cu(H_2PO4)_2$	-6.71	1.95E-07	1.24E-02	99.88
CuH_2PO_4	-7.13	7.38E-08	4.69E-03	99.95

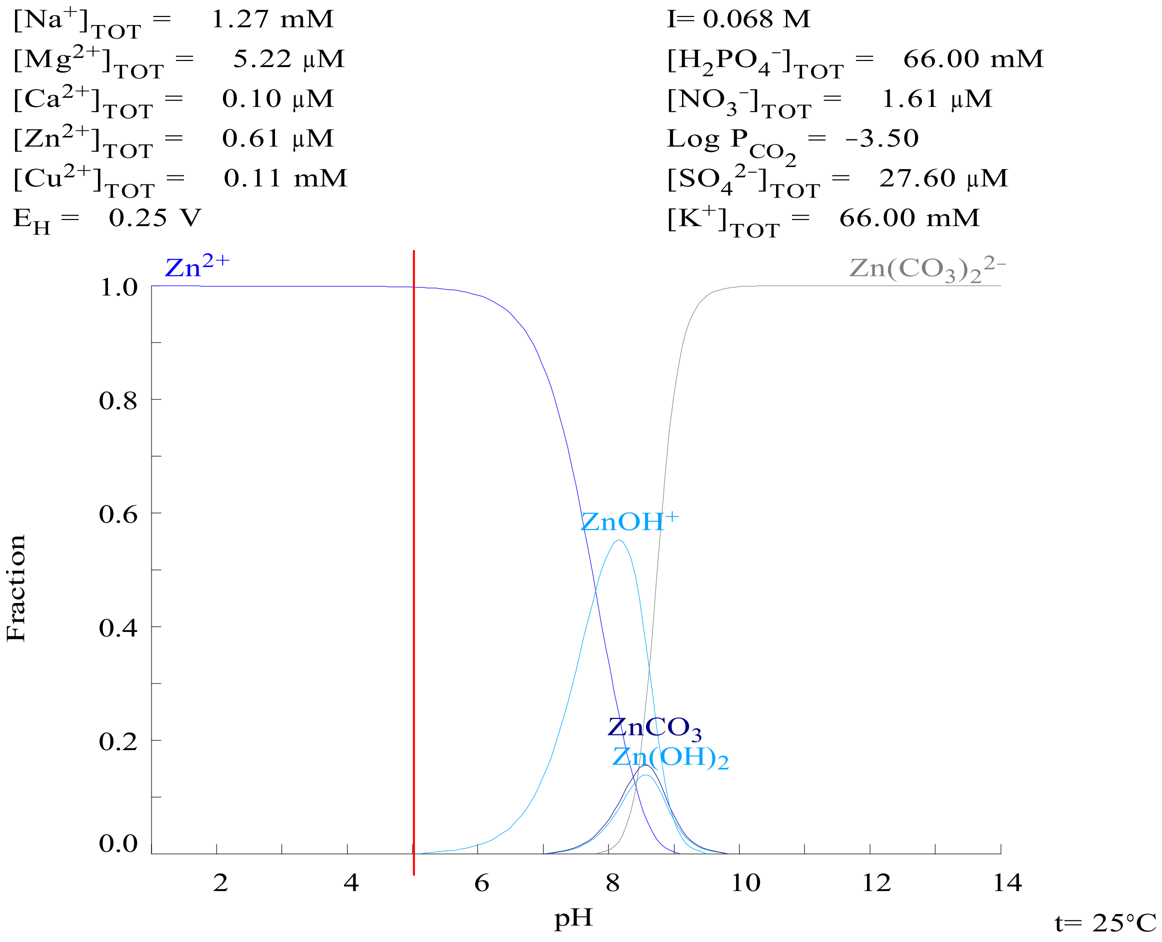


Figure C.213. Fraction diagram of zinc for copper gutter section immersed into pH 5 water after one day of exposure.

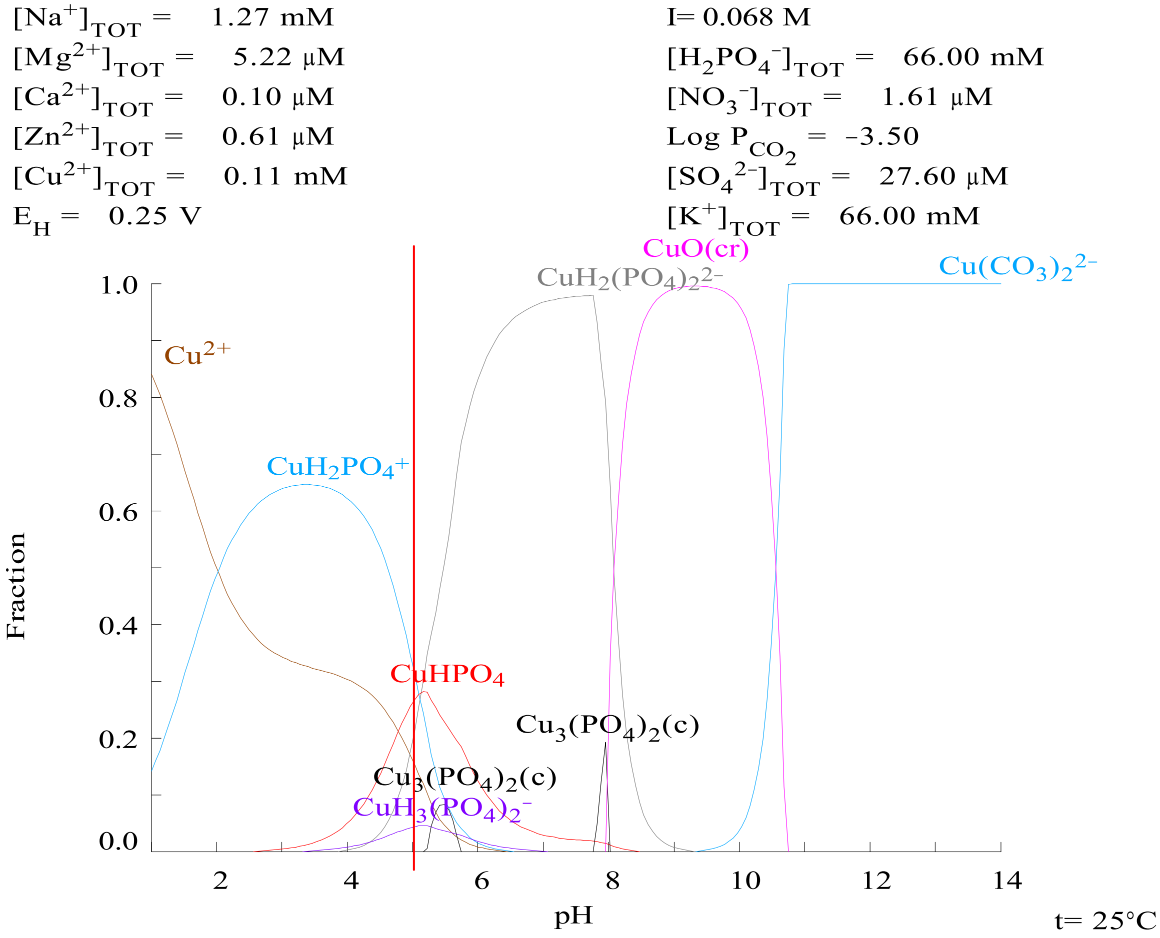


Figure C.214. Fraction diagram of copper for copper gutter section immersed into pH 5 water after one day of exposure.

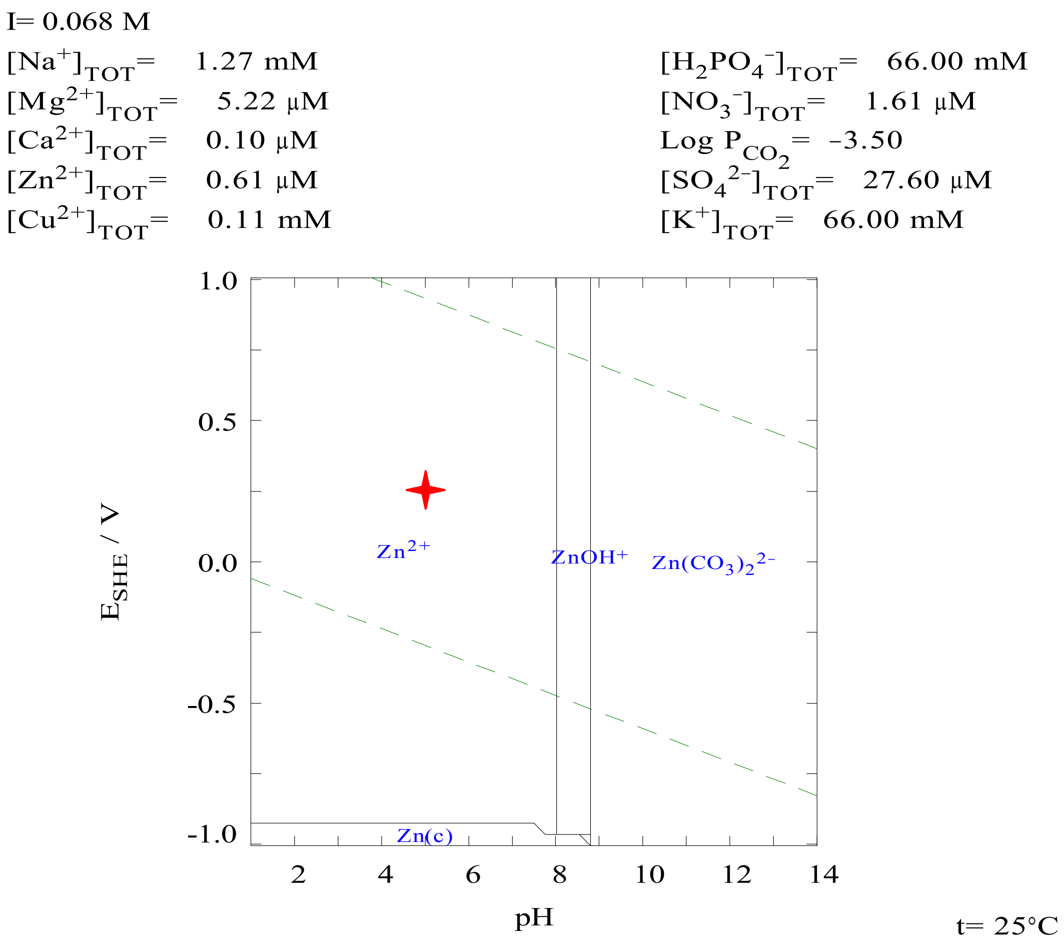


Figure C.215. Pourbaix diagram of zinc for copper gutter section immersed into pH 5 water after one day of exposure.

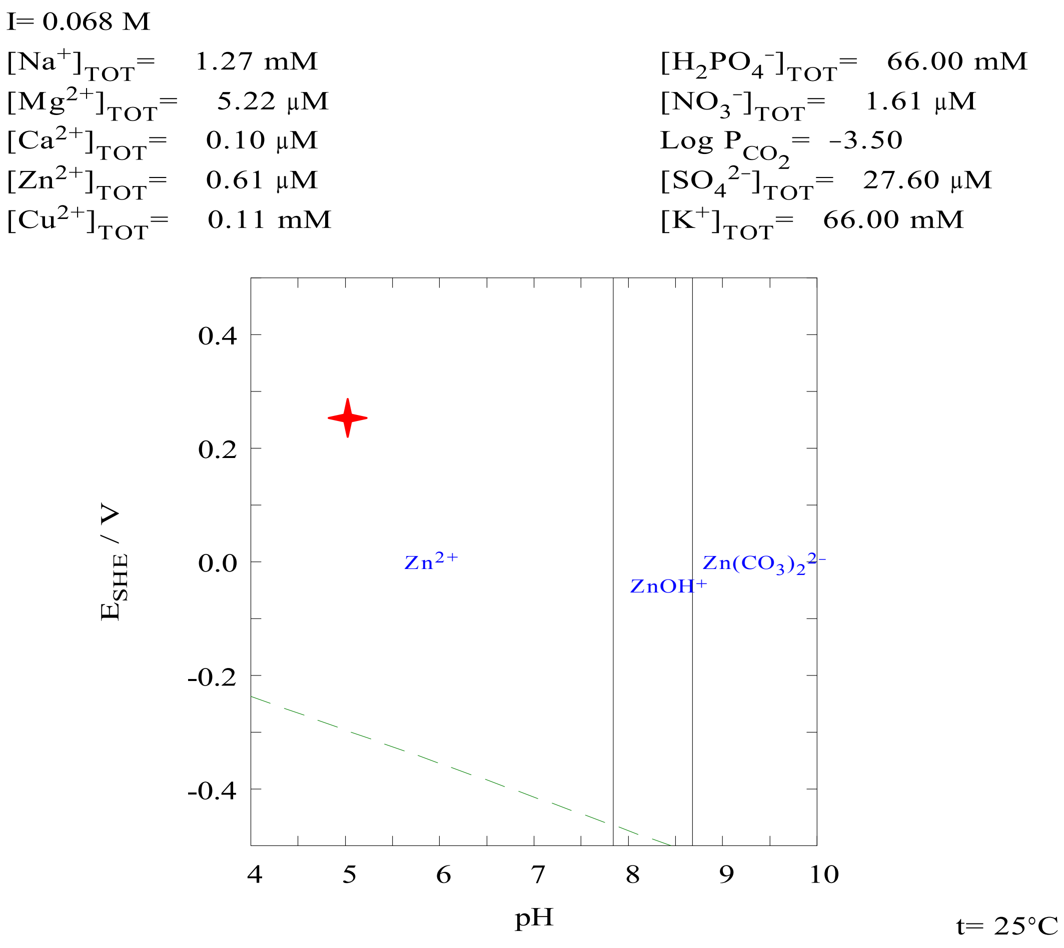


Figure C.216. Pourbaix diagram of zinc for copper gutter section immersed into pH 5 water after one day of exposure. Study area.

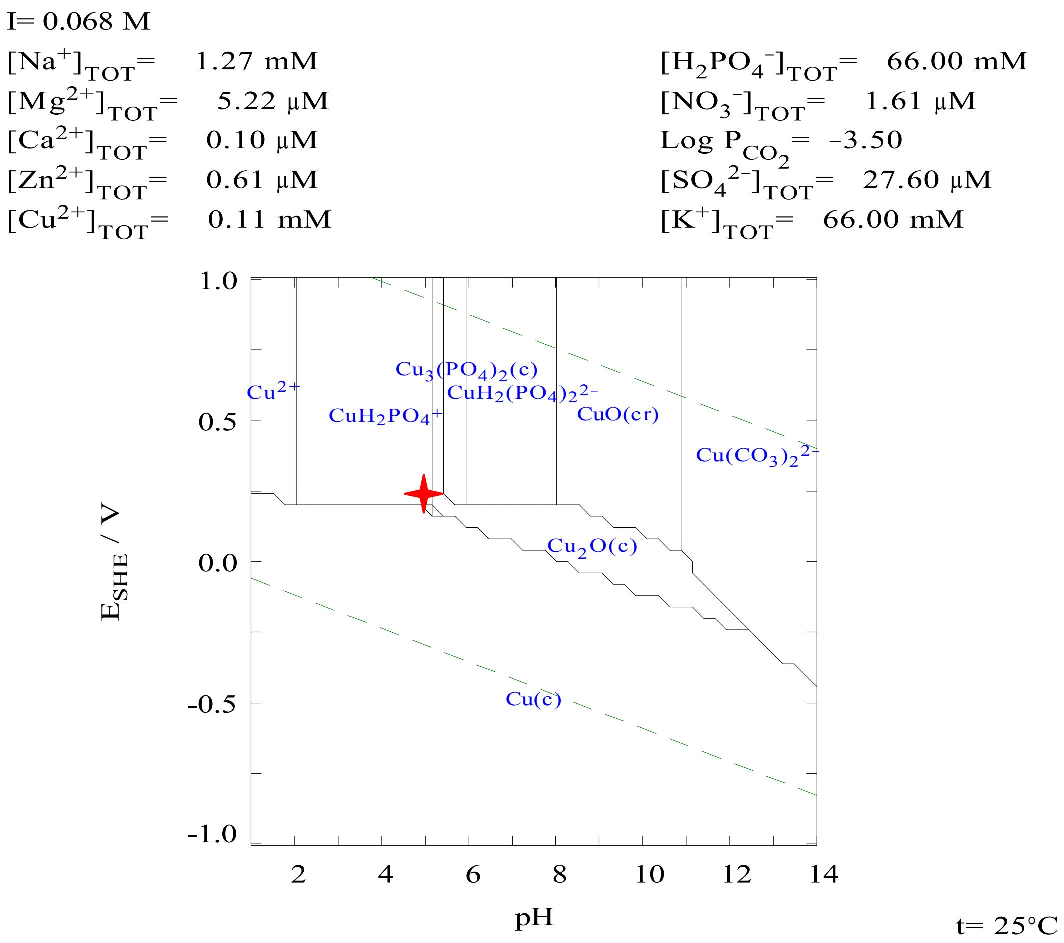
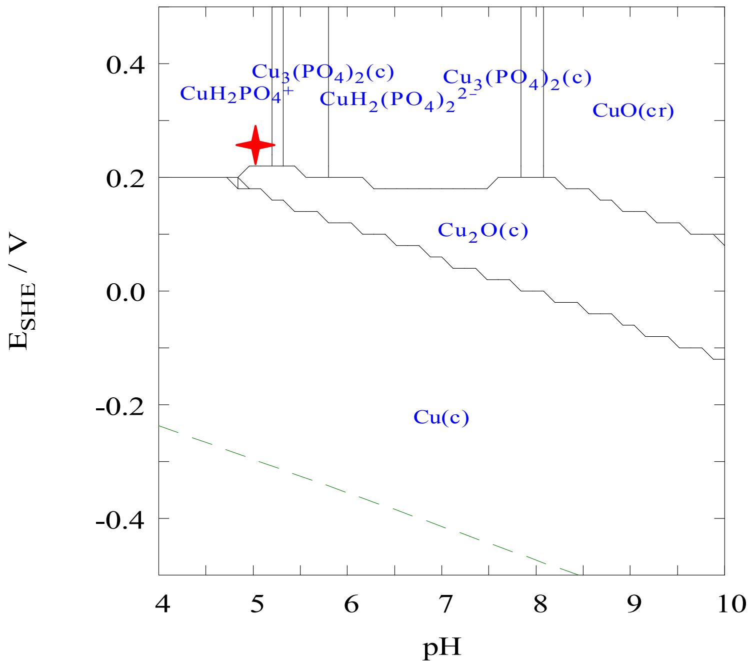


Figure C.217. Pourbaix diagram of copper for copper gutter section immersed into pH 5 water after one day of exposure.

I= 0.068 M

$[Na^+]_{TOT}$= 1.27 mM
$[Mg^{2+}]_{TOT}$= 5.22 μM
$[Ca^{2+}]_{TOT}$= 0.10 μM
$[Zn^{2+}]_{TOT}$= 0.61 μM
$[Cu^{2+}]_{TOT}$= 0.11 mM

$[H_2PO_4^-]_{TOT}$= 66.00 mM
$[NO_3^-]_{TOT}$= 1.61 μM
Log P_{CO_2}= -3.50
$[SO_4^{2-}]_{TOT}$= 27.60 μM
$[K^+]_{TOT}$= 66.00 mM



t= 25°C

Figure C.218. Pourbaix diagram of copper for copper gutter section immersed into pH 5 water after one day of exposure. Study area.

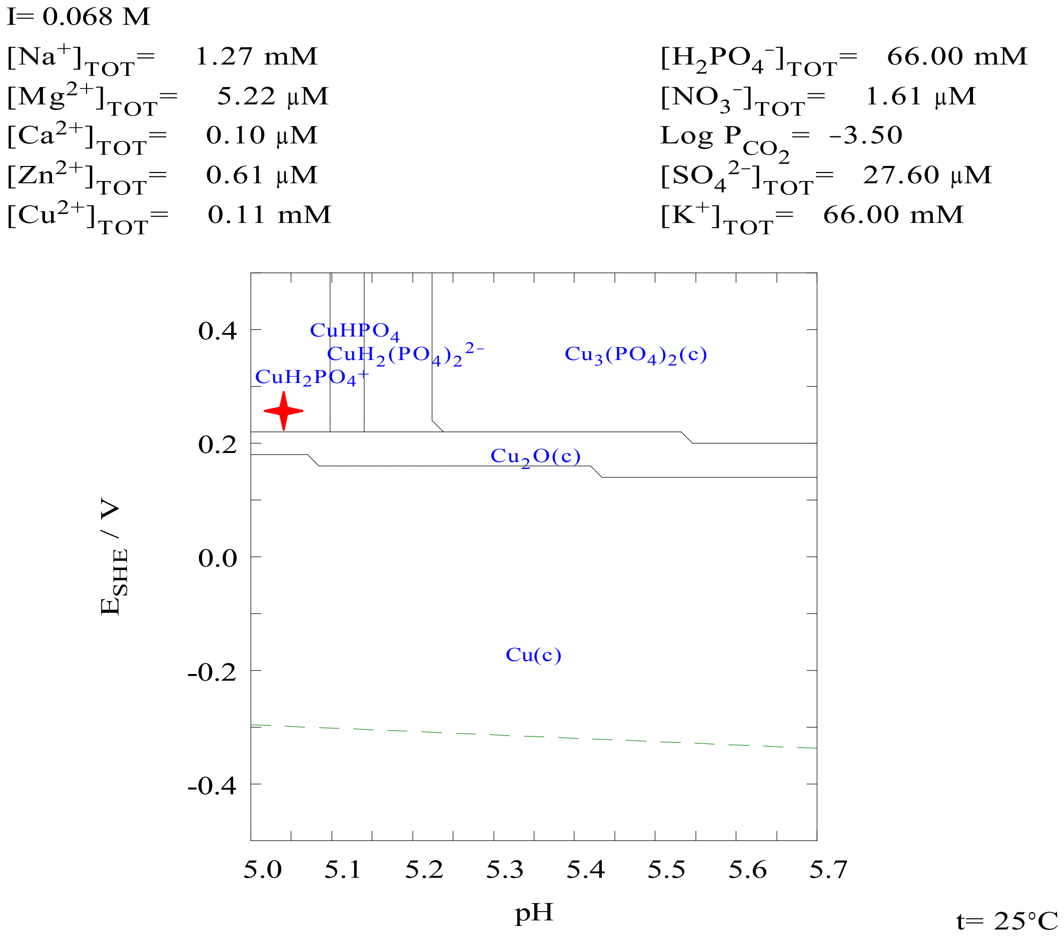


Figure C.219. Pourbaix diagram of copper for copper gutter section immersed into pH 5 water after one day of exposure. Study area.

Copper Gutter, pH 8 Water, After One Day of Exposure

$[Na^+]_{TOT}$ = 129.00 mM
$[Mg^{2+}]_{TOT}$ = 3.91 μM
$[Ca^{2+}]_{TOT}$ = 1.50 μM
$[Zn^{2+}]_{TOT}$ = 0.31 μM
$[Cu^{2+}]_{TOT}$ = 4.56 μM
E_H = 0.16 V

I= 0.196 M
$[HPO_4^{2-}]_{TOT}$ = 64.60 mM
$[NO_3^-]_{TOT}$ = 30.60 μM
Log P_{CO_2} = -3.50
$[SO_4^{2-}]_{TOT}$ = 24.80 μM
$[K^+]_{TOT}$ = 2.07 mM

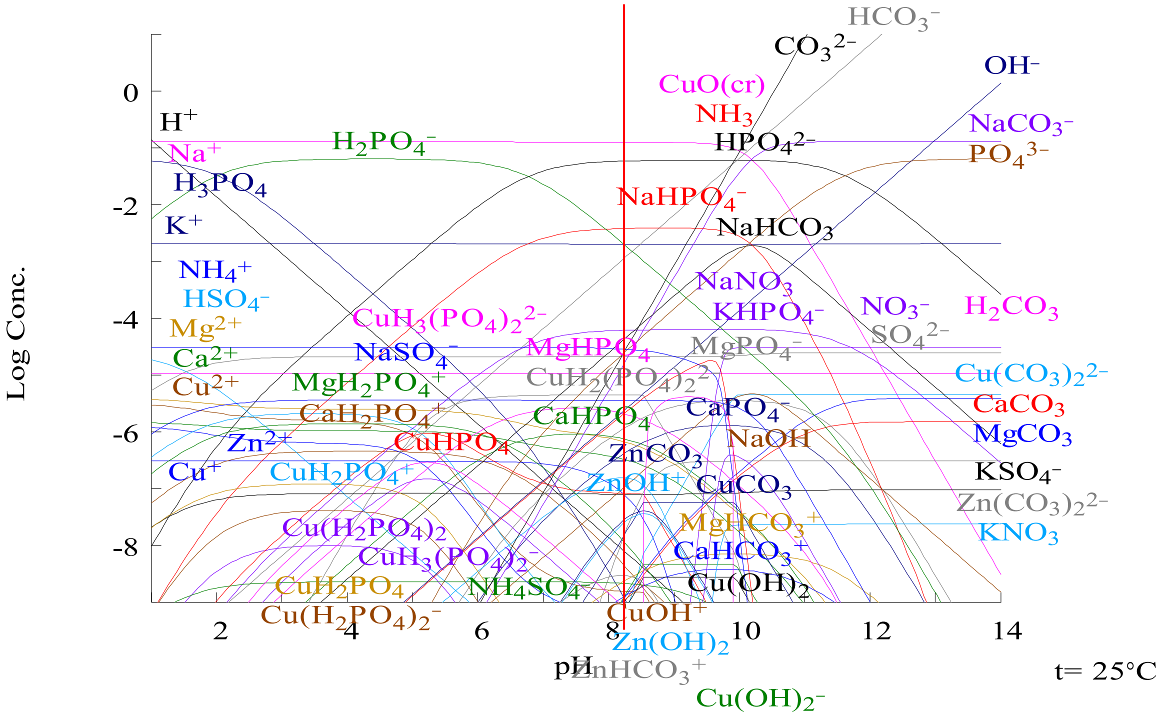


Figure C.220. Phase diagram for copper gutter section immersed into pH 8 water after one day of exposure.

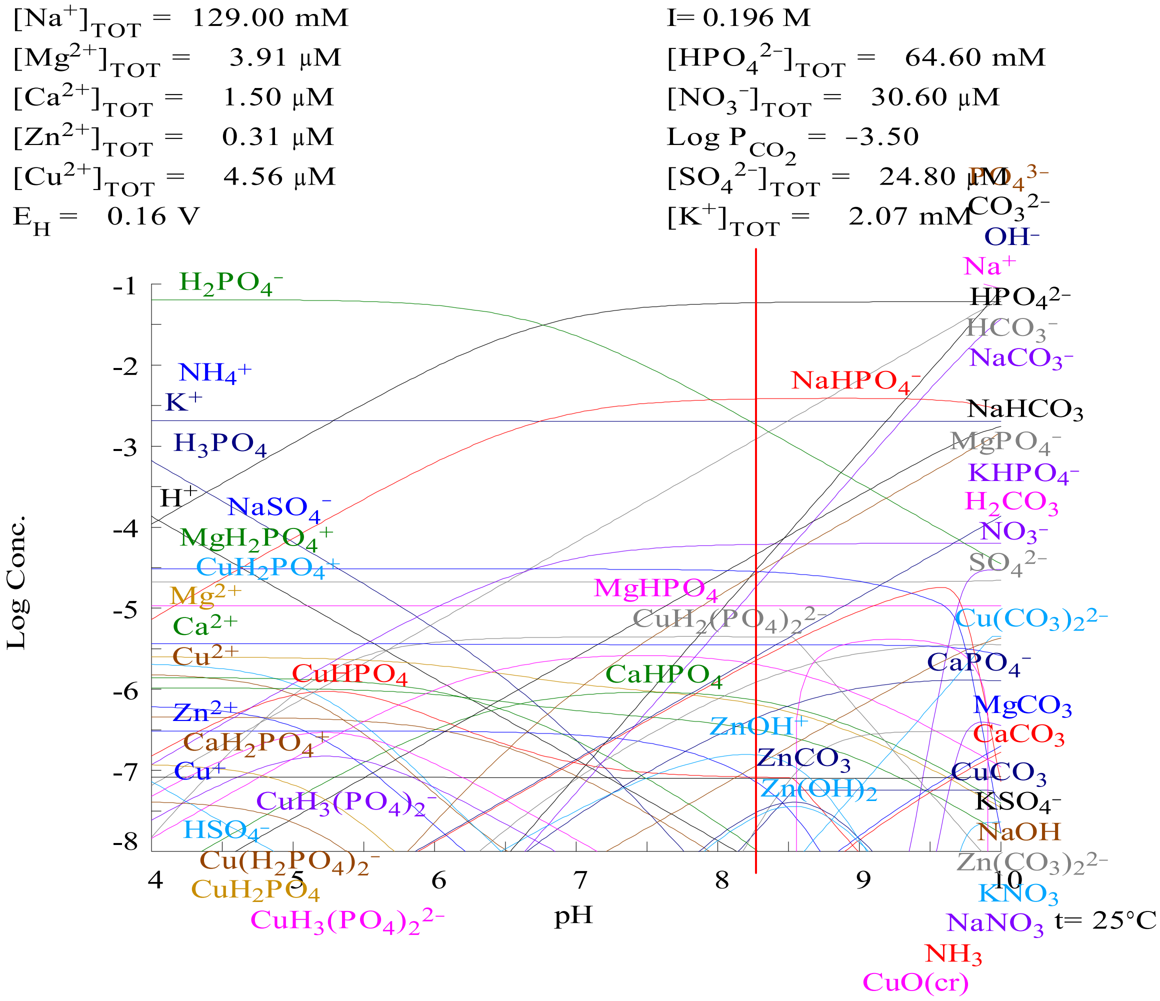


Figure C.221. Phase diagram for copper gutter section immersed into pH 8 water after one day of exposure. Study area.

Table C.53. The predominant species of zinc. Copper gutter section, pH 8 water, one day exposure.

Component	Log Concentration (mol/L)	Concentration (mol/L)	Zn Concentration (mg/L as Zn)	Cumulative Percentage of Zn
$ZnOH^+$	-6.81	1.55E-07	1.01E-02	50.53
Zn^{2+}	-7.15	7.05E-08	4.61E-03	73.57
ZnCO3	-7.51	3.07E-08	2.01E-03	83.59
$Zn(OH)_2$	-7.56	2.73E-08	1.78E-03	92.50
$Zn(CO_3)_2^{2-}$	-7.70	2.00E-08	1.31E-03	99.03
$ZnHCO_3^+$	-8.53	2.95E-09	1.93E-04	99.99

Table C.54. The predominant species of copper. Copper gutter section, pH 8 water, one day exposure.

Component	Log Concentration (mol/L)	Concentration (mol/L)	Cu Concentration (mg/L as Cu)	Cumulative Percentage of Cu
$CuH_2(PO_4)_2^{2-}$	-5.35	4.45E-06	2.83E-01	97.62
$CuHPO_4$	-7.08	8.25E-08	5.24E-03	99.43
CuCO3	-7.74	1.81E-08	1.15E-03	99.83
Cu^{2+}	-8.81	1.55E-09	9.83E-05	99.86
$Cu(OH)_2^-$	-8.83	1.49E-09	9.49E-05	99.89
$Cu(OH)^+$	-8.93	1.18E-09	7.47E-05	99.92

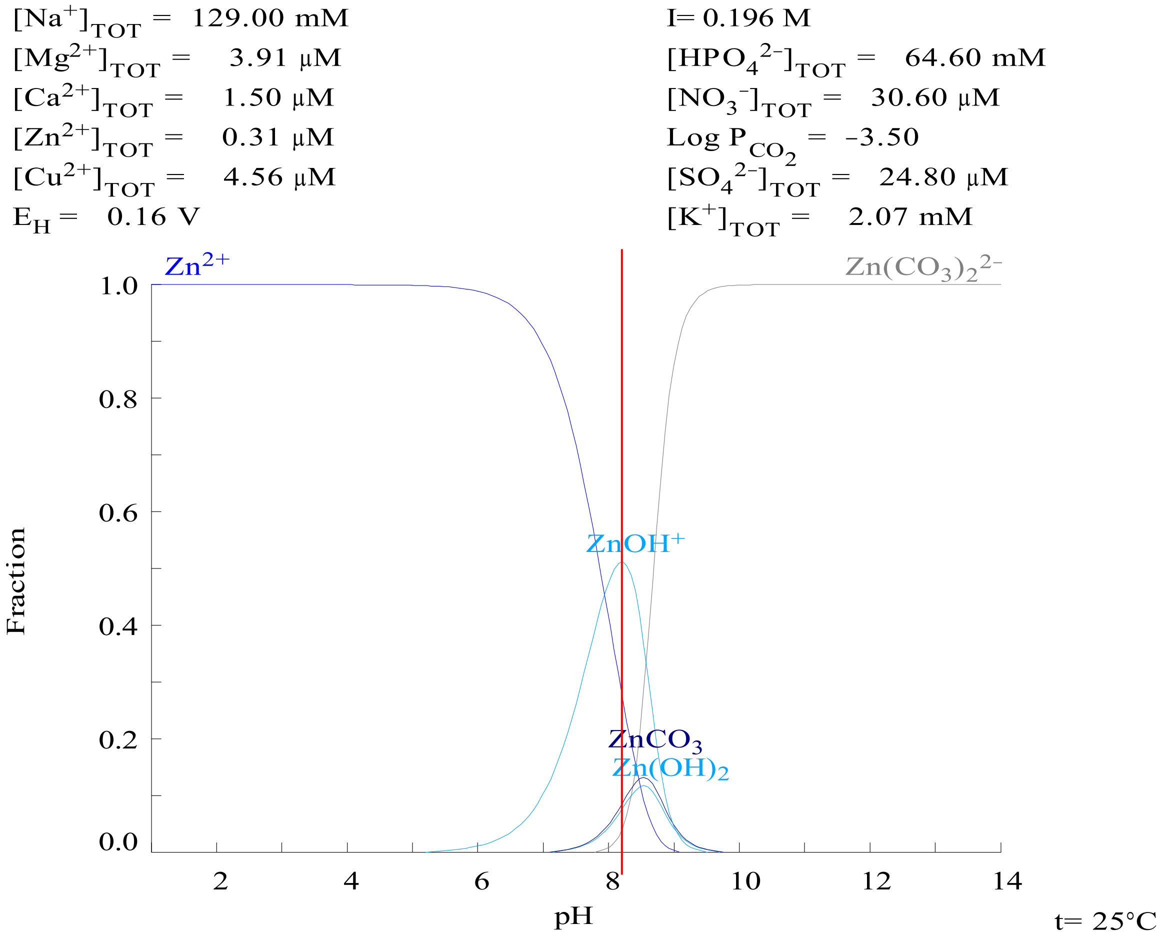


Figure C.222. Fraction diagram of zinc for copper gutter section immersed into pH 8 water after one day of exposure.

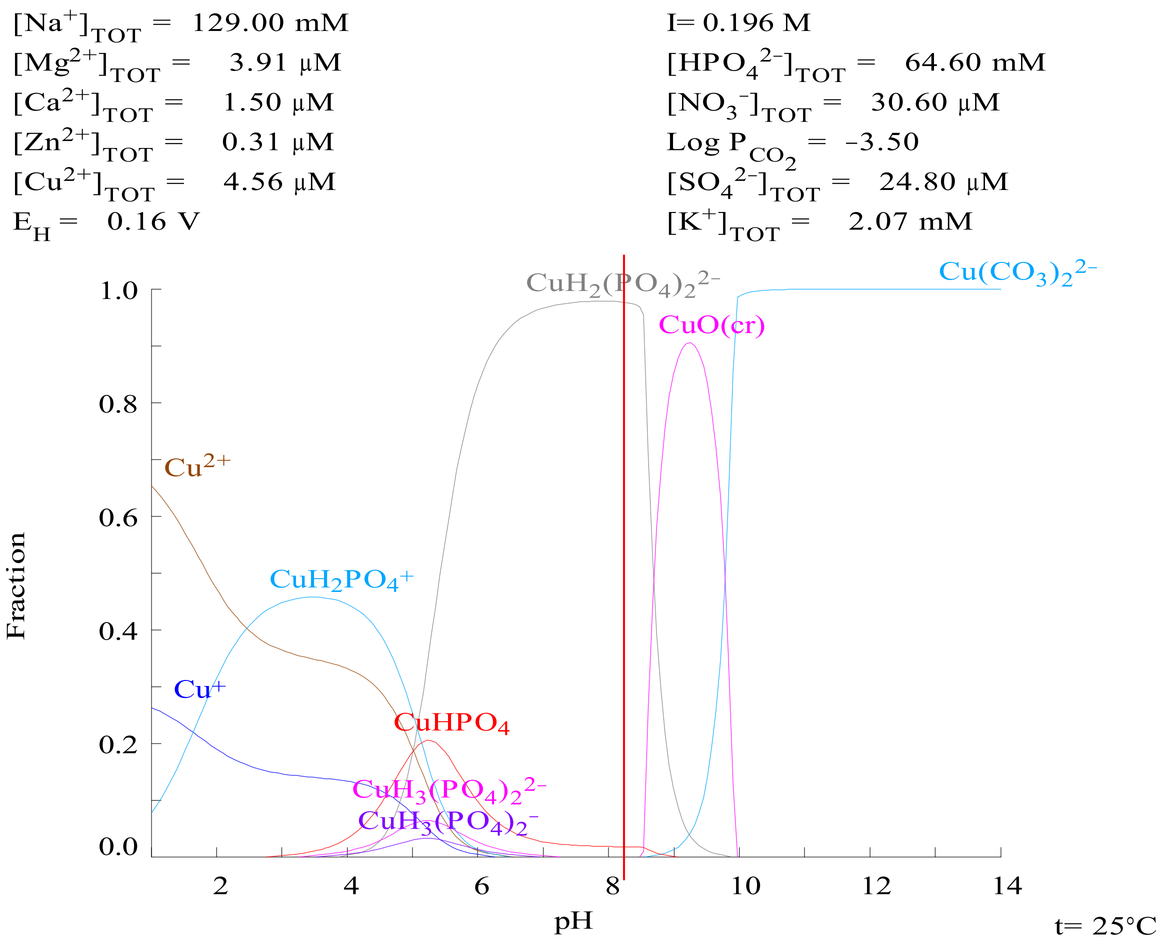


Figure C.223. Fraction diagram of copper for copper gutter section immersed into pH 8 water after one day of exposure.

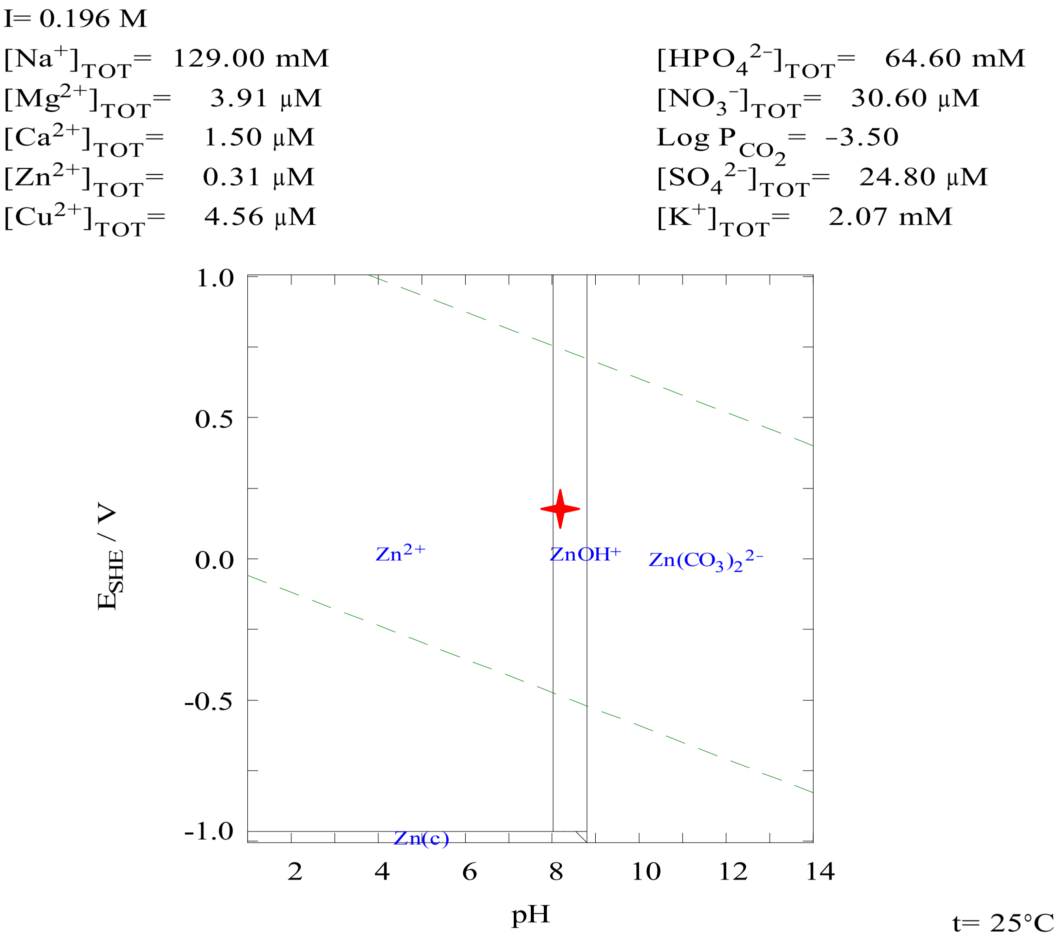


Figure C.224. Pourbaix diagram of zinc for copper gutter section immersed into pH 8 water after one day of exposure.

I= 0.196 M

$[Na^+]_{TOT}$= 129.00 mM
$[Mg^{2+}]_{TOT}$= 3.91 μM
$[Ca^{2+}]_{TOT}$= 1.50 μM
$[Zn^{2+}]_{TOT}$= 0.31 μM
$[Cu^{2+}]_{TOT}$= 4.56 μM

$[HPO_4^{2-}]_{TOT}$= 64.60 mM
$[NO_3^-]_{TOT}$= 30.60 μM
Log P_{CO_2}= -3.50
$[SO_4^{2-}]_{TOT}$= 24.80 μM
$[K^+]_{TOT}$= 2.07 mM

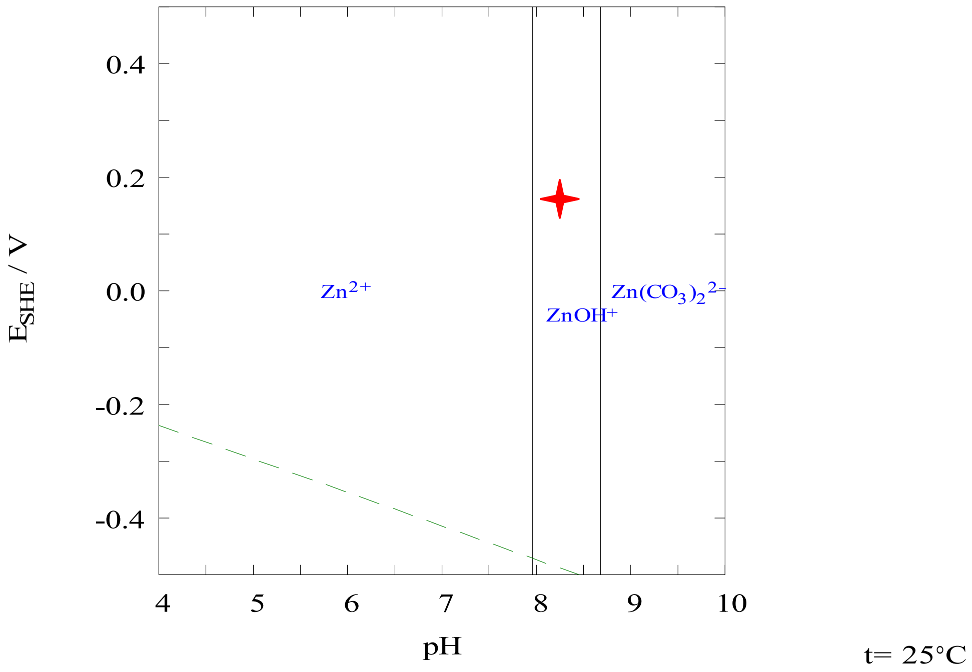


Figure C.225.Pourbaix diagram of zinc for copper gutter section immersed into pH 8 water after one day of exposure. Study area.

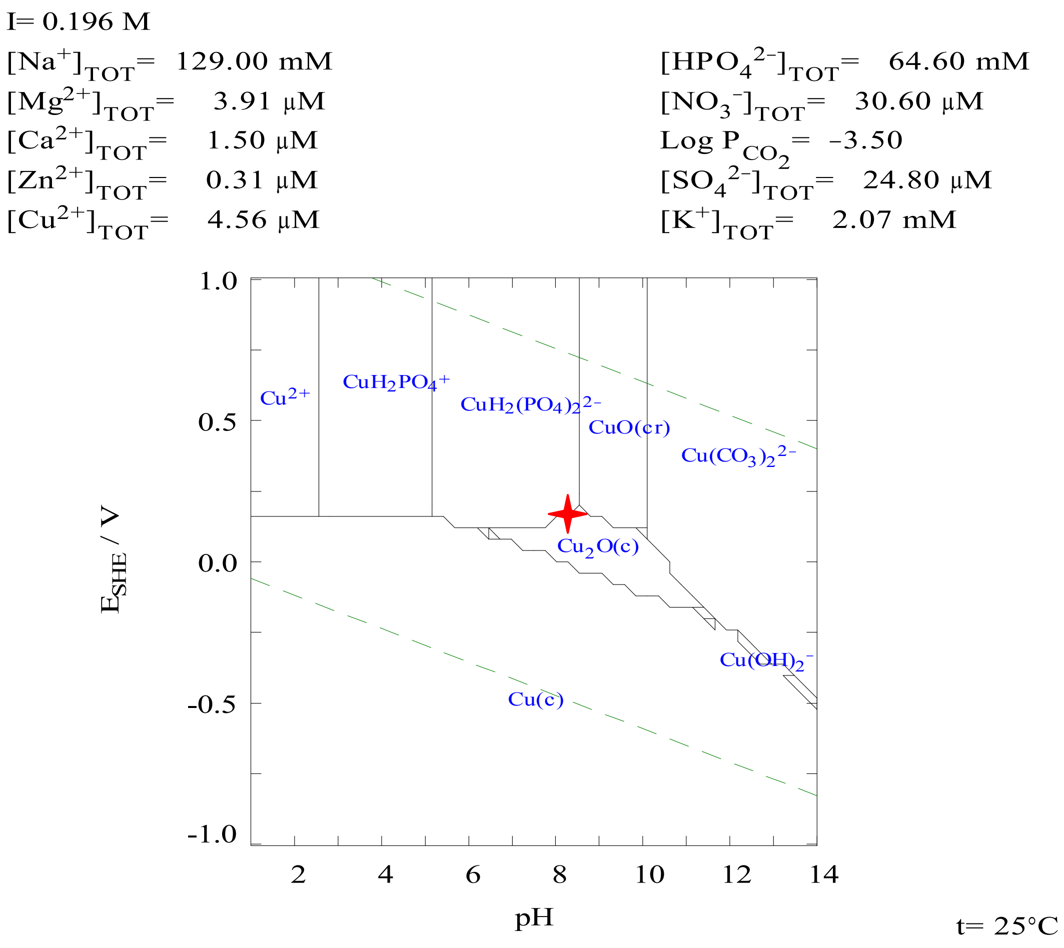


Figure C.226. Pourbaix diagram of copper for copper gutter section immersed into pH 8 water after one day of exposure.

$I = 0.196$ M

$[Na^+]_{TOT} =$ 129.00 mM

$[Mg^{2+}]_{TOT} =$ 3.91 μM

$[Ca^{2+}]_{TOT} =$ 1.50 μM

$[Zn^{2+}]_{TOT} =$ 0.31 μM

$[Cu^{2+}]_{TOT} =$ 4.56 μM

$[HPO_4^{2-}]_{TOT} =$ 64.60 mM

$[NO_3^-]_{TOT} =$ 30.60 μM

$\text{Log } P_{CO_2} = -3.50$

$[SO_4^{2-}]_{TOT} =$ 24.80 μM

$[K^+]_{TOT} =$ 2.07 mM

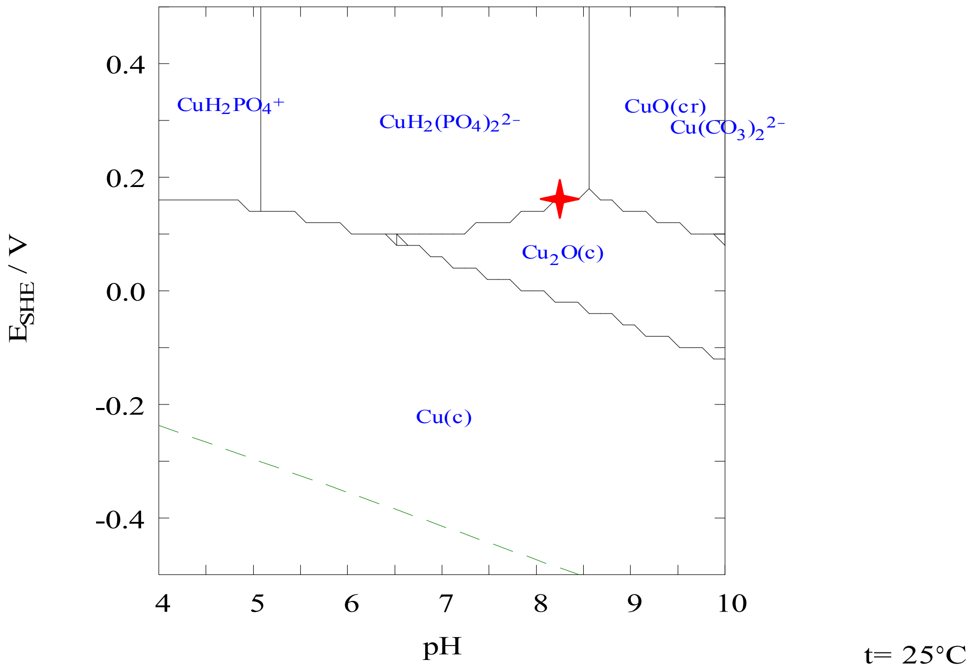


Figure C.227.Pourbaix diagram of copper for copper gutter section immersed into pH 8 water after one day of exposure. Study area.

Steel Pipe, Bay Water, After Three Months of Exposure

$[SO_4^{2-}]_{TOT}$ = 7.02 mM
$[Cl^-]_{TOT}$ = 94.50 mM
$[Mg^{2+}]_{TOT}$ = 12.00 mM
$[Ca^{2+}]_{TOT}$ = 3.47 mM
$[Fe^{2+}]_{TOT}$ = 34.90 μM
$[Zn^{2+}]_{TOT}$ = 1.20 mM
E_H = -0.18 V

I= 0.087 M
Log P_{CO_2} = -3.50
$[K^+]_{TOT}$ = 1.72 mM
$[Na^+]_{TOT}$ = 76.60 mM
$[B(OH)_3]_{TOT}$ = 0.39 mM
$[Br^-]_{TOT}$ = 0.16 mM
$[NO_3^-]_{TOT}$ = 3.39 μM

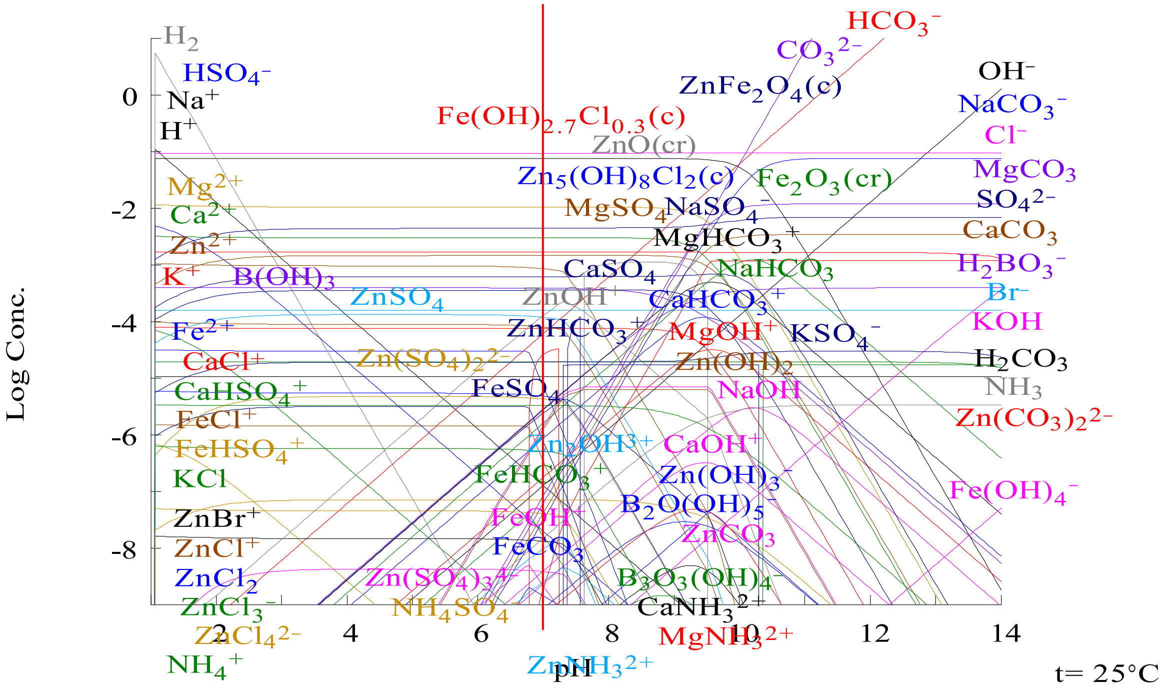


Figure C.228. Phase diagram for steel pipe section immersed into bay water after three months of exposure.

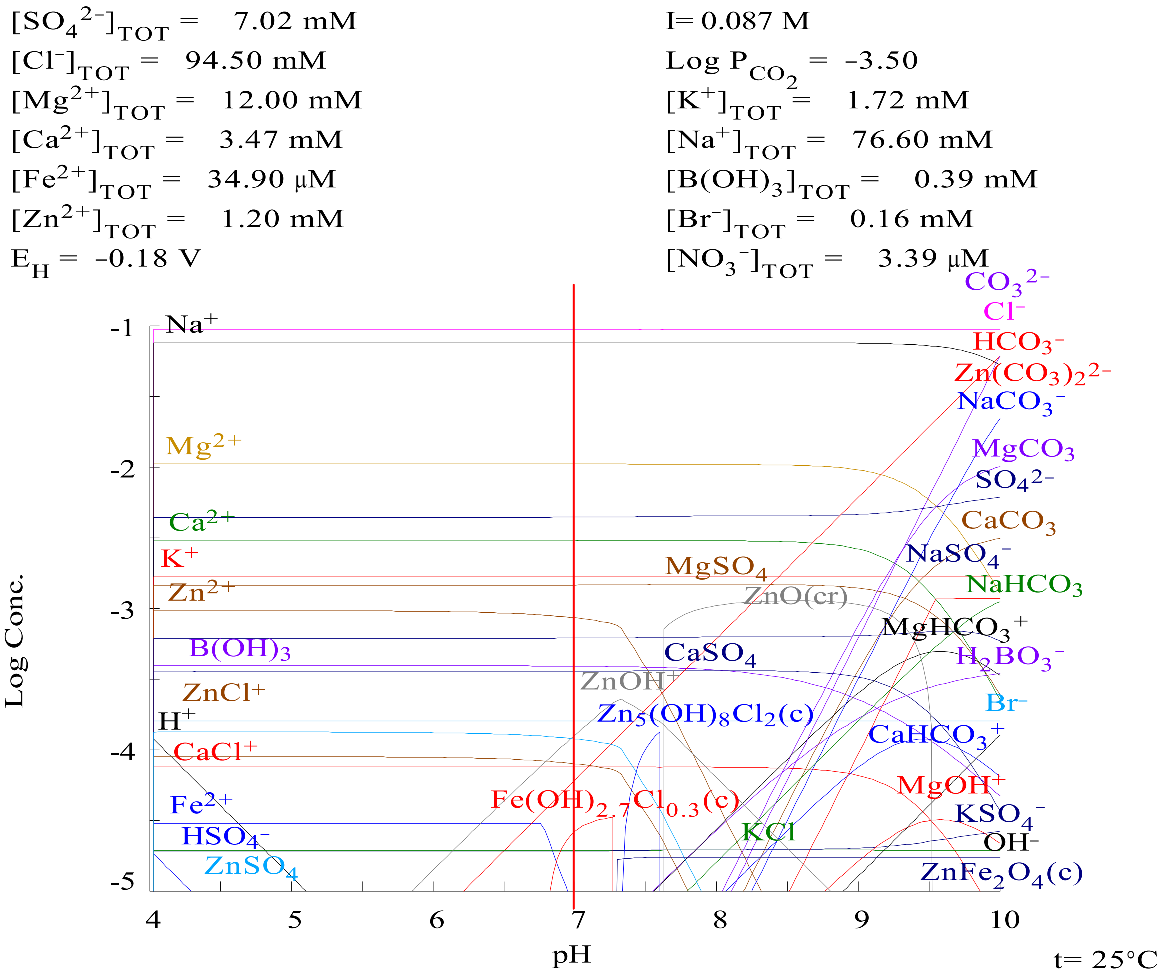


Figure C.229. Phase diagram for steel pipe section immersed into bay water after three months of exposure. Study area.

Table C.55. The predominant species of zinc. Steel pipe section, bay water, three months exposure.

Component	Log Concentration (mol/L)	Concentration (mol/L)	Zn Concentration (mg/L as Zn)	Cumulative Percentage of Zn
Zn^{2+}	-3.06	8.64E-04	56.48	71.96
$ZnOH^+$	-3.91	1.22E-04	7.96	82.09
$ZnSO_4$	-3.92	1.20E-04	7.86	92.11
$ZnCl^+$	-4.10	8.02E-05	5.24	98.79
$ZnCl_2$	-5.31	4.88E-06	3.19E-01	99.19
$Zn(SO4)_2^{2-}$	-5.36	4.32E-06	2.82E-01	99.55
$ZnHCO_3^+$	-5.63	2.32E-06	1.52E-01	99.75
$ZnCO_3$	-5.89	1.29E-06	8.45E-02	99.85
$Zn(OH)_2$	-5.94	1.15E-06	7.51E-02	99.95

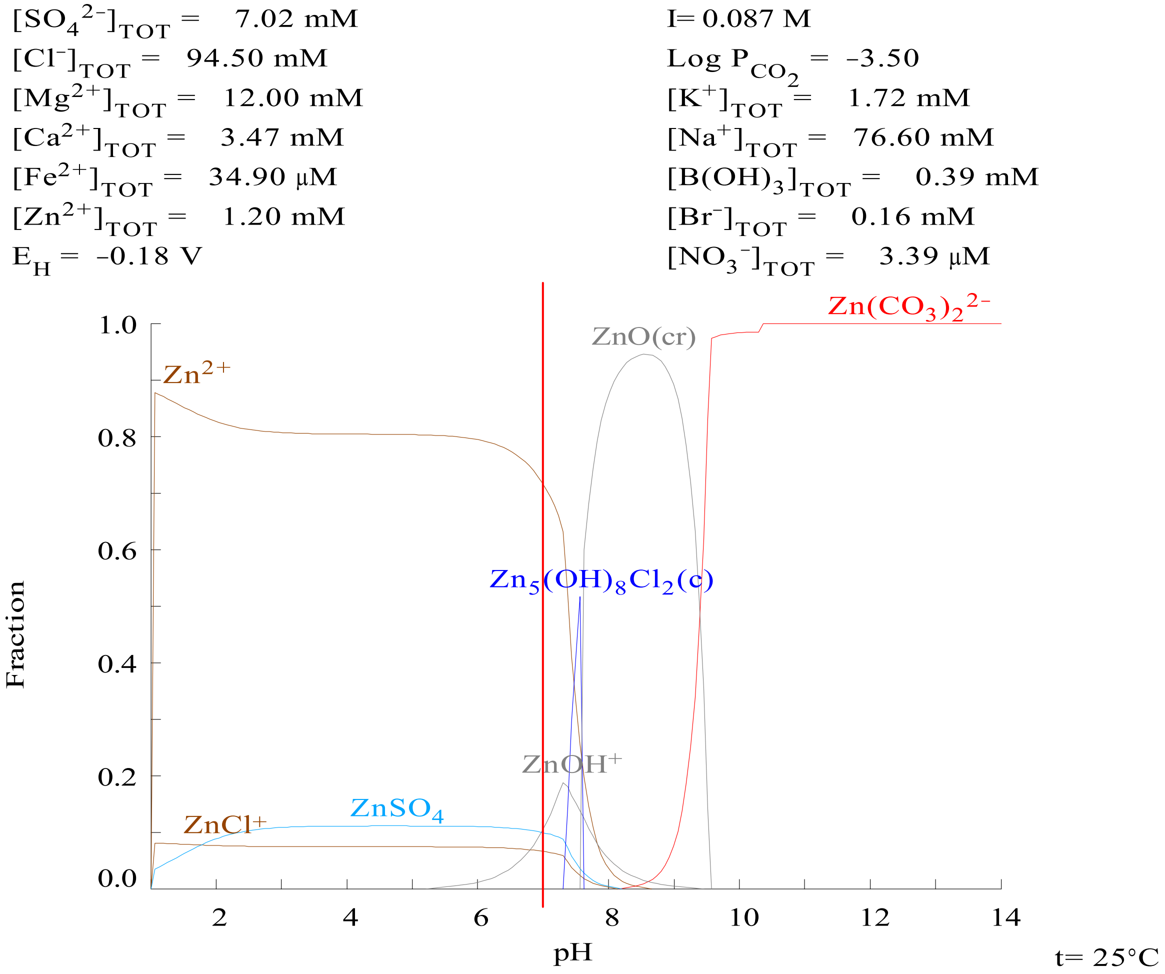


Figure C.230. Fraction diagram of zinc for steel pipe section immersed into bay water after three months of exposure.

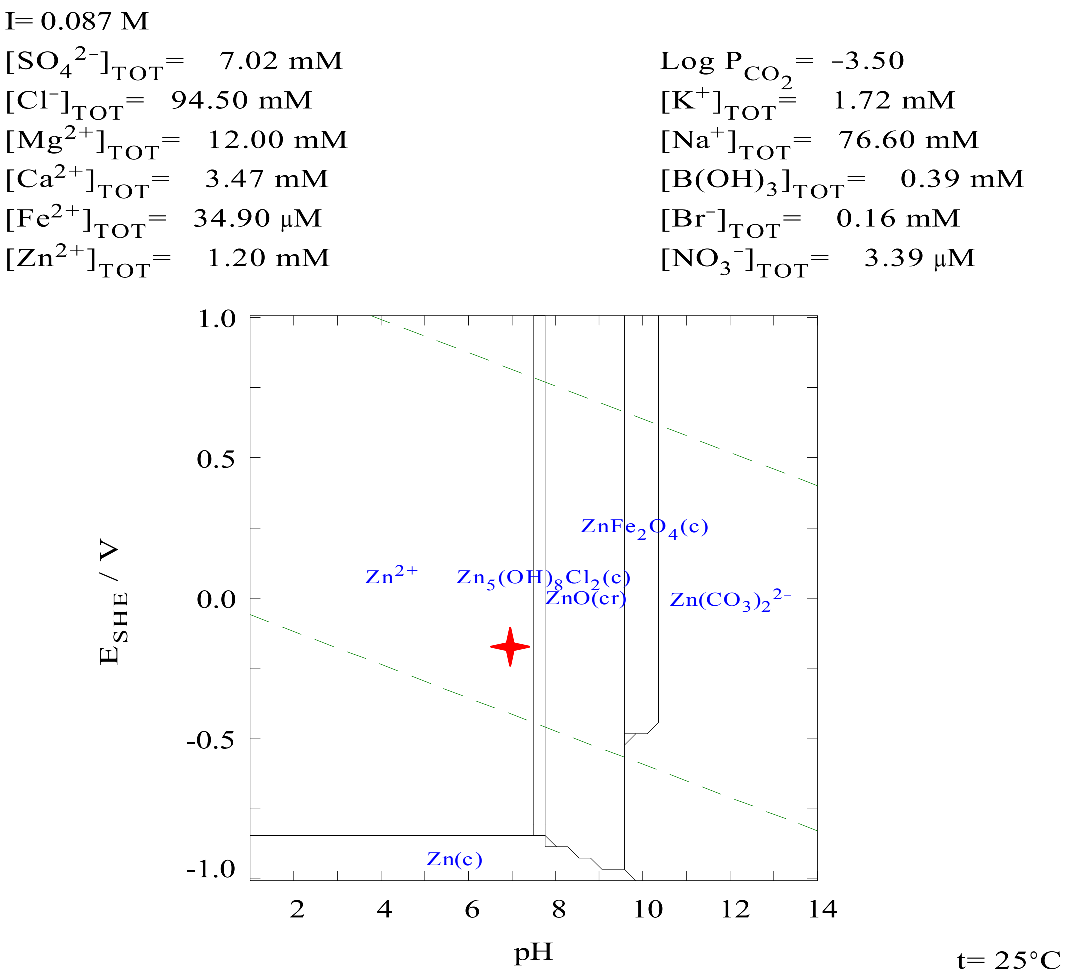


Figure C.231. Pourbaix diagram of zinc for steel pipe section immersed into bay water after three months of exposure.

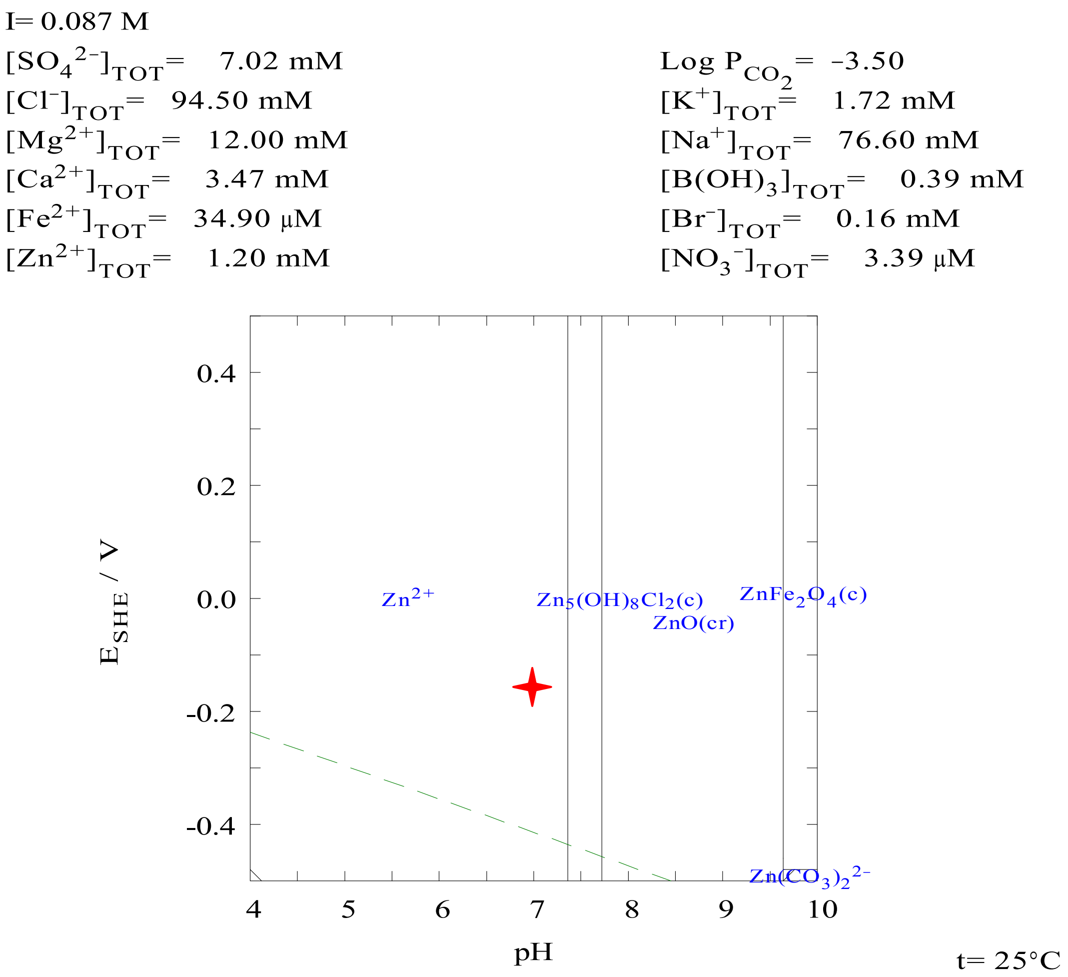


Figure C.232. Pourbaix diagram of zinc for steel pipe section immersed into bay water after three months of exposure. Study area.

Steel Gutter, Bay Water, After Three Months of Exposure

$[K^+]_{TOT}$ = 1.72 mM
$[Na^+]_{TOT}$ = 76.60 mM
$[Mg^{2+}]_{TOT}$ = 11.80 mM
$[Ca^{2+}]_{TOT}$ = 4.32 mM
$[Fe^{2+}]_{TOT}$ = 41.20 µM
$[Zn^{2+}]_{TOT}$ = 0.56 mM
E_H = -0.18 V

I= 0.087 M
Log P_{CO_2} = -3.50
$[B(OH)_3]_{TOT}$ = 0.39 mM
$[Br^-]_{TOT}$ = 0.16 mM
$[NO_3^-]_{TOT}$ = 3.39 µM
$[SO_4^{2-}]_{TOT}$ = 7.02 mM
$[Cl^-]_{TOT}$ = 94.50 mM

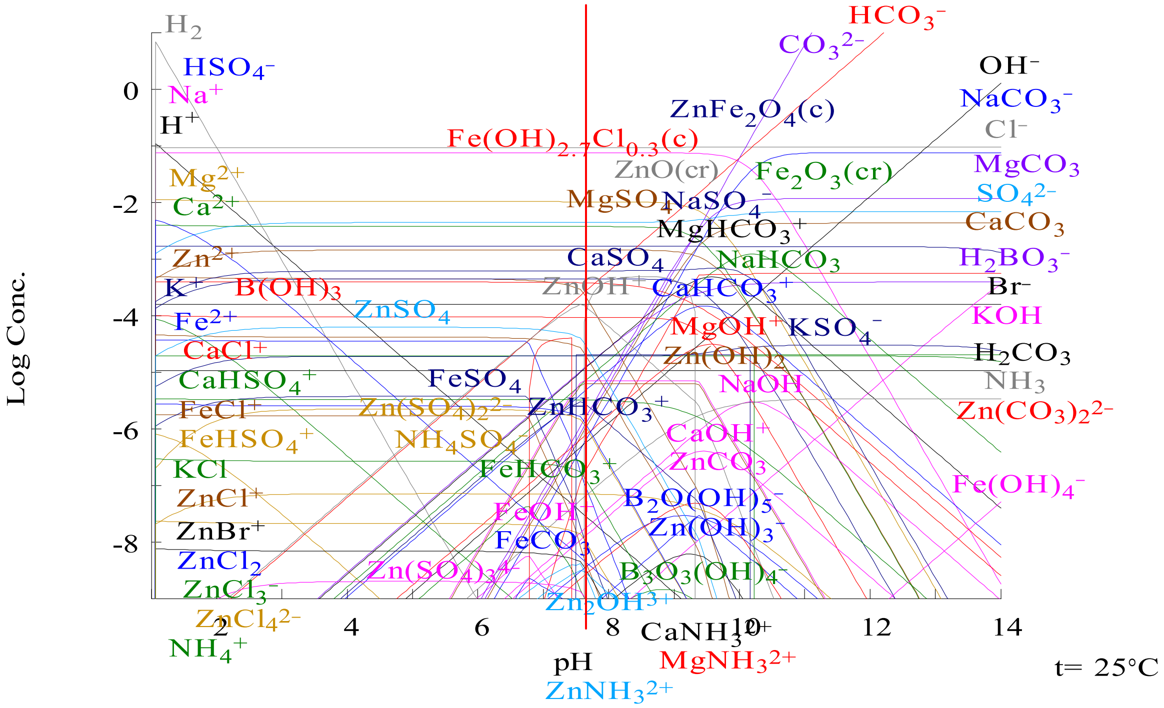


Figure C.233. Phase diagram for steel gutter section immersed into bay water after three months of exposure.

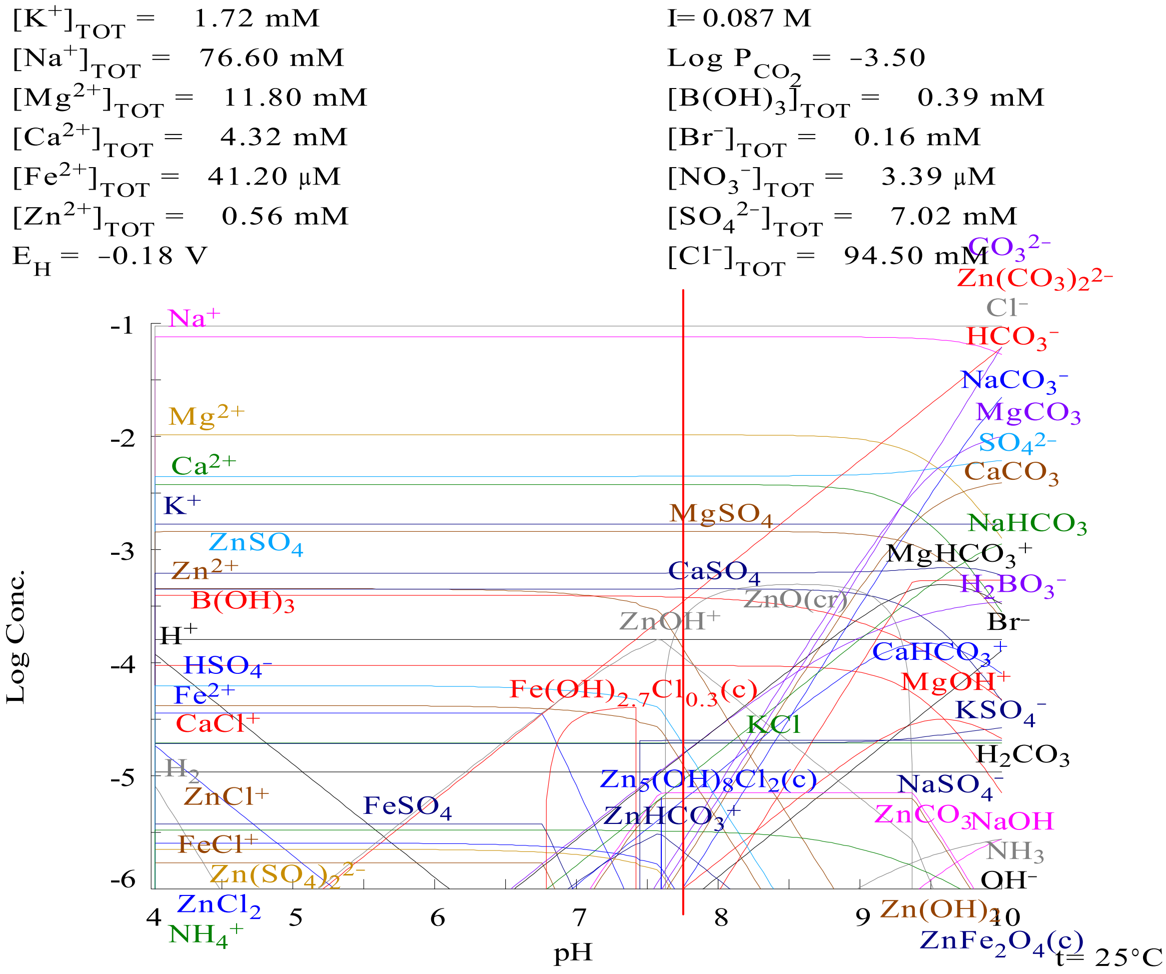


Figure C.234. Phase diagram for steel gutter section immersed into bay water after three months of exposure. Study area.

Table C.56.The predominant species of zinc. Steel gutter section, bay water, three months exposure.

Component	Log Concentration (mol/L)	Concentration (mol/L)	Zn Concentration (mg/L as Zn)	Cumulative Percentage of Zn
ZnO(cr)	-3.52	3.04E-04	19.92	54.27
Zn^{2+}	-4.00	9.93E-05	6.49	71.97
$ZnOH^+$	-4.01	9.67E-05	6.33	89.21
$ZnFe_2O_4$(c)	-4.69	2.06E-05	1.35	92.88
$ZnSO_4$	-4.86	1.39E-05	0.91	95.36
$ZnCl^+$	-5.04	9.22E-06	0.60	97.00
$ZnCO_3$	-5.15	7.11E-06	0.46	98.27
$Zn(OH)_2$	-5.20	6.32E-06	0.41	99.40
$ZnHCO_3^+$	-5.73	1.84E-06	0.12	99.72
$ZnCl_2$	-6.25	5.61E-07	0.04	99.83
$Zn(SO4)_2^{2-}$	-6.30	5.05E-07	0.03	99.91

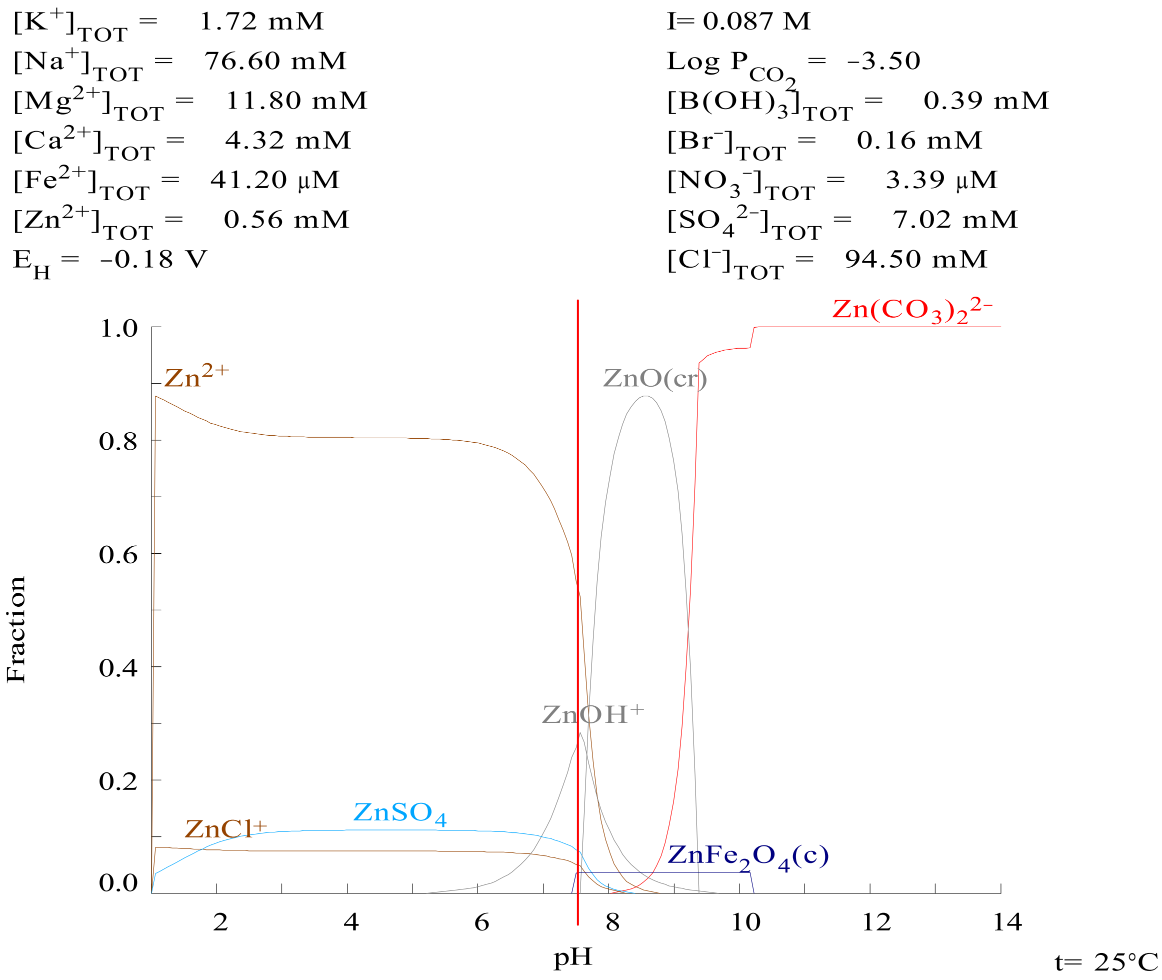


Figure C.235. Fraction diagram of zinc for steel gutter section immersed into bay water after three months of exposure.

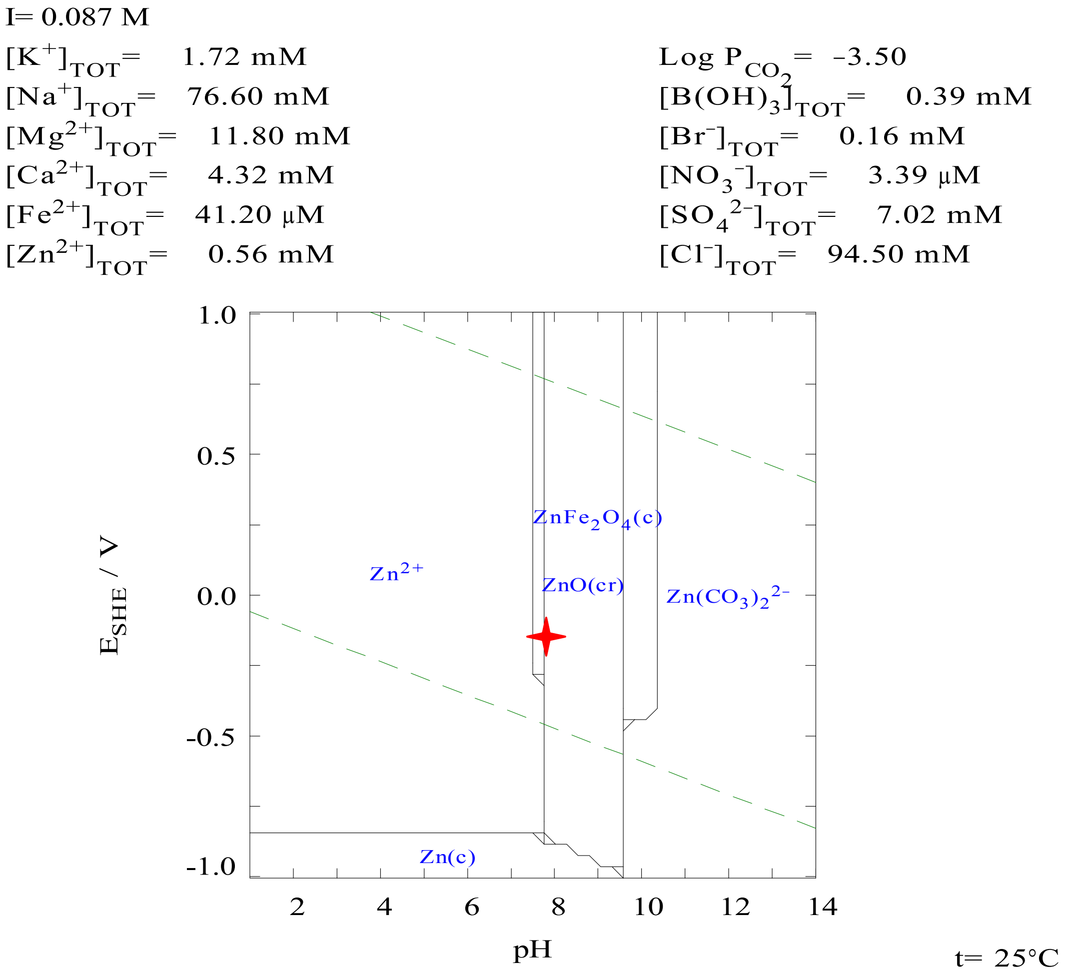


Figure C.236. Pourbaix diagram of zinc for steel gutter section immersed into bay water after three months of exposure.

I= 0.087 M

$[K^+]_{TOT}$= 1.72 mM

$[Na^+]_{TOT}$= 76.60 mM

$[Mg^{2+}]_{TOT}$= 11.80 mM

$[Ca^{2+}]_{TOT}$= 4.32 mM

$[Fe^{2+}]_{TOT}$= 41.20 μM

$[Zn^{2+}]_{TOT}$= 0.56 mM

Log P_{CO_2}= -3.50

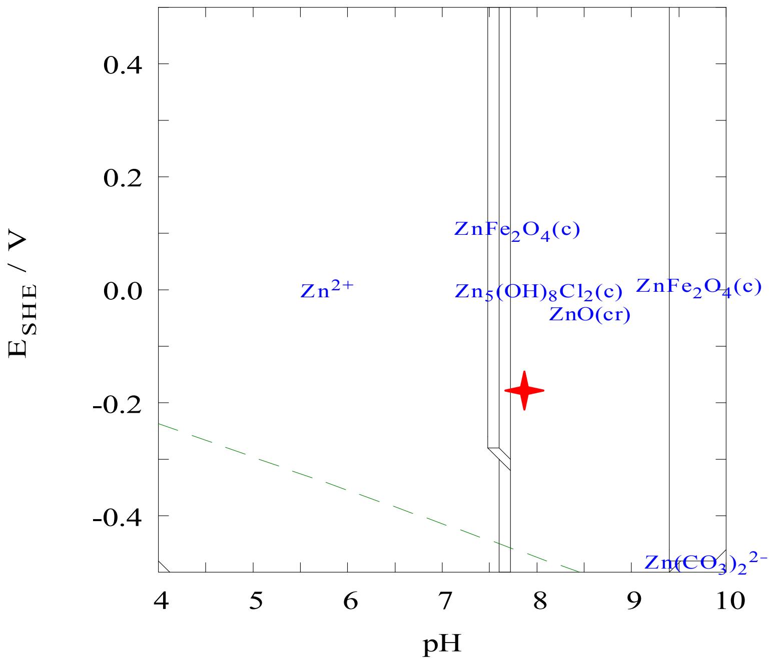
$[B(OH)_3]_{TOT}$= 0.39 mM

$[Br^-]_{TOT}$= 0.16 mM

$[NO_3^-]_{TOT}$= 3.39 μM

$[SO_4^{2-}]_{TOT}$= 7.02 mM

$[Cl^-]_{TOT}$= 94.50 mM



t= 25°C

Figure C.237. Pourbaix diagram of zinc for steel gutter section immersed into bay water after three months of exposure. Study area.

Copper Gutter, Bay Water, After Three Months of Exposure

$[NO_3^-]_{TOT}$ = 3.39 μM
$[SO_4^{2-}]_{TOT}$ = 7.02 mM
$[Cl^-]_{TOT}$ = 94.50 mM
$[Mg^{2+}]_{TOT}$ = 11.10 mM
$[Ca^{2+}]_{TOT}$ = 3.37 mM
$[Fe^{2+}]_{TOT}$ = 37.60 μM
E_H = -0.14 V

I= 0.085 M
$[Cu^{2+}]_{TOT}$ = 0.56 mM
Log P_{CO_2} = -3.50
$[K^+]_{TOT}$ = 1.72 mM
$[Na^+]_{TOT}$ = 76.60 mM
$[B(OH)_3]_{TOT}$ = 0.39 mM
$[Br^-]_{TOT}$ = 0.16 mM

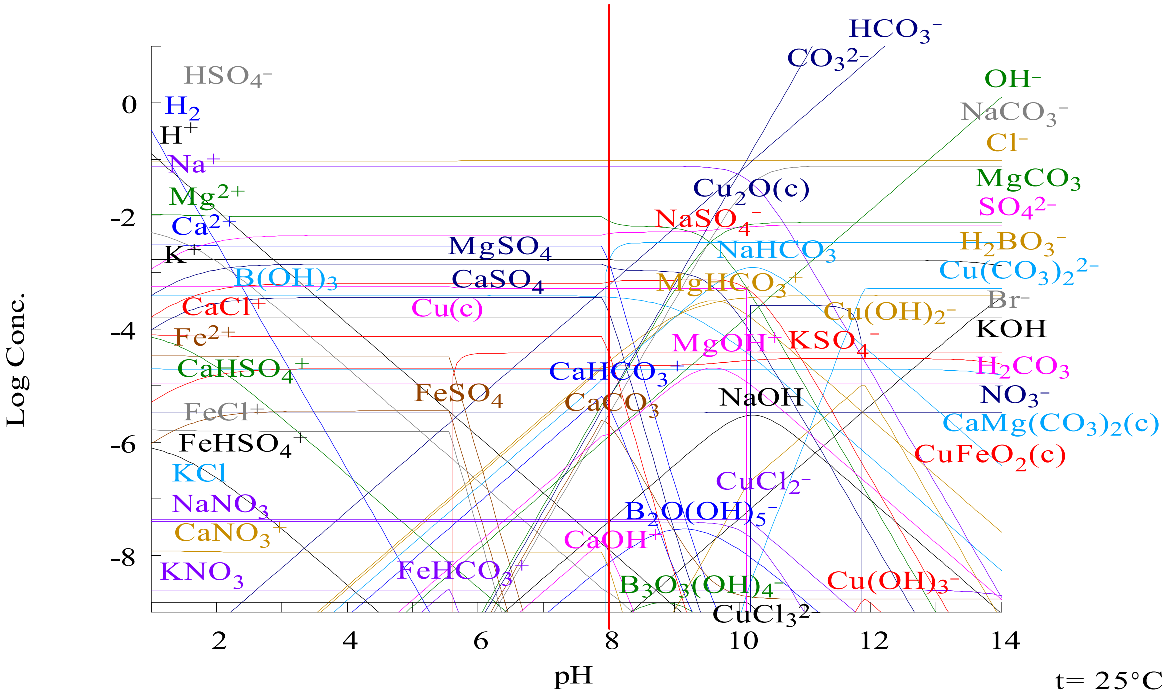


Figure C.238. Phase diagram for copper gutter section immersed into bay water after three months of exposure.

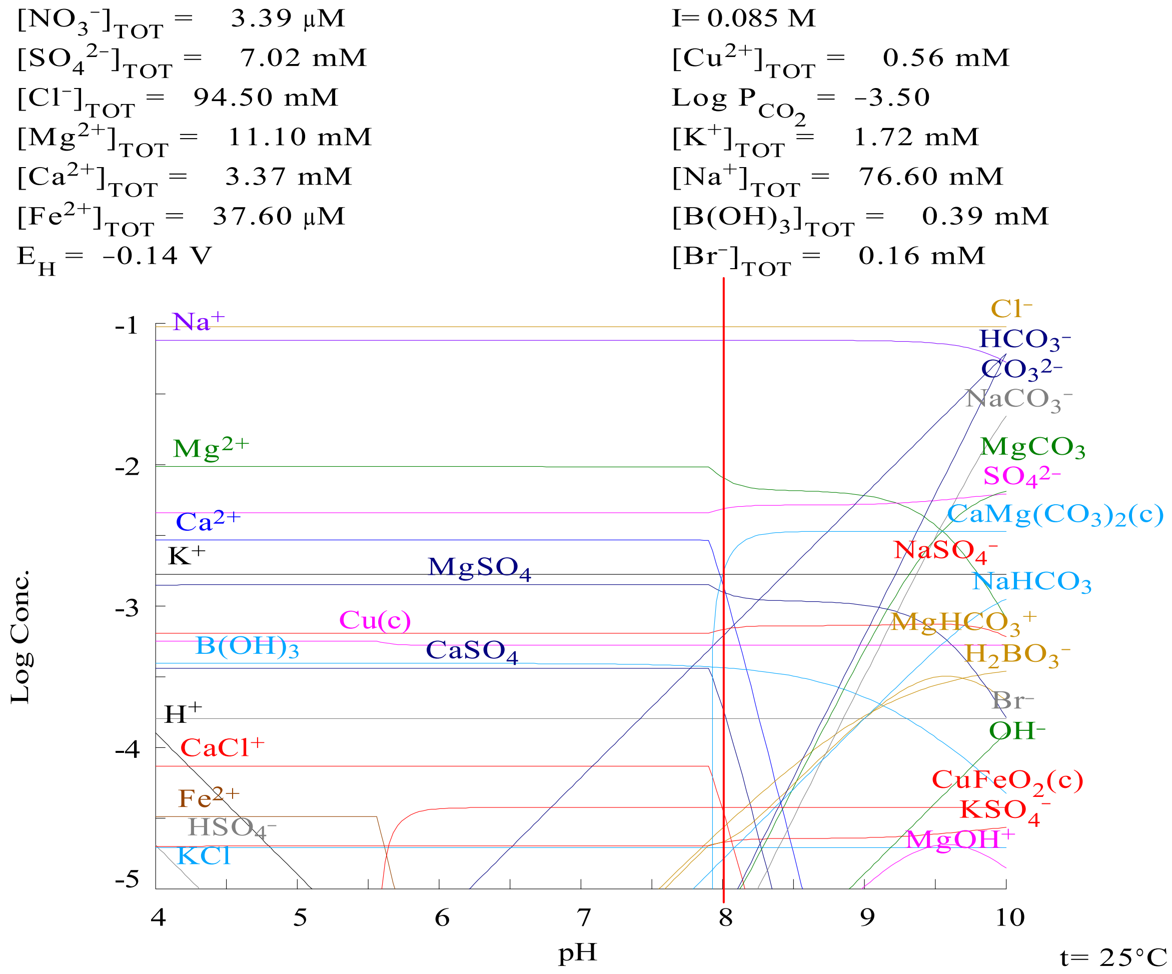


Figure C.239. Phase diagram for copper gutter section immersed into bay water after three months of exposure. Study area.

Table C.57. The predominant species of copper. Copper gutter section, bay water, three months exposure.

Component	Log Concentration (mol/L)	Concentration (mol/L)	Cu Concentration (mg/L as Cu)	Cumulative Percentage of Cu
Cu(c)	-3.28	5.27E-04	33.51	93.34
$CuFeO_2$(c)	-4.42	3.76E-05	2.39	99.99

Footnote: Cu^+ was calculated to be 1.03E-06mg/L; Cu^{2+} was calculated to be 1.5E-11 mg/L

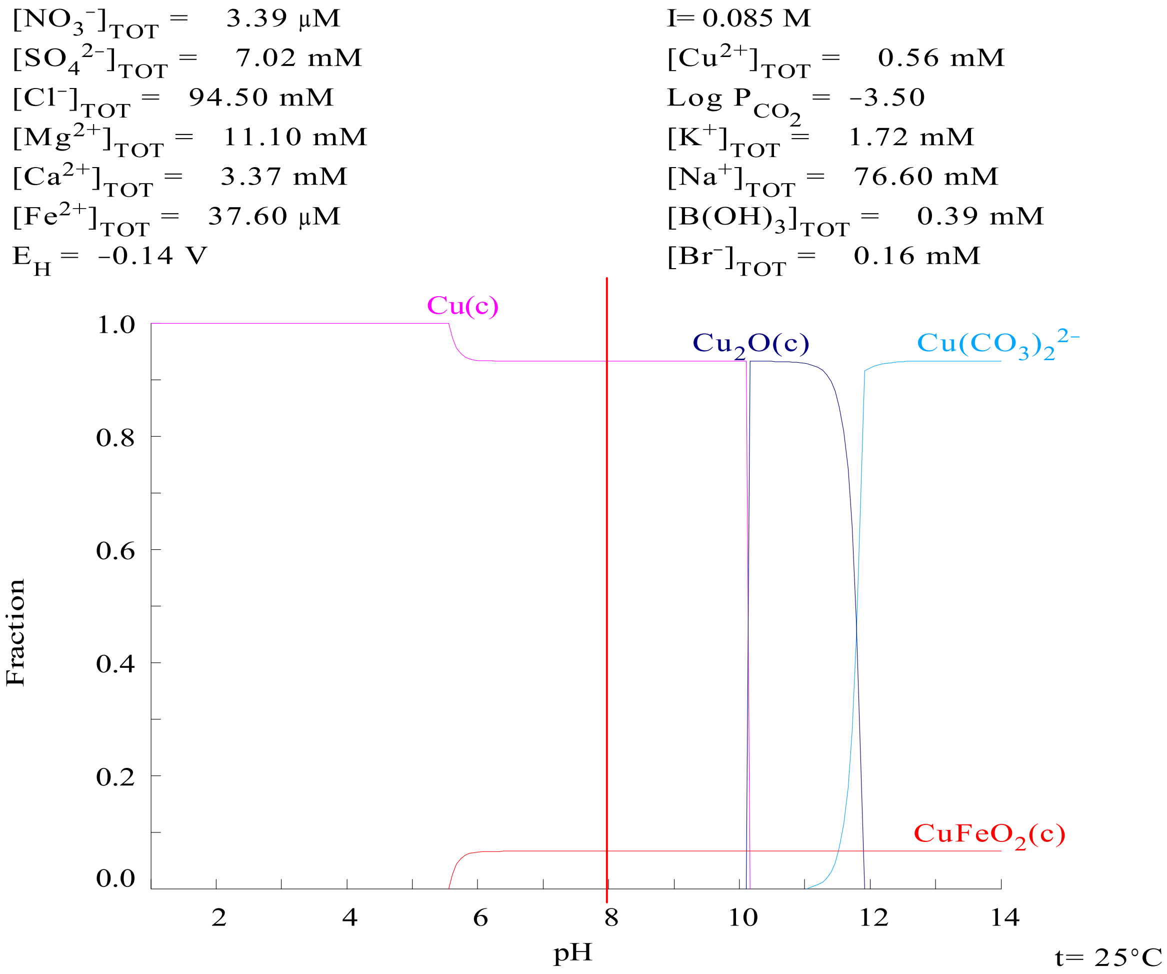
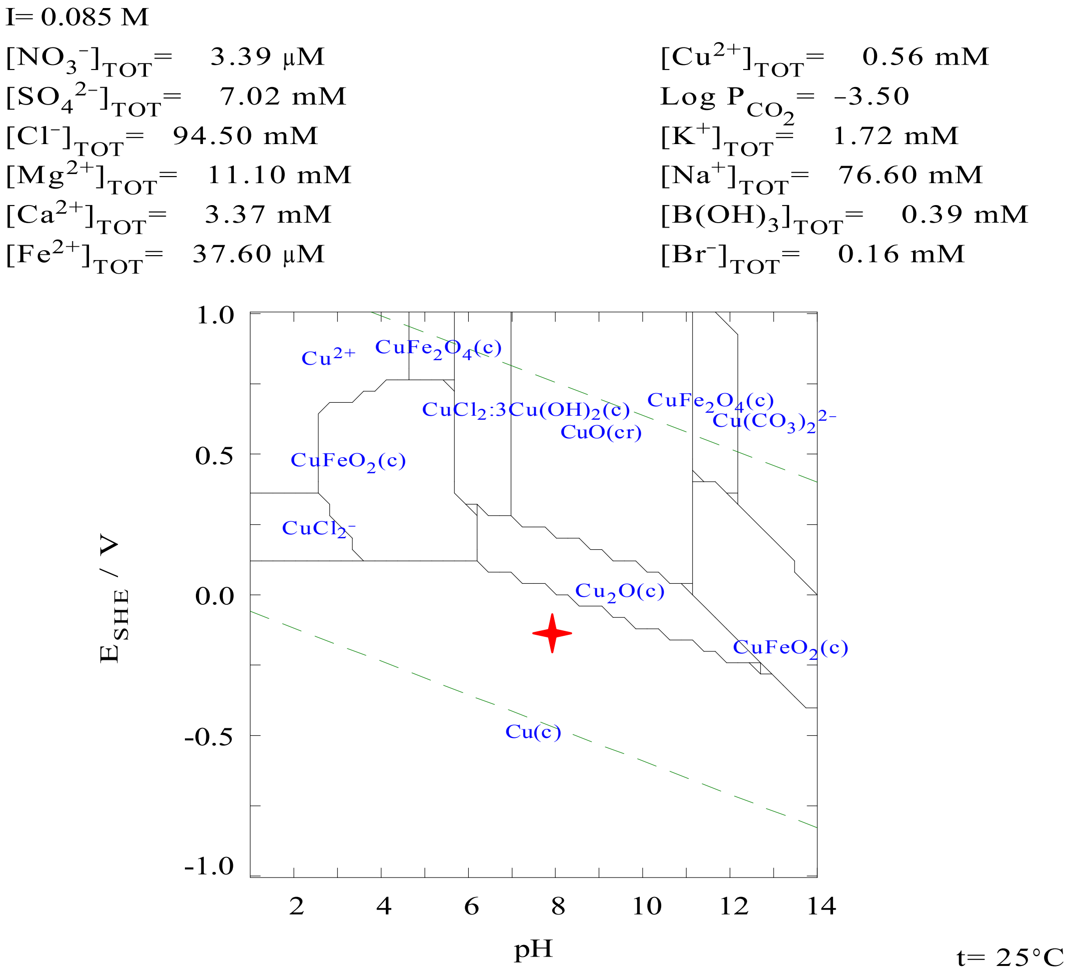


Figure C.240. Fraction diagram of copper for copper gutter section immersed into bay water after three months of exposure.



I= 0.085 M

$[NO_3^-]_{TOT}$= 3.39 μM

$[SO_4^{2-}]_{TOT}$= 7.02 mM

$[Cl^-]_{TOT}$= 94.50 mM

$[Mg^{2+}]_{TOT}$= 11.10 mM

$[Ca^{2+}]_{TOT}$= 3.37 mM

$[Fe^{2+}]_{TOT}$= 37.60 μM

$[Cu^{2+}]_{TOT}$= 0.56 mM

Log P_{CO_2}= -3.50

$[K^+]_{TOT}$= 1.72 mM

$[Na^+]_{TOT}$= 76.60 mM

$[B(OH)_3]_{TOT}$= 0.39 mM

$[Br^-]_{TOT}$= 0.16 mM

Figure C.241. Pourbaix diagram of copper for copper gutter section immersed into bay water after three months of exposure.

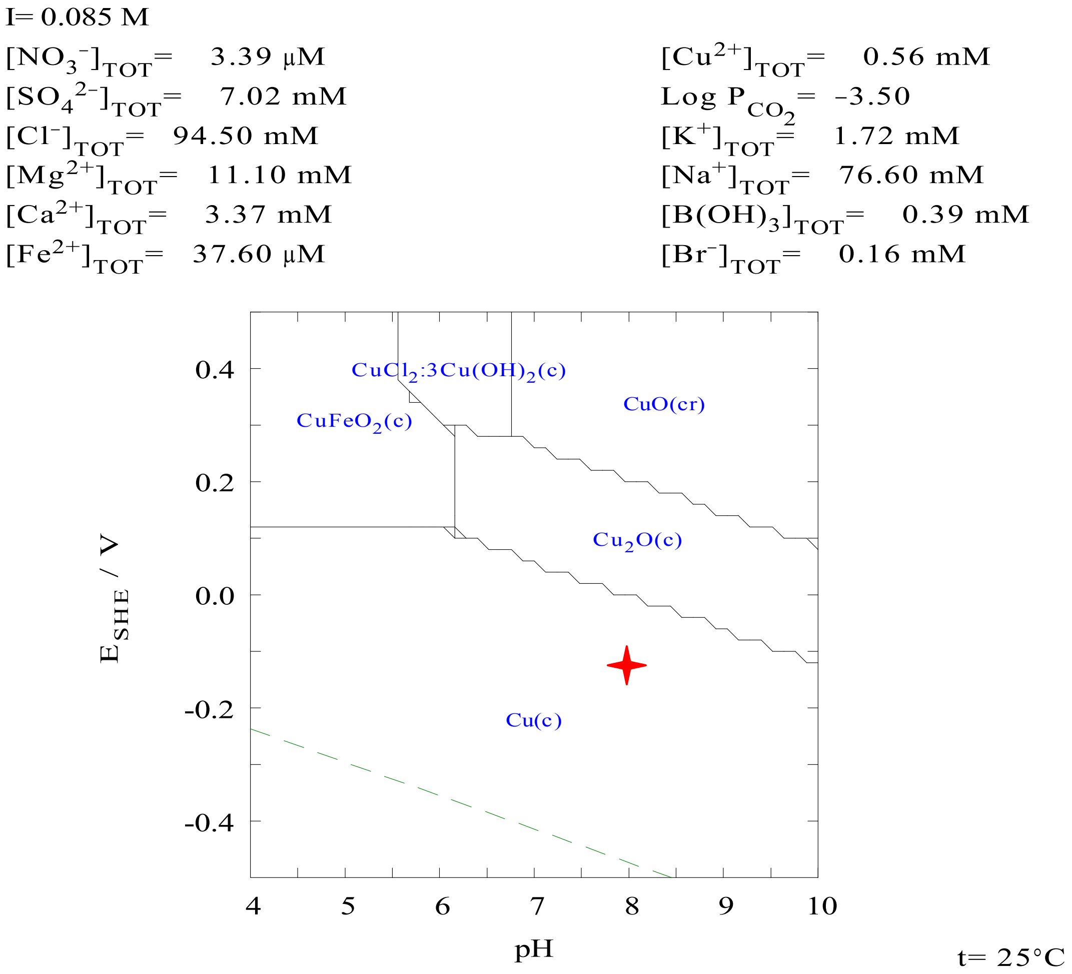


Figure C.242. Pourbaix diagram of copper for copper gutter section immersed into bay water after three months of exposure. Study area.

Steel Pipe, River Water, After Three Months of Exposure

I= 0.008 M

$[K^+]_{TOT}$ = 0.15 mM

$[Na^+]_{TOT}$ = 2.89 mM

$[Mg^{2+}]_{TOT}$ = 0.64 mM

$[Ca^{2+}]_{TOT}$ = 0.16 mM

$[Fe^{2+}]_{TOT}$ = 25.40 μM

$[Zn^{2+}]_{TOT}$ = 1.04 mM

E_H = -0.13 V

Log P_{CO_2} = -3.50

$[B(OH)_3]_{TOT}$ = 52.50 μM

$[Br^-]_{TOT}$ = 2.88 μM

$[NO_3^-]_{TOT}$ = 11.00 μM

$[F^-]_{TOT}$ = 14.70 μM

$[SO_4^{2-}]_{TOT}$ = 1.10 mM

$[Cl^-]_{TOT}$ = 2.51 mM

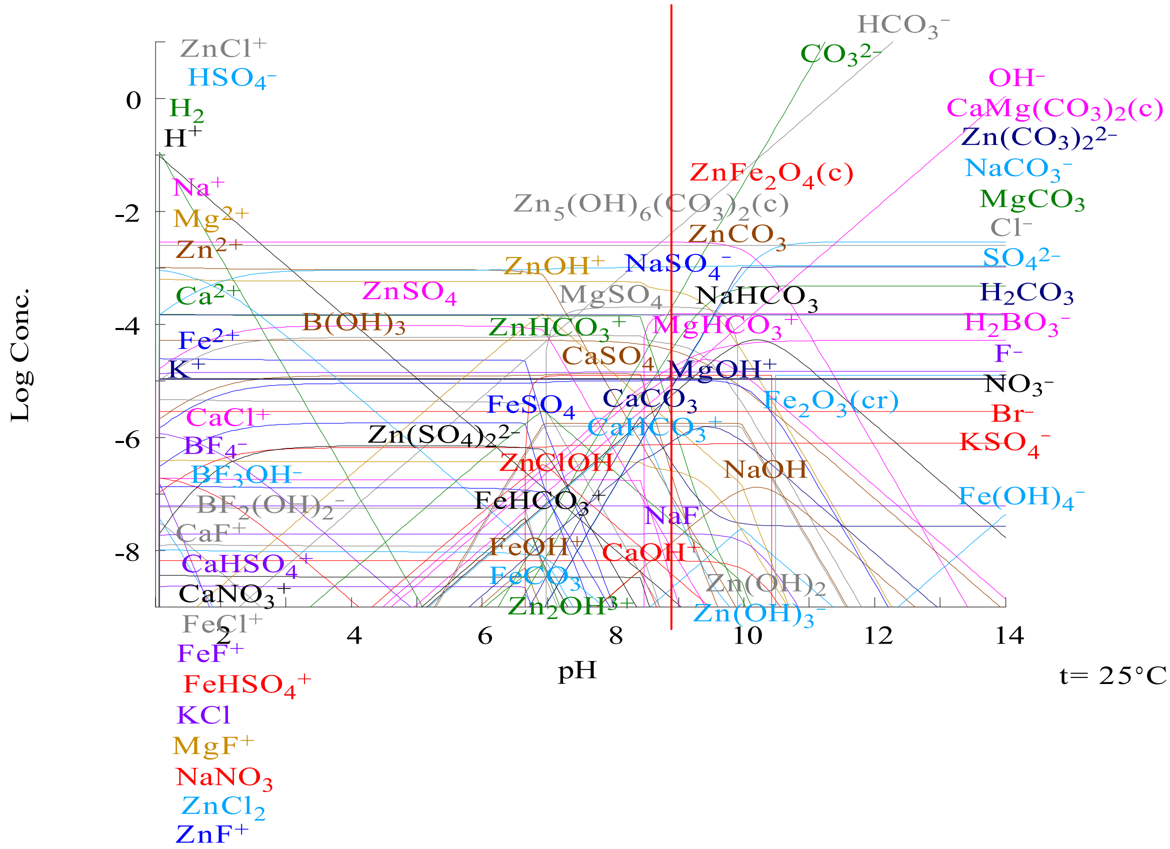


Figure C.243. Phase diagram for steel pipe section immersed into river water after three months of exposure.

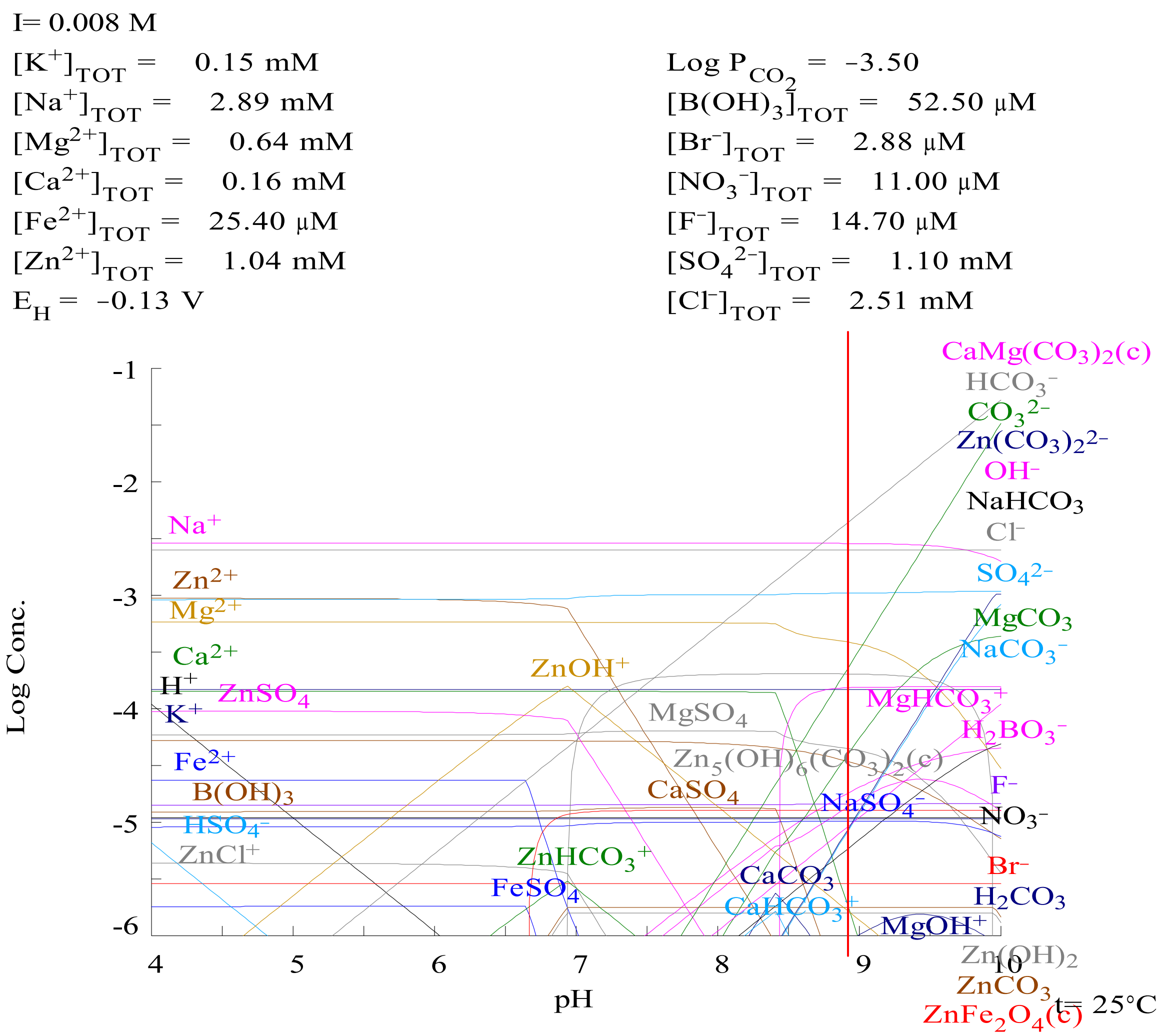


Figure C.244. Phase diagram for steel pipe section immersed into river water after three months of exposure. Study area.

Table C.58. The predominant species of zinc. Steel pipe section, river water, three months exposure.

Component	Log Concentration (mol/L)	Concentration (mol/L)	Zn Concentration (mg/L as Zn)	Cumulative Percentage of Zn
$Zn_5(OH)_6(CO_3)_2$ (c)	-3.69	2.0E-04	66.41	97.62
$ZnFe_2O_4$(c)	-4.90	1.3E-05	0.83	98.84
$Zn(CO3)_2^{2-}$	-5.18	6.7E-06	0.44	99.48
$ZnOH^+$	-5.73	1.9E-06	1.23E-01	99.66
$ZnCO_3$	-5.75	1.8E-06	1.16E-01	99.83
$Zn(OH)_2$	-5.80	1.6E-06	1.03E-01	99.98
Zn^{2+}	-6.97	1.1E-07	7.03E-03	99.995

I= 0.008 M

$[K^+]_{TOT}$ = 0.15 mM

$[Na^+]_{TOT}$ = 2.89 mM

$[Mg^{2+}]_{TOT}$ = 0.64 mM

$[Ca^{2+}]_{TOT}$ = 0.16 mM

$[Fe^{2+}]_{TOT}$ = 25.40 μM

$[Zn^{2+}]_{TOT}$ = 1.04 mM

E_H = -0.13 V

Log P_{CO_2} = -3.50

$[B(OH)_3]_{TOT}$ = 52.50 μM

$[Br^-]_{TOT}$ = 2.88 μM

$[NO_3^-]_{TOT}$ = 11.00 μM

$[F^-]_{TOT}$ = 14.70 μM

$[SO_4^{2-}]_{TOT}$ = 1.10 mM

$[Cl^-]_{TOT}$ = 2.51 mM

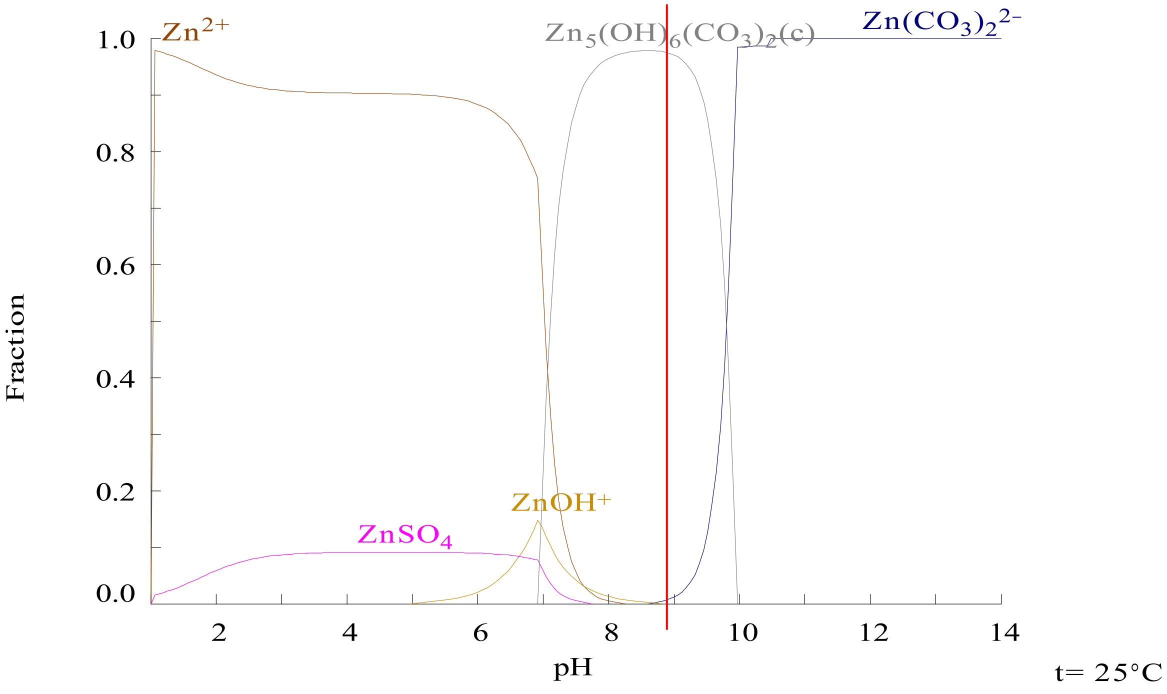


Figure C.245. Fraction diagram of zinc for steel pipe section immersed into river water after three months of exposure.

$[Cl^-]_{TOT}$= 2.51 mM
$[K^+]_{TOT}$= 0.15 mM
$[Na^+]_{TOT}$= 2.89 mM
$[Mg^{2+}]_{TOT}$= 0.64 mM
$[Ca^{2+}]_{TOT}$= 0.16 mM
$[Fe^{2+}]_{TOT}$= 25.40 μM
$[Zn^{2+}]_{TOT}$= 1.04 mM

I= 0.008 M
Log P_{CO_2}= -3.50
$[B(OH)_3]_{TOT}$= 52.50 μM
$[Br^-]_{TOT}$= 2.88 μM
$[NO_3^-]_{TOT}$= 11.00 μM
$[F^-]_{TOT}$= 14.70 μM
$[SO_4^{2-}]_{TOT}$= 1.10 mM

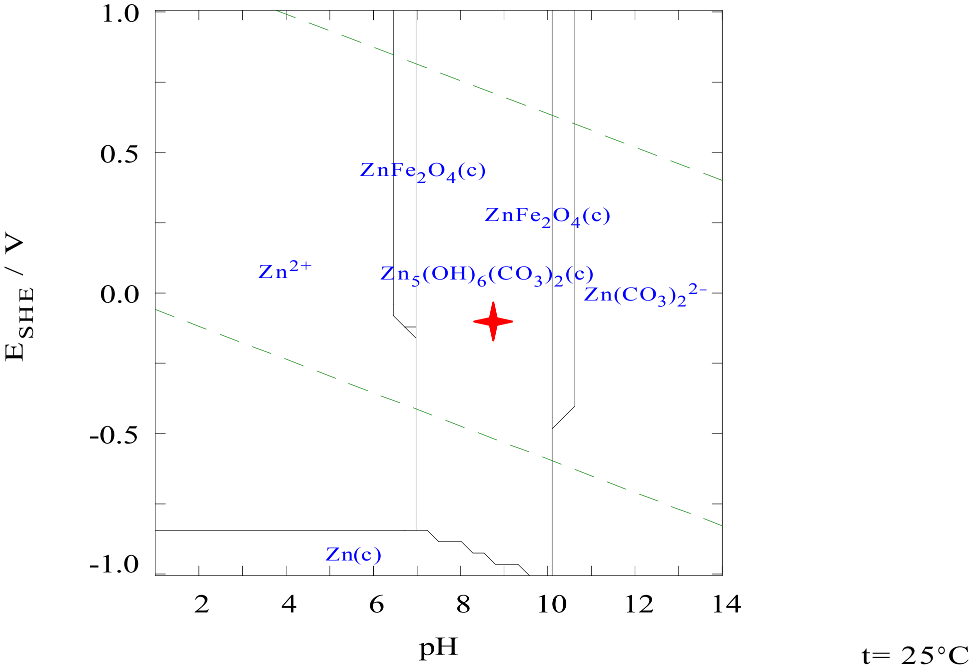


Figure C.246. Pourbaix diagram of zinc for steel pipe section immersed into river water after three months of exposure.

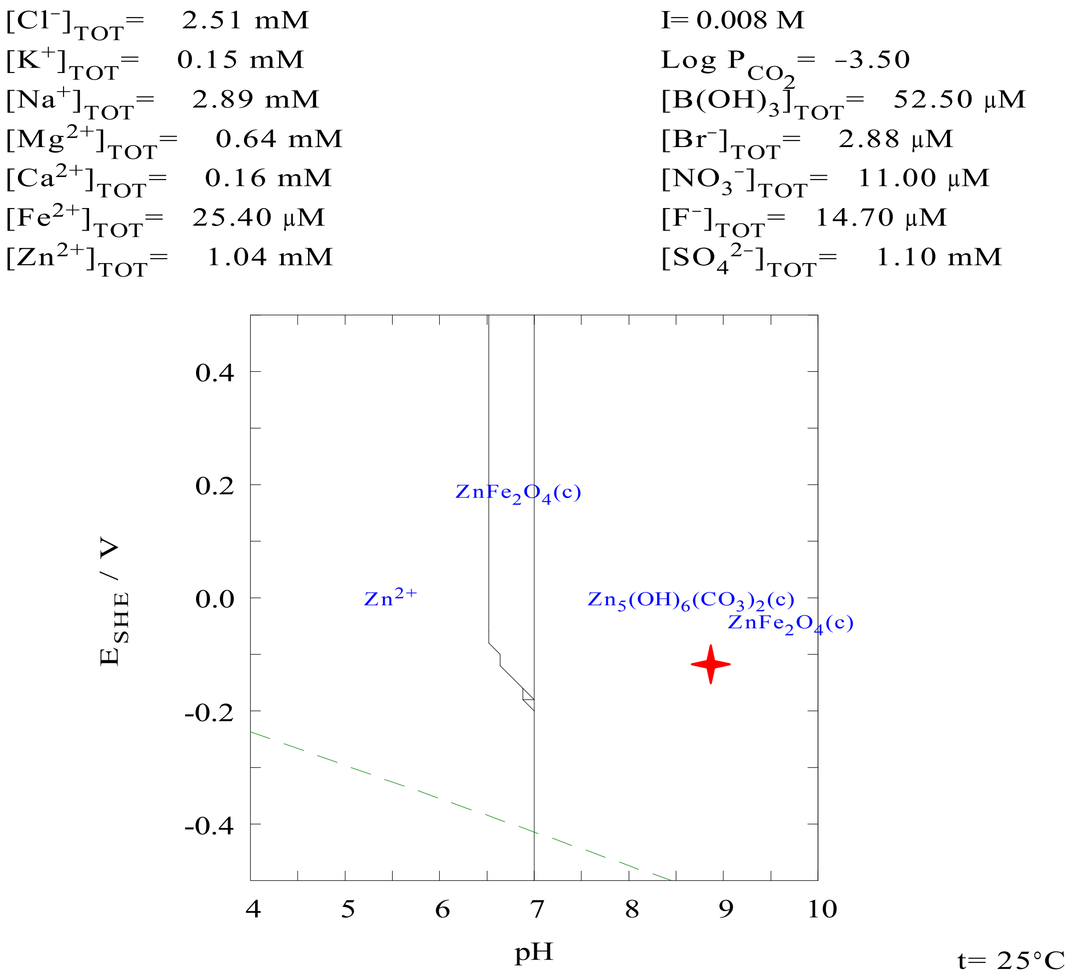


Figure C.247. Pourbaix diagram of zinc for steel pipe section immersed into river water after three months of exposure. Study area.

Steel Gutter, River Water, After Three Months of Exposure

I= 0.012 M

$[Na^{+}]_{TOT}$ = 1.73 mM

$[Mg^{2+}]_{TOT}$ = 32.00 µM

$[Ca^{2+}]_{TOT}$ = 0.60 mM

$[Fe^{2+}]_{TOT}$ = 25.80 µM

$[Al^{3+}]_{TOT}$ = 3.71 µM

$[Zn^{2+}]_{TOT}$ = 2.91 mM

$[Pb^{2+}]_{TOT}$ = 0.28 µM

E_H = -0.10 V

Log P_{CO_2} = -3.50

$[B(OH)_3]_{TOT}$ = 73.50 µM

$[Br^{-}]_{TOT}$ = 4.03 µM

$[NO_3^{-}]_{TOT}$ = 15.40 µM

$[F^{-}]_{TOT}$ = 20.60 µM

$[SO_4^{2-}]_{TOT}$ = 1.54 mM

$[Cl^{-}]_{TOT}$ = 3.51 mM

$[K^{+}]_{TOT}$ = 89.30 µM

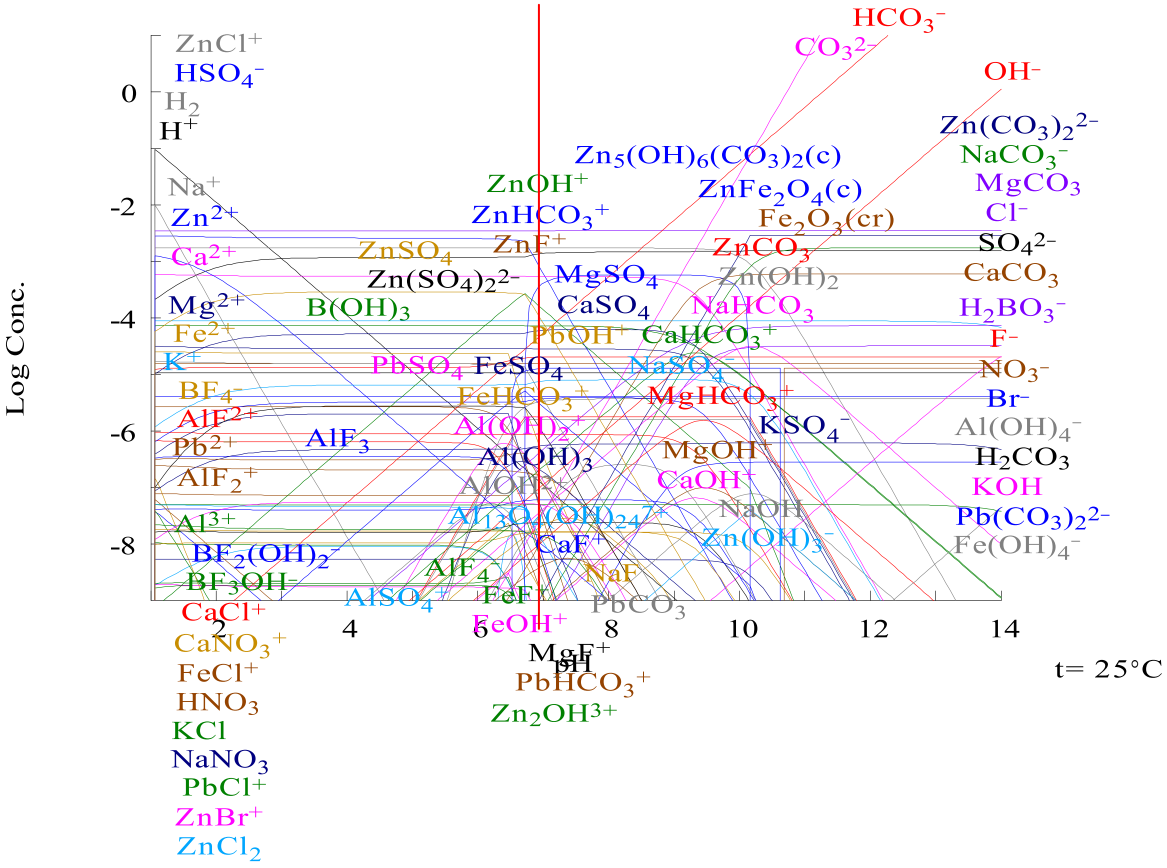


Figure C.248. Phase diagram for steel gutter section immersed into river water after three months of exposure.

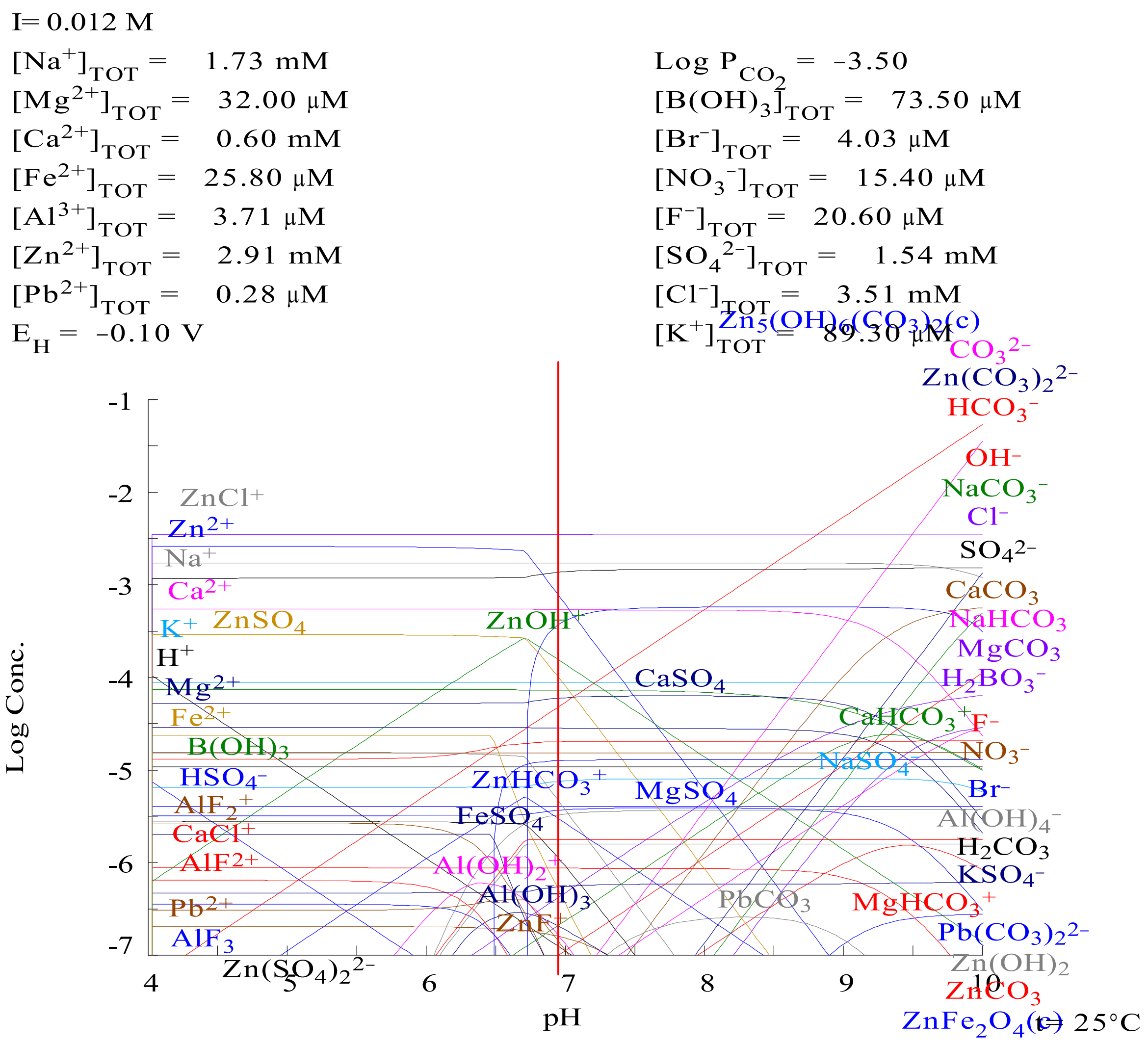


Figure C.249. Phase diagram for steel gutter section immersed into river water after three months of exposure. Study area.

Table C.59. The predominant species of lead. Steel gutter section, river water, three months exposure.

Component	Log Concentration (mol/L)	Concentration (mol/L)	Pb Concentration (mg/L as Pb)	Cumulative Percentage of Pb
Pb^{2+}	-6.79	1.61E-07	3.35E-02	57.63
$PbSO_4$	-7.30	5.01E-08	1.04E-02	75.50
$PbCO_3$	-7.52	3.04E-08	6.30E-03	86.35
$PbOH^+$	-7.71	1.95E-08	4.04E-03	93.32
$PbCl^+$	-7.84	1.43E-08	2.97E-03	98.44
$PbHCO_3^+$	-8.42	3.81E-09	7.89E-04	99.80
$Pb(SO4)_2^{2-}$	-9.45	3.58E-10	7.41E-05	99.93

Table C.60. The predominant species of zinc. Steel gutter section, river water, three months exposure.

Component	Log Concentration (mol/L)	Concentration (mol/L)	Zn Concentration (mg/L as Zn)	Cumulative Percentage of Zn
$Zn_5(OH)_6(CO_3)_2(c)$	-3.44	3.60E-04	1.18E+02	61.79
Zn^{2+}	-3.09	8.20E-04	5.36E+01	89.97
$ZnOH^+$	-3.79	1.61E-04	1.05E+01	95.49
$ZnSO_4$	-3.97	1.06E-04	6.93E+00	99.13
$ZnFe_2O_4(c)$	-4.90	1.26E-05	8.24E-01	99.56
$ZnCl^+$	-5.31	4.92E-06	3.22E-01	99.73
$ZnHCO_3^+$	-5.51	3.06E-06	2.00E-01	99.84
$ZnCO_3$	-5.75	1.77E-06	1.16E-01	99.899
$Zn(OH)_2$	-5.80	1.58E-06	1.03E-01	99.954

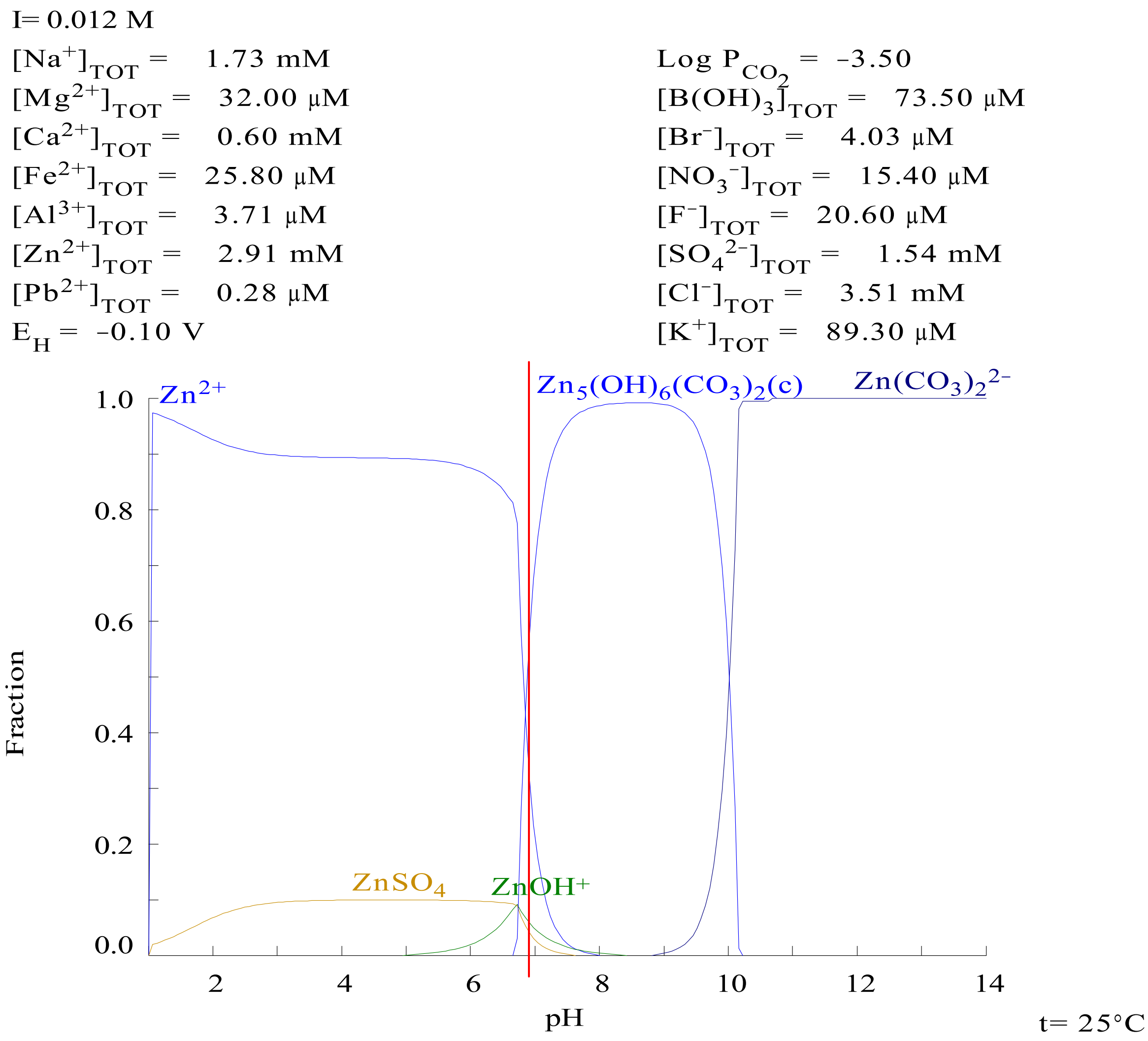


Figure C.250. Fraction diagram of zinc for steel gutter section immersed into river water after three months of exposure.

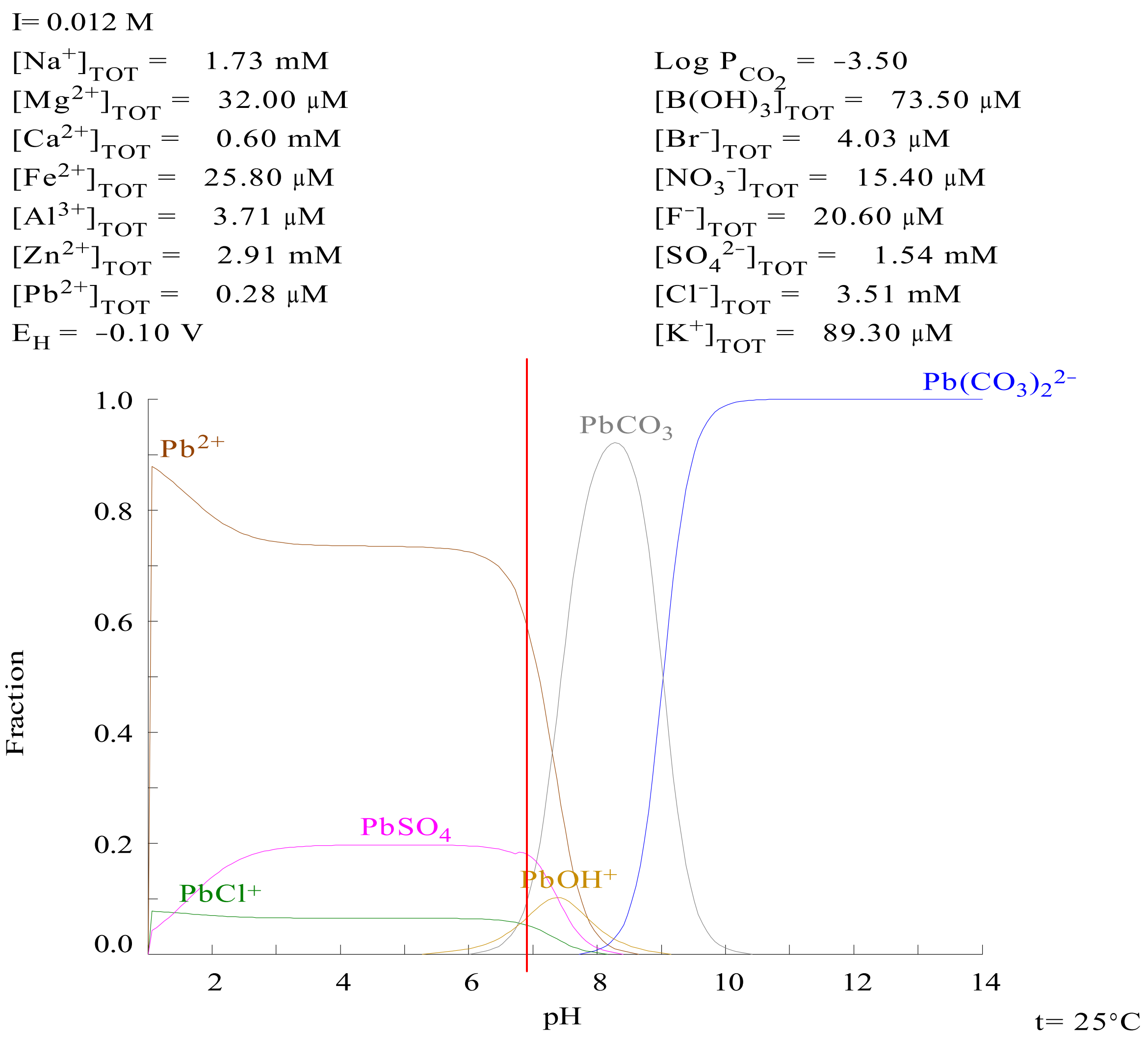


Figure C.251. Fraction diagram of lead for steel gutter section immersed into river water after three months of exposure.

$[K^{+}]_{TOT}$= 89.30 µM
$[Na^{+}]_{TOT}$= 1.73 mM
$[Mg^{2+}]_{TOT}$= 32.00 µM
$[Ca^{2+}]_{TOT}$= 0.60 mM
$[Fe^{2+}]_{TOT}$= 25.80 µM
$[Al^{3+}]_{TOT}$= 3.71 µM
$[Zn^{2+}]_{TOT}$= 2.91 mM
$[Pb^{2+}]_{TOT}$= 0.28 µM

I= 0.012 M
Log P_{CO_2}= -3.50
$[B(OH)_3]_{TOT}$= 73.50 µM
$[Br^{-}]_{TOT}$= 4.03 µM
$[NO_3^{-}]_{TOT}$= 15.40 µM
$[F^{-}]_{TOT}$= 20.60 µM
$[SO_4^{2-}]_{TOT}$= 1.54 mM
$[Cl^{-}]_{TOT}$= 3.51 mM

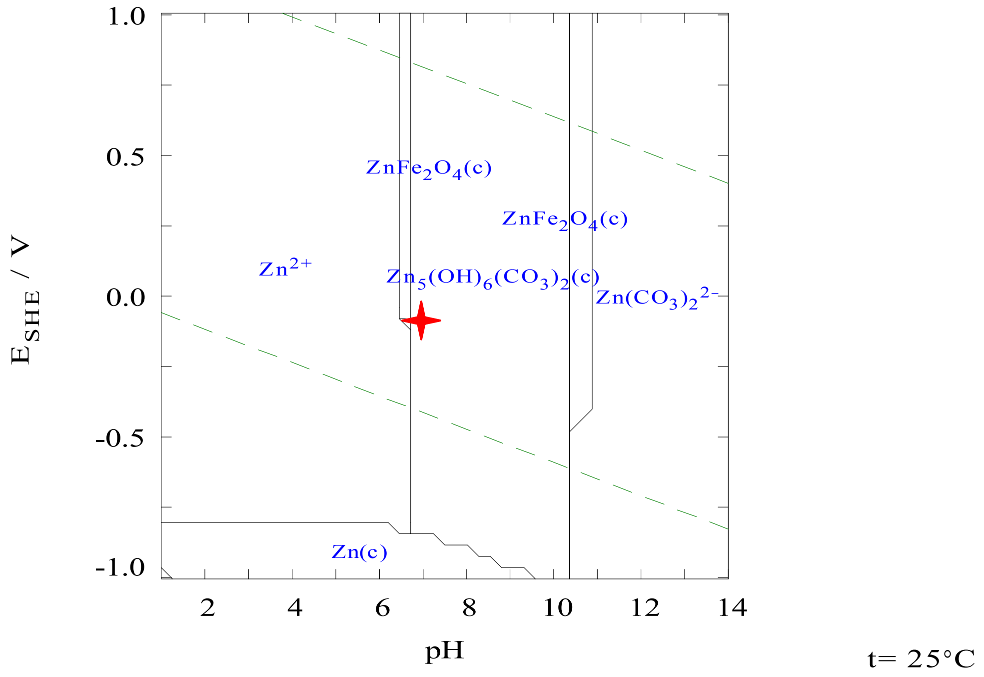


Figure C.252. Pourbaix diagram of zinc for steel gutter section immersed into river water after three months of exposure.

$[K^+]_{TOT}$= 89.30 µM
$[Na^+]_{TOT}$= 1.73 mM
$[Mg^{2+}]_{TOT}$= 32.00 µM
$[Ca^{2+}]_{TOT}$= 0.60 mM
$[Fe^{2+}]_{TOT}$= 25.80 µM
$[Al^{3+}]_{TOT}$= 3.71 µM
$[Zn^{2+}]_{TOT}$= 2.91 mM
$[Pb^{2+}]_{TOT}$= 0.28 µM

I= 0.012 M
Log P_{CO_2}= -3.50
$[B(OH)_3]_{TOT}$= 73.50 µM
$[Br^-]_{TOT}$= 4.03 µM
$[NO_3^-]_{TOT}$= 15.40 µM
$[F^-]_{TOT}$= 20.60 µM
$[SO_4^{2-}]_{TOT}$= 1.54 mM
$[Cl^-]_{TOT}$= 3.51 mM

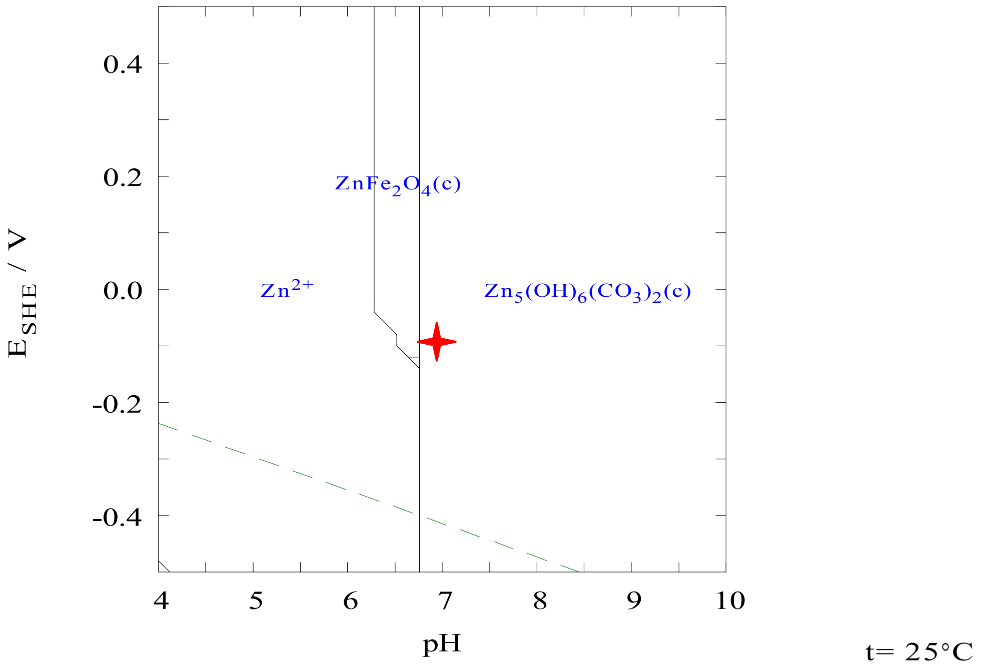


Figure C.253. Pourbaix diagram of zinc for steel gutter section immersed into river water after three months of exposure. Study area.

$[K^+]_{TOT}$= 89.30 μM
$[Na^+]_{TOT}$= 1.73 mM
$[Mg^{2+}]_{TOT}$= 32.00 μM
$[Ca^{2+}]_{TOT}$= 0.60 mM
$[Fe^{2+}]_{TOT}$= 25.80 μM
$[Al^{3+}]_{TOT}$= 3.71 μM
$[Zn^{2+}]_{TOT}$= 2.91 mM
$[Pb^{2+}]_{TOT}$= 0.28 μM

I= 0.012 M
Log P_{CO_2}= -3.50
$[B(OH)_3]_{TOT}$= 73.50 μM
$[Br^-]_{TOT}$= 4.03 μM
$[NO_3^-]_{TOT}$= 15.40 μM
$[F^-]_{TOT}$= 20.60 μM
$[SO_4^{2-}]_{TOT}$= 1.54 mM
$[Cl^-]_{TOT}$= 3.51 mM

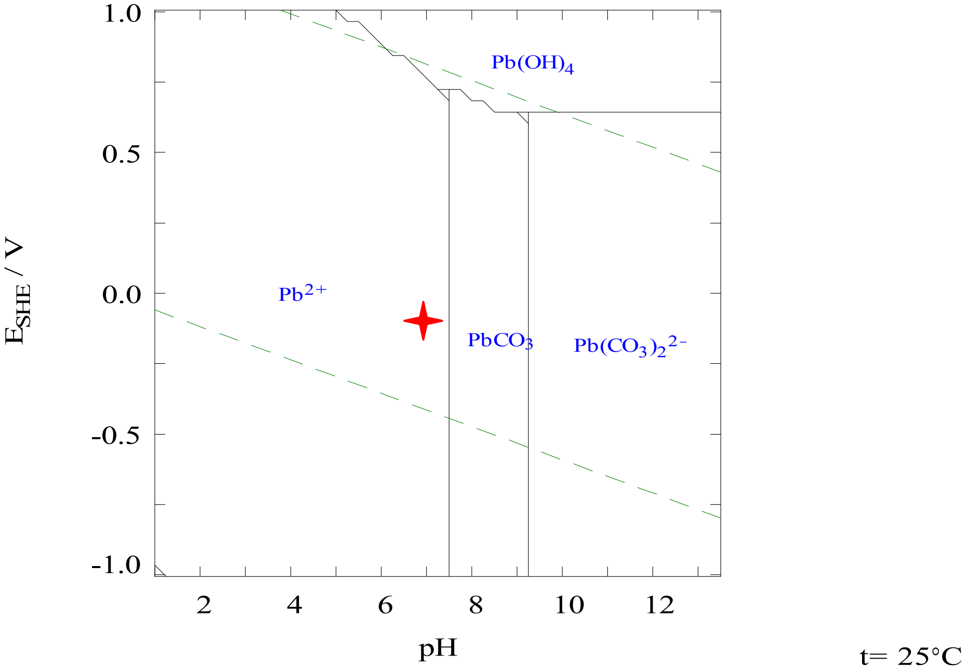


Figure C.254. Pourbaix diagram of lead for steel gutter section immersed into river water after three months of exposure.

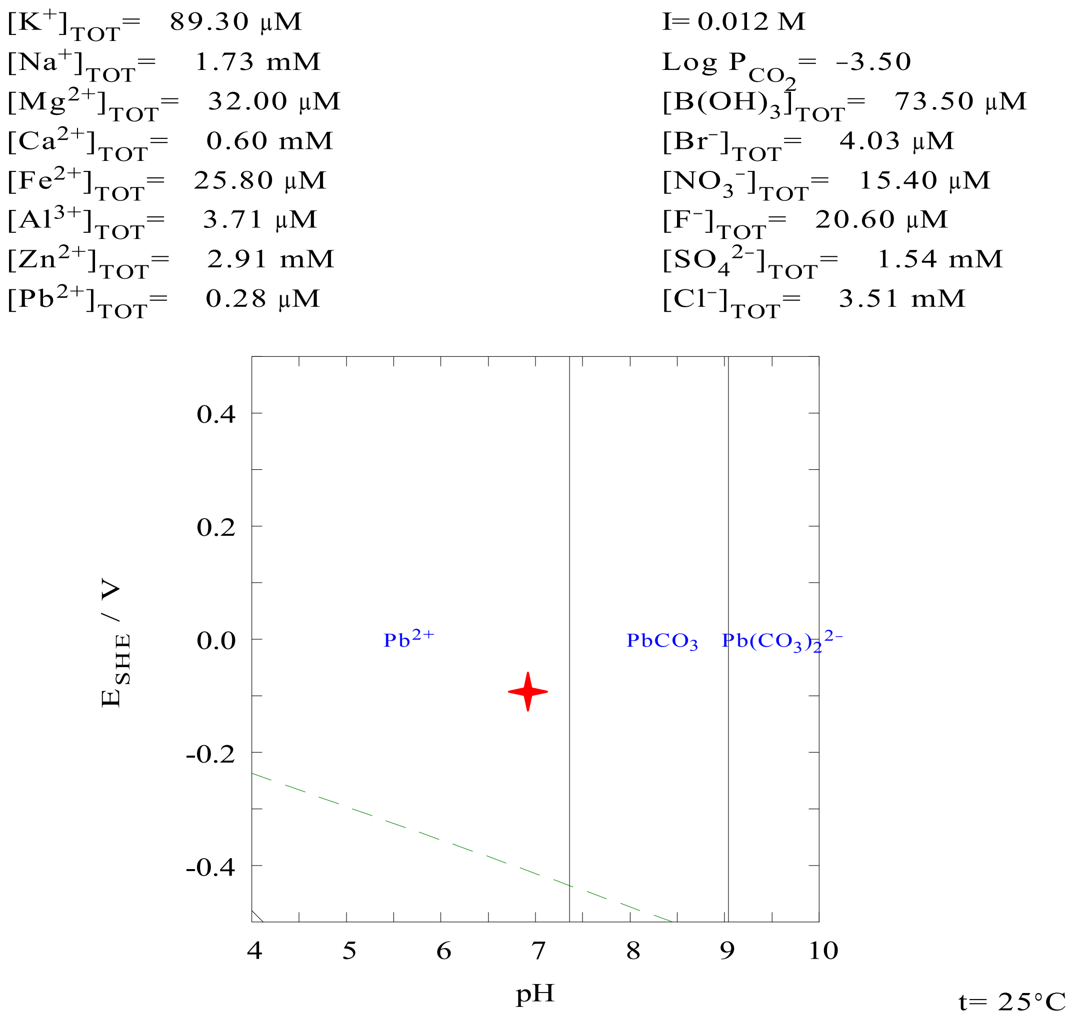


Figure C.255. Pourbaix diagram of lead for steel gutter section immersed into river water after three months of exposure. Study area.

Copper Gutter, River Water, After Three Months of Exposure

$[K^+]_{TOT}$ = 0.15 mM
$[Na^+]_{TOT}$ = 2.89 mM
$[Mg^{2+}]_{TOT}$ = 0.89 mM
$[Ca^{2+}]_{TOT}$ = 1.00 mM
$[Fe^{2+}]_{TOT}$ = 31.90 μM
$[Zn^{2+}]_{TOT}$ = 7.65 μM
$[Cu^{2+}]_{TOT}$ = 86.10 μM
E_H = -0.06 V

I= 0.009 M
Log P_{CO_2} = -3.50
$[B(OH)_3]_{TOT}$ = 52.50 μM
$[Br^-]_{TOT}$ = 2.88 μM
$[NO_3^-]_{TOT}$ = 11.00 μM
$[F^-]_{TOT}$ = 14.70 μM
$[SO_4^{2-}]_{TOT}$ = 1.10 mM
$[Cl^-]_{TOT}$ = 2.51 mM

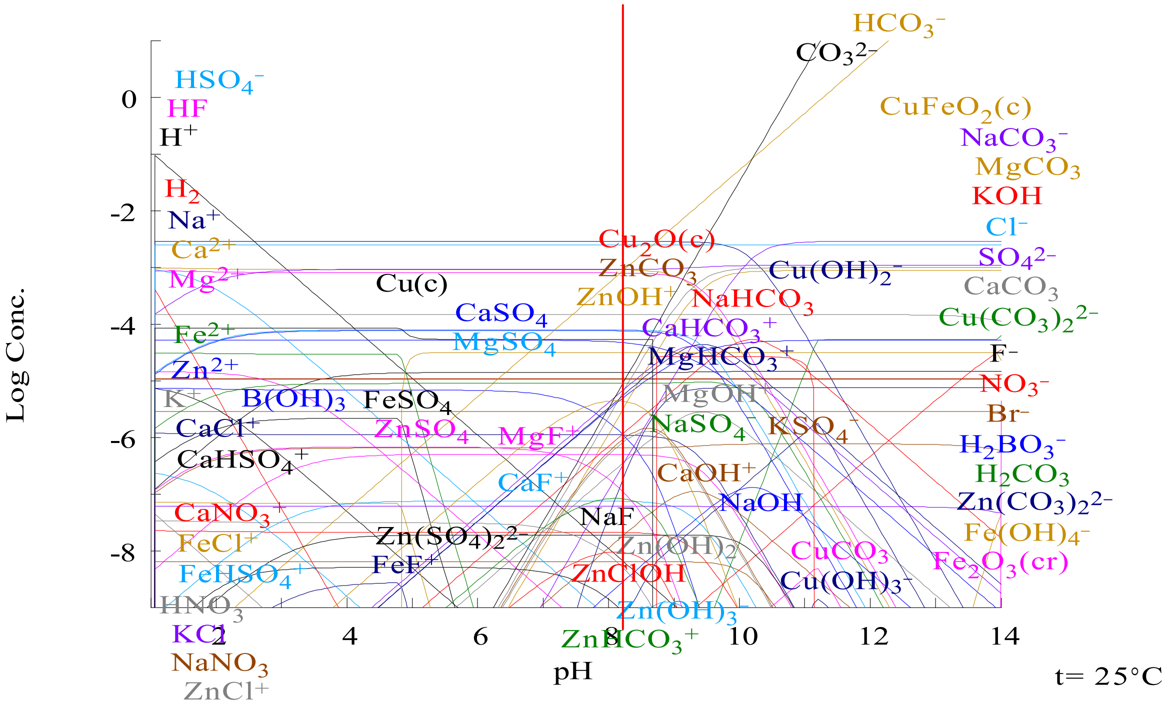


Figure C.256. Phase diagram for copper gutter section immersed into river water after three months of exposure.

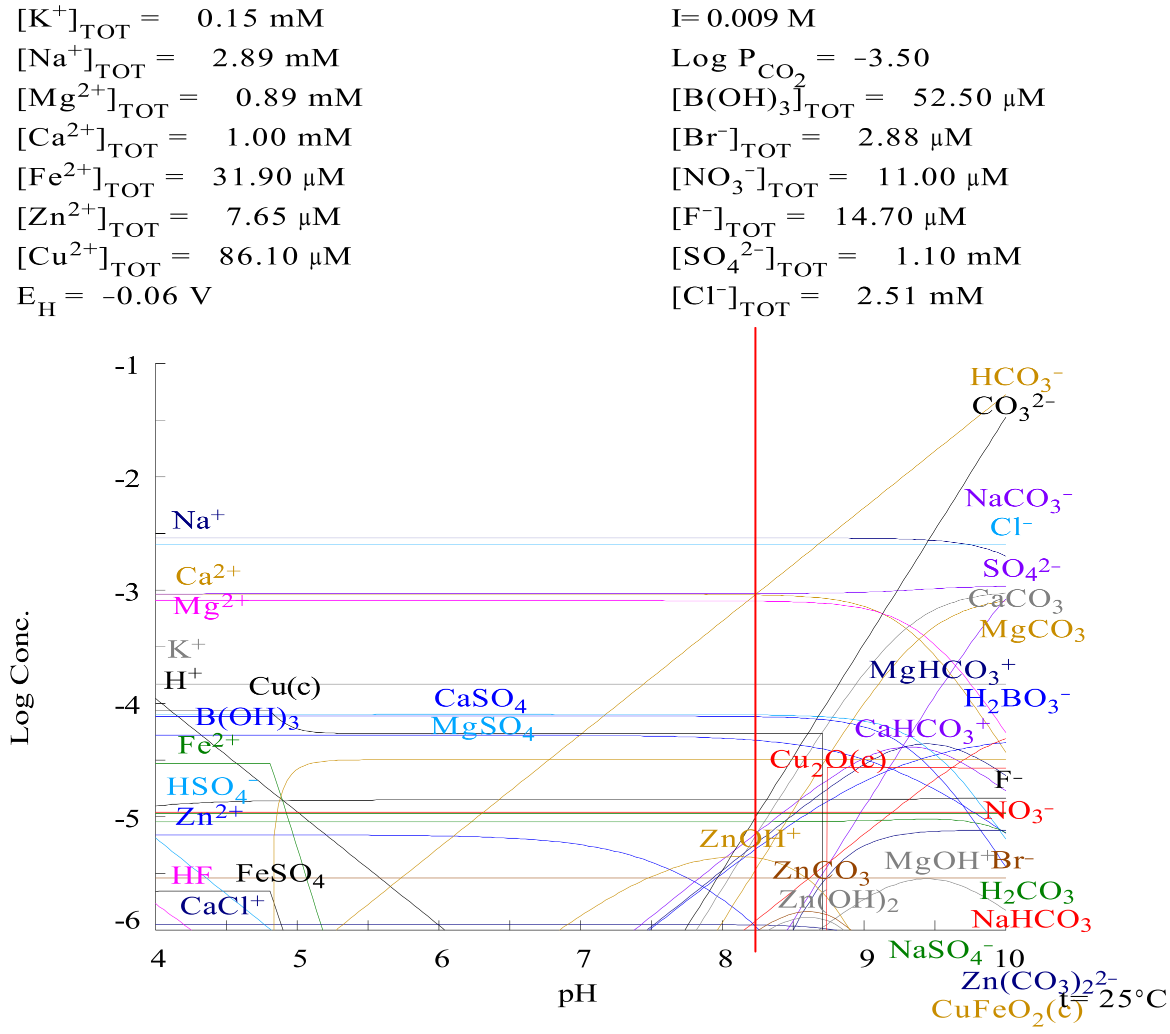


Figure C.257. Phase diagram for copper gutter section immersed into river water after three months of exposure. Study area.

Table C.61. The predominant species of copper. Copper gutter section, river water, three months exposure.

Component	Log Concentration (mol/L)	Concentration (mol/L)	Cu Concentration (mg/L as Cu)	Cumulative Percentage of Cu
Cu(c)	-4.27E	5.42E-05	3.44	62.947
$CuFeO_2$(c)	-4.50E	3.19E-05	2.03	99.997

Footnote: Cu^+ was calculated to be 2.17E-05 mg/L; Cu^{2+} was calculated to be 4.87E-09 mg/L

Table C.62. The predominant species of zinc. Copper gutter section, river water, three months exposure.

Component	Log Concentration (mol/L)	Concentration (mol/L)	Zn Concentration (mg/L as Zn)	Cumulative Percentage of Zn
$ZnOH^+$	-5.38	4.18E-06	2.73E-01	54.62
$ZnCO_3$	-5.96	1.11E-06	7.24E-02	69.10
$Zn(OH)_2$	-6.01	9.85E-07	6.44E-02	81.97
Zn^{2+}	-6.06	8.63E-07	5.64E-02	93.25
$Zn(CO3)_2^{2-}$	-6.47	3.37E-07	2.21E-02	97.66
$ZnSO_4$	-7.07	8.54E-08	5.59E-03	98.78
$ZnHCO_3^+$	-7.10	7.96E-08	5.21E-03	99.82
ZnClOH	-8.04	9.02E-09	5.90E-04	99.93

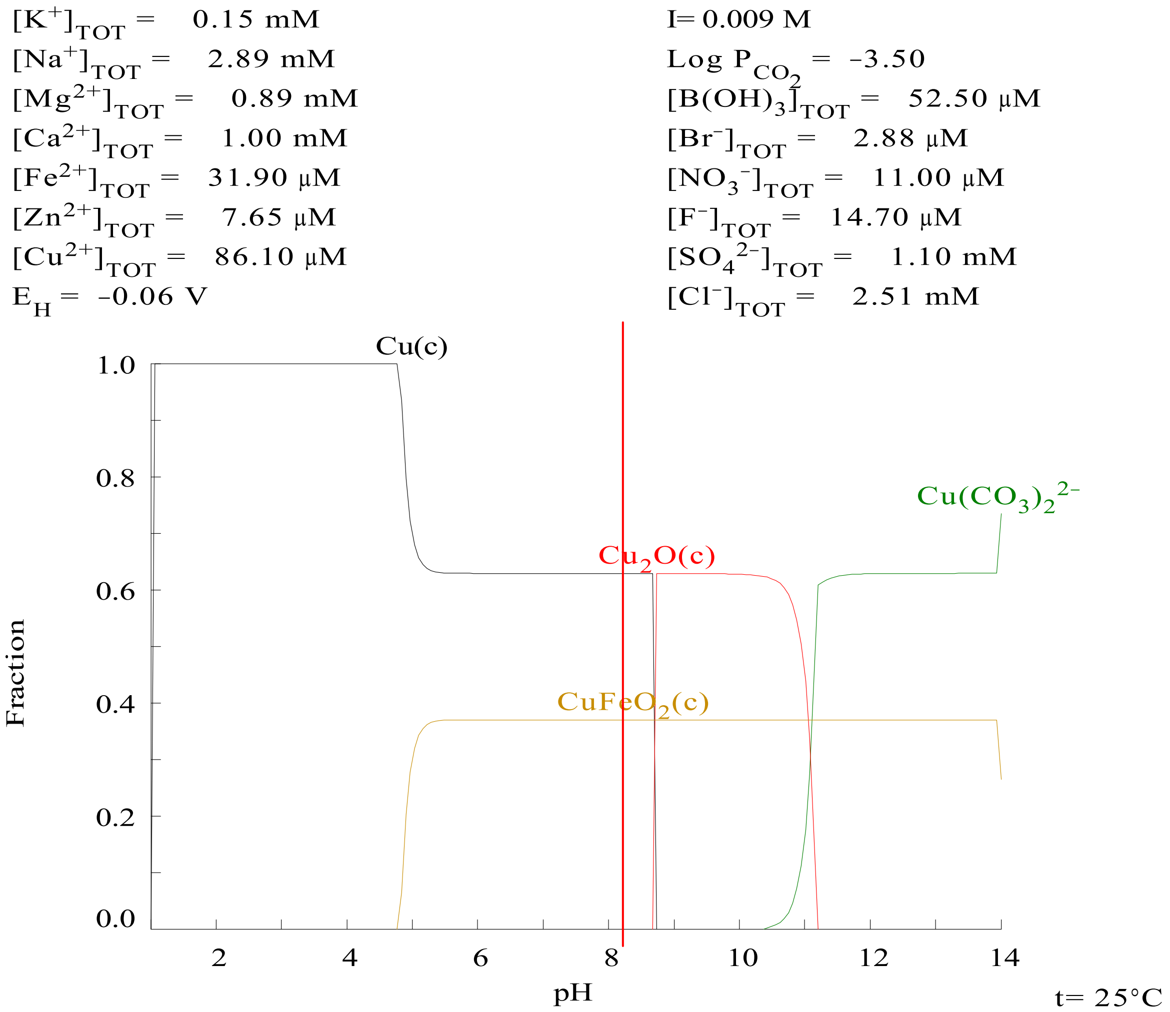


Figure C.258. Fraction diagram of copper for copper gutter section immersed into river water after three months of exposure.

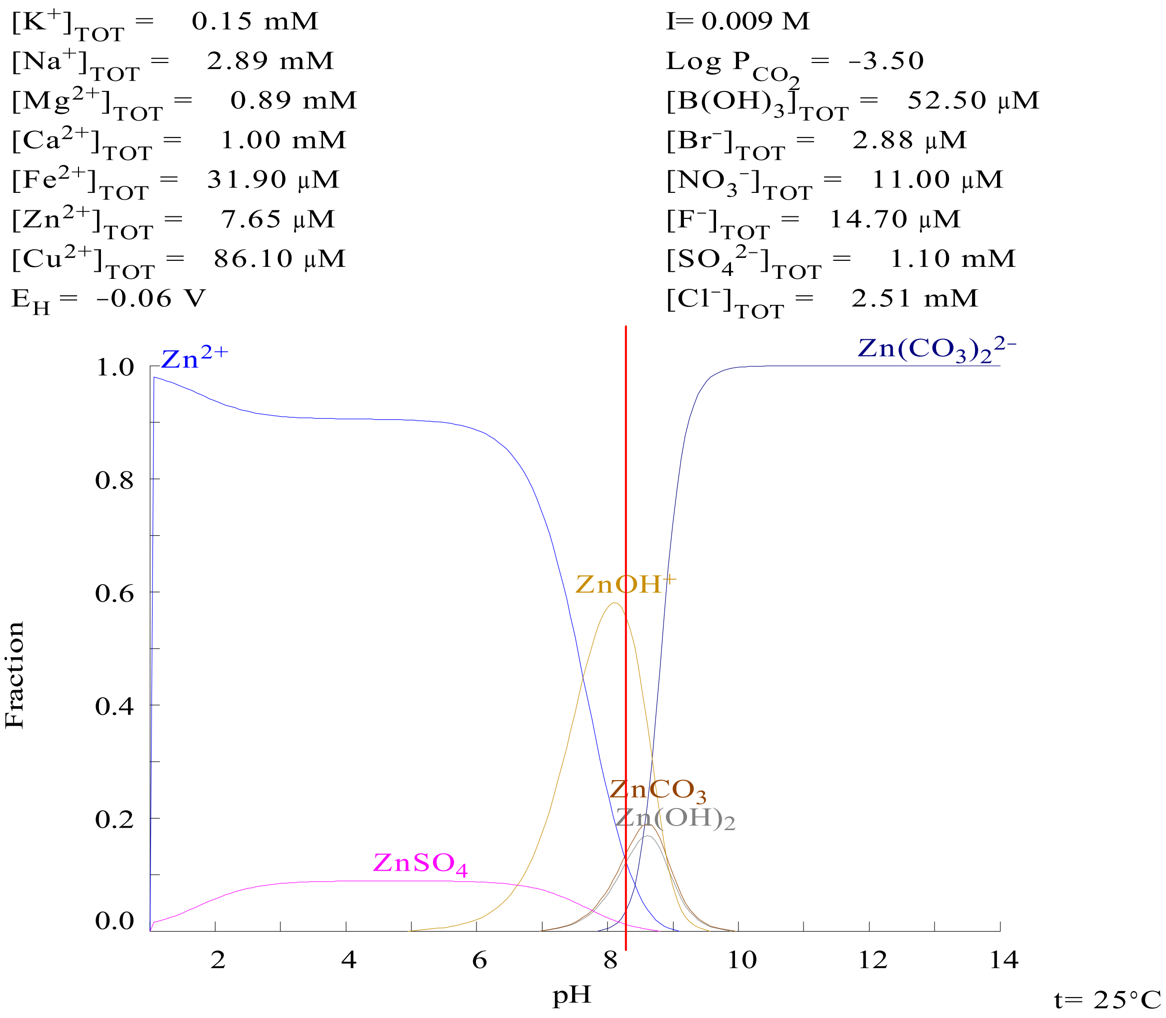


Figure C.259. Fraction diagram of zinc for copper gutter section immersed into river water after three months of exposure.

I= 0.009 M

$[K^+]_{TOT}$= 0.15 mM
$[Na^+]_{TOT}$= 2.89 mM
$[Mg^{2+}]_{TOT}$= 0.89 mM
$[Ca^{2+}]_{TOT}$= 1.00 mM
$[Fe^{2+}]_{TOT}$= 31.90 µM
$[Zn^{2+}]_{TOT}$= 7.65 µM
$[Cu^{2+}]_{TOT}$= 86.10 µM

Log P_{CO_2}= -3.50
$[B(OH)_3]_{TOT}$= 52.50 µM
$[Br^-]_{TOT}$= 2.88 µM
$[NO_3^-]_{TOT}$= 11.00 µM
$[F^-]_{TOT}$= 14.70 µM
$[SO_4^{2-}]_{TOT}$= 1.10 mM
$[Cl^-]_{TOT}$= 2.51 mM

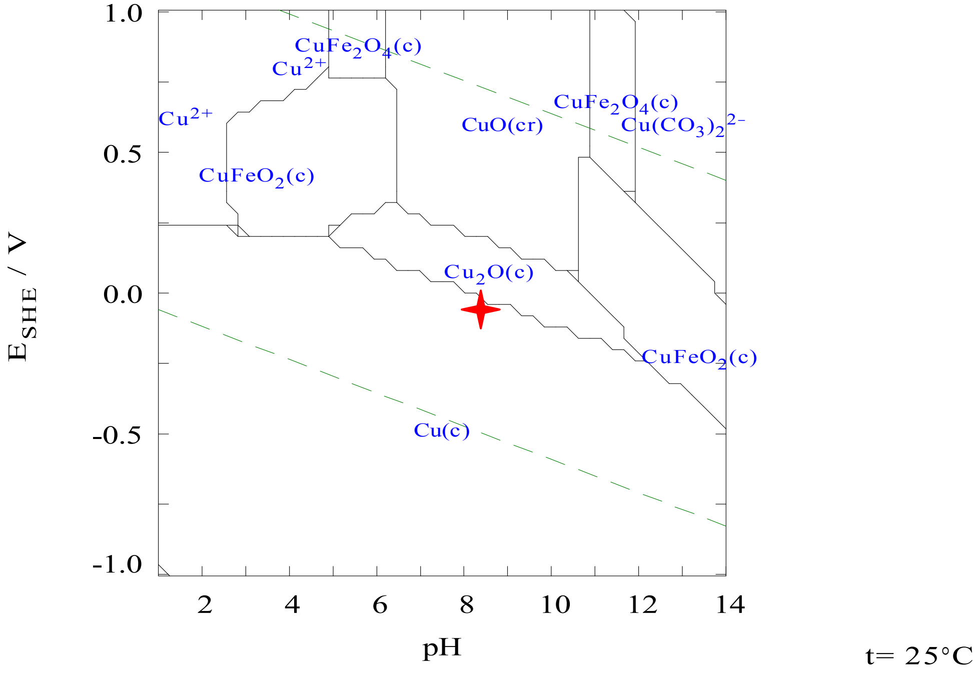


Figure C.260. Pourbaix diagram of copper for copper gutter section immersed into river water after three months of exposure.

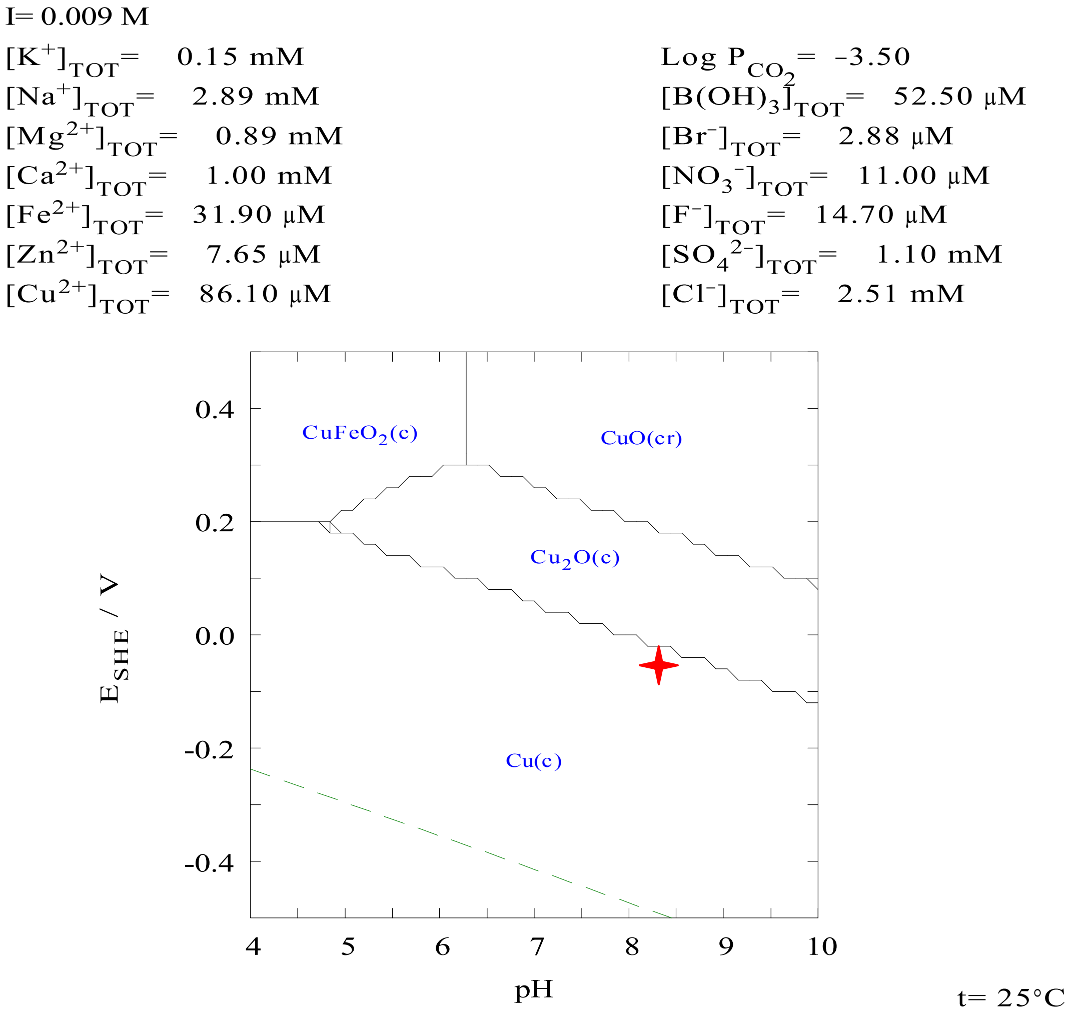


Figure C.261. Pourbaix diagram of copper for copper gutter section immersed into river water after three months of exposure. Study area.

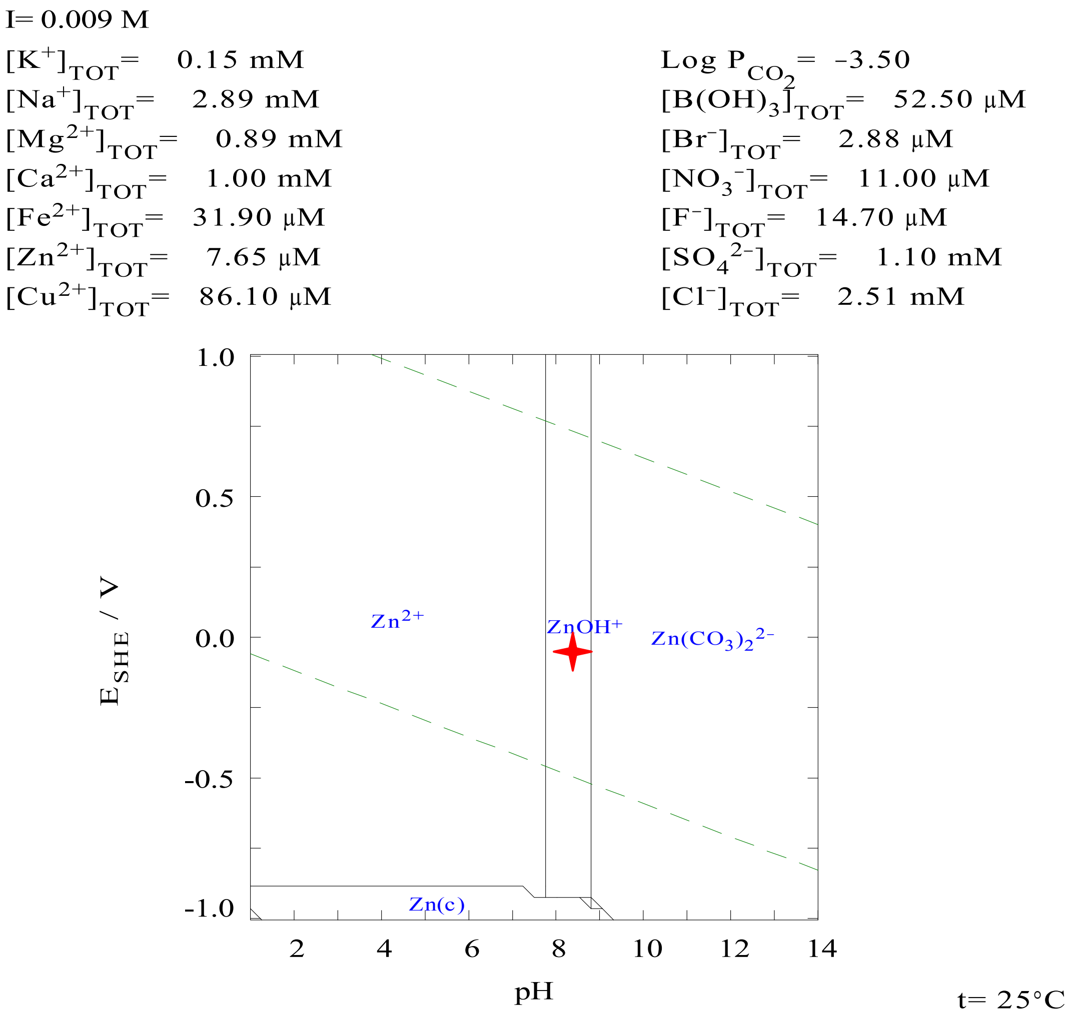


Figure C.262. Pourbaix diagram of zinc for copper gutter section immersed into river water after three months of exposure.

I= 0.009 M

$[K^{+}]_{TOT}$= 0.15 mM
$[Na^{+}]_{TOT}$= 2.89 mM
$[Mg^{2+}]_{TOT}$= 0.89 mM
$[Ca^{2+}]_{TOT}$= 1.00 mM
$[Fe^{2+}]_{TOT}$= 31.90 µM
$[Zn^{2+}]_{TOT}$= 7.65 µM
$[Cu^{2+}]_{TOT}$= 86.10 µM

Log P_{CO_2}= -3.50
$[B(OH)_3]_{TOT}$= 52.50 µM
$[Br^{-}]_{TOT}$= 2.88 µM
$[NO_3^{-}]_{TOT}$= 11.00 µM
$[F^{-}]_{TOT}$= 14.70 µM
$[SO_4^{2-}]_{TOT}$= 1.10 mM
$[Cl^{-}]_{TOT}$= 2.51 mM

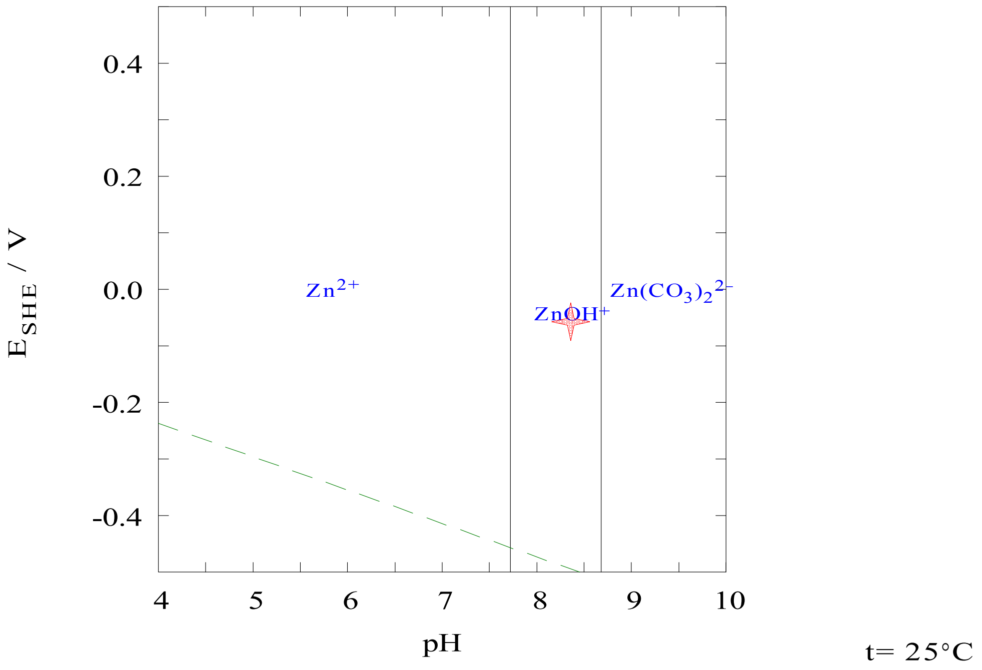


Figure C.263. Pourbaix diagram of zinc for copper gutter section immersed into river water after three months of exposure. Study area.

PVC Pipe, River Water, After Three Months of Exposure

$[K^+]_{TOT}$ = 0.15 mM
$[Na^+]_{TOT}$ = 2.89 mM
$[Mg^{2+}]_{TOT}$ = 1.08 mM
$[Ca^{2+}]_{TOT}$ = 1.04 mM
$[Fe^{2+}]_{TOT}$ = 11.10 µM
$[Al^{3+}]_{TOT}$ = 7.41 µM
$[Zn^{2+}]_{TOT}$ = 0.46 µM
E_H = -0.12 V

I= 0.010 M
Log P_{CO_2} = -3.50
$[B(OH)_3]_{TOT}$ = 52.50 µM
$[Br^-]_{TOT}$ = 2.88 µM
$[NO_3^-]_{TOT}$ = 11.00 µM
$[F^-]_{TOT}$ = 14.70 µM
$[SO_4^{2-}]_{TOT}$ = 1.10 mM
$[Cl^-]_{TOT}$ = 2.51 mM

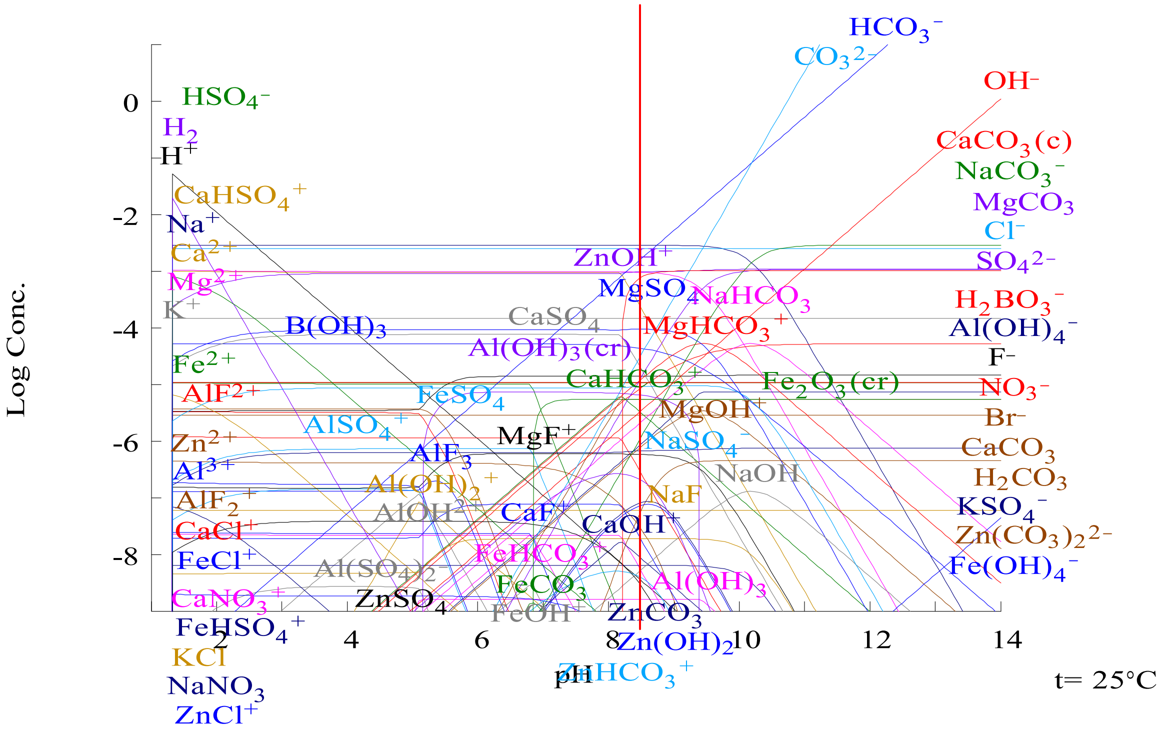


Figure C.264. Phase diagram for PVC pipe section immersed into river water after three months of exposure.

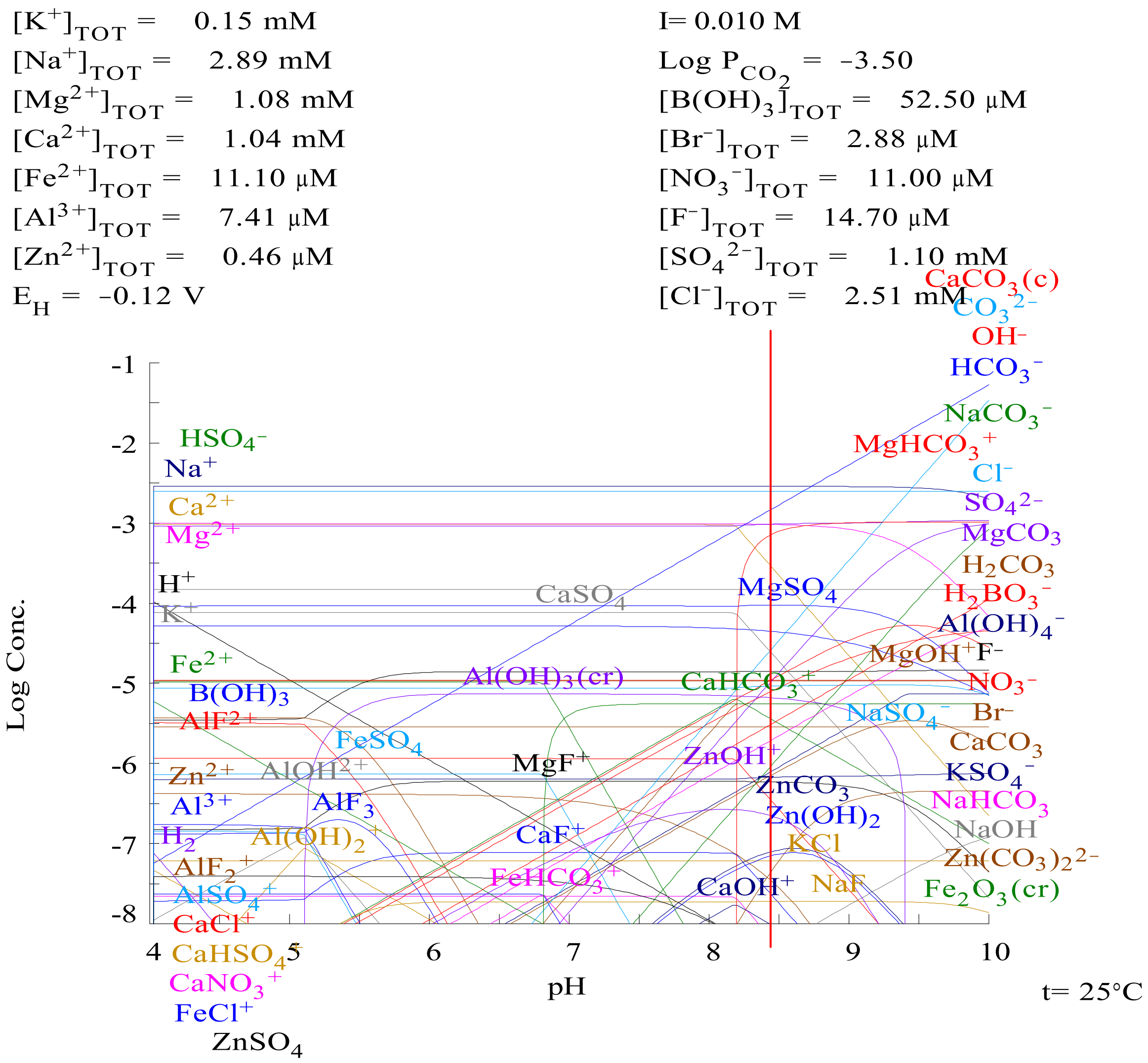


Figure C.265. Phase diagram for PVC pipe section immersed into river water after three months of exposure. Study area.

Table C.63. The predominant species of zinc. PVC pipe section, river water, three months exposure.

Component	Log Concentration (mol/L)	Concentration (mol/L)	Zn Concentration (mg/L as Zn)	Cumulative Percentage of Zn
$ZnOH^+$	-6.64	2.31E-07	1.51E-02	50.43
$ZnCO_3$	-7.12	7.60E-08	4.97E-03	66.98
$Zn(OH)_2$	-7.17	6.76E-08	4.42E-03	81.70
Zn^{2+}	-7.41	3.90E-08	2.55E-03	90.19
$Zn(CO3)_2^{2-}$	-7.44	3.65E-08	2.39E-03	98.15
$ZnHCO_3^+$	-8.36	4.41E-09	2.89E-04	99.11
$ZnSO_4$	-8.42	3.84E-09	2.51E-04	99.95

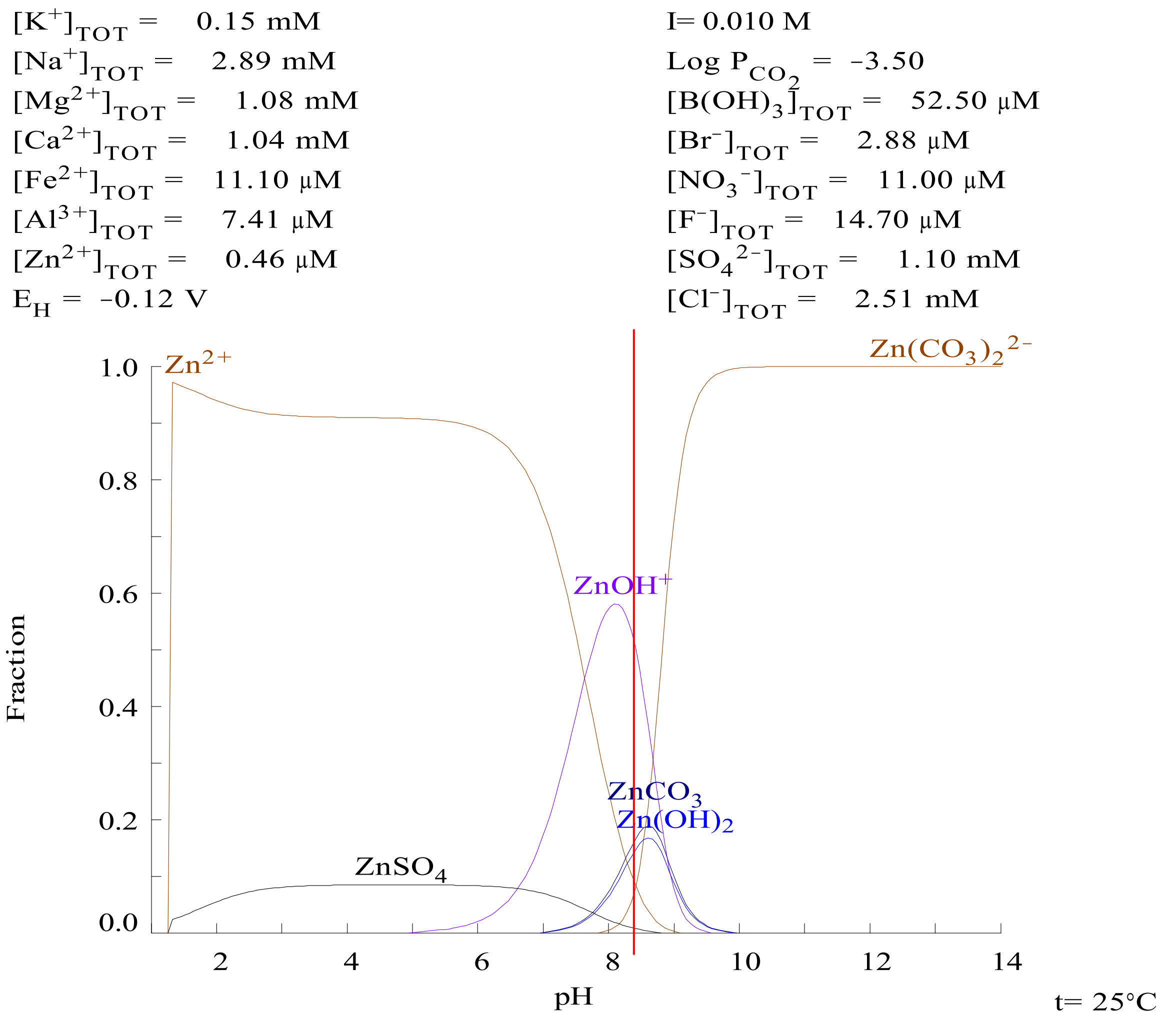


Figure C.266. Fraction diagram of zinc for PVC pipe section immersed into river water after three months of exposure.

I= 0.010 M
$[K^+]_{TOT}$= 0.15 mM
$[Na^+]_{TOT}$= 2.89 mM
$[Mg^{2+}]_{TOT}$= 1.08 mM
$[Ca^{2+}]_{TOT}$= 1.04 mM
$[Fe^{2+}]_{TOT}$= 11.10 μM
$[Al^{3+}]_{TOT}$= 7.41 μM
$[Zn^{2+}]_{TOT}$= 0.46 μM

Log P_{CO_2}= -3.50
$[B(OH)_3]_{TOT}$= 52.50 μM
$[Br^-]_{TOT}$= 2.88 μM
$[NO_3^-]_{TOT}$= 11.00 μM
$[F^-]_{TOT}$= 14.70 μM
$[SO_4^{2-}]_{TOT}$= 1.10 mM
$[Cl^-]_{TOT}$= 2.51 mM

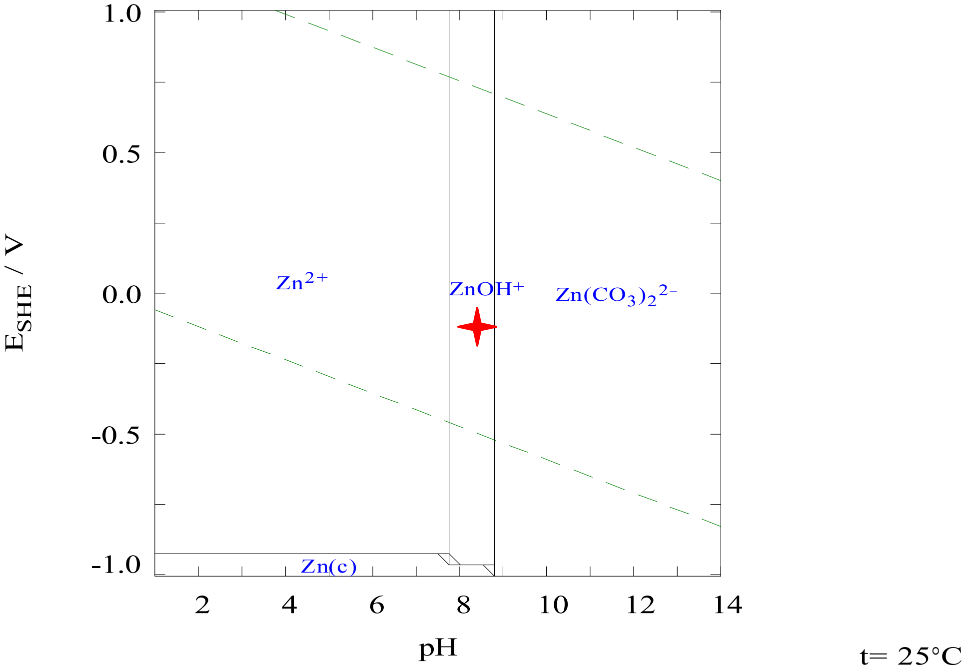


Figure C.267. Pourbaix diagram of zinc for PVC pipe section immersed into river water after three months of exposure.

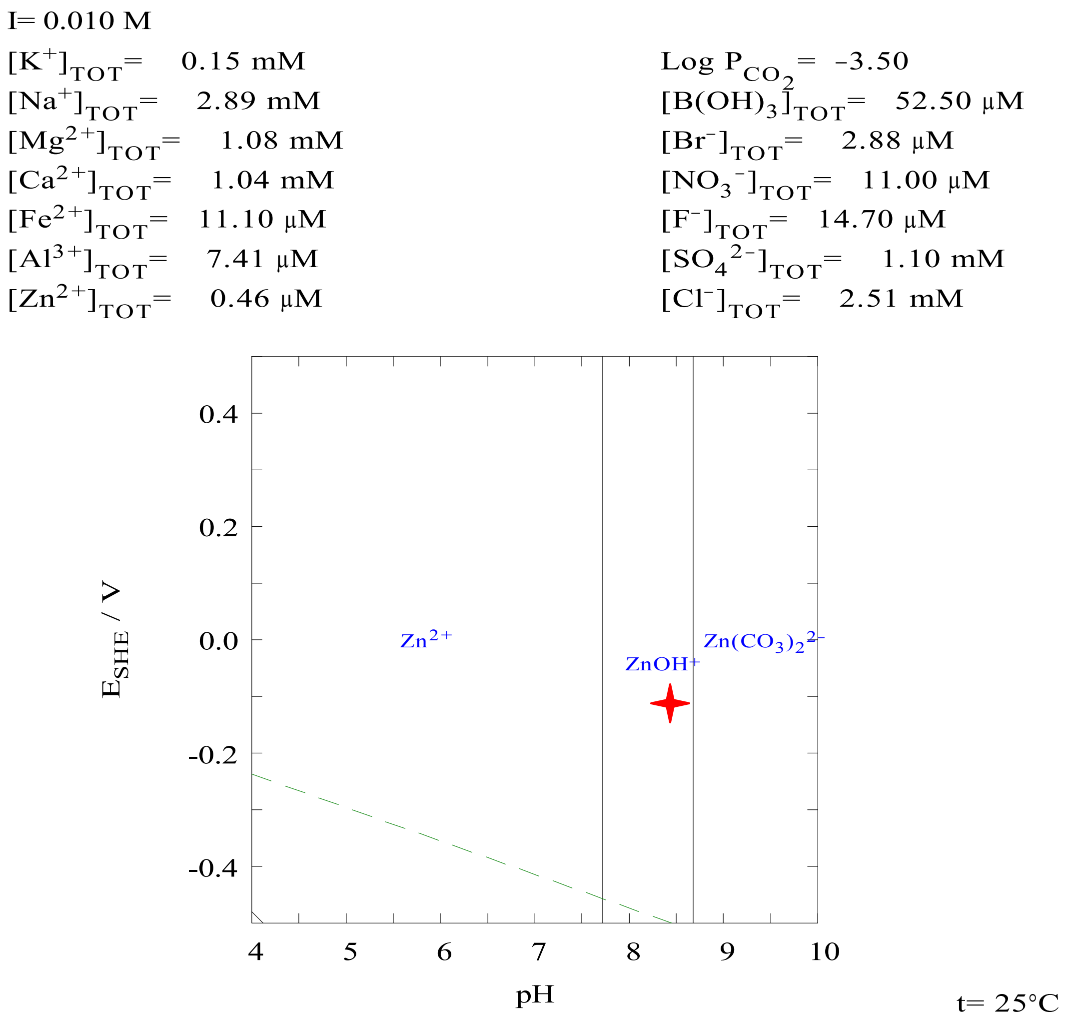


Figure C.268. Pourbaix diagram of zinc for PVC pipe section immersed into river water after three months of exposure. Study area.

HDPE Pipe, River Water, After Three Months of Exposure

$[K^+]_{TOT}$ = 0.15 mM
$[Na^+]_{TOT}$ = 2.89 mM
$[Mg^{2+}]_{TOT}$ = 1.01 mM
$[Ca^{2+}]_{TOT}$ = 0.92 mM
$[Fe^{2+}]_{TOT}$ = 7.70 µM
$[Al^{3+}]_{TOT}$ = 11.10 µM
$[Zn^{2+}]_{TOT}$ = 0.46 µM
E_H = -0.12 V

I= 0.009 M
Log P_{CO_2} = -3.50
$[B(OH)_3]_{TOT}$ = 52.50 µM
$[Br^-]_{TOT}$ = 2.88 µM
$[NO_3^-]_{TOT}$ = 11.00 µM
$[F^-]_{TOT}$ = 14.70 µM
$[SO_4^{2-}]_{TOT}$ = 1.10 mM
$[Cl^-]_{TOT}$ = 2.51 mM

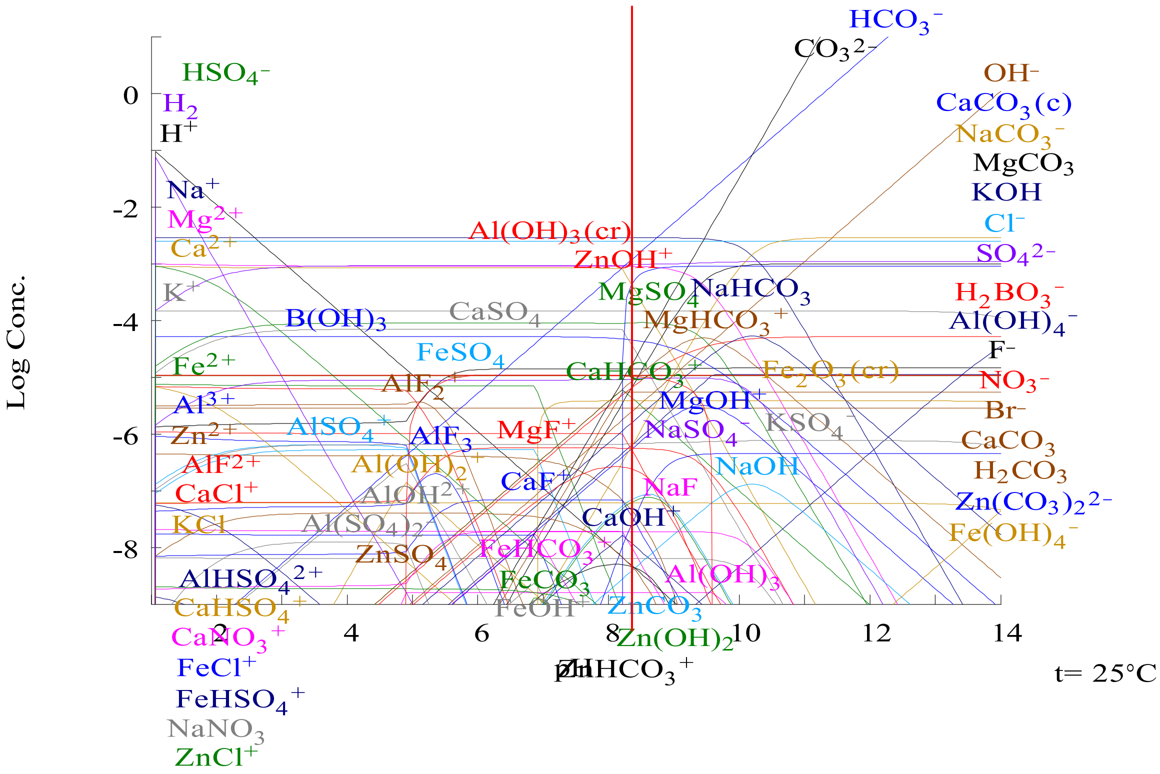


Figure C.269. Phase diagram for HDPE pipe section immersed into river water after three months of exposure.

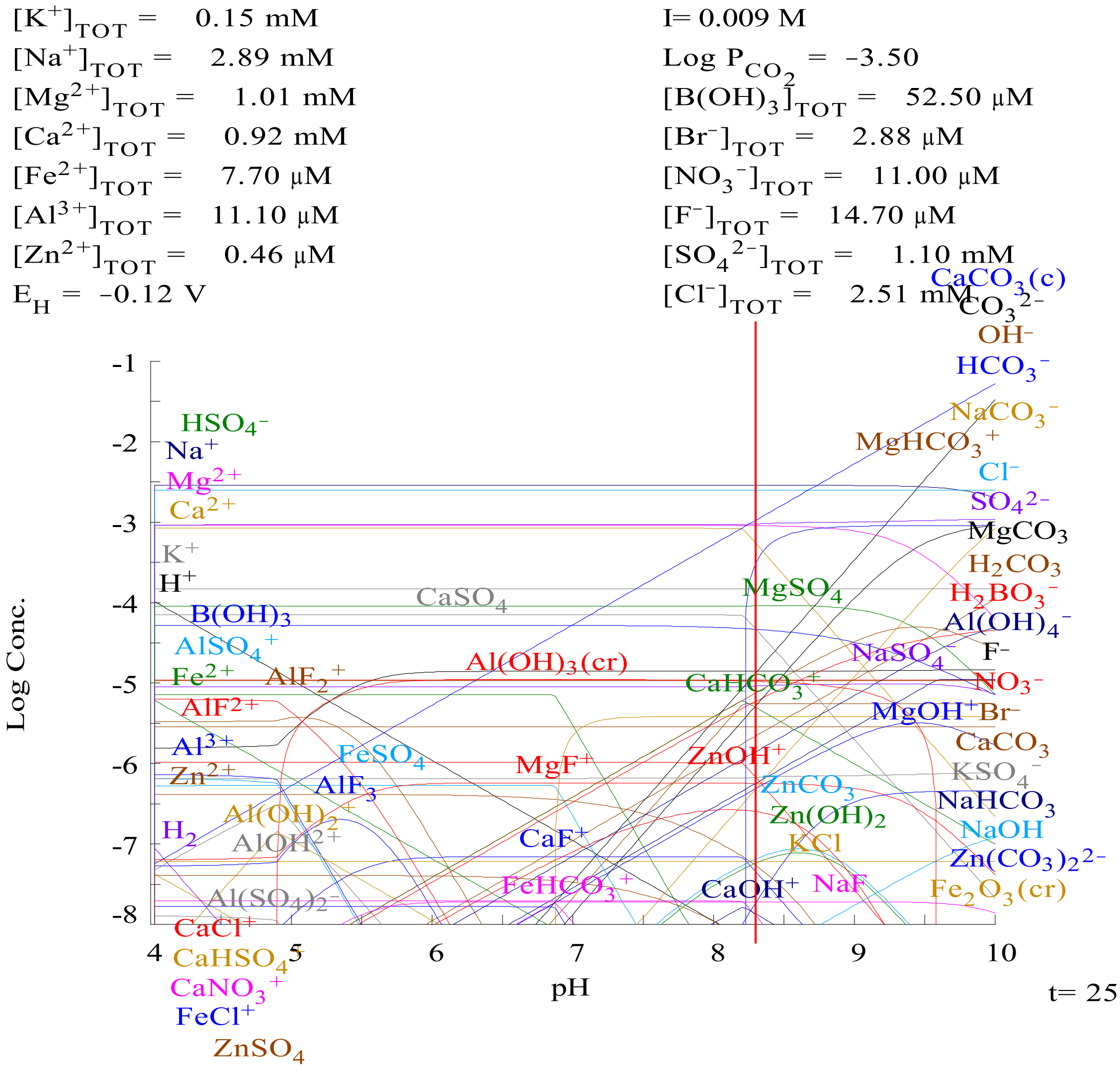


Figure C.270. Phase diagram for HDPE pipe section immersed into river water after three months of exposure. Study area.

Table C.64. The predominant species of zinc. HDPE pipe section, river water, three months exposure.

Component	Log Concentration (mol/L)	Concentration (mol/L)	Zn Concentration (mg/L as Zn)	Cumulative Percentage of Zn
$ZnOH^+$	-6.61	2.45E-07	1.61E-02	53.46
$ZnCO_3$	-7.16	6.97E-08	4.56E-03	68.65
$Zn(OH)_2$	-7.21	6.20E-08	4.05E-03	82.15
Zn^{2+}	-7.33	4.73E-08	3.09E-03	92.45
$Zn(CO3)_2^{2-}$	-7.61	2.44E-08	1.59E-03	97.76
$ZnSO_4$	-8.32	4.80E-09	3.14E-04	98.80
$ZnHCO_3^+$	-8.33	4.68E-09	3.06E-04	99.82
ZnClOH	-9.28	5.30E-10	3.46E-05	99.94
$ZnCl^+$	-9.67	2.15E-10	1.40E-05	99.99

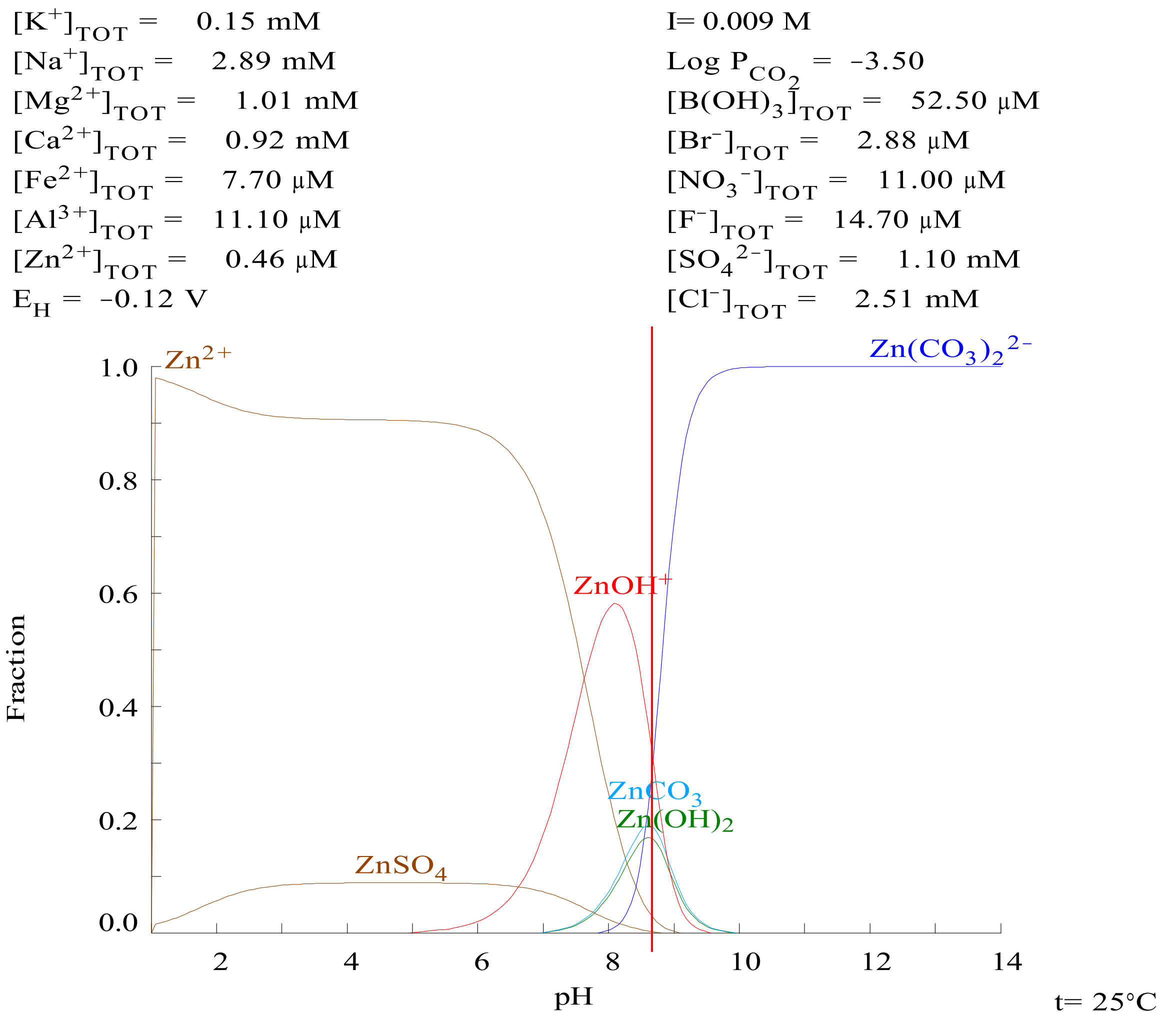


Figure C.271. Fraction diagram of zinc for HDPE pipe section immersed into river water after three months of exposure.

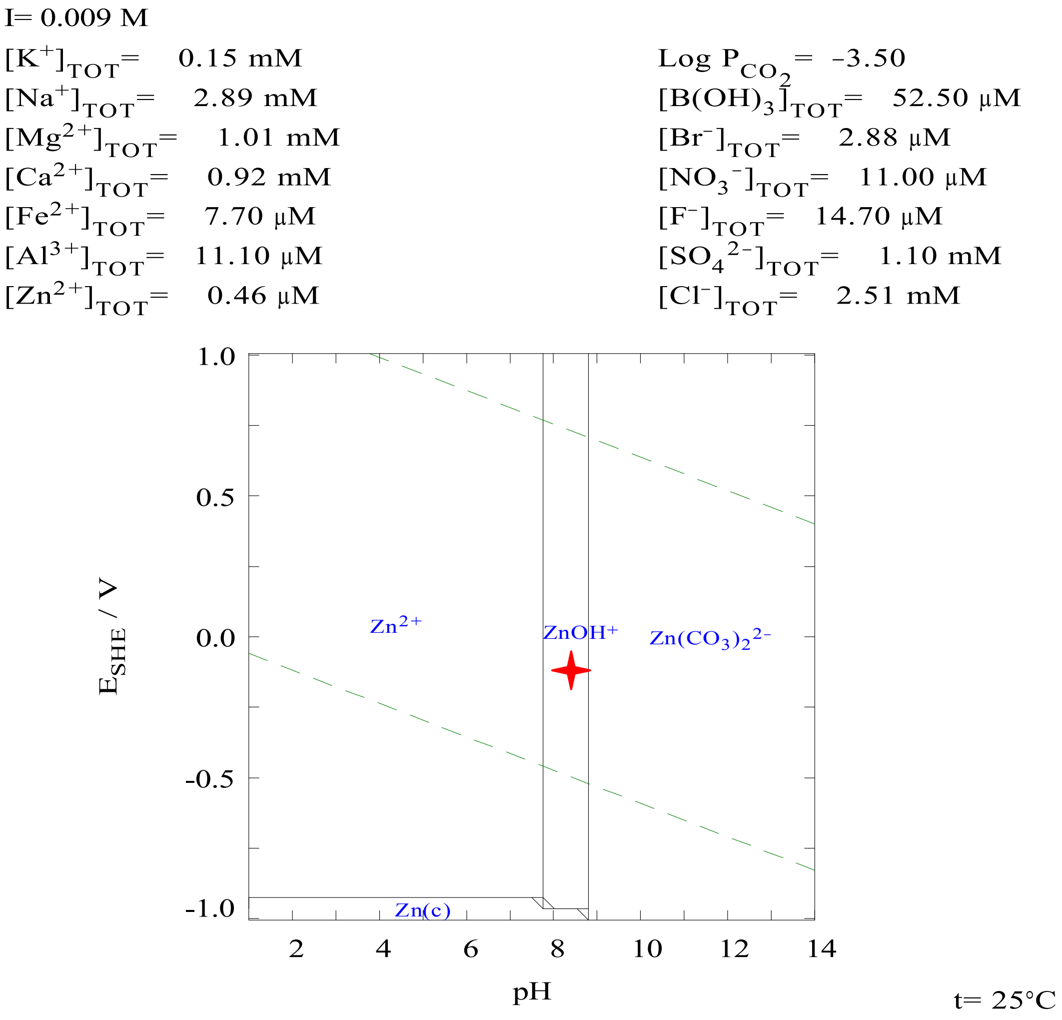
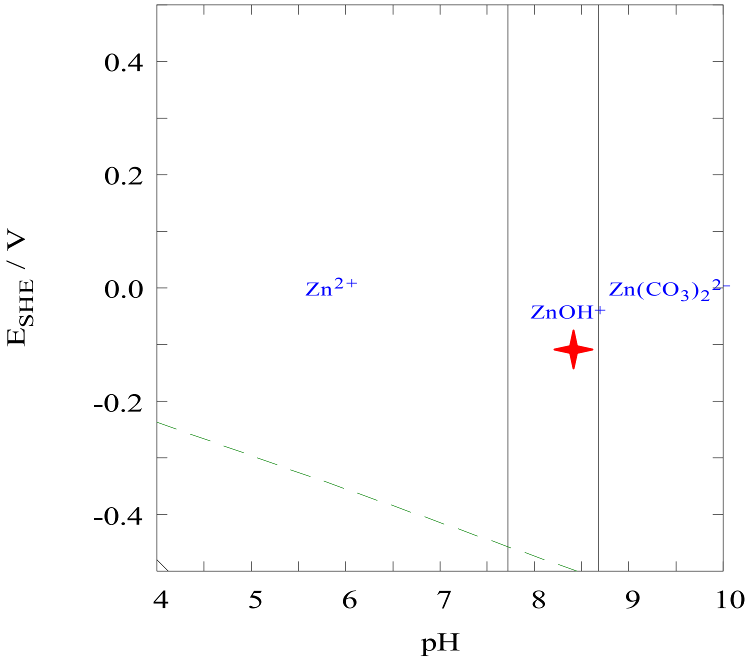


Figure C.272. Pourbaix diagram of zinc for HDPE pipe section immersed into river water after three months of exposure.

I= 0.009 M

$[K^+]_{TOT}$= 0.15 mM
$[Na^+]_{TOT}$= 2.89 mM
$[Mg^{2+}]_{TOT}$= 1.01 mM
$[Ca^{2+}]_{TOT}$= 0.92 mM
$[Fe^{2+}]_{TOT}$= 7.70 μM
$[Al^{3+}]_{TOT}$= 11.10 μM
$[Zn^{2+}]_{TOT}$= 0.46 μM

Log P_{CO_2}= -3.50
$[B(OH)_3]_{TOT}$= 52.50 μM
$[Br^-]_{TOT}$= 2.88 μM
$[NO_3^-]_{TOT}$= 11.00 μM
$[F^-]_{TOT}$= 14.70 μM
$[SO_4^{2-}]_{TOT}$= 1.10 mM
$[Cl^-]_{TOT}$= 2.51 mM



t= 25°C

Figure C.273. Pourbaix diagram of zinc for HDPE pipe section immersed into river water after three months of exposure. Study area.

Aluminum Gutter, River Water, After Three Months of Exposure

$[K^+]_{TOT}$ = 0.15 mM
$[Na^+]_{TOT}$ = 2.89 mM
$[Mg^{2+}]_{TOT}$ = 0.96 mM
$[Ca^{2+}]_{TOT}$ = 1.00 mM
$[Fe^{2+}]_{TOT}$ = 8.24 μM
$[Al^{3+}]_{TOT}$ = 37.10 μM
$[Zn^{2+}]_{TOT}$ = 0.46 μM
E_H = -0.12 V

I= 0.009 M
Log P_{CO_2} = -3.50
$[B(OH)_3]_{TOT}$ = 52.50 μM
$[Br^-]_{TOT}$ = 2.88 μM
$[NO_3^-]_{TOT}$ = 11.00 μM
$[F^-]_{TOT}$ = 14.70 μM
$[SO_4^{2-}]_{TOT}$ = 1.10 mM
$[Cl^-]_{TOT}$ = 2.51 mM

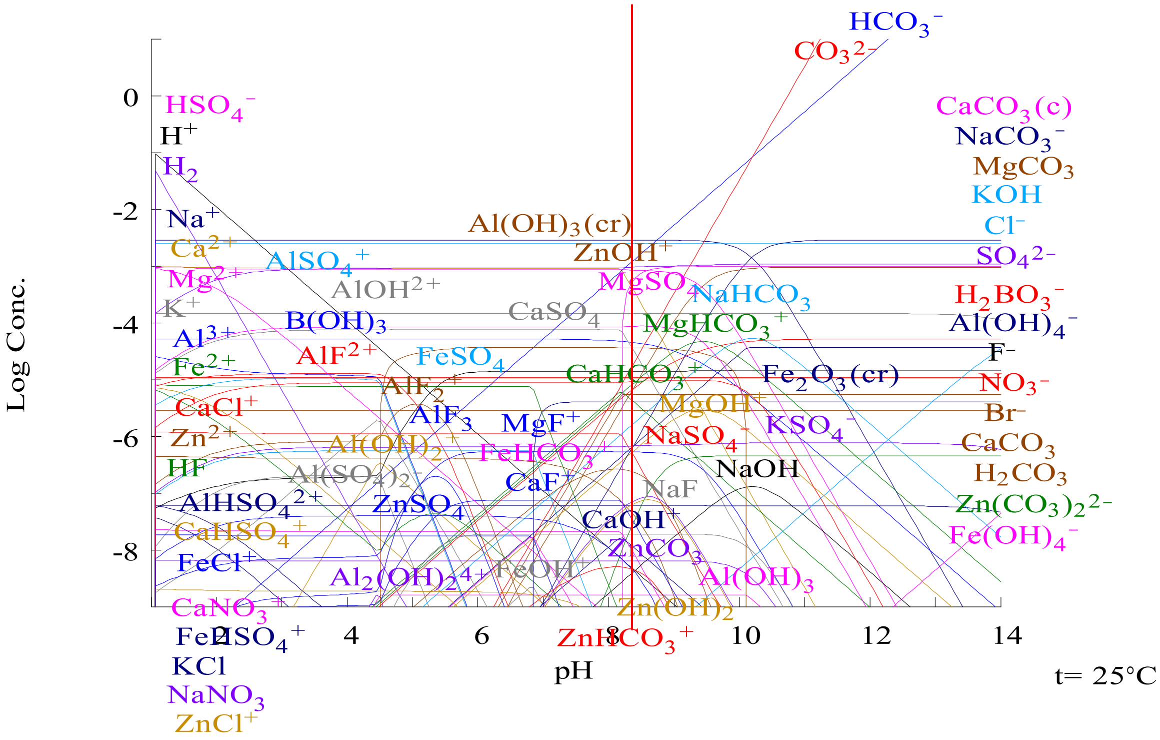


Figure C.274. Phase diagram for Aluminum gutter section immersed into river water after three months of exposure.

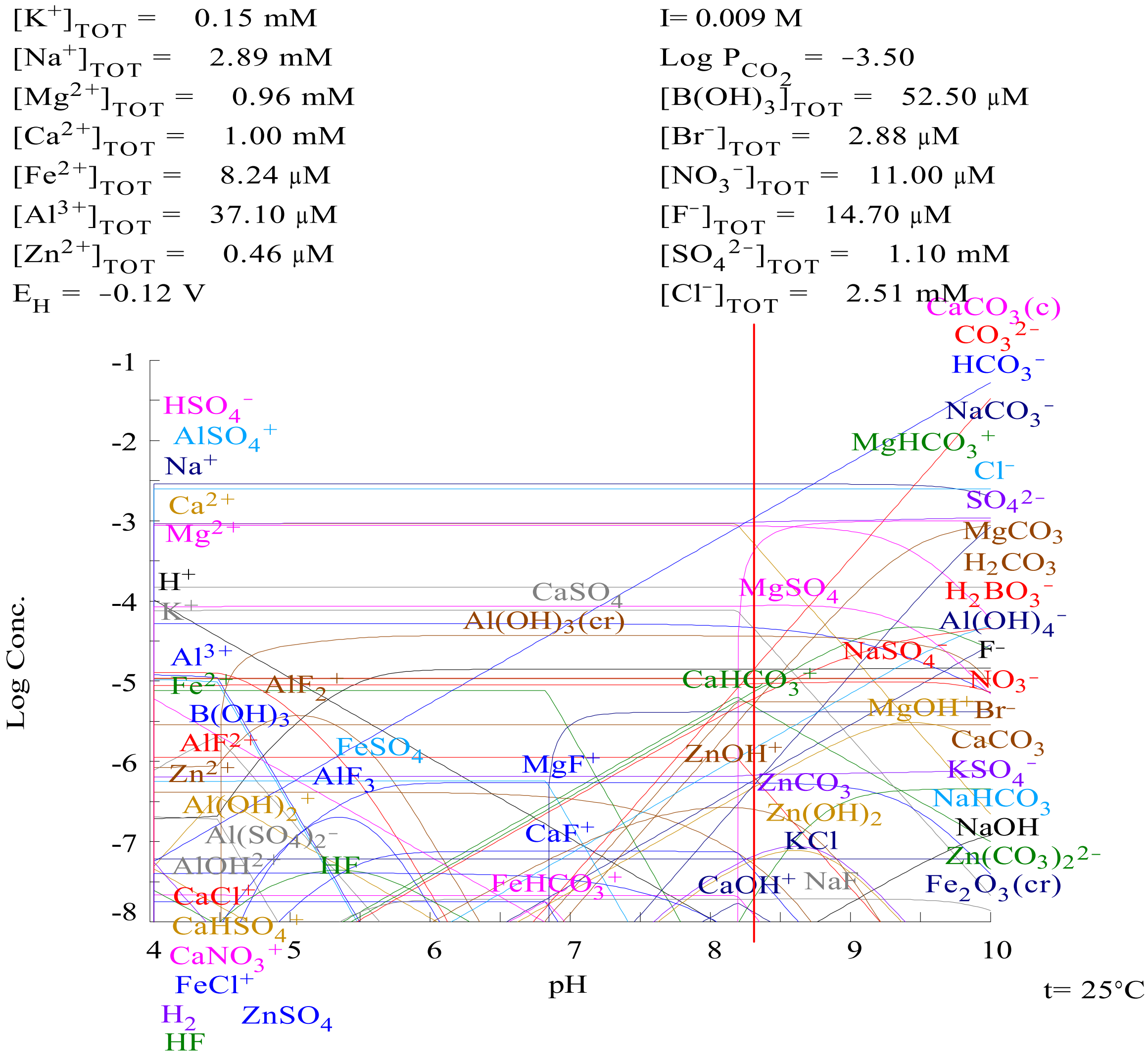


Figure C.275. Phase diagram for aluminum gutter section immersed into river water after three months of exposure. Study area.

Table C.65. The predominant species of zinc. Aluminum gutter section, river water, three months exposure.

Component	Log Concentration (mol/L)	Concentration (mol/L)	Zn Concentration (mg/L as Zn)	Cumulative Percentage of Zn
$ZnOH^+$	-6.61	2.45E-07	1.61E-02	53.46
$ZnCO_3$	-7.16	6.97E-08	4.56E-03	68.64
$Zn(OH)_2$	-7.21	6.20E-08	4.05E-03	82.14
Zn^{2+}	-7.33	4.73E-08	3.09E-03	92.45
$Zn(CO3)_2^{2-}$	-7.61	2.44E-08	1.59E-03	97.75
$ZnSO_4$	-8.32	4.82E-09	3.15E-04	98.80
$ZnHCO_3^+$	-8.33	4.68E-09	3.06E-04	99.82
ZnClOH	-9.28	5.30E-10	3.46E-05	99.94
$ZnCl^+$	-9.67	2.15E-10	1.40E-05	99.99

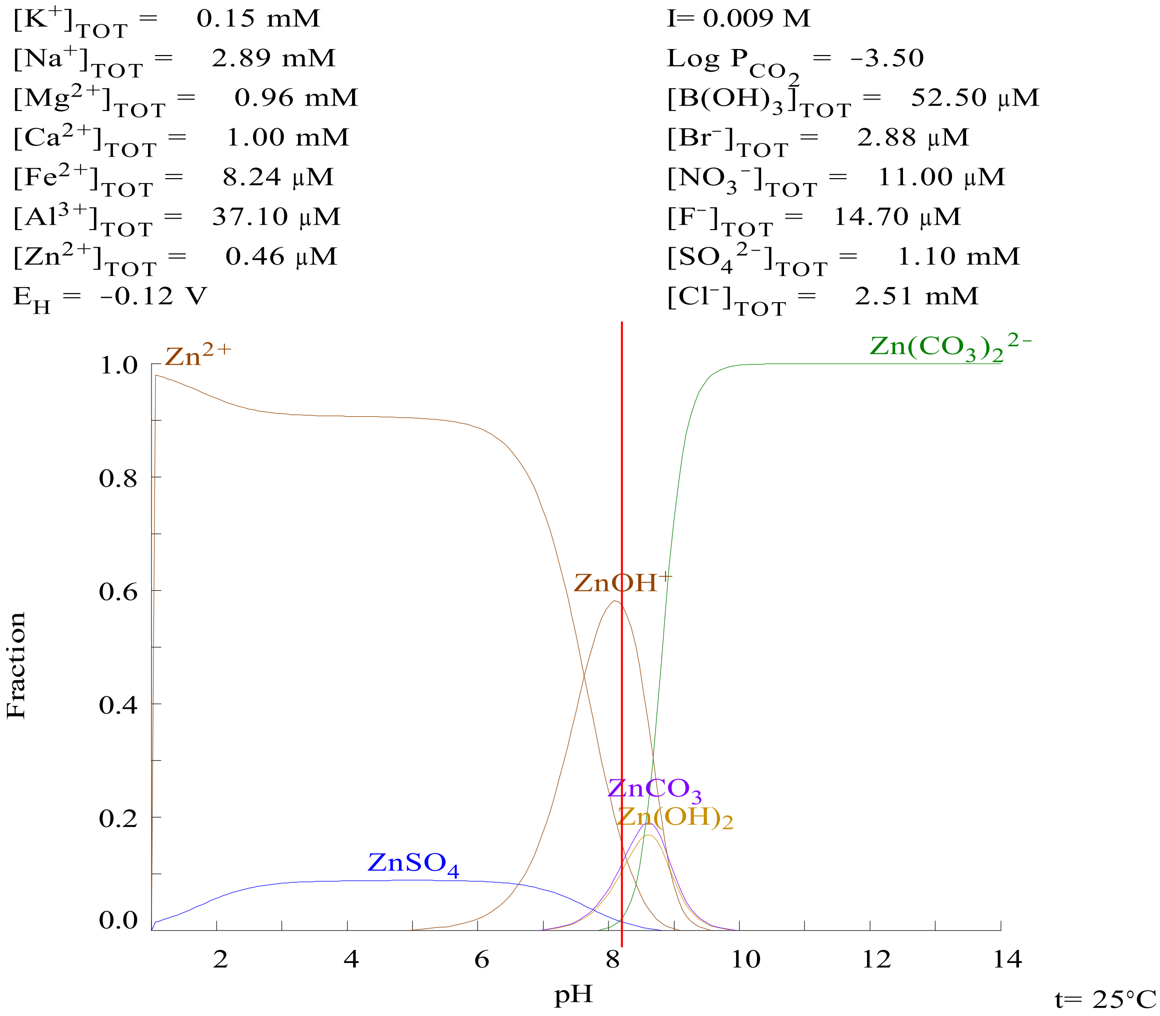


Figure C.276. Fraction diagram of zinc for aluminum gutter section immersed into river water after three months of exposure.

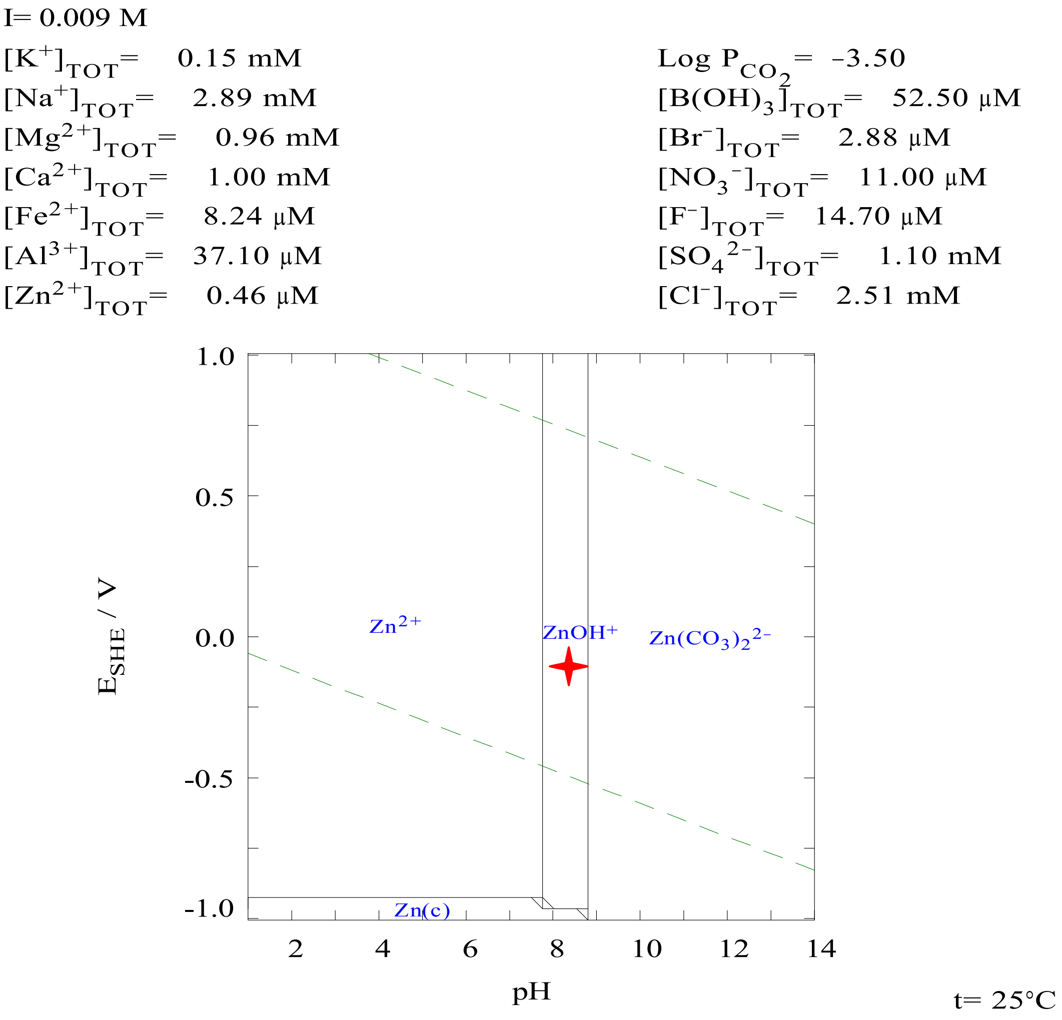


Figure C.277. Pourbaix diagram of zinc for aluminum gutter section immersed into river water after three months of exposure.

$I = 0.009$ M

$[K^+]_{TOT} =$ 0.15 mM

$[Na^+]_{TOT} =$ 2.89 mM

$[Mg^{2+}]_{TOT} =$ 0.96 mM

$[Ca^{2+}]_{TOT} =$ 1.00 mM

$[Fe^{2+}]_{TOT} =$ 8.24 μM

$[Al^{3+}]_{TOT} =$ 37.10 μM

$[Zn^{2+}]_{TOT} =$ 0.46 μM

$\log P_{CO_2} = -3.50$

$[B(OH)_3]_{TOT} =$ 52.50 μM

$[Br^-]_{TOT} =$ 2.88 μM

$[NO_3^-]_{TOT} =$ 11.00 μM

$[F^-]_{TOT} =$ 14.70 μM

$[SO_4^{2-}]_{TOT} =$ 1.10 mM

$[Cl^-]_{TOT} =$ 2.51 mM

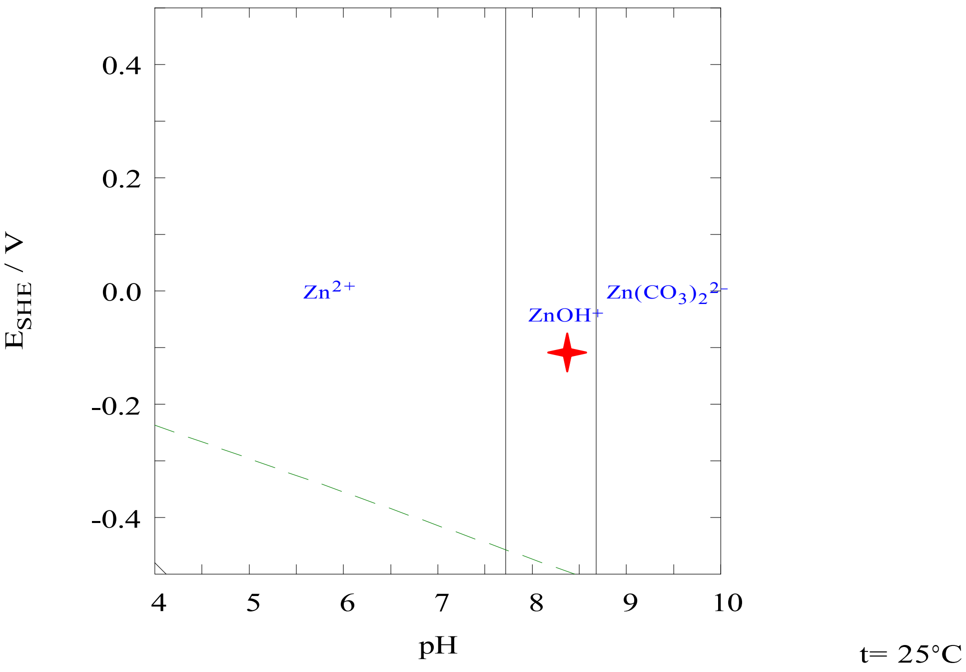


Figure C.278. Pourbaix diagram of zinc for aluminum gutter section immersed into river water after three months of exposure. Study area.

HDPE Pipe, River Water, Time Zero

I= 0.008 M
$[K^+]_{TOT}$ = 0.15 mM
$[Na^+]_{TOT}$ = 2.89 mM
$[Mg^{2+}]_{TOT}$ = 0.84 mM
$[Ca^{2+}]_{TOT}$ = 0.62 mM
$[Fe^{2+}]_{TOT}$ = 3.76 μM
$[Zn^{2+}]_{TOT}$ = 0.31 μM
E_H = -0.14 V

Log P_{CO_2} = -3.50
$[B(OH)_3]_{TOT}$ = 52.50 μM
$[Br^-]_{TOT}$ = 2.88 μM
$[NO_3^-]_{TOT}$ = 11.00 μM
$[F^-]_{TOT}$ = 14.70 μM
$[SO_4^{2-}]_{TOT}$ = 1.10 mM
$[Cl^-]_{TOT}$ = 2.51 mM

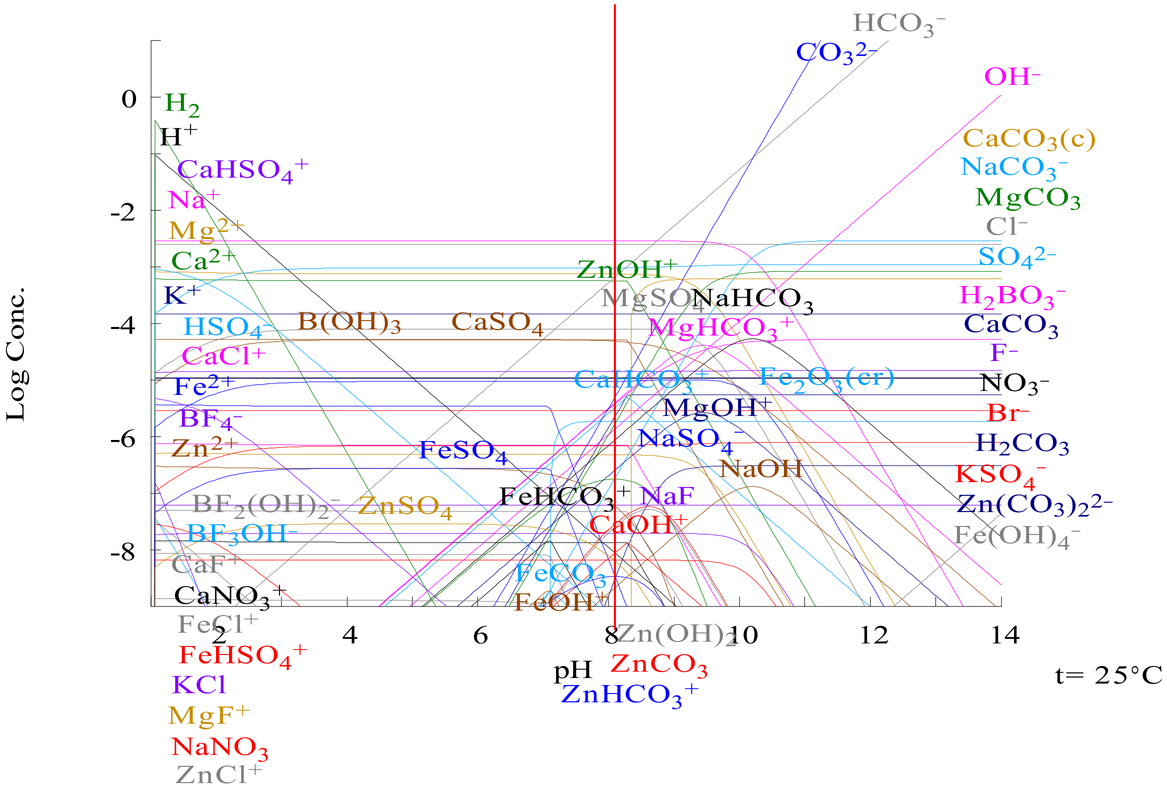


Figure C.279. Phase diagram for the container of HDPE pipe section at time zero in river water.

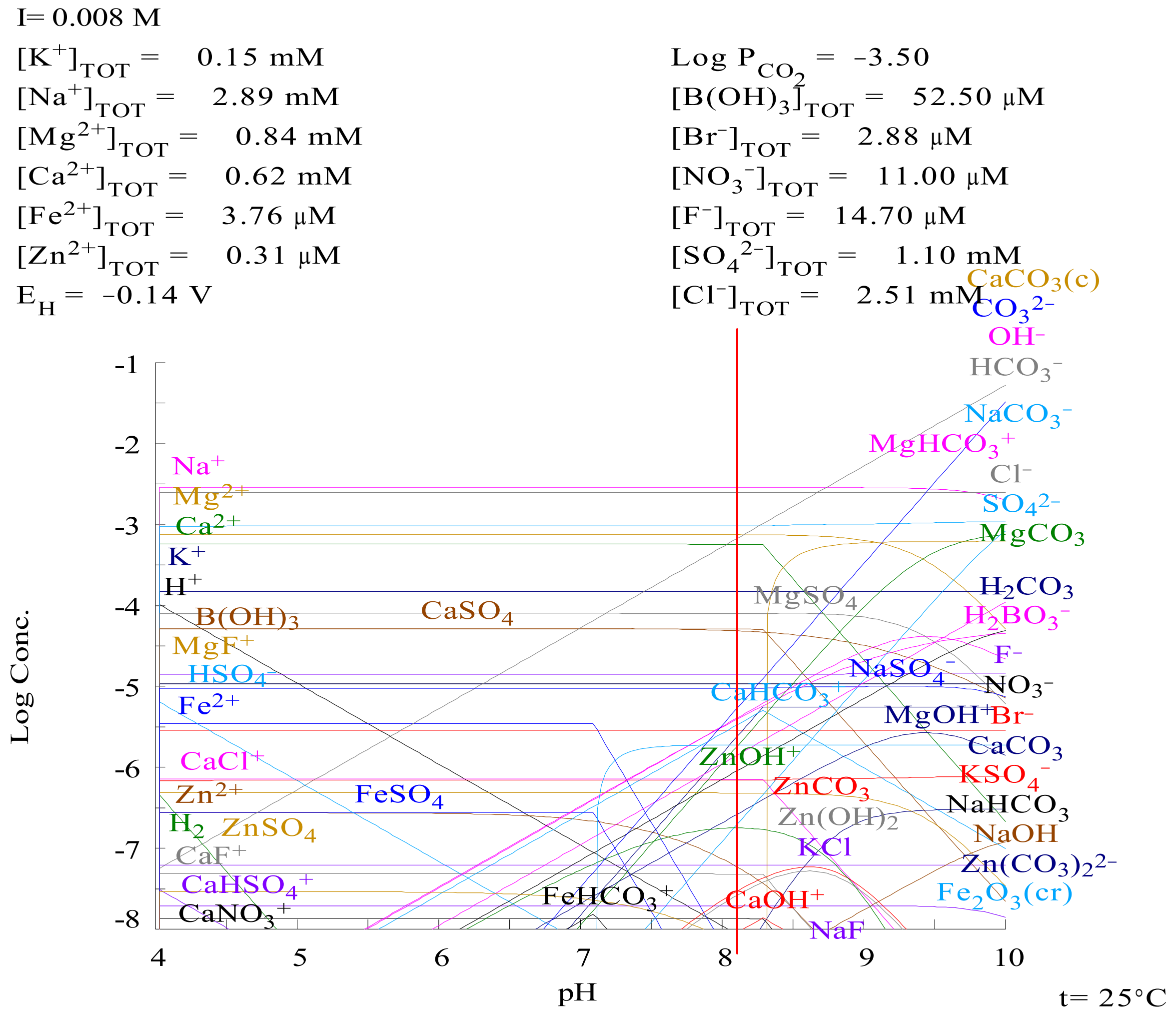


Figure C.280. Phase diagram for the container of HDPE pipe section at time zero in river water. Study area.

Table C.66. The predominant species of zinc. Container for HDPE pipe section, river water, time zero.

Component	Log Concentration (mol/L)	Concentration (mol/L)	Zn as Zn Concentration (mg/L)	Cumulative Percentage of Zn
$ZnOH^+$	-6.75	1.78E-07	1.16E-02	58.17
Zn^{2+}	-7.28	5.29E-08	3.46E-03	75.46
$ZnCO_3$	-7.49	3.24E-08	2.12E-03	86.06
$Zn(OH)_2$	-7.54	2.88E-08	1.89E-03	95.48
$ZnSO_4$	-8.25	5.60E-09	3.66E-04	97.31
$Zn(CO3)_2^{2-}$	-8.34	4.53E-09	2.96E-04	98.79
$ZnHCO_3^+$	-8.47	3.39E-09	2.22E-04	99.90

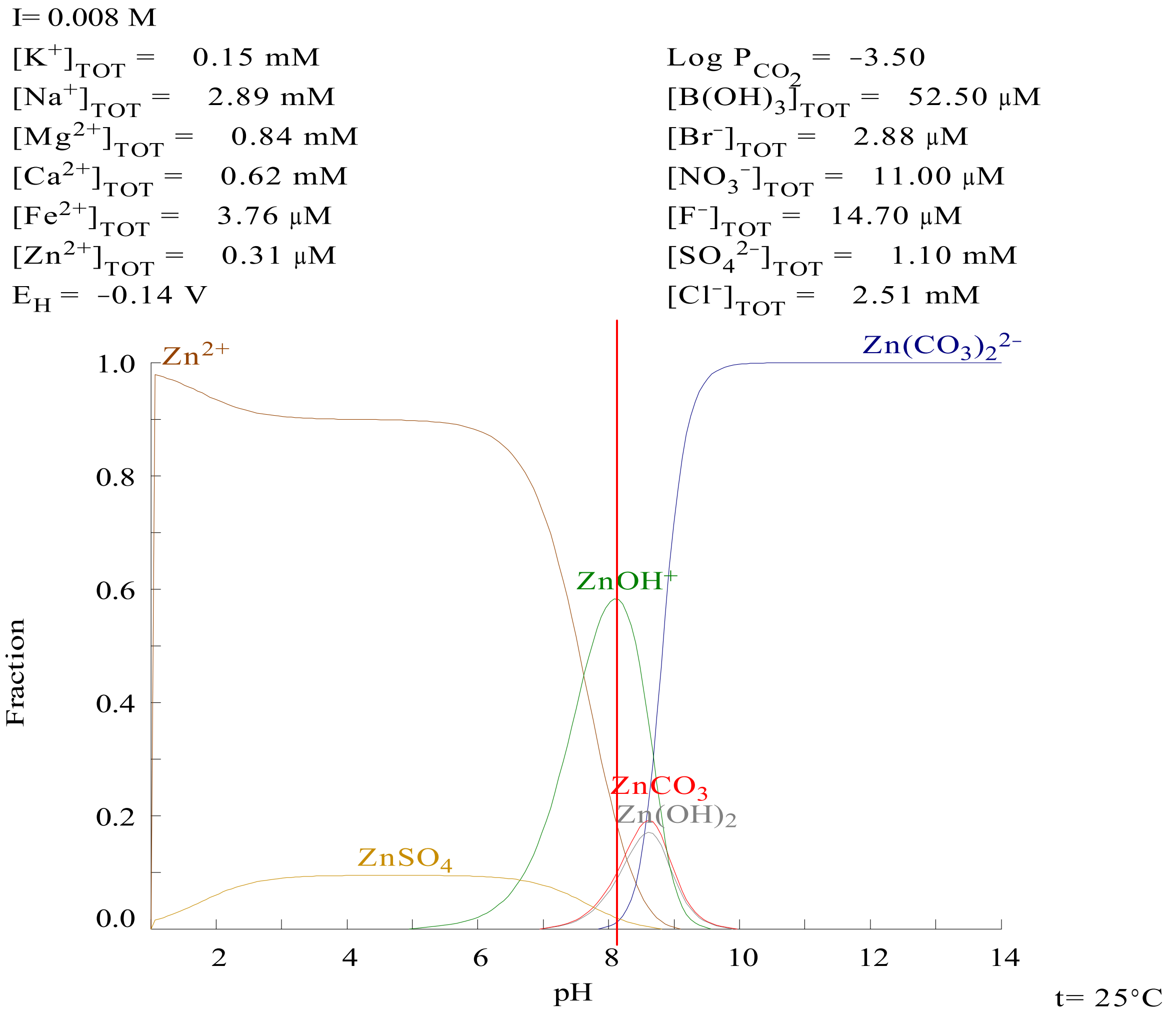


Figure C.281. Fraction diagram of zinc for the container of HDPE pipe section at time zero in river water.

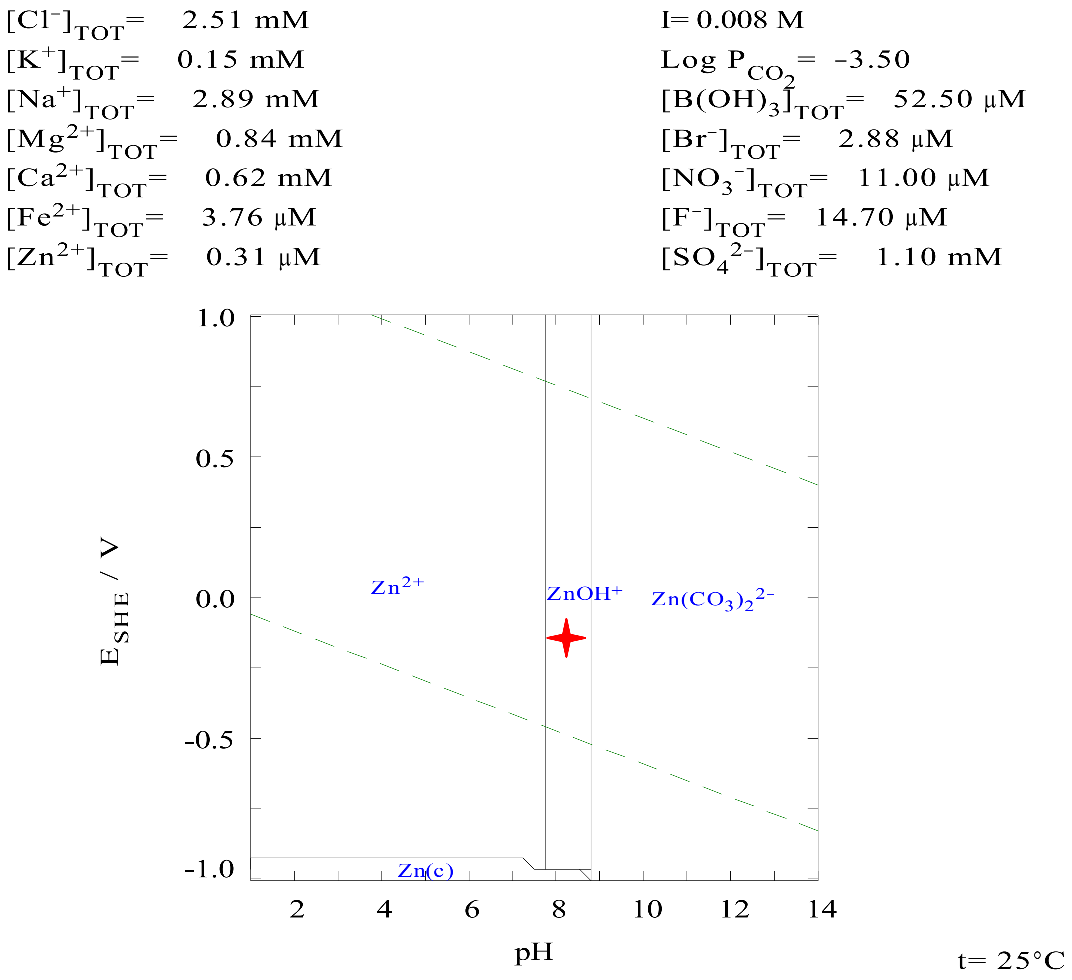


Figure C.282. Pourbaix diagram of zinc for the container of HDPE pipe section at time zero in river water.

$[Cl^-]_{TOT}$= 2.51 mM
$[K^+]_{TOT}$= 0.15 mM
$[Na^+]_{TOT}$= 2.89 mM
$[Mg^{2+}]_{TOT}$= 0.84 mM
$[Ca^{2+}]_{TOT}$= 0.62 mM
$[Fe^{2+}]_{TOT}$= 3.76 µM
$[Zn^{2+}]_{TOT}$= 0.31 µM

I= 0.008 M
Log P_{CO_2}= -3.50
$[B(OH)_3]_{TOT}$= 52.50 µM
$[Br^-]_{TOT}$= 2.88 µM
$[NO_3^-]_{TOT}$= 11.00 µM
$[F^-]_{TOT}$= 14.70 µM
$[SO_4^{2-}]_{TOT}$= 1.10 mM

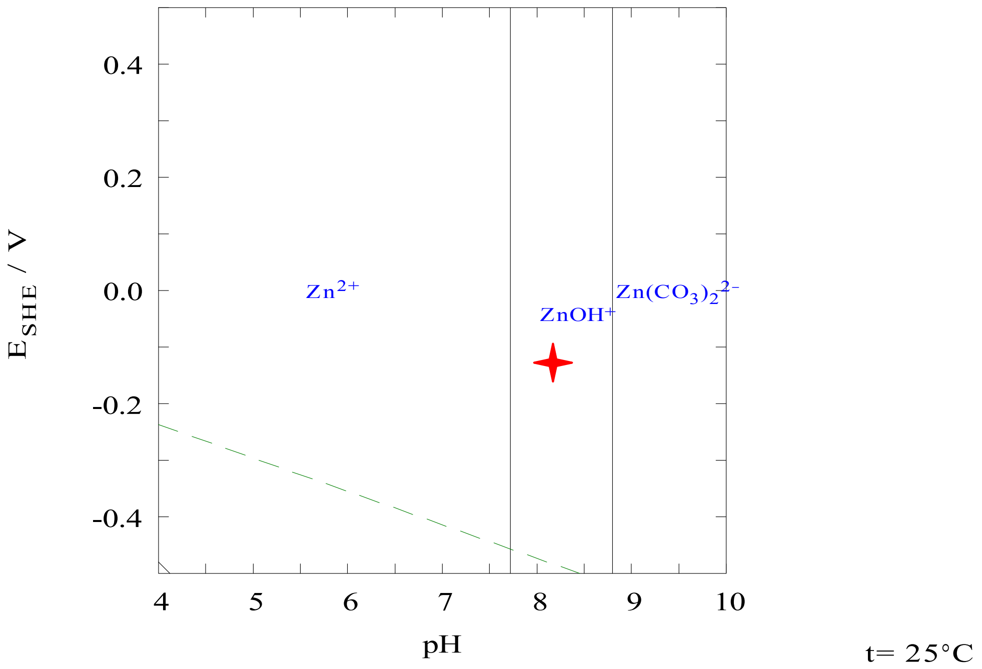


Figure C.283. Pourbaix diagram of zinc for the container of HDPE pipe section at time zero in river water. Study area.

Aluminum Gutter, River Water, Time Zero

I= 0.008 M

$[K^+]_{TOT}$ = 0.15 mM

$[Na^+]_{TOT}$ = 2.89 mM

$[Mg^{2+}]_{TOT}$ = 0.84 mM

$[Ca^{2+}]_{TOT}$ = 0.51 mM

$[Fe^{2+}]_{TOT}$ = 3.94 μM

$[Zn^{2+}]_{TOT}$ = 0.31 μM

E_H = -0.14 V

Log P_{CO_2} = -3.50

$[B(OH)_3]_{TOT}$ = 52.50 μM

$[Br^-]_{TOT}$ = 2.88 μM

$[NO_3^-]_{TOT}$ = 11.00 μM

$[F^-]_{TOT}$ = 14.70 μM

$[SO_4^{2-}]_{TOT}$ = 1.10 mM

$[Cl^-]_{TOT}$ = 2.51 mM

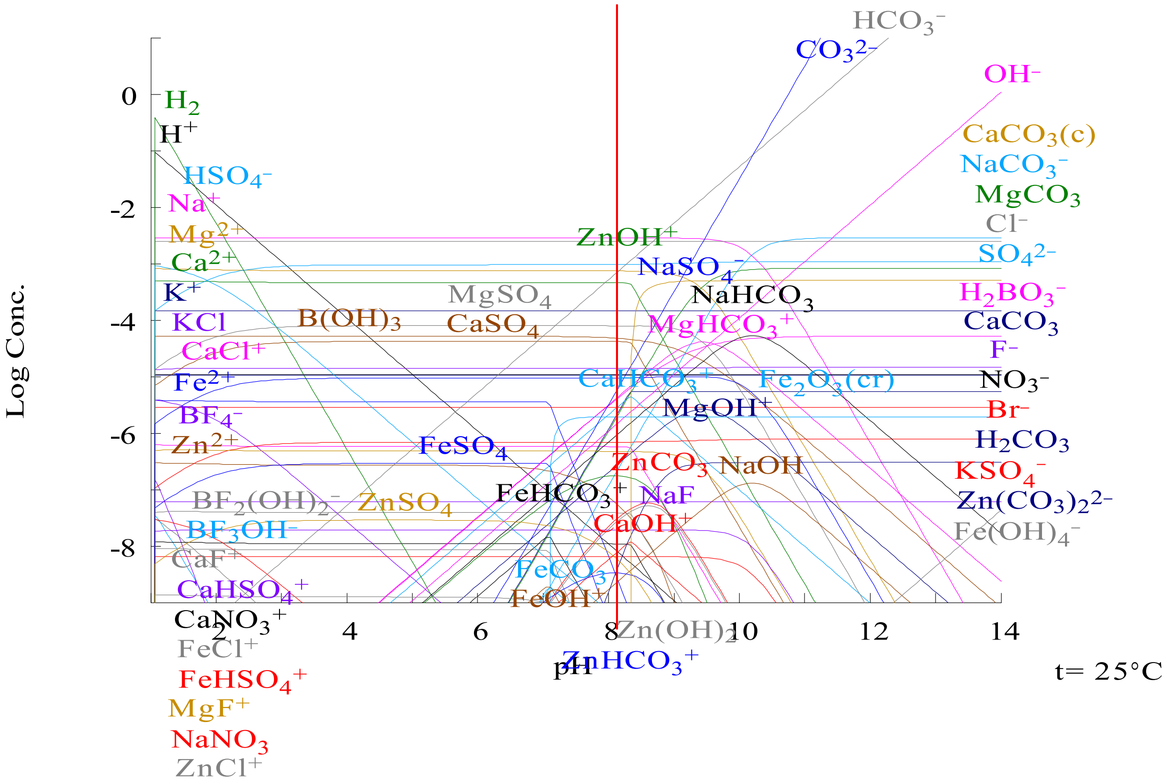


Figure C.284. Phase diagram for the container of aluminum gutter section at time zero in river water.

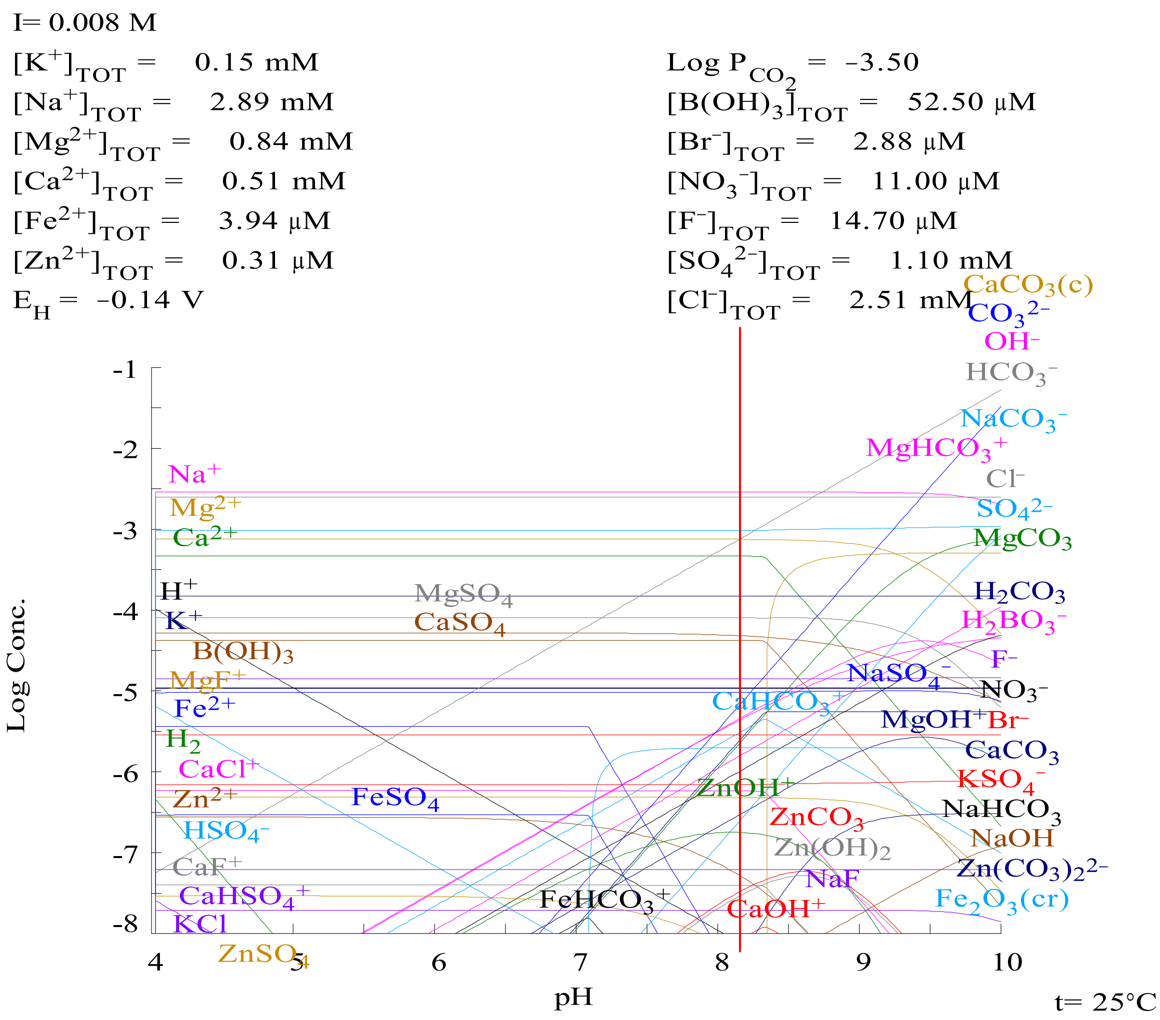


Figure 285. Phase diagram for the container of aluminum gutter section at time zero in river water. Study area.

Table 67. The predominant species of zinc. Container for aluminum gutter section, river water, time zero.

Component	Log Concentration (mol/L)	Concentration (mol/L)	Zn as Zn Concentration (mg/L)	Cumulative Percentage of Zn
$ZnOH^+$	-6.75	1.78E-07	1.16E-02	58.16
Zn^{2+}	-7.28	5.29E-08	3.46E-03	75.45
$ZnCO_3$	-7.49	3.24E-08	2.12E-03	86.05
$Zn(OH)_2$	-7.54	2.88E-08	1.89E-03	95.47
$ZnSO_4$	-8.25	5.65E-09	3.69E-04	97.31
$Zn(CO3)_2^{2-}$	-8.34	4.53E-09	2.96E-04	98.79
$ZnHCO_3^+$	-8.47	3.39E-09	2.22E-04	99.90

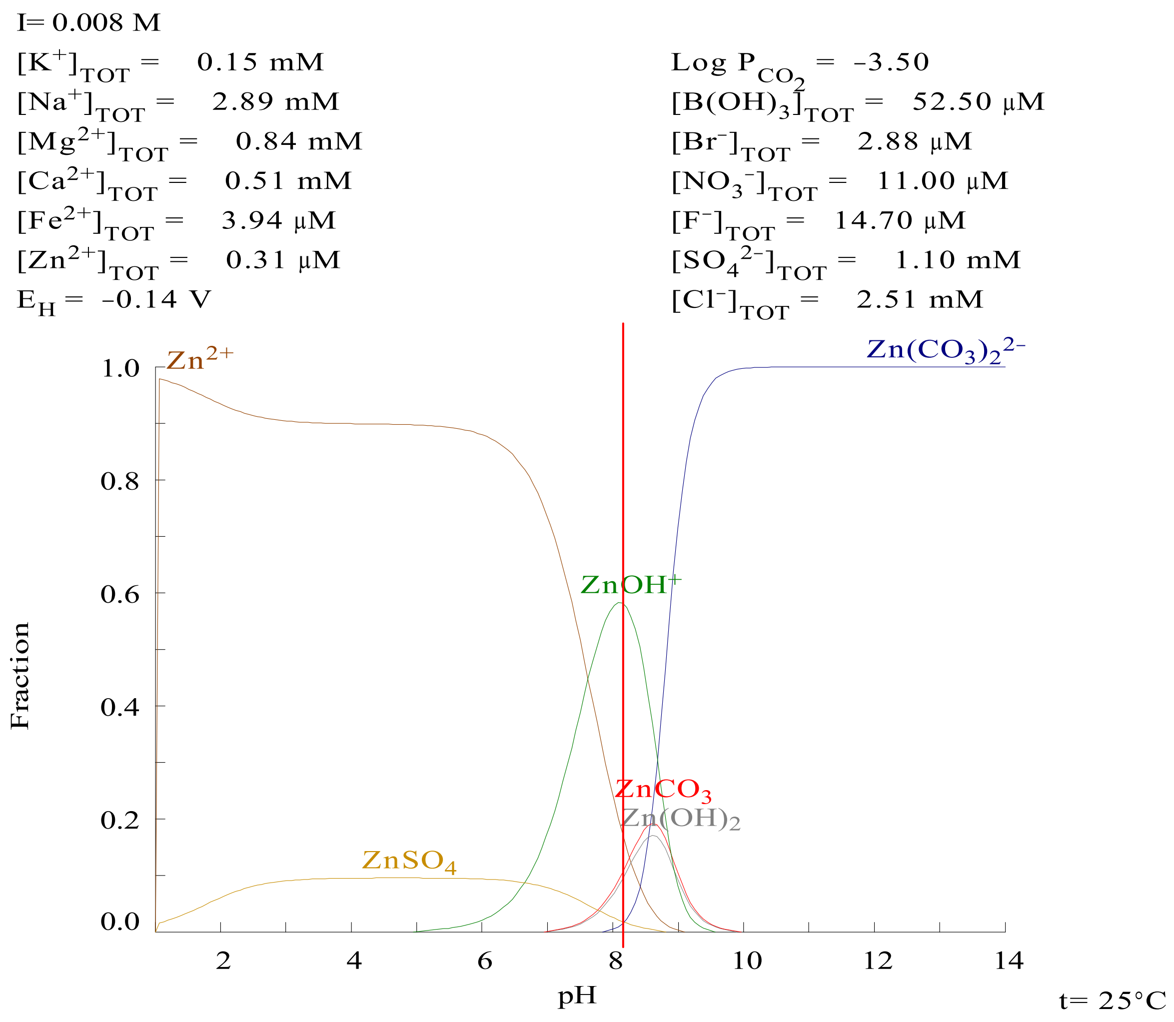


Figure C.286. Fraction diagram of zinc for the container of aluminum gutter section at time zero in river water.

$[\mathrm{Cl^-}]_{\mathrm{TOT}}=$ 2.51 mM
$[\mathrm{K^+}]_{\mathrm{TOT}}=$ 0.15 mM
$[\mathrm{Na^+}]_{\mathrm{TOT}}=$ 2.89 mM
$[\mathrm{Mg^{2+}}]_{\mathrm{TOT}}=$ 0.84 mM
$[\mathrm{Ca^{2+}}]_{\mathrm{TOT}}=$ 0.51 mM
$[\mathrm{Fe^{2+}}]_{\mathrm{TOT}}=$ 3.94 μM
$[\mathrm{Zn^{2+}}]_{\mathrm{TOT}}=$ 0.31 μM

I= 0.008 M
Log $P_{\mathrm{CO_2}}=$ -3.50
$[\mathrm{B(OH)_3}]_{\mathrm{TOT}}=$ 52.50 μM
$[\mathrm{Br^-}]_{\mathrm{TOT}}=$ 2.88 μM
$[\mathrm{NO_3^-}]_{\mathrm{TOT}}=$ 11.00 μM
$[\mathrm{F^-}]_{\mathrm{TOT}}=$ 14.70 μM
$[\mathrm{SO_4^{2-}}]_{\mathrm{TOT}}=$ 1.10 mM

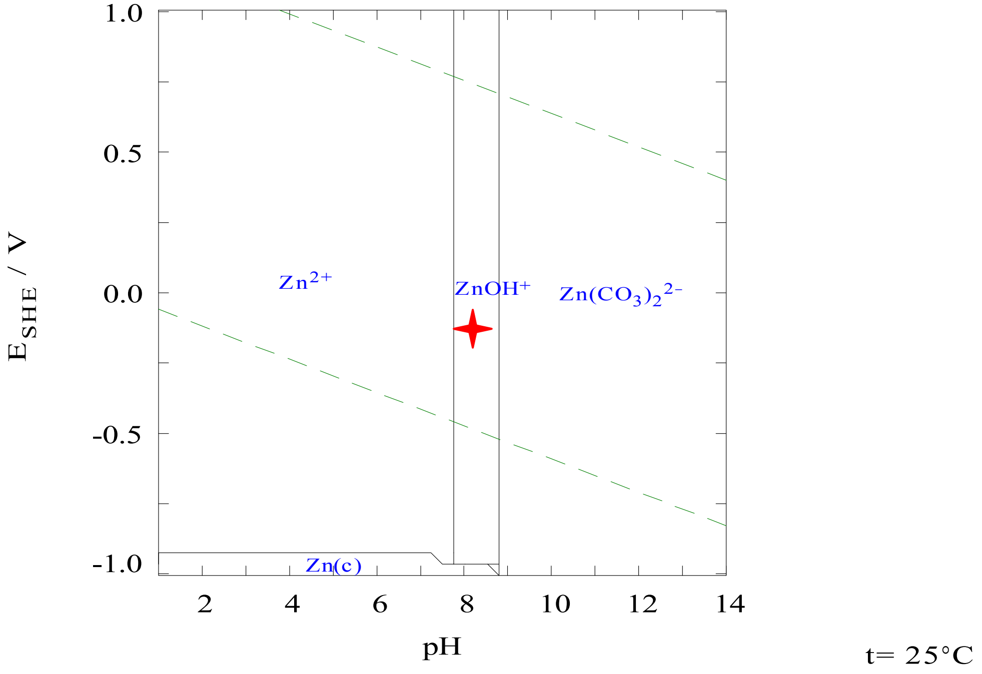


Figure C.287. Pourbaix diagram of zinc for the container of aluminum gutter section at time zero in river water.

$[Cl^-]_{TOT}=$ 2.51 mM
$[K^+]_{TOT}=$ 0.15 mM
$[Na^+]_{TOT}=$ 2.89 mM
$[Mg^{2+}]_{TOT}=$ 0.84 mM
$[Ca^{2+}]_{TOT}=$ 0.51 mM
$[Fe^{2+}]_{TOT}=$ 3.94 μM
$[Zn^{2+}]_{TOT}=$ 0.31 μM

I= 0.008 M
Log $P_{CO_2}=$ -3.50
$[B(OH)_3]_{TOT}=$ 52.50 μM
$[Br^-]_{TOT}=$ 2.88 μM
$[NO_3^-]_{TOT}=$ 11.00 μM
$[F^-]_{TOT}=$ 14.70 μM
$[SO_4^{2-}]_{TOT}=$ 1.10 mM

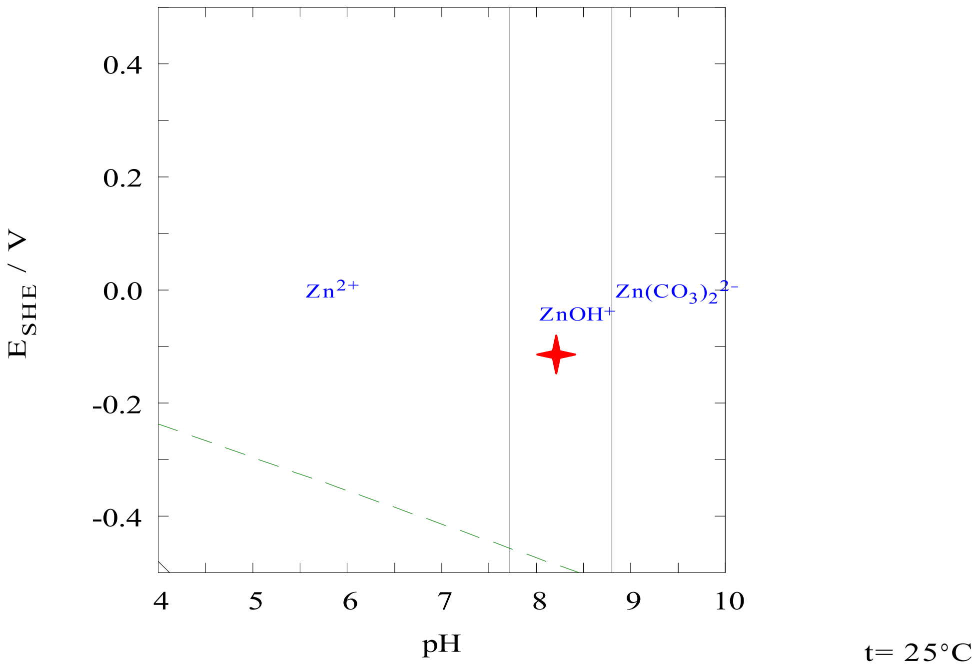


Figure C.288. Pourbaix diagram of zinc for the container of aluminum gutter section at time zero in river water. Study area.

Steel Gutter, River Water, Time Zero

I= 0.007 M
$[K^+]_{TOT}$ = 0.15 mM
$[Na^+]_{TOT}$ = 2.89 mM
$[Mg^{2+}]_{TOT}$ = 0.87 mM
$[Ca^{2+}]_{TOT}$ = 0.57 mM
$[Fe^{2+}]_{TOT}$ = 3.40 μM
$[Zn^{2+}]_{TOT}$ = 0.31 μM
E_H = -0.15 V

Log P_{CO_2} = -3.50
$[B(OH)_3]_{TOT}$ = 52.50 μM
$[Br^-]_{TOT}$ = 2.88 μM
$[NO_3^-]_{TOT}$ = 11.00 μM
$[F^-]_{TOT}$ = 14.70 μM
$[SO_4^{2-}]_{TOT}$ = 1.10 mM
$[Cl^-]_{TOT}$ = 2.51 mM

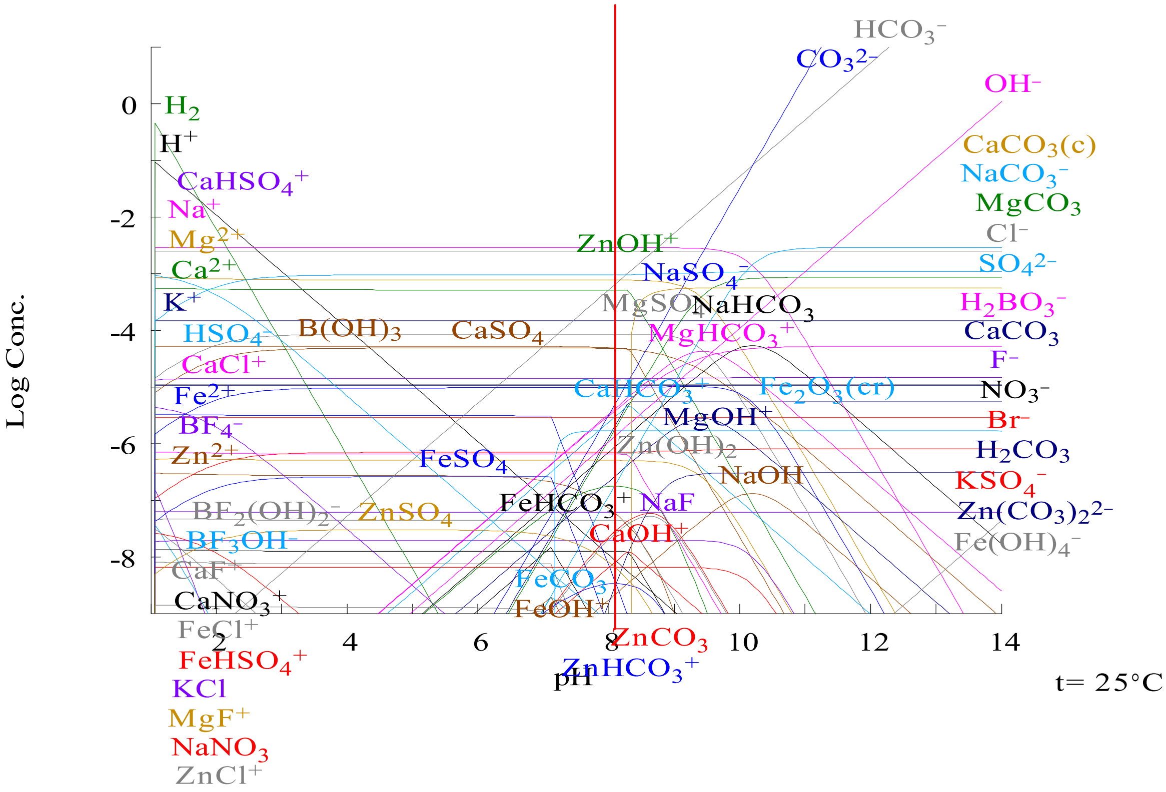


Figure C.289. Phase diagram for the container of steel gutter section at time zero in river water.

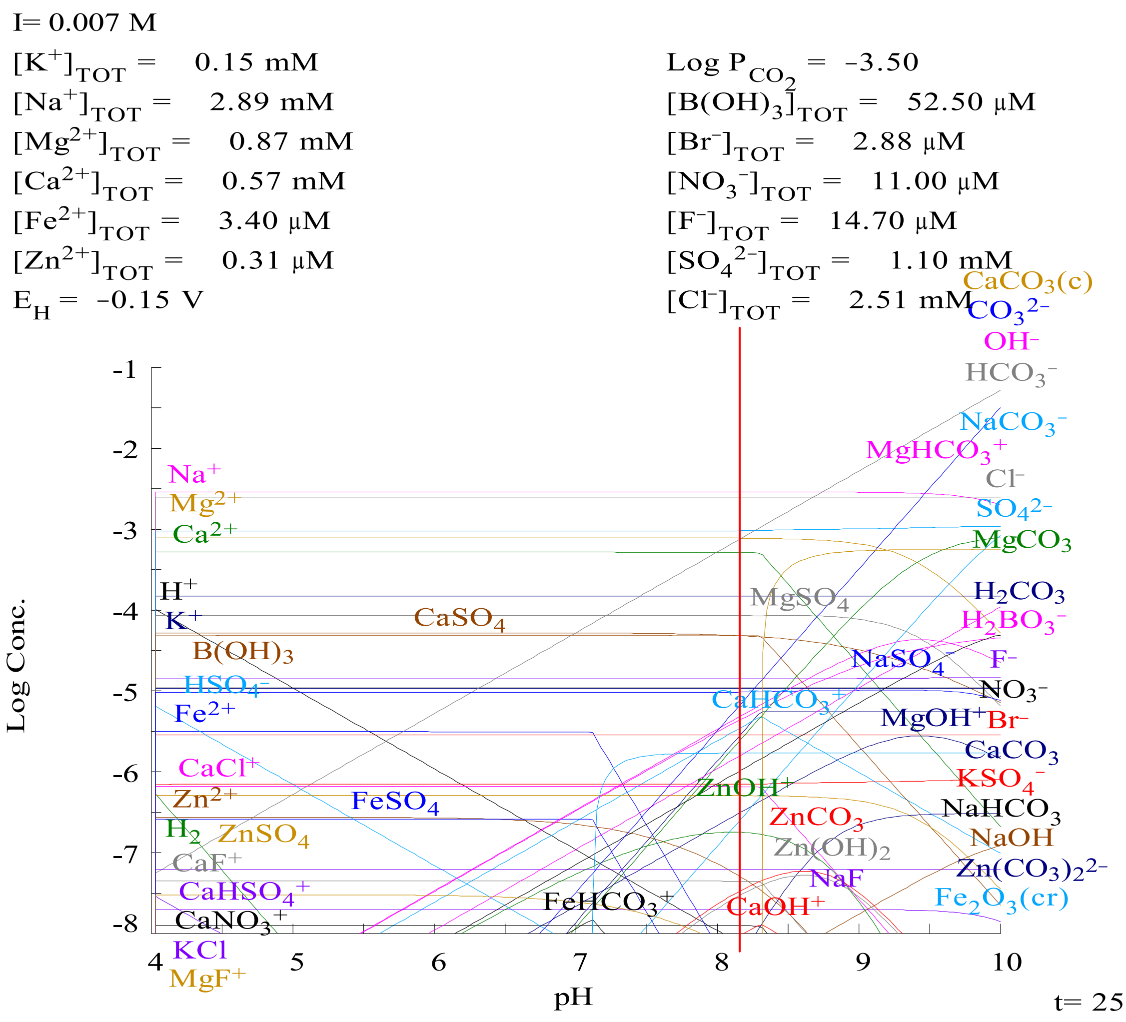


Figure C.290. Phase diagram for the container of steel gutter section at time zero in river water. Study area.

Table C.68. The predominant species of zinc. Container for steel gutter section, river water, time zero.

Component	Log Concentration (mol/L)	Concentration (mol/L)	Zn as Zn Concentration (mg/L)	Cumulative Percentage of Zn
$ZnOH^+$	-6.76	1.76E-07	1.15E-02	57.44
Zn^{2+}	-7.35	4.43E-08	2.89E-03	71.89
$ZnCO_3$	-7.43	3.74E-08	2.45E-03	84.11
$Zn(OH)_2$	-7.48	3.32E-08	2.17E-03	94.98
$Zn(CO3)_2^{2-}$	-8.16	6.89E-09	4.50E-04	97.23
$ZnSO_4$	-8.31	4.88E-09	3.19E-04	98.82
$ZnHCO_3^+$	-8.48	3.35E-09	2.19E-04	99.91

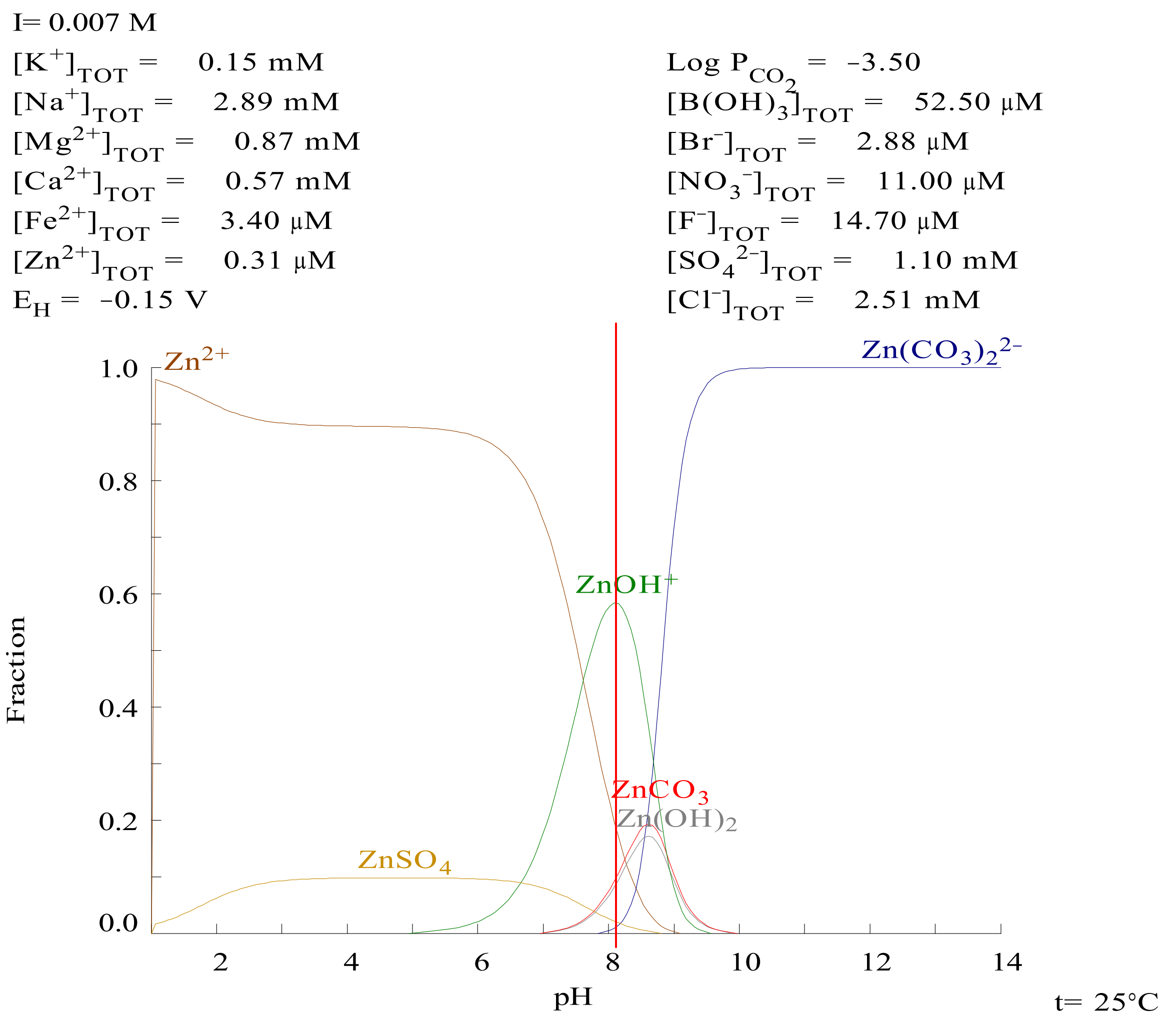


Figure C.291. Fraction diagram of zinc for the container of steel gutter section at time zero in river water.

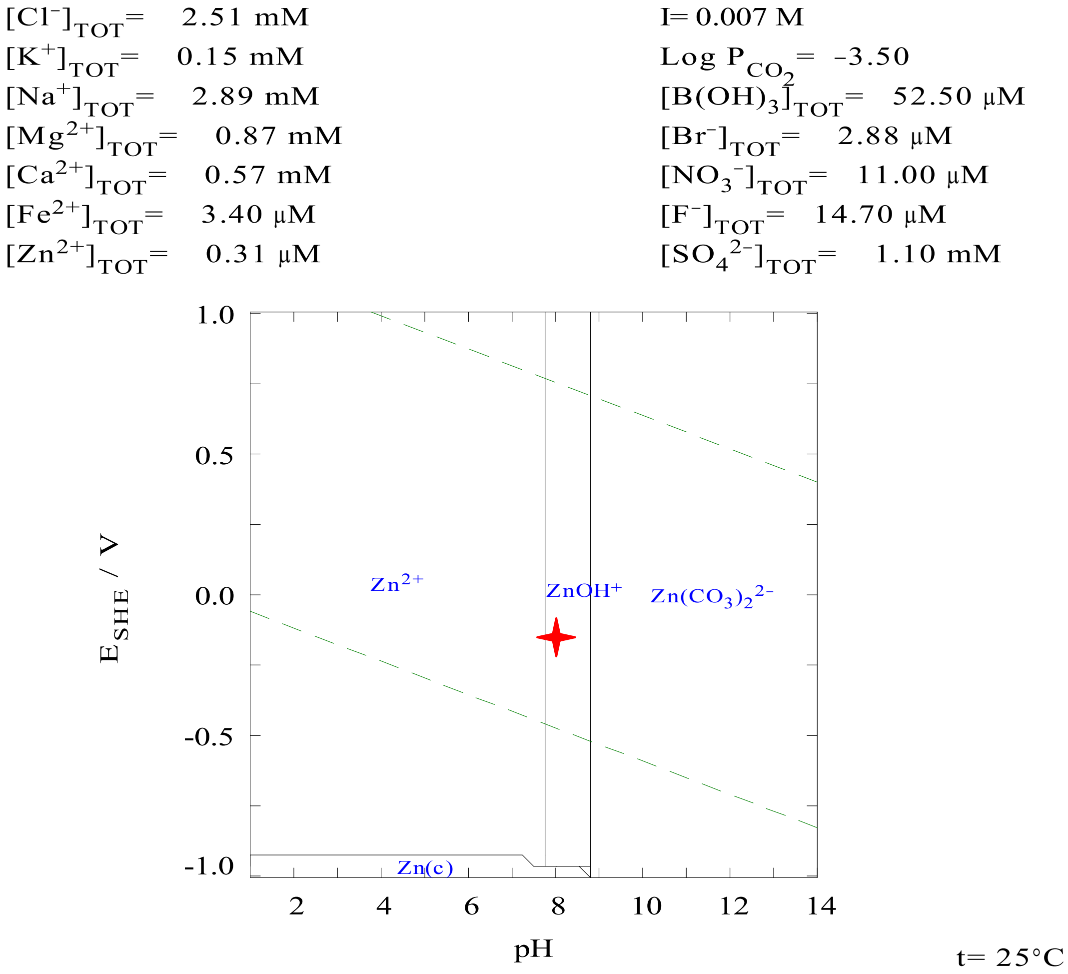


Figure C.292. Pourbaix diagram of zinc for the container of steel gutter section at time zero in river water.

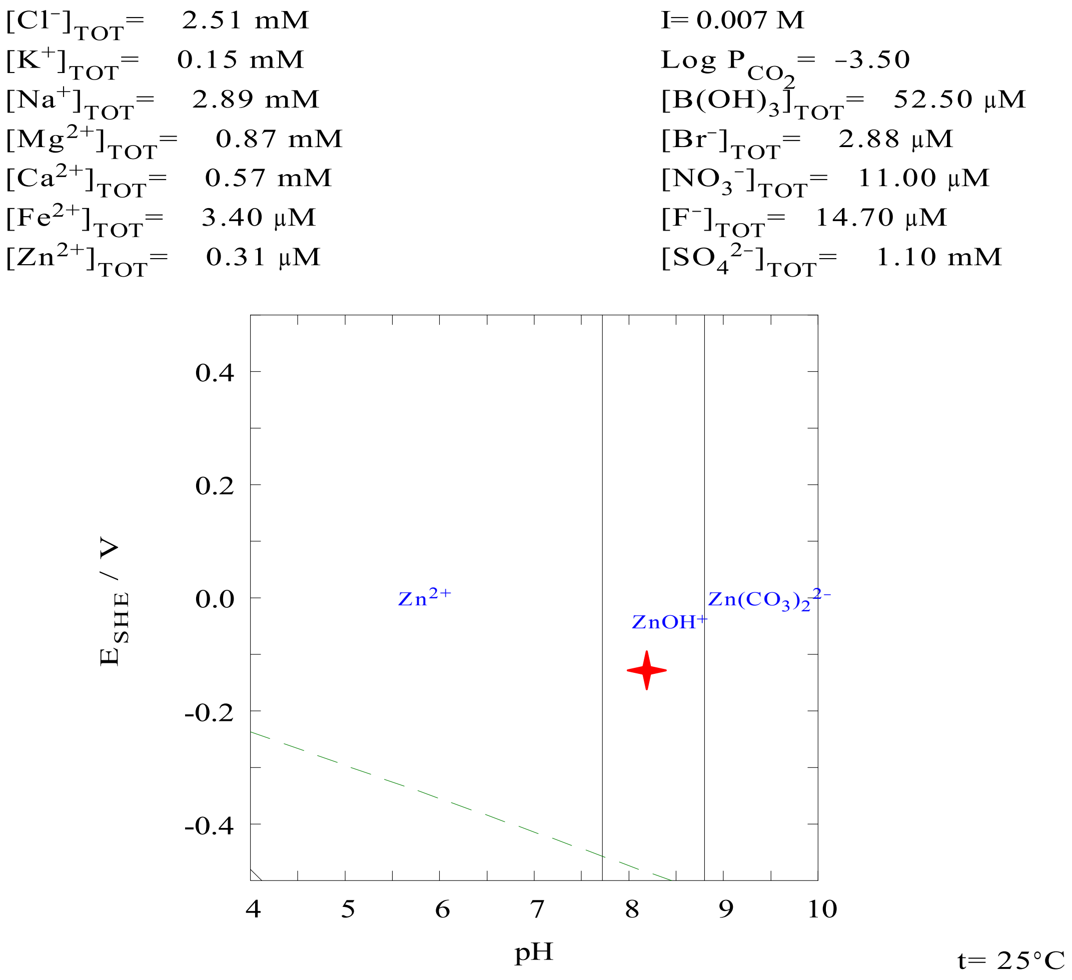


Figure C.293. Pourbaix diagram of zinc for the container of steel gutter section at time zero in river water. Study area.

Copper Cutter, River Water, Time Zero

I= 0.009 M

$[K^+]_{TOT}$ = 0.15 mM

$[Na^+]_{TOT}$ = 2.89 mM

$[Mg^{2+}]_{TOT}$ = 1.06 mM

$[Ca^{2+}]_{TOT}$ = 1.02 mM

$[Fe^{2+}]_{TOT}$ = 3.58 μM

$[Zn^{2+}]_{TOT}$ = 0.31 μM

E_H = -0.15 V

Log P_{CO_2} = -3.50

$[B(OH)_3]_{TOT}$ = 52.50 μM

$[Br^-]_{TOT}$ = 2.88 μM

$[NO_3^-]_{TOT}$ = 11.00 μM

$[F^-]_{TOT}$ = 14.70 μM

$[SO_4^{2-}]_{TOT}$ = 1.10 mM

$[Cl^-]_{TOT}$ = 2.51 mM

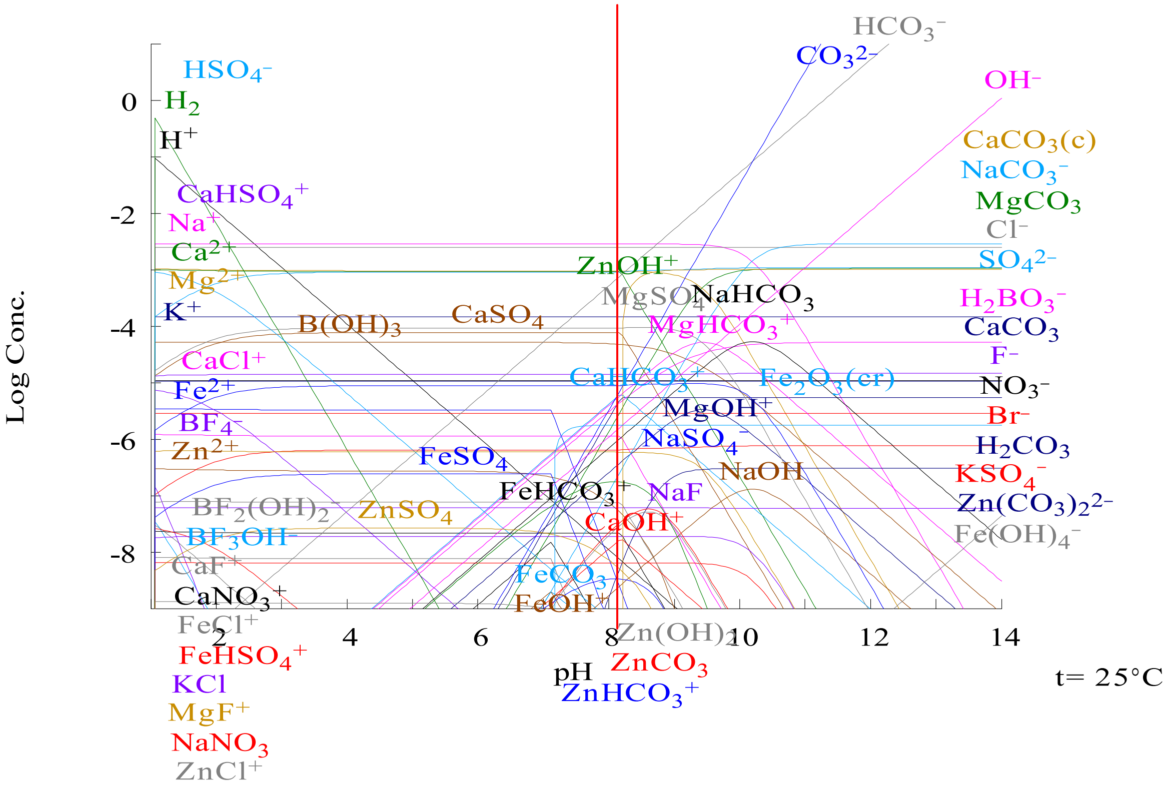


Figure C.294. Phase diagram for the container of copper gutter section at time zero in river water.

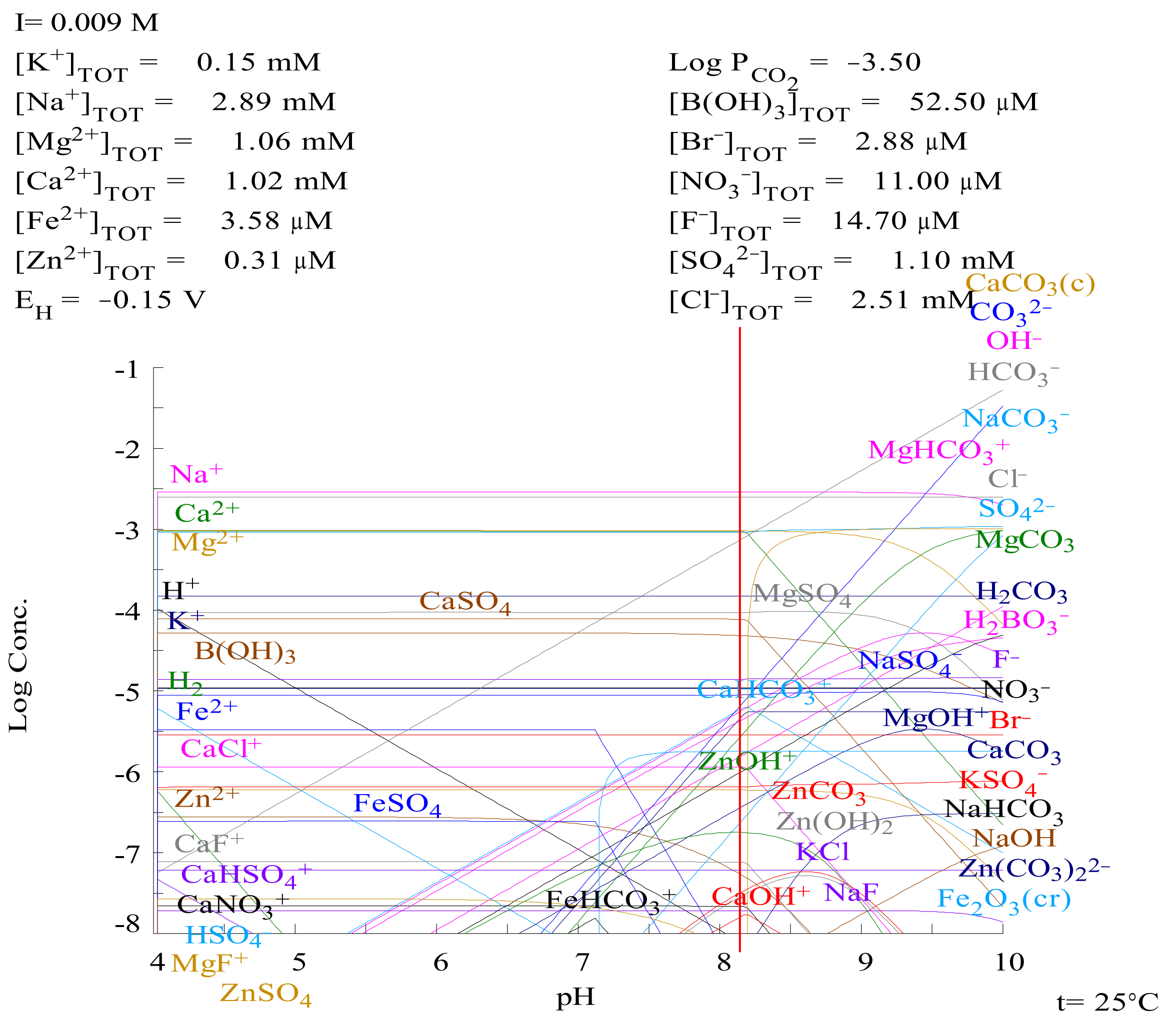


Figure C.295. Phase diagram for the container of copper gutter section at time zero in river water. Study area.

Table C.69. The predominant species of zinc. Container for copper gutter section, river water, time zero.

Component	Log Concentration (mol/L)	Concentration (mol/L)	Zn as Zn Concentration (mg/L)	Cumulative Percentage of Zn
$ZnOH^+$	-6.75E+00	1.78E-07	1.16E-02	58.13
Zn^{2+}	-7.27E+00	5.37E-08	3.51E-03	75.68
$ZnCO_3$	-7.49E+00	3.22E-08	2.11E-03	86.22
$Zn(OH)_2$	-7.54E+00	2.87E-08	1.88E-03	95.59
$ZnSO_4$	-8.28E+00	5.23E-09	3.42E-04	97.29
$Zn(CO3)_2^{2-}$	-8.34E+00	4.59E-09	3.00E-04	98.80
$ZnHCO_3^+$	-8.47E+00	3.39E-09	2.22E-04	99.90

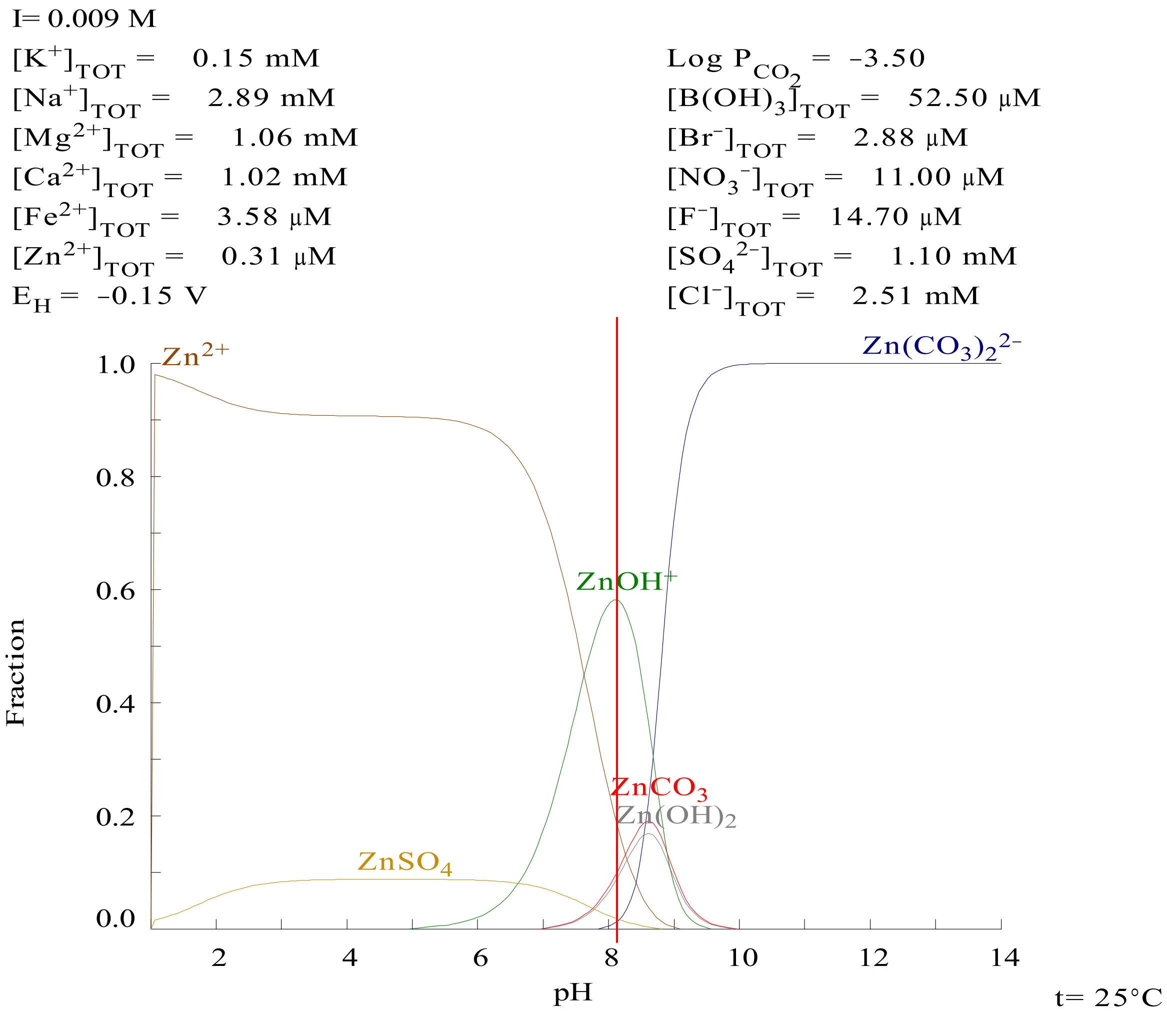


Figure C.296. Fraction diagram of zinc for the container of copper gutter section at time zero in river water.

$[Cl^-]_{TOT}=$ 2.51 mM
$[K^+]_{TOT}=$ 0.15 mM
$[Na^+]_{TOT}=$ 2.89 mM
$[Mg^{2+}]_{TOT}=$ 1.06 mM
$[Ca^{2+}]_{TOT}=$ 1.02 mM
$[Fe^{2+}]_{TOT}=$ 3.58 μM
$[Zn^{2+}]_{TOT}=$ 0.31 μM

I= 0.009 M
Log $P_{CO_2}=$ -3.50
$[B(OH)_3]_{TOT}=$ 52.50 μM
$[Br^-]_{TOT}=$ 2.88 μM
$[NO_3^-]_{TOT}=$ 11.00 μM
$[F^-]_{TOT}=$ 14.70 μM
$[SO_4^{2-}]_{TOT}=$ 1.10 mM

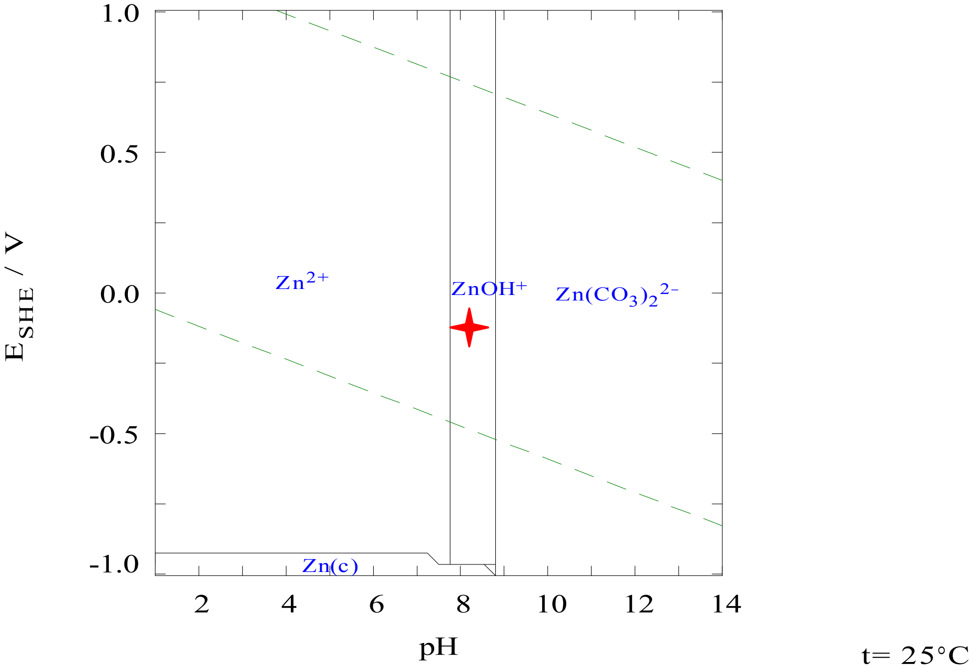


Figure C.297. Pourbaix diagram of zinc for the container of copper gutter section at time zero in river water.

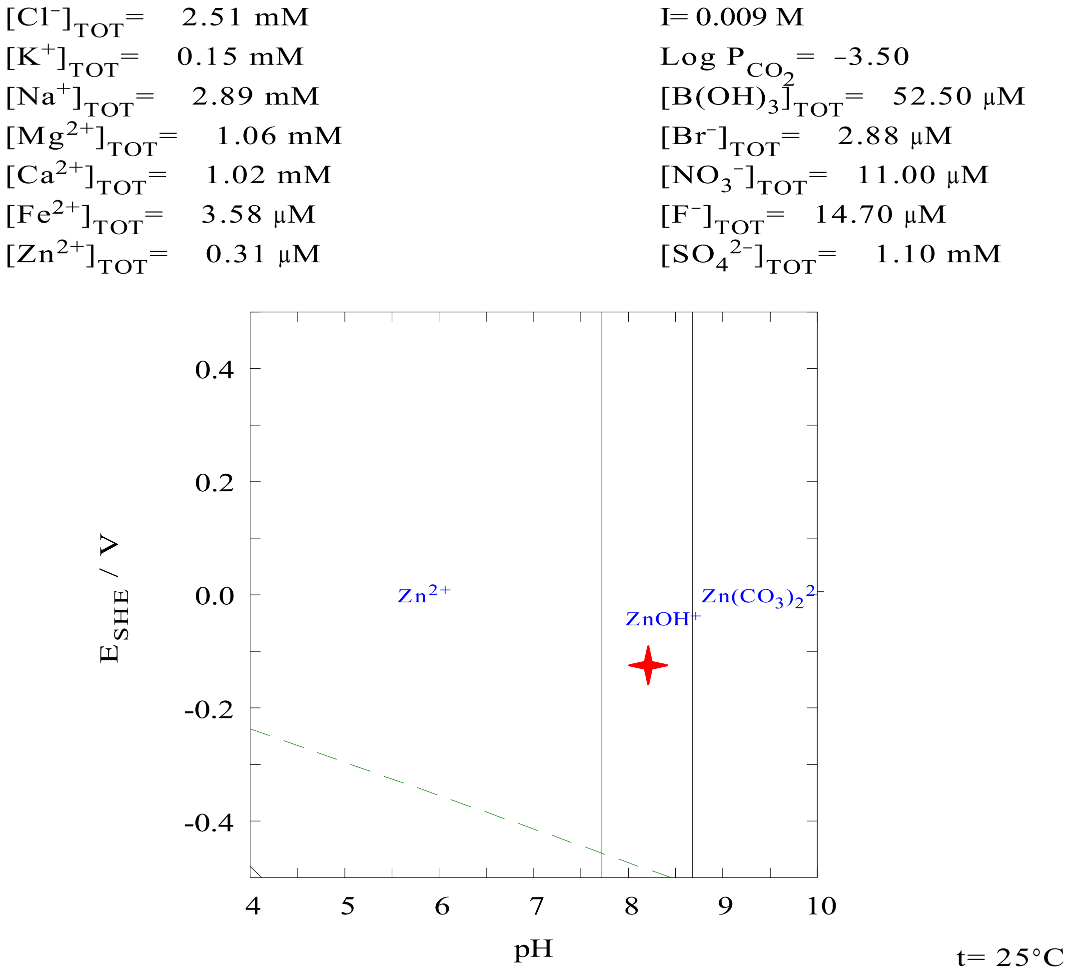


Figure C.298. Pourbaix diagram of zinc for the container of copper gutter section at time zero in river water. Study area.

Steel Pipe, Bay Water, After One Day of Exposure

I= 0.078 M

$[Na^+]_{TOT}$ = 76.60 mM

$[Mg^{2+}]_{TOT}$ = 9.43 mM

$[Ca^{2+}]_{TOT}$ = 2.15 mM

$[Fe^{2+}]_{TOT}$ = 11.60 µM

$[Zn^{2+}]_{TOT}$ = 0.13 mM

$[Pb^{2+}]_{TOT}$ = 57.90 nM

E_H = -0.15 V

Log P_{CO_2} = -3.50

$[B(OH)_3]_{TOT}$ = 0.39 mM

$[Br^-]_{TOT}$ = 0.16 mM

$[NO_3^-]_{TOT}$ = 3.39 µM

$[SO_4^{2-}]_{TOT}$ = 7.02 mM

$[Cl^-]_{TOT}$ = 94.50 mM

$[K^+]_{TOT}$ = 1.72 mM

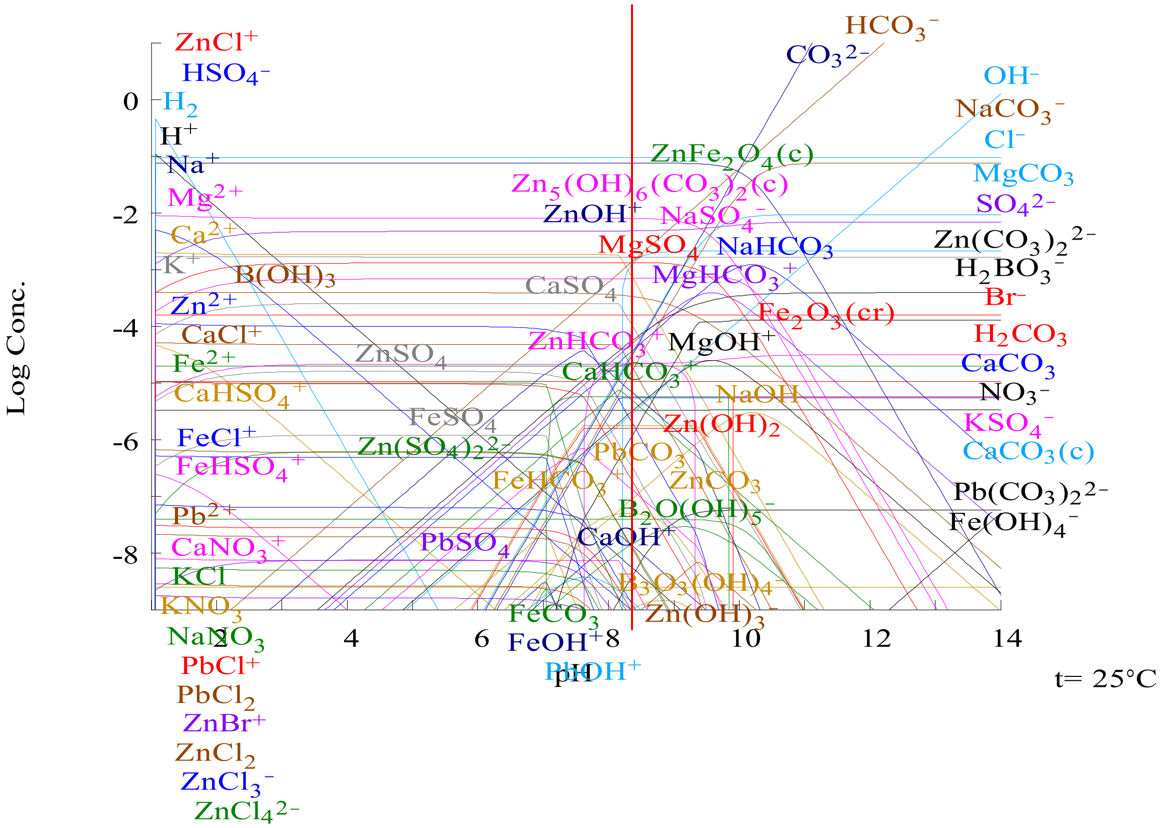


Figure C.299. Phase diagram for steel pipe section immersed into bay water after one day of exposure.

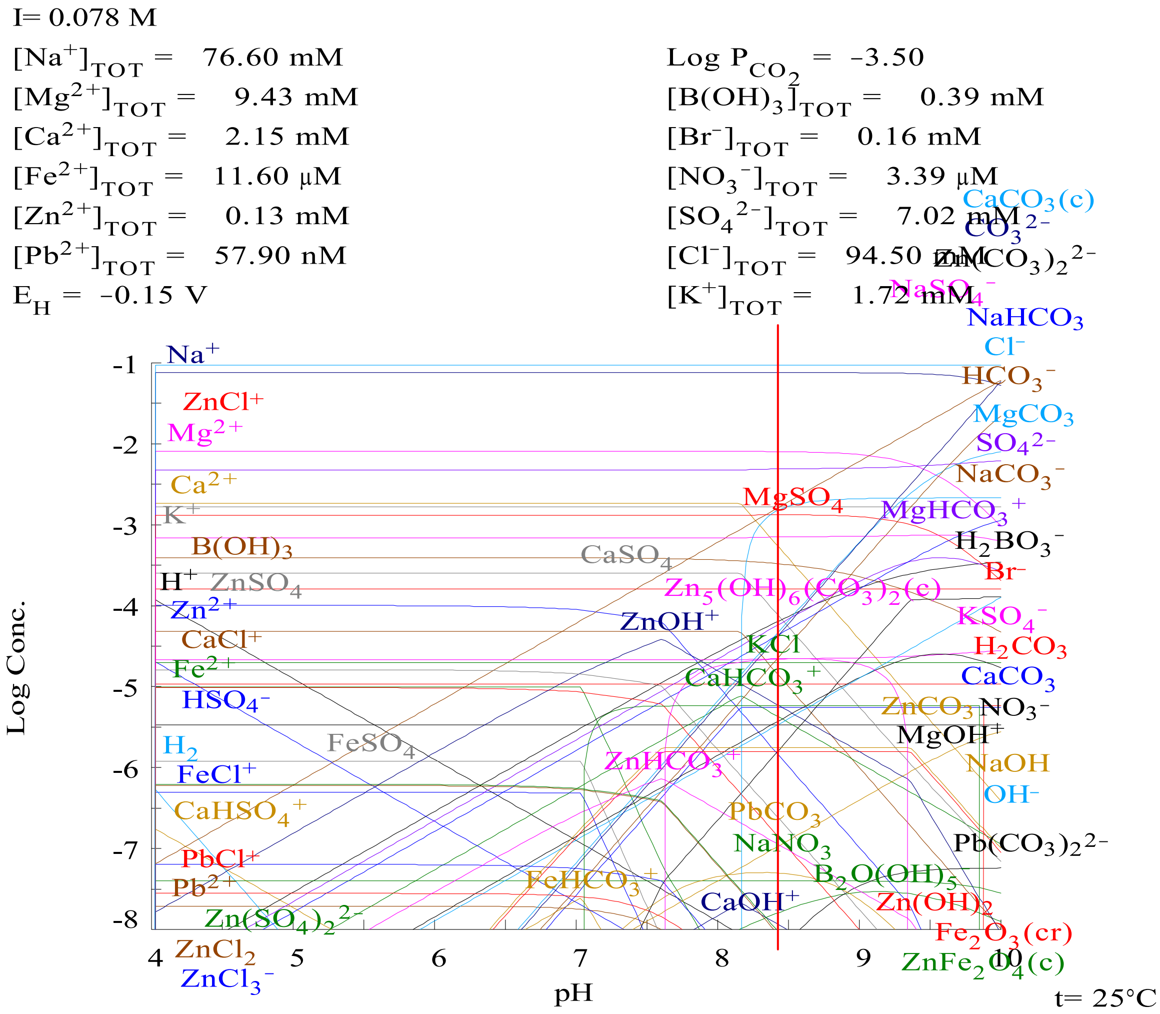


Figure C.300. Phase diagram for steel pipe section immersed into bay water after one day of exposure. Study area.

Table C.70. The predominant species of zinc. Steel pipe section, bay water, one day exposure.

Component	Log Concentration (mol/L)	Concentration (mol/L)	Zn as Zn Concentration (mg/L)	Cumulative Percentage of Zn
$Zn_5(OH)_6(CO_3)_2$(c)	-4.66	2.18E-05	7.14E+00	85.22
$ZnOH^+$	-5.21	6.16E-06	4.03E-01	90.03
$ZnFe_2O_4$(c)	-5.24	5.80E-06	3.79E-01	94.56
$ZnCO_3$	-5.75	1.78E-06	1.16E-01	95.95
$Zn(OH)_2$	-5.80	1.58E-06	1.03E-01	97.18
Zn^{2+}	-5.80	1.58E-06	1.03E-01	98.41
$Zn(CO3)_2^{2-}$	-5.83	1.48E-06	9.66E-02	99.57
$ZnSO_4$	-6.58	2.61E-07	1.71E-02	99.77
$ZnCl^+$	-6.82	1.52E-07	9.97E-03	99.89
$ZnHCO_3^+$	-6.93	1.17E-07	7.67E-03	99.98

Table C.71. The predominant species of lead. Steel pipe section, bay water, one day exposure.

Component	Log Concentration (mol/L)	Concentration (mol/L)	Pb as Pb Concentration (mg/L)	Cumulative Percentage of Pb
$PbCO_3$	-7.30	5.01E-08	1.04E-02	86.24
$Pb(CO3)_2^{2-}$	-8.31	4.90E-09	1.01E-03	94.68
$PbOH^+$	-8.91	1.23E-09	2.55E-04	96.79
$PbCl^+$	-9.14	7.30E-10	1.51E-04	98.05
Pb^{2+}	-9.29	5.10E-10	1.06E-04	98.93
$PbHCO_3^+$	-9.62	2.40E-10	4.97E-05	99.34
$PbSO_4$	-9.69	2.03E-10	4.21E-05	99.69
$Pb(OH)_2$	-1.00	9.75E-11	2.02E-05	99.86
$PbCl_2$	-1.02	6.85E-11	1.42E-05	99.98

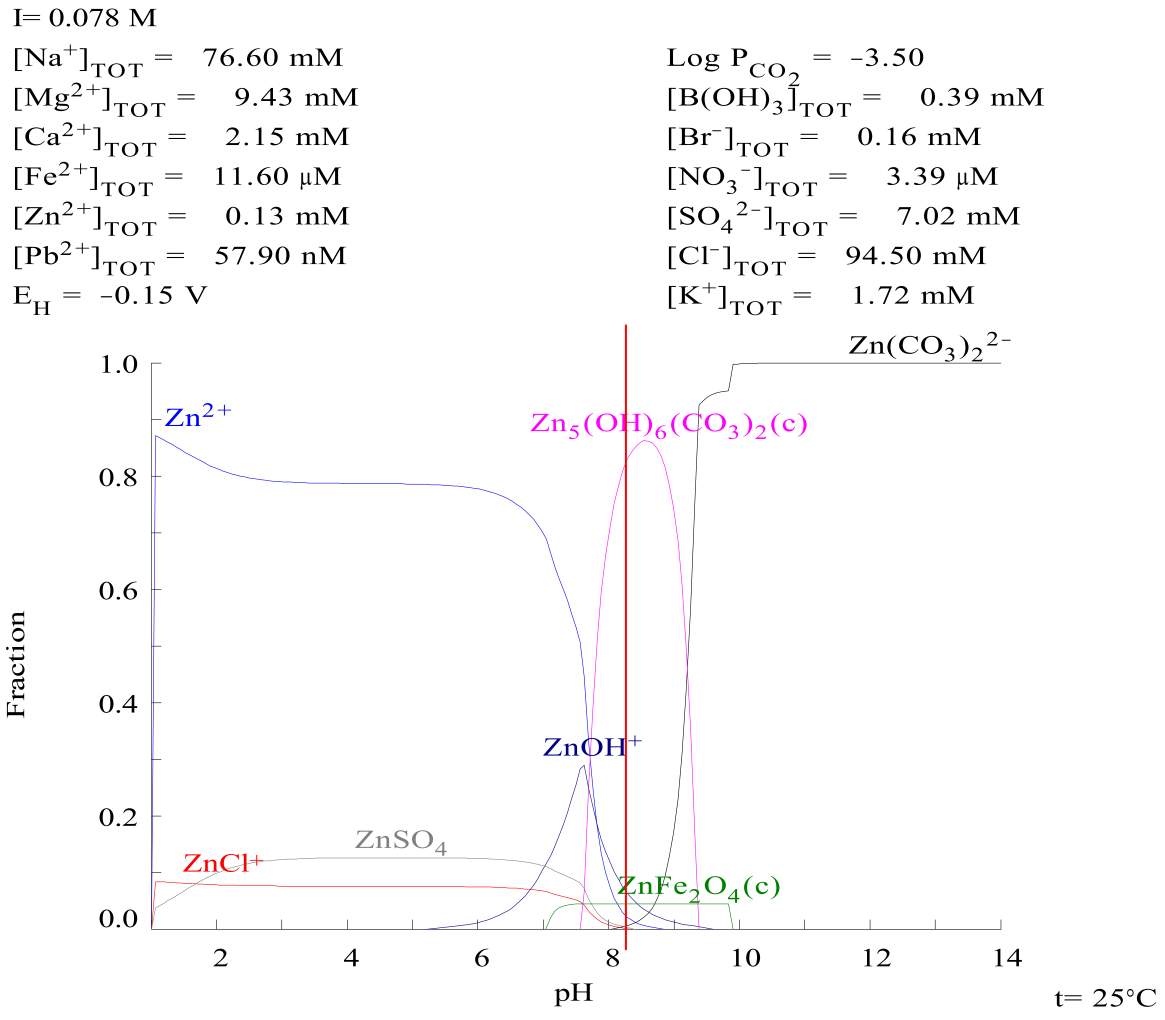


Figure C.301. Fraction diagram of zinc for steel pipe section immersed into bay water after one day of exposure.

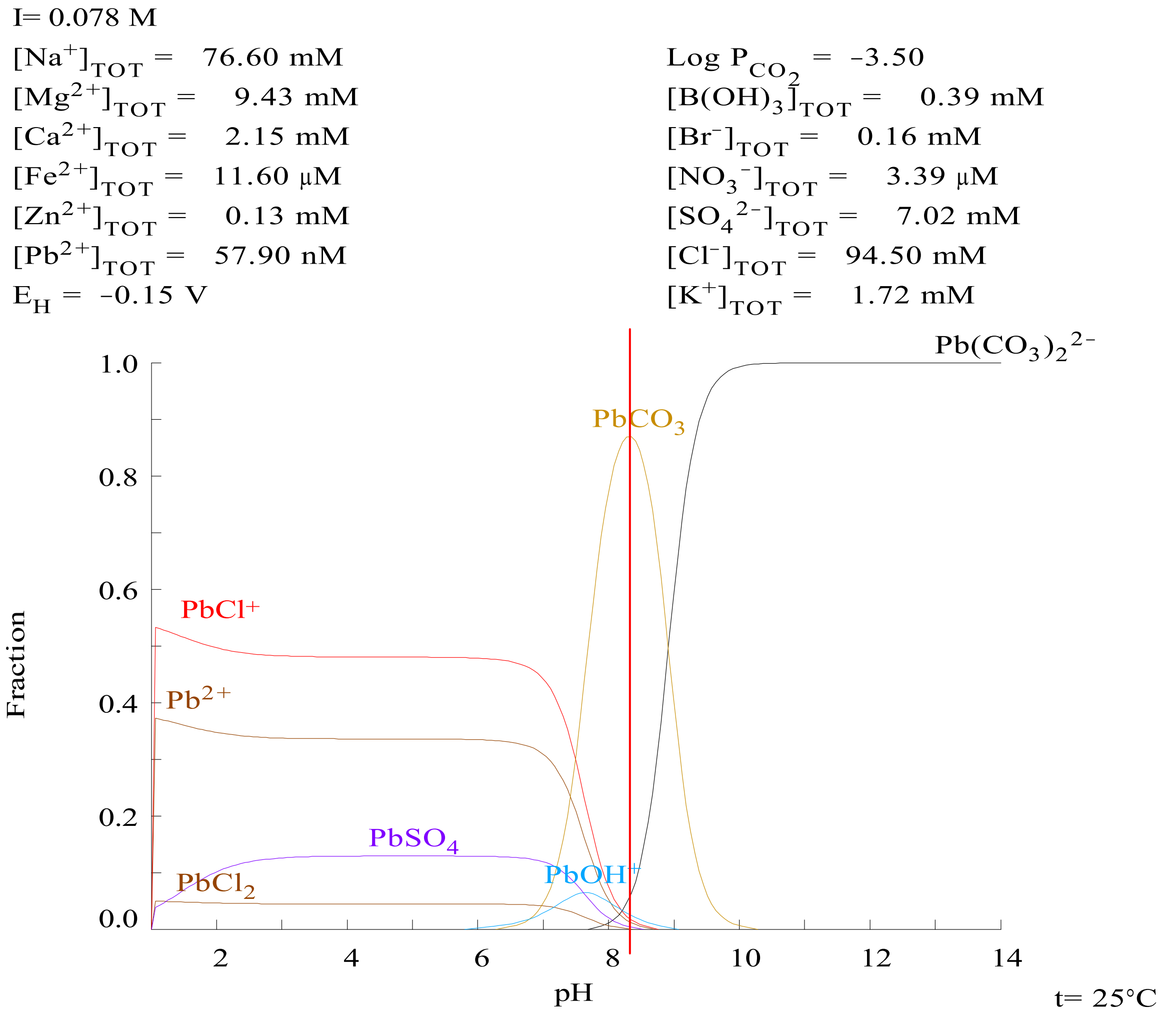


Figure C.302. Fraction diagram of lead for steel pipe section immersed into bay water after one day of exposure.

$[K^+]_{TOT}$= 1.72 mM
$[Na^+]_{TOT}$= 76.60 mM
$[Mg^{2+}]_{TOT}$= 9.43 mM
$[Ca^{2+}]_{TOT}$= 2.15 mM
$[Fe^{2+}]_{TOT}$= 11.60 μM
$[Zn^{2+}]_{TOT}$= 0.13 mM
$[Pb^{2+}]_{TOT}$= 57.90 nM

I= 0.078 M
Log P_{CO_2} = -3.50
$[B(OH)_3]_{TOT}$= 0.39 mM
$[Br^-]_{TOT}$= 0.16 mM
$[NO_3^-]_{TOT}$= 3.39 μM
$[SO_4^{2-}]_{TOT}$= 7.02 mM
$[Cl^-]_{TOT}$= 94.50 mM

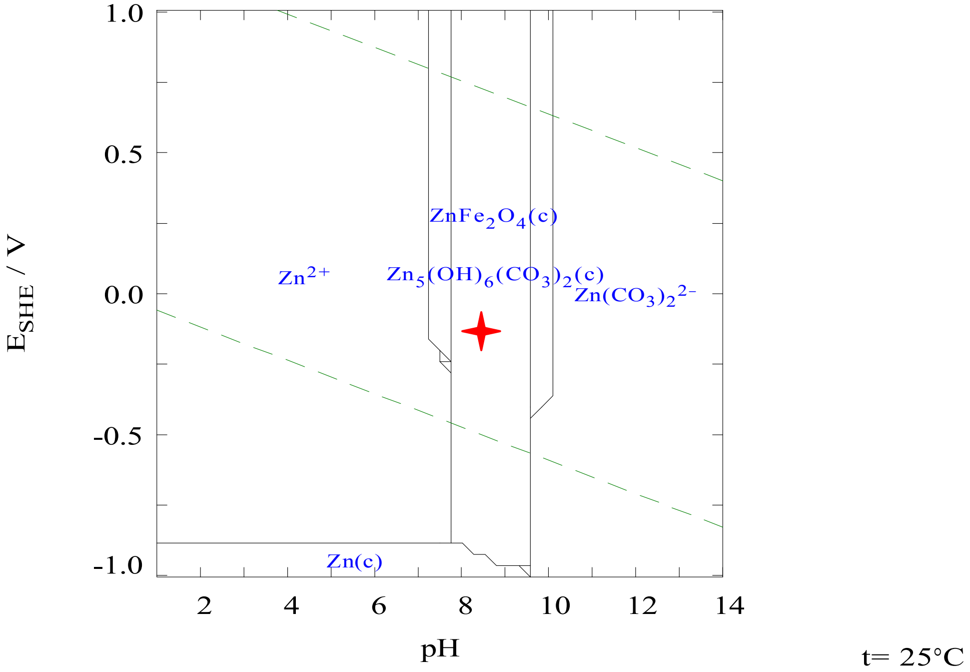


Figure C.303. Pourbaix diagram of zinc for steel pipe section immersed into bay water after one day of exposure.

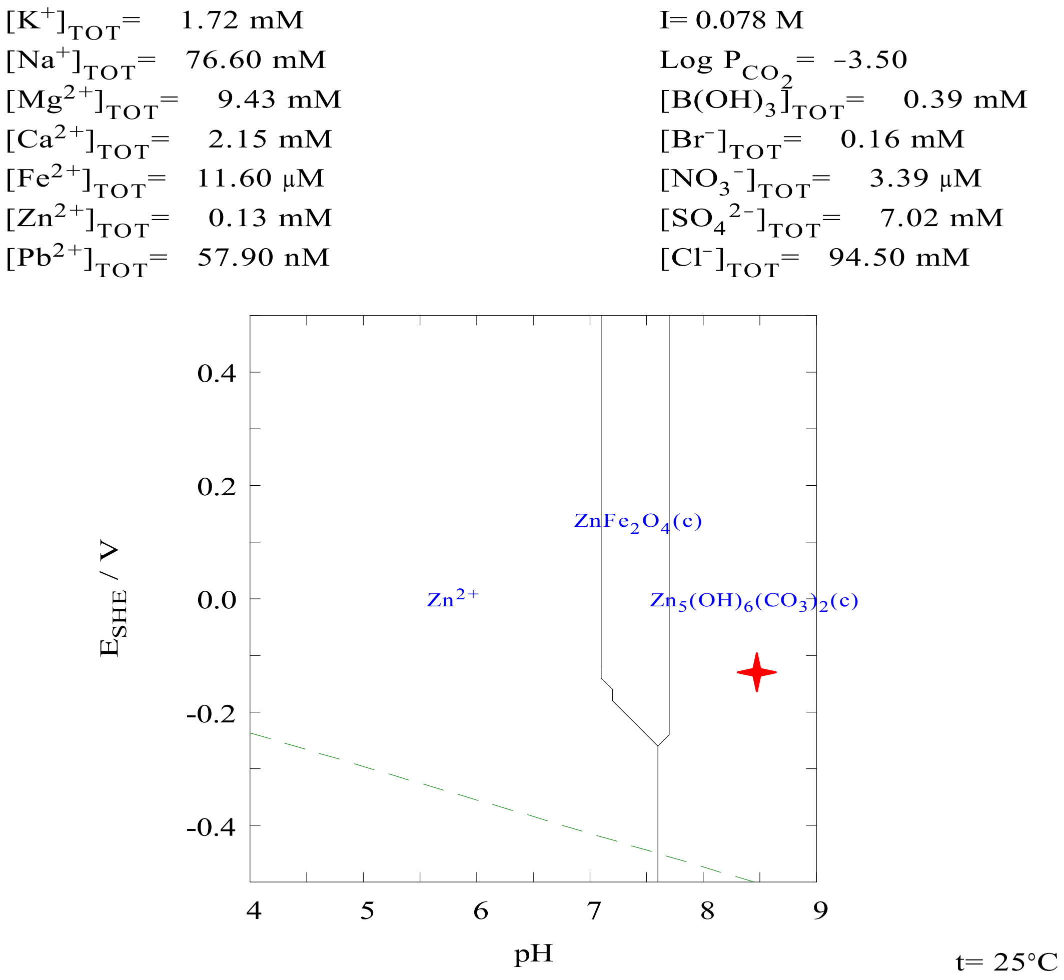


Figure 304. Pourbaix diagram of zinc for steel pipe section immersed into bay water after one day of exposure. Study area.

$[K^+]_{TOT}=$ 1.72 mM
$[Na^+]_{TOT}=$ 76.60 mM
$[Mg^{2+}]_{TOT}=$ 9.43 mM
$[Ca^{2+}]_{TOT}=$ 2.15 mM
$[Fe^{2+}]_{TOT}=$ 11.60 μM
$[Zn^{2+}]_{TOT}=$ 0.13 mM
$[Pb^{2+}]_{TOT}=$ 57.90 nM

I= 0.078 M
Log $P_{CO_2}=$ -3.50
$[B(OH)_3]_{TOT}=$ 0.39 mM
$[Br^-]_{TOT}=$ 0.16 mM
$[NO_3^-]_{TOT}=$ 3.39 μM
$[SO_4^{2-}]_{TOT}=$ 7.02 mM
$[Cl^-]_{TOT}=$ 94.50 mM

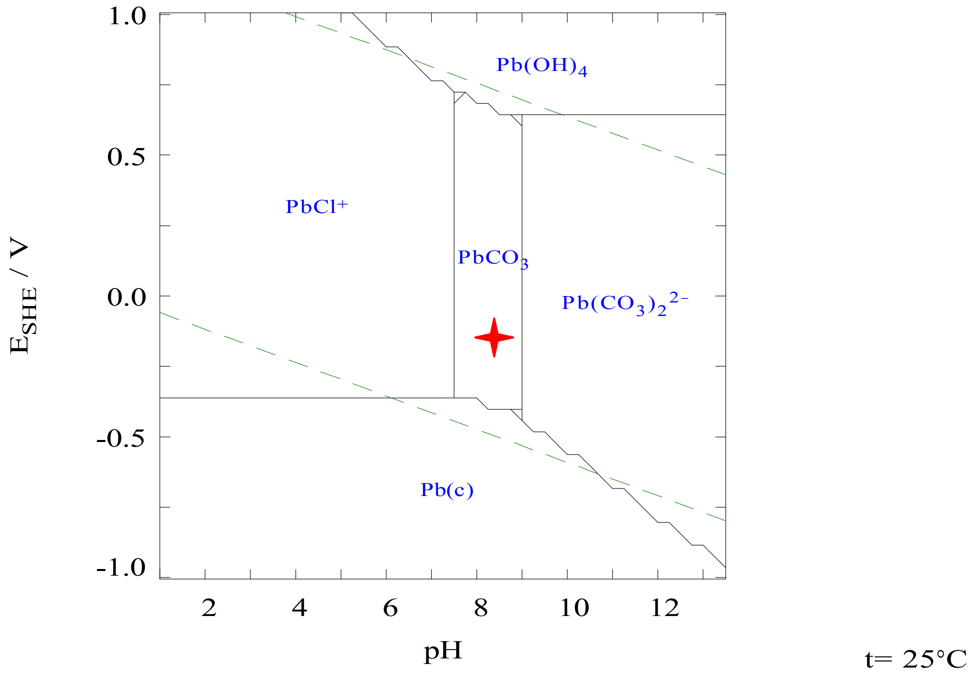


Figure C.305. Pourbaix diagram of lead for steel pipe section immersed into bay water after one day of exposure.

$[K^+]_{TOT}$= 1.72 mM
$[Na^+]_{TOT}$= 76.60 mM
$[Mg^{2+}]_{TOT}$= 9.43 mM
$[Ca^{2+}]_{TOT}$= 2.15 mM
$[Fe^{2+}]_{TOT}$= 11.60 μM
$[Zn^{2+}]_{TOT}$= 0.13 mM
$[Pb^{2+}]_{TOT}$= 57.90 nM

I= 0.078 M
Log P_{CO_2} = -3.50
$[B(OH)_3]_{TOT}$= 0.39 mM
$[Br^-]_{TOT}$= 0.16 mM
$[NO_3^-]_{TOT}$= 3.39 μM
$[SO_4^{2-}]_{TOT}$= 7.02 mM
$[Cl^-]_{TOT}$= 94.50 mM

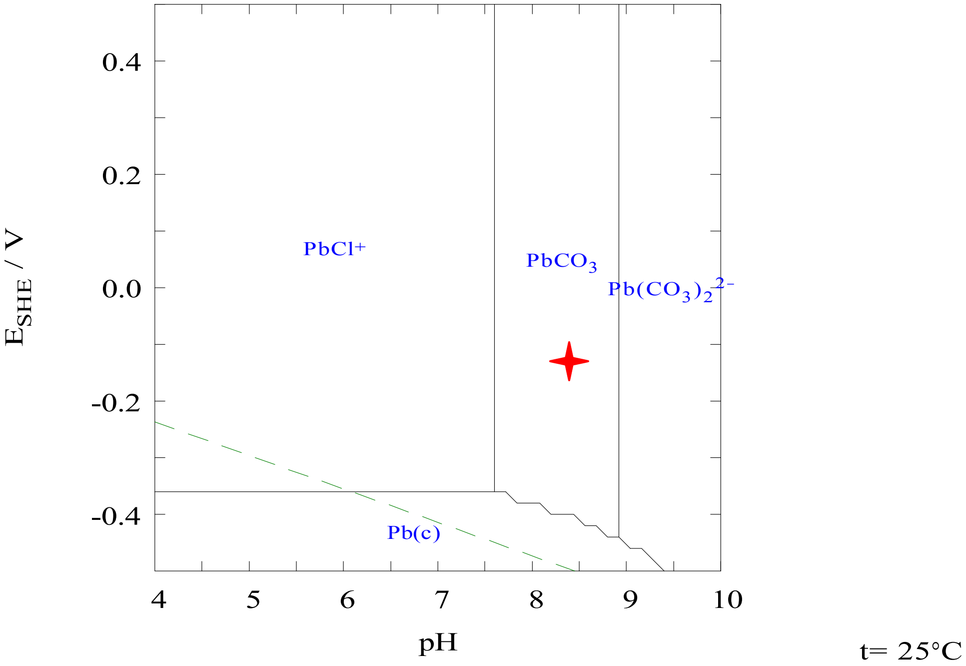


Figure C.306. Pourbaix diagram of lead for steel pipe section immersed into bay water after one day of exposure. Study area.

Steel Gutter, Bay Water, After One Day of Exposure

I= 0.078 M
$[Na^+]_{TOT}$ = 76.60 mM
$[Mg^{2+}]_{TOT}$ = 9.43 mM
$[Ca^{2+}]_{TOT}$ = 2.15 mM
$[Fe^{2+}]_{TOT}$ = 14.00 μM
$[Zn^{2+}]_{TOT}$ = 74.00 μM
$[Pb^{2+}]_{TOT}$ = 24.10 nM
E_H = -0.15 V

Log P_{CO_2} = -3.50
$[B(OH)_3]_{TOT}$ = 0.39 mM
$[Br^-]_{TOT}$ = 0.16 mM
$[NO_3^-]_{TOT}$ = 3.39 μM
$[SO_4^{2-}]_{TOT}$ = 7.02 mM
$[Cl^-]_{TOT}$ = 94.50 mM
$[K^+]_{TOT}$ = 1.72 mM

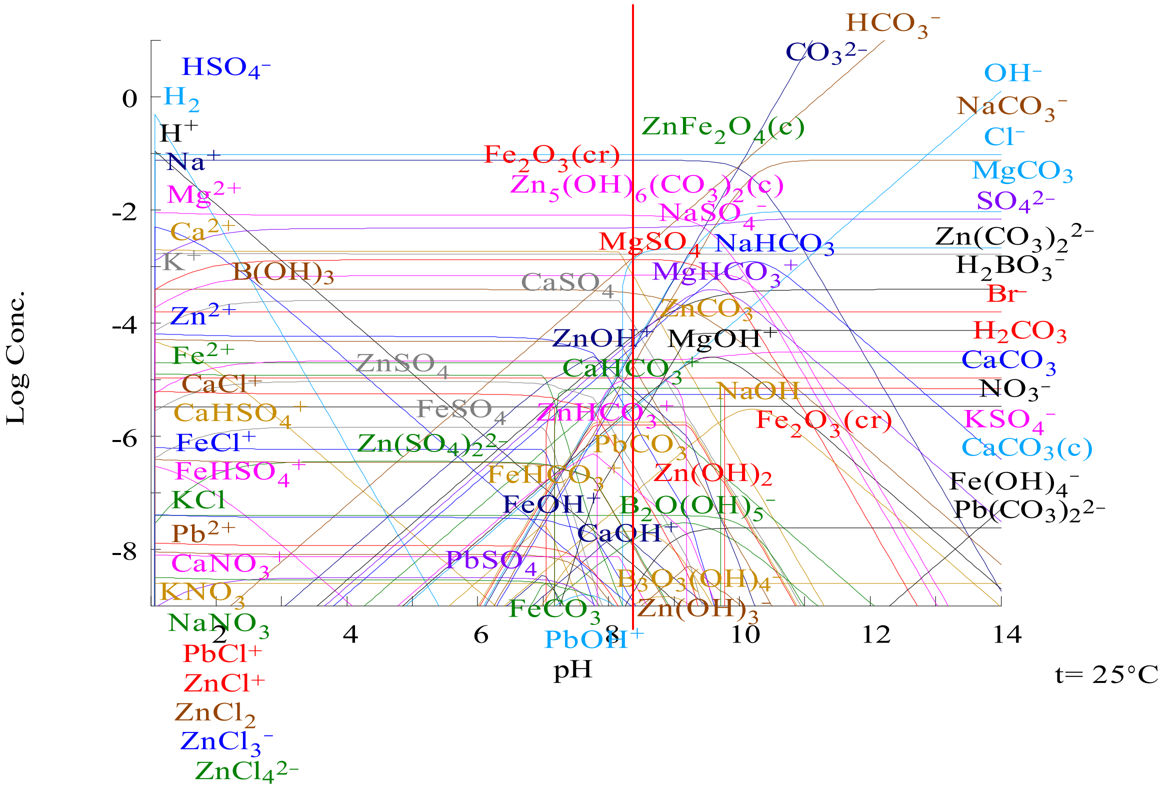


Figure C.307. Phase diagram for steel gutter section immersed into bay water after one day of exposure.

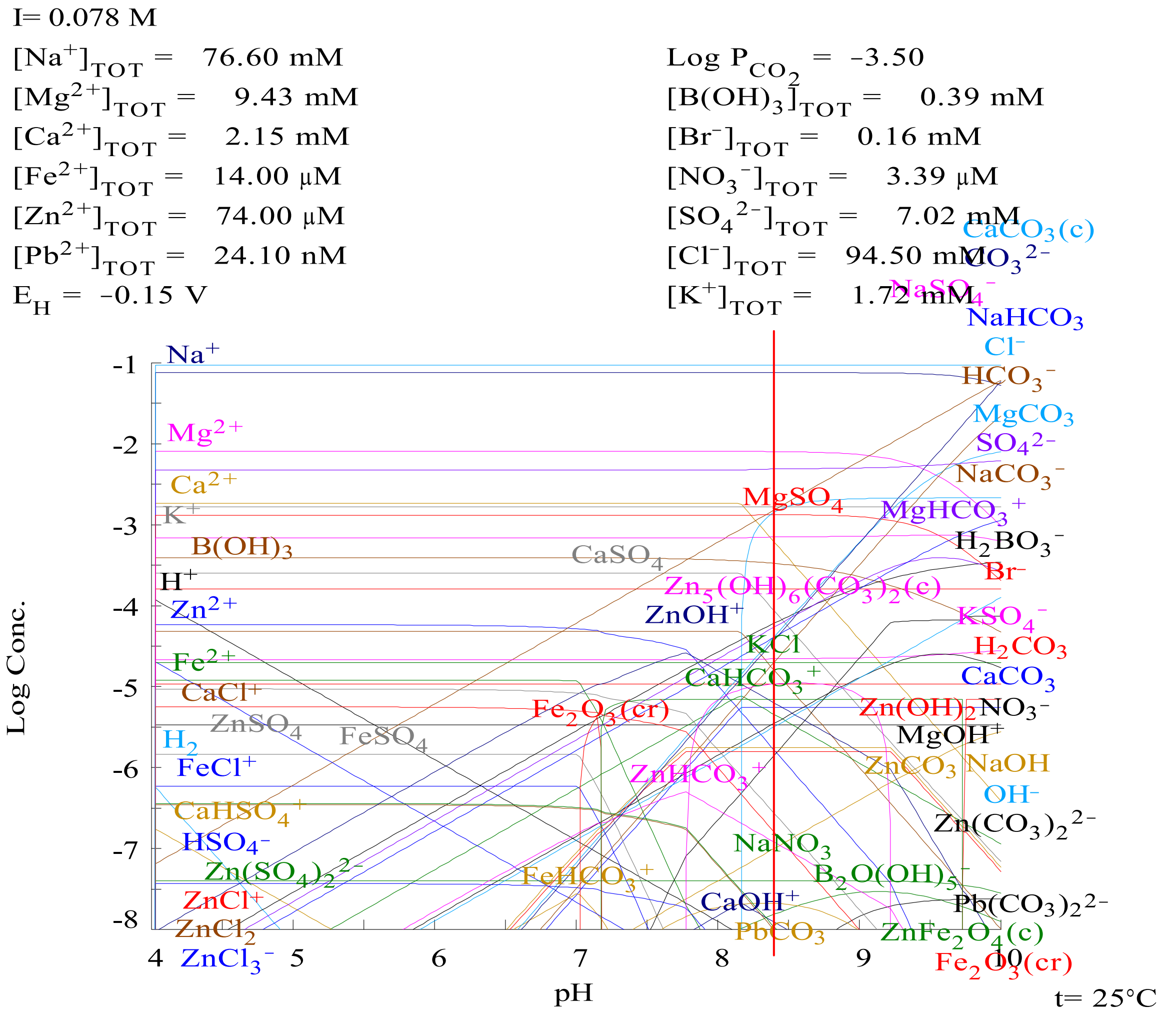


Figure C.308. Phase diagram for steel gutter section immersed into bay water after one day of exposure. Study area.

Table C.72. The predominant species of zinc. Steel gutter section, bay water, one day exposure.

Component	Log Concentration (mol/L)	Concentration (mol/L)	Zn as Zn Concentration (mg/L)	Cumulative Percentage of Zn
$Zn_5(OH)_6(CO_3)_2$(c)	-4.97	1.08E-05	3.52E+00	72.82
$ZnFe_2O_4$(c)	-5.15	7.00E-06	4.58E-01	82.28
$ZnOH^+$	-5.21	6.16E-06	4.03E-01	90.60
$ZnCO_3$	-5.75	1.78E-06	1.16E-01	93.00
$Zn(OH)_2$	-5.80	1.58E-06	1.03E-01	95.13
Zn^{2+}	-5.80	1.58E-06	1.03E-01	97.26
$Zn(CO3)_2^{2-}$	-5.83	1.48E-06	9.66E-02	99.25
$ZnSO_4$	-6.58	2.61E-07	1.71E-02	99.61
$ZnCl^+$	-6.82	1.52E-07	9.97E-03	99.81
$ZnHCO_3^+$	-6.93	1.17E-07	7.67E-03	99.97

Table C.73. The predominant species of lead. Steel gutter section, bay water, one day exposure.

Component	Log Concentration (mol/L)	Concentration (mol/L)	Pb as Pb Concentration (mg/L)	Cumulative Percentage of Pb
$PbCO_3$	-7.68	2.09E-08	4.34E-03	86.24
$Pb(CO3)_2^{2-}$	-8.69	2.05E-09	4.24E-04	94.68
$PbOH^+$	-9.29	5.14E-10	1.06E-04	96.79
$PbCl^+$	-9.52	3.05E-10	6.32E-05	98.05
Pb^{2+}	-9.67	2.13E-10	4.42E-05	98.93
$PbHCO_3^+$	-1.00	1.00E-10	2.08E-05	99.34
$PbSO_4$	-1.01	8.48E-11	1.76E-05	99.69
$Pb(OH)_2$	-1.04	4.07E-11	8.43E-06	99.86
$PbCl_2$	-1.05	2.86E-11	5.93E-06	99.98

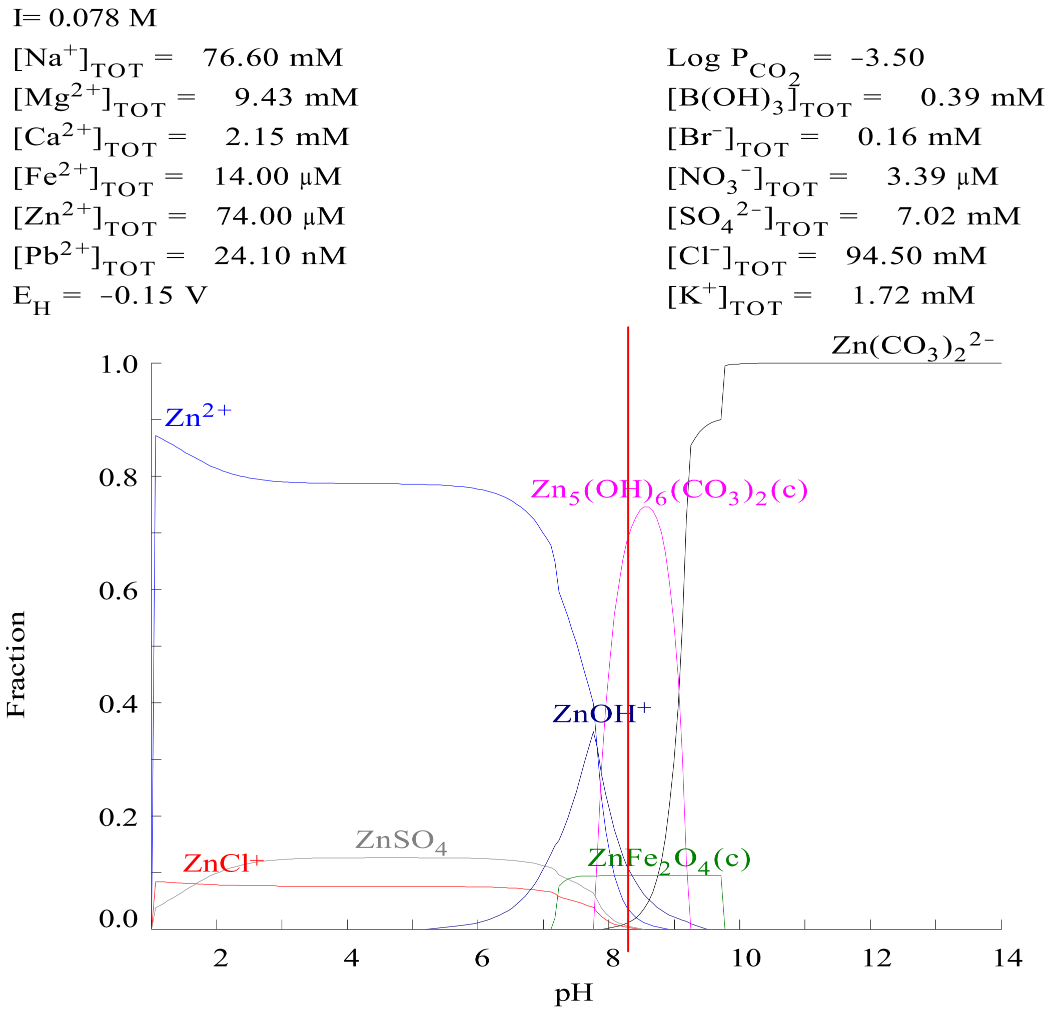


Figure C.309. Fraction diagram of zinc for steel gutter section immersed into bay water after one day of exposure.

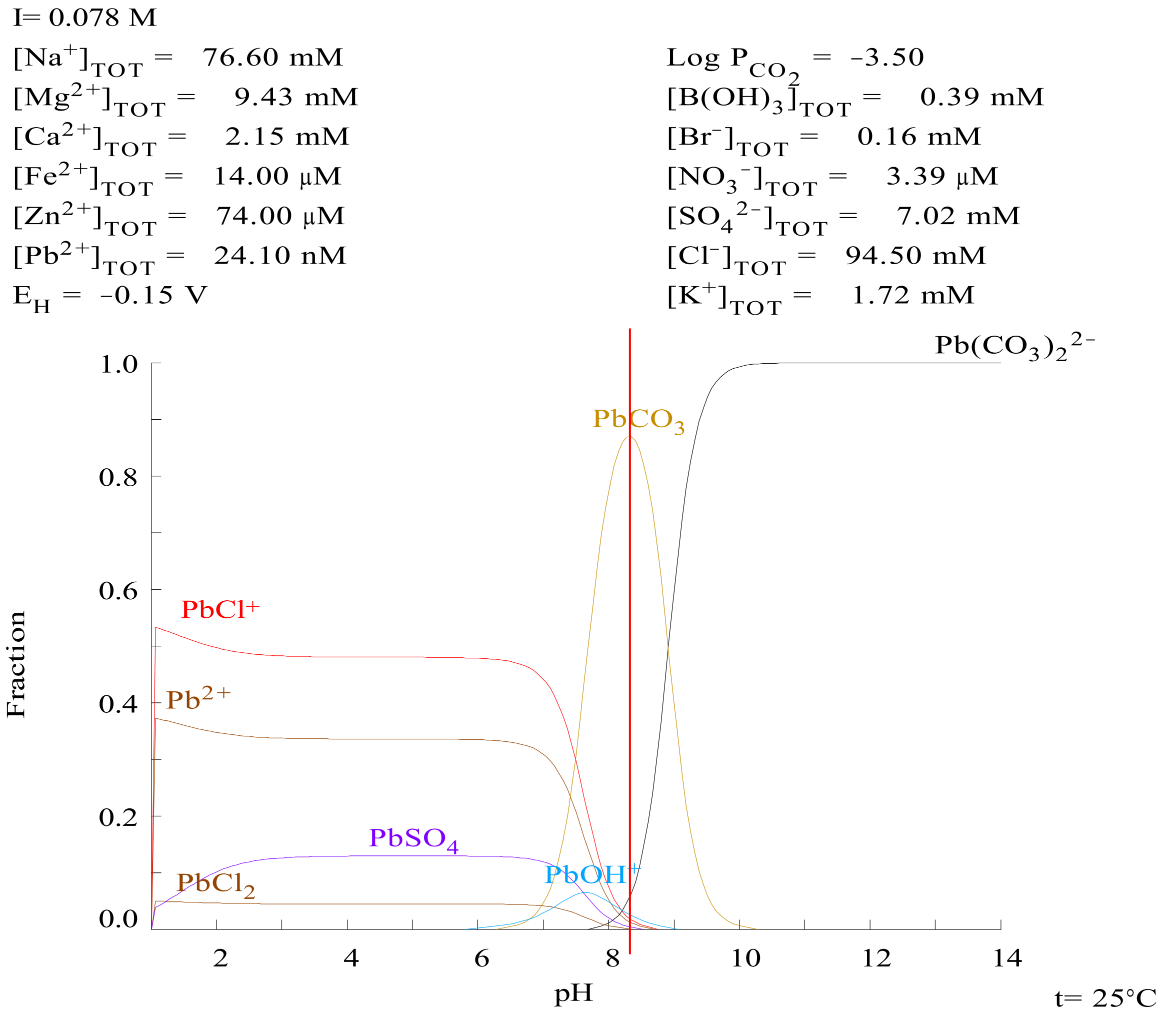


Figure C.310. Fraction diagram of lead for steel gutter section immersed into bay water after one day of exposure.

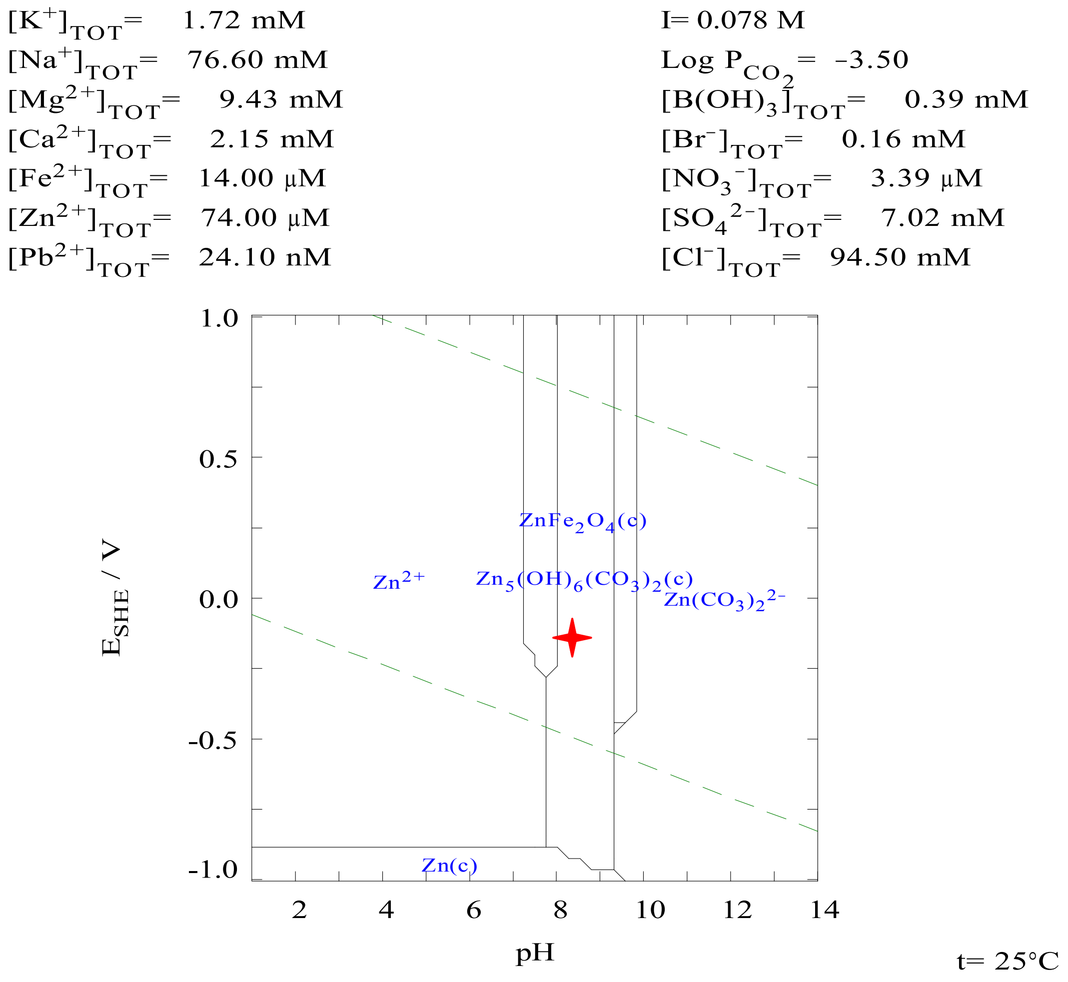


Figure C.311. Pourbaix diagram of zinc for steel gutter section immersed into bay water after one day of exposure.

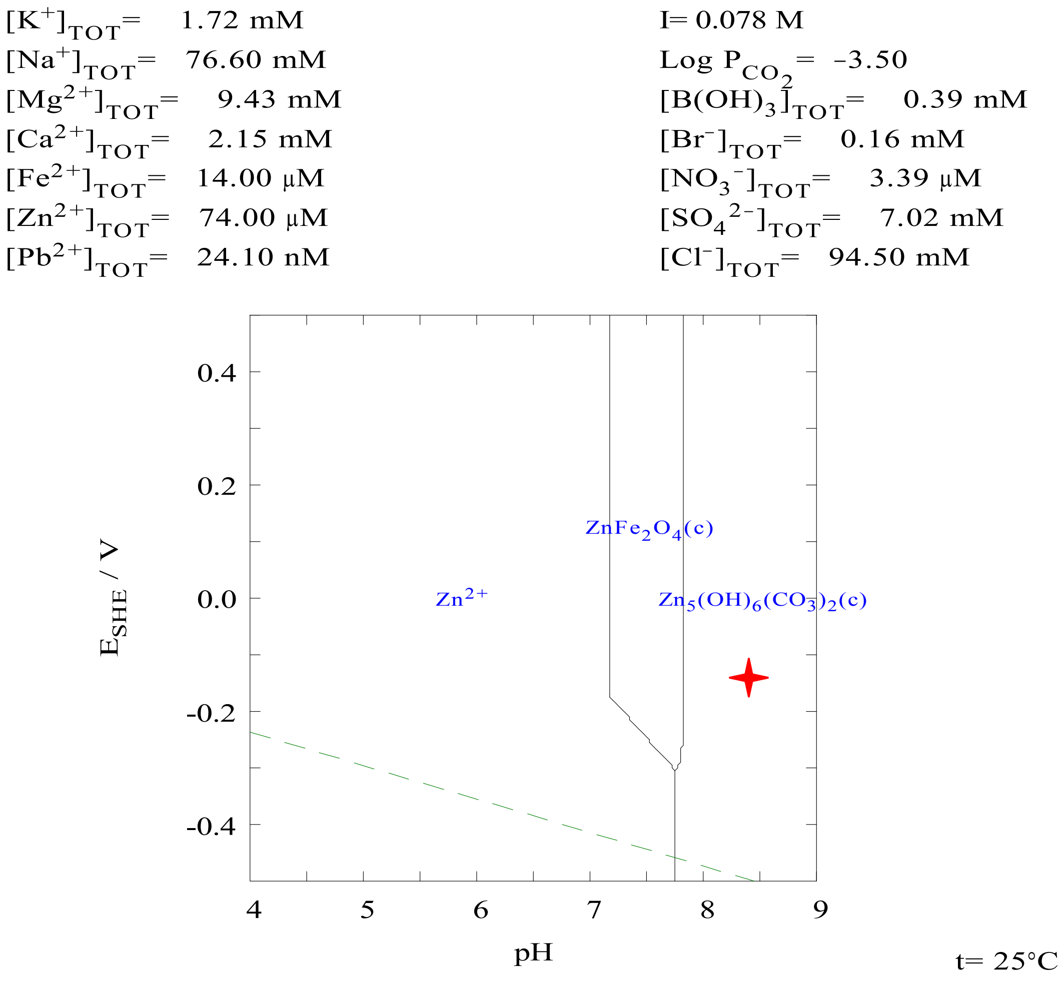


Figure C.312. Pourbaix diagram of zinc for steel gutter section immersed into bay water after one day of exposure. Study area.

$[K^+]_{TOT}=$ 1.72 mM
$[Na^+]_{TOT}=$ 76.60 mM
$[Mg^{2+}]_{TOT}=$ 9.43 mM
$[Ca^{2+}]_{TOT}=$ 2.15 mM
$[Fe^{2+}]_{TOT}=$ 14.00 µM
$[Zn^{2+}]_{TOT}=$ 74.00 µM
$[Pb^{2+}]_{TOT}=$ 24.10 nM

I= 0.078 M
Log $P_{CO_2}=$ -3.50
$[B(OH)_3]_{TOT}=$ 0.39 mM
$[Br^-]_{TOT}=$ 0.16 mM
$[NO_3^-]_{TOT}=$ 3.39 µM
$[SO_4^{2-}]_{TOT}=$ 7.02 mM
$[Cl^-]_{TOT}=$ 94.50 mM

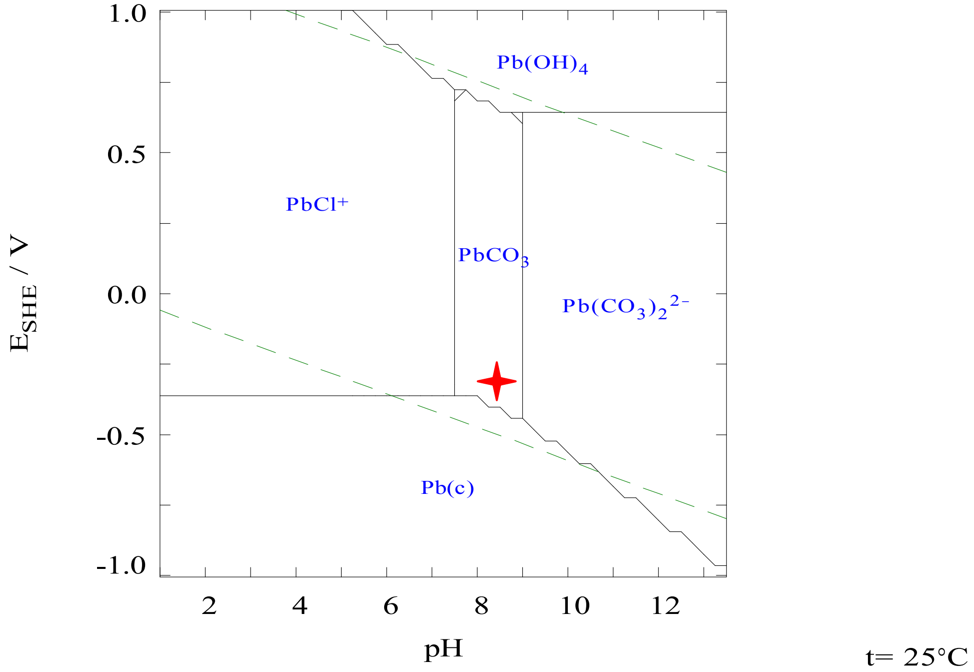


Figure C.313. Pourbaix diagram of lead for steel gutter section immersed into bay water after one day of exposure.

$[K^+]_{TOT}$= 1.72 mM
$[Na^+]_{TOT}$= 76.60 mM
$[Mg^{2+}]_{TOT}$= 9.43 mM
$[Ca^{2+}]_{TOT}$= 2.15 mM
$[Fe^{2+}]_{TOT}$= 14.00 μM
$[Zn^{2+}]_{TOT}$= 74.00 μM
$[Pb^{2+}]_{TOT}$= 24.10 nM

I= 0.078 M
Log P_{CO_2}= -3.50
$[B(OH)_3]_{TOT}$= 0.39 mM
$[Br^-]_{TOT}$= 0.16 mM
$[NO_3^-]_{TOT}$= 3.39 μM
$[SO_4^{2-}]_{TOT}$= 7.02 mM
$[Cl^-]_{TOT}$= 94.50 mM

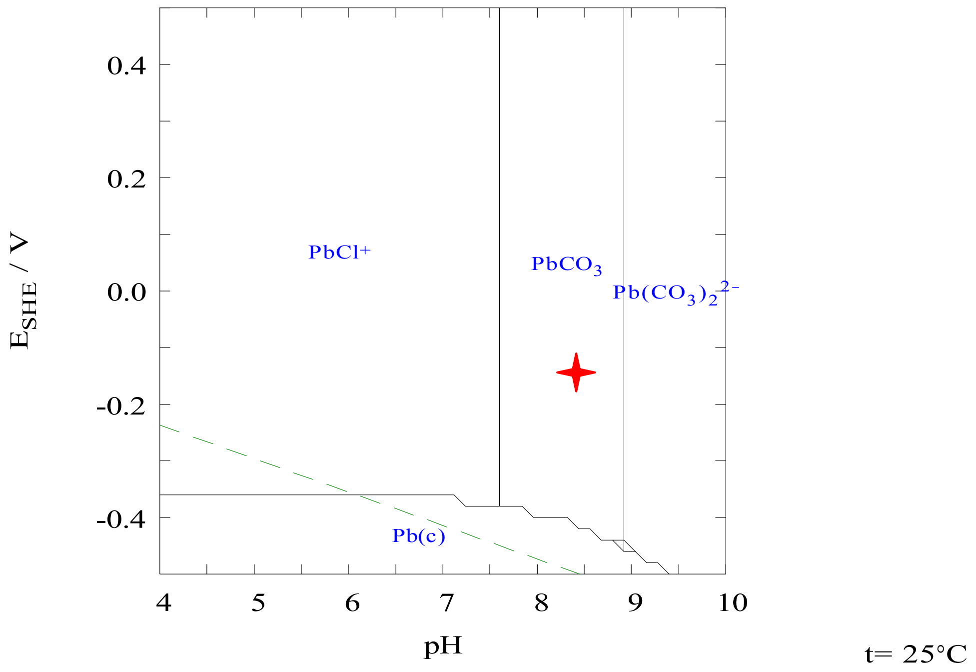


Figure C.314. Pourbaix diagram of lead for steel gutter section immersed into bay water after one day of exposure. Study area.

Copper Gutter, Bay Water, After One Day of Exposure

I= 0.078 M
$[Na^+]_{TOT}$ = 76.60 mM
$[Mg^{2+}]_{TOT}$ = 9.30 mM
$[Ca^{2+}]_{TOT}$ = 2.26 mM
$[Fe^{2+}]_{TOT}$ = 13.30 µM
$[Zn^{2+}]_{TOT}$ = 0.76 µM
$[Cu^{2+}]_{TOT}$ = 33.20 µM
E_H = -0.13 V

Log P_{CO_2} = -3.50
$[B(OH)_3]_{TOT}$ = 0.39 mM
$[Br^-]_{TOT}$ = 0.16 mM
$[NO_3^-]_{TOT}$ = 3.39 µM
$[SO_4^{2-}]_{TOT}$ = 7.02 mM
$[Cl^-]_{TOT}$ = 94.50 mM
$[K^+]_{TOT}$ = 1.72 mM

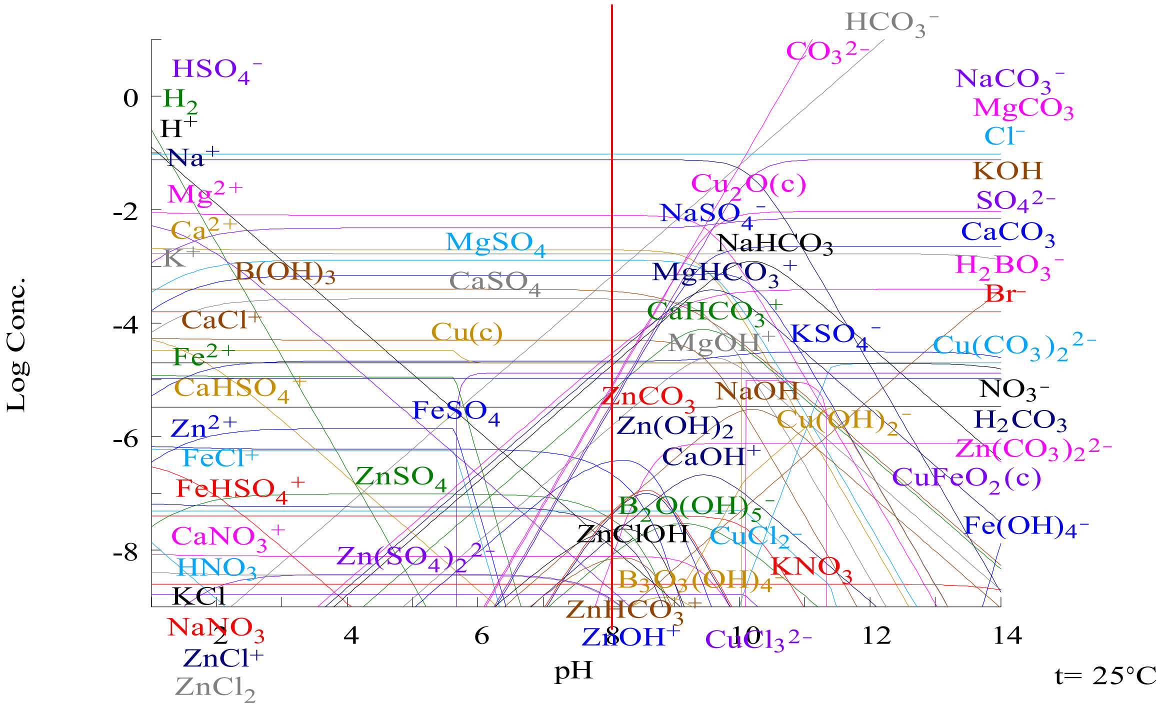


Figure C.315. Phase diagram for copper gutter section immersed into bay water after one day of exposure.

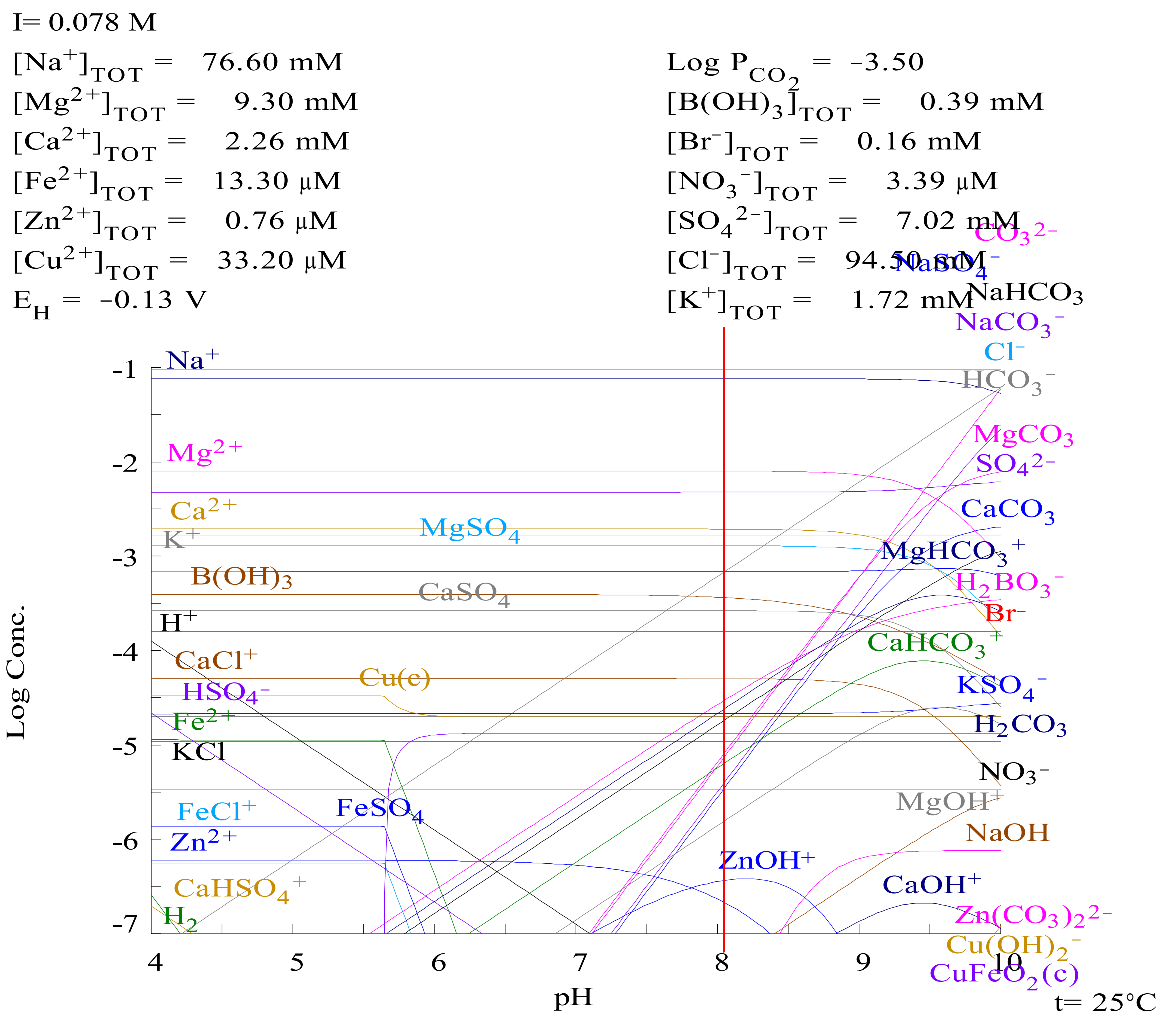


Figure C.316. Phase diagram for copper gutter section immersed into bay water after one day of exposure. Study area.

Table C.74. The predominant species of copper. Copper gutter section, bay water, one day exposure.

Component	Log Concentration (mol/L)	Concentration (mol/L)	Cu as Cu Concentration (mg/L)	Cumulative Percentage of Cu
Cu(c)	-4.70	1.98E-05	1.26E+00	59.79
$CuFeO_2$(c)	-4.88	1.33E-05	8.45E-01	99.85
$CuCl_2^-$	-7.31	4.95E-08	3.15E-03	99.99

Table C.75. The predominant species of zinc. Copper gutter section, bay water, one day exposure.

Component	Log Concentration (mol/L)	Concentration (mol/L)	Zn as Zn Concentration (mg/L)	Cumulative Percentage of Zn
$ZnOH^+$	-6.43	3.73E-07	2.44E-02	48.74
Zn^{2+}	-6.70	2.02E-07	1.32E-02	75.10
$ZnCO_3$	-7.29	5.09E-08	3.33E-03	81.75
$Zn(OH)_2$	-7.34	4.52E-08	2.96E-03	87.66
$ZnSO_4$	-7.49	3.26E-08	2.13E-03	91.92
ZnClOH	-7.64	2.31E-08	1.51E-03	94.94
$ZnCl^+$	-7.71	1.95E-08	1.28E-03	97.49
$Zn(CO3)_2^{2-}$	-8.02	9.48E-09	6.20E-04	98.73
$ZnHCO_3^+$	-8.15	7.10E-09	4.65E-04	99.66
$Zn(SO4)_2^{2-}$	-8.90	1.26E-09	8.23E-05	99.82
$ZnCl_2$	-8.92	1.21E-09	7.91E-05	99.98

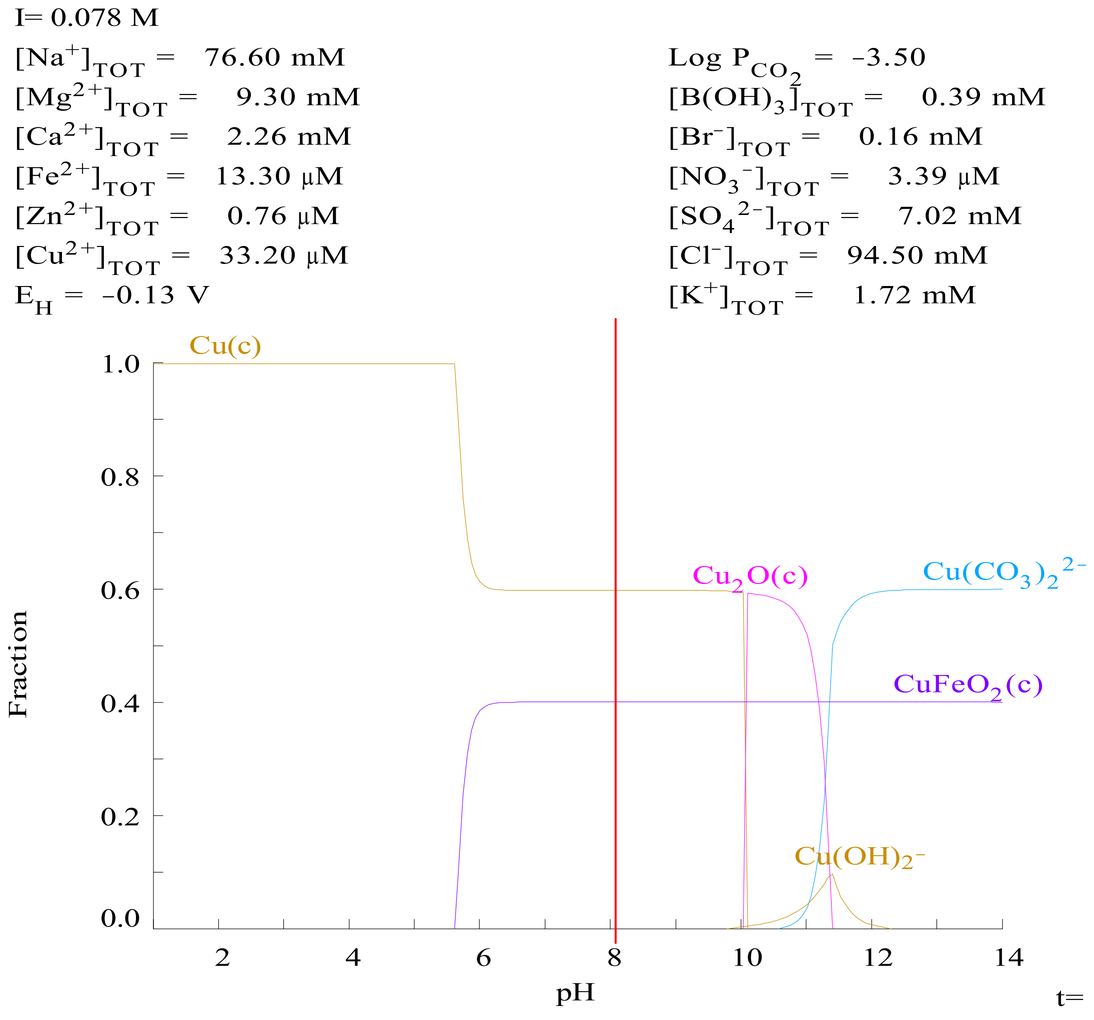


Figure C.317. Fraction diagram of copper for copper gutter section immersed into bay water after one day of exposure.

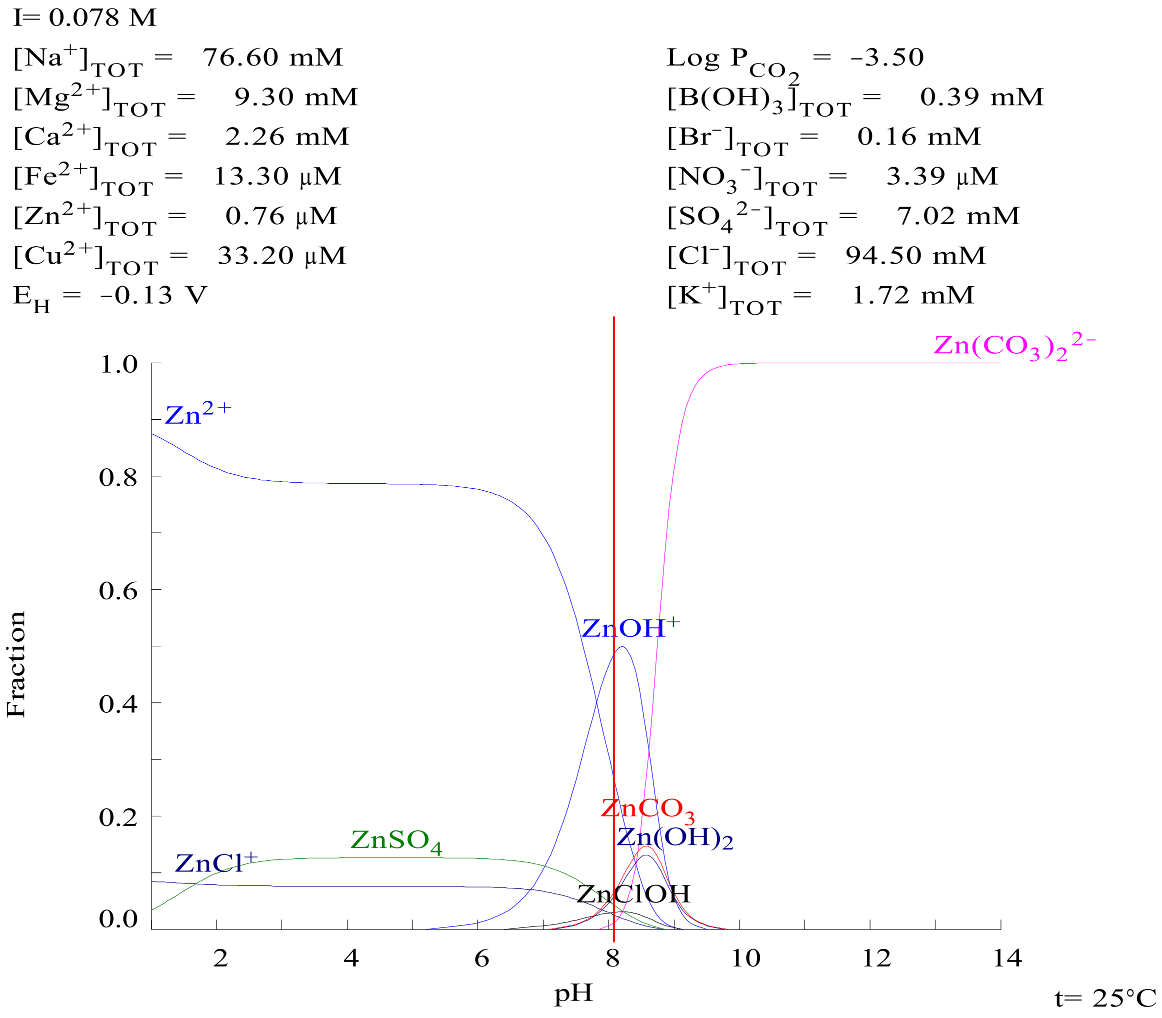


Figure C.318. Fraction diagram of zinc for copper gutter section immersed into bay water after one day of exposure.

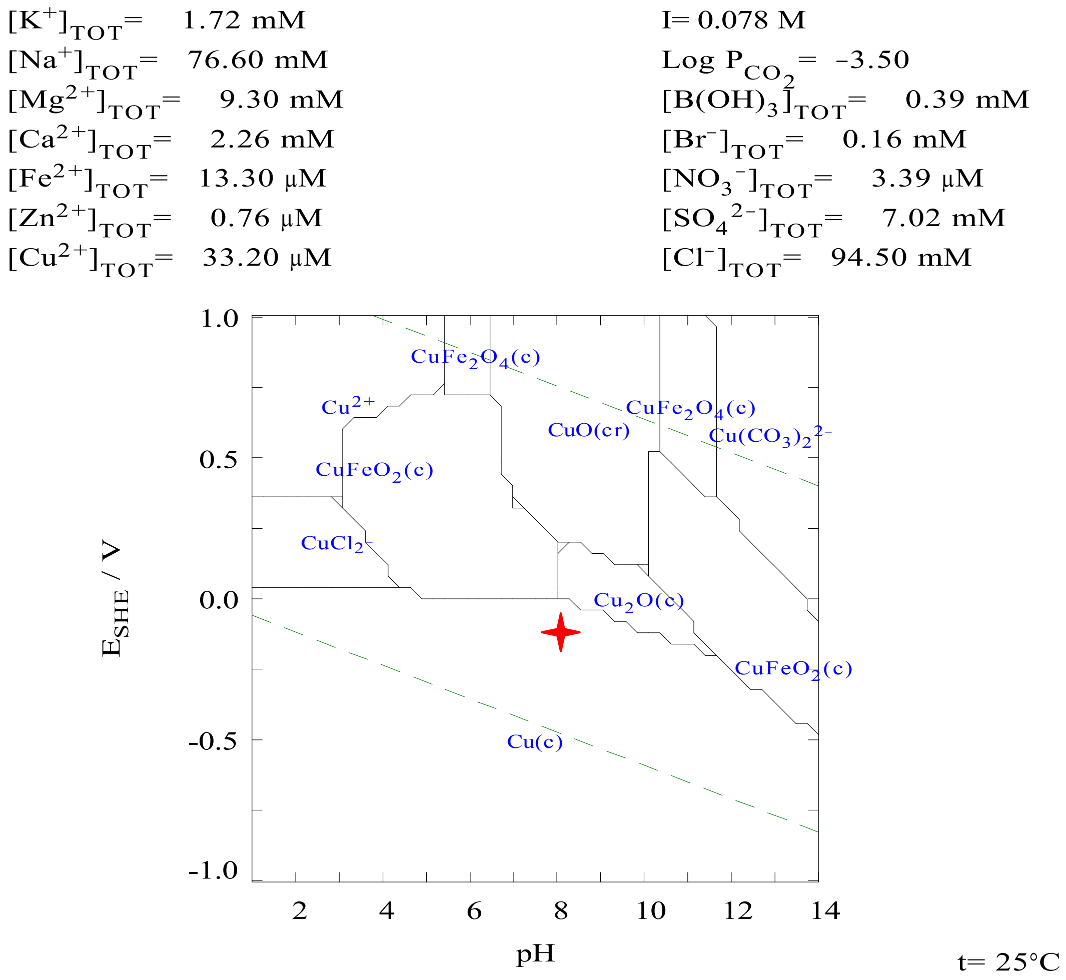


Figure C.319. Pourbaix diagram of copper for copper gutter section immersed into bay water after one day of exposure.

$[K^+]_{TOT}$= 1.72 mM
$[Na^+]_{TOT}$= 76.60 mM
$[Mg^{2+}]_{TOT}$= 9.30 mM
$[Ca^{2+}]_{TOT}$= 2.26 mM
$[Fe^{2+}]_{TOT}$= 13.30 μM
$[Zn^{2+}]_{TOT}$= 0.76 μM
$[Cu^{2+}]_{TOT}$= 33.20 μM

I= 0.078 M
Log P_{CO_2} = -3.50
$[B(OH)_3]_{TOT}$= 0.39 mM
$[Br^-]_{TOT}$= 0.16 mM
$[NO_3^-]_{TOT}$= 3.39 μM
$[SO_4^{2-}]_{TOT}$= 7.02 mM
$[Cl^-]_{TOT}$= 94.50 mM

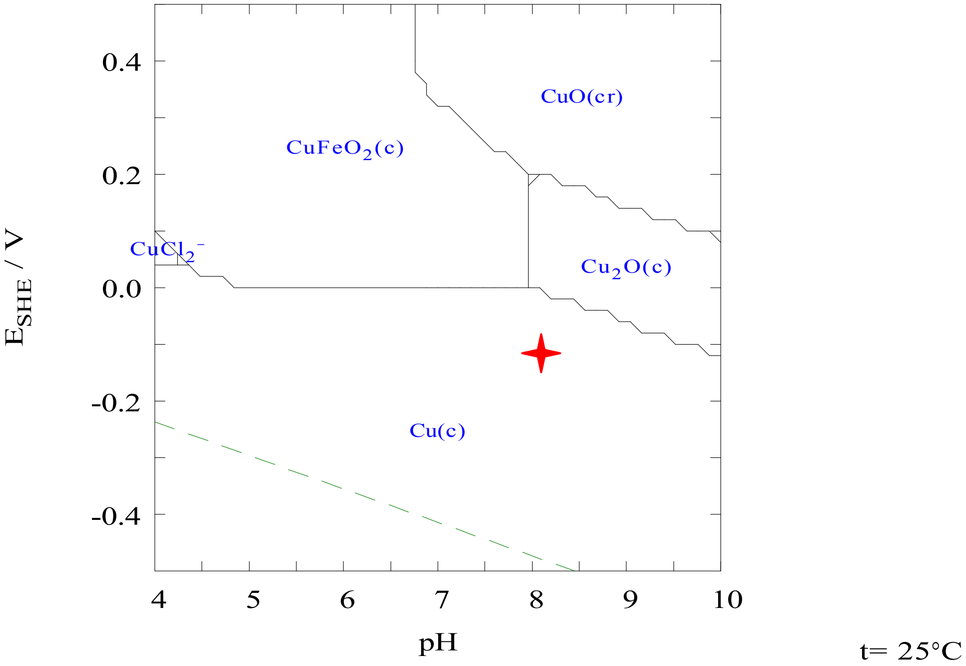


Figure C.320. Pourbaix diagram of copper for copper gutter section immersed into bay water after one day of exposure. Study area.

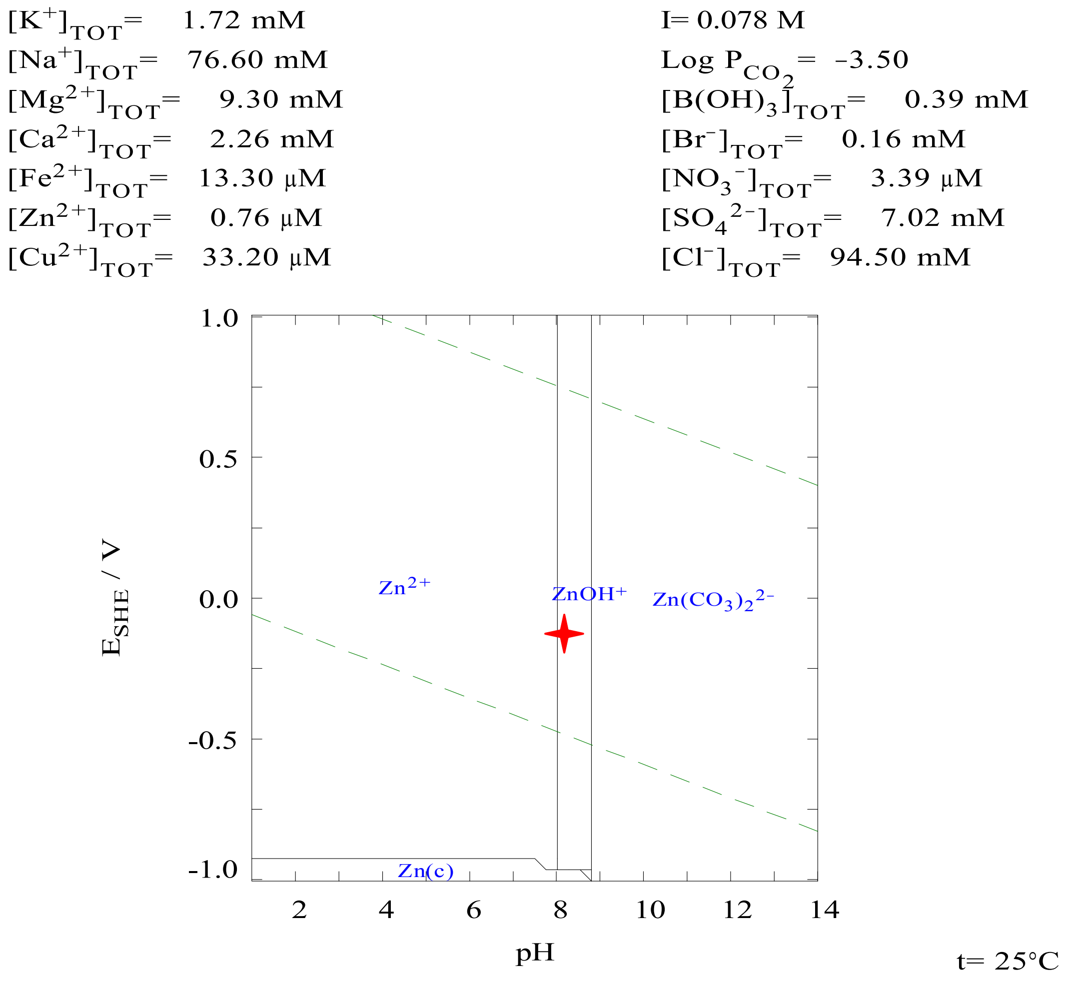


Figure C.321. Pourbaix diagram of zinc for copper gutter section immersed into bay water after one day of exposure.

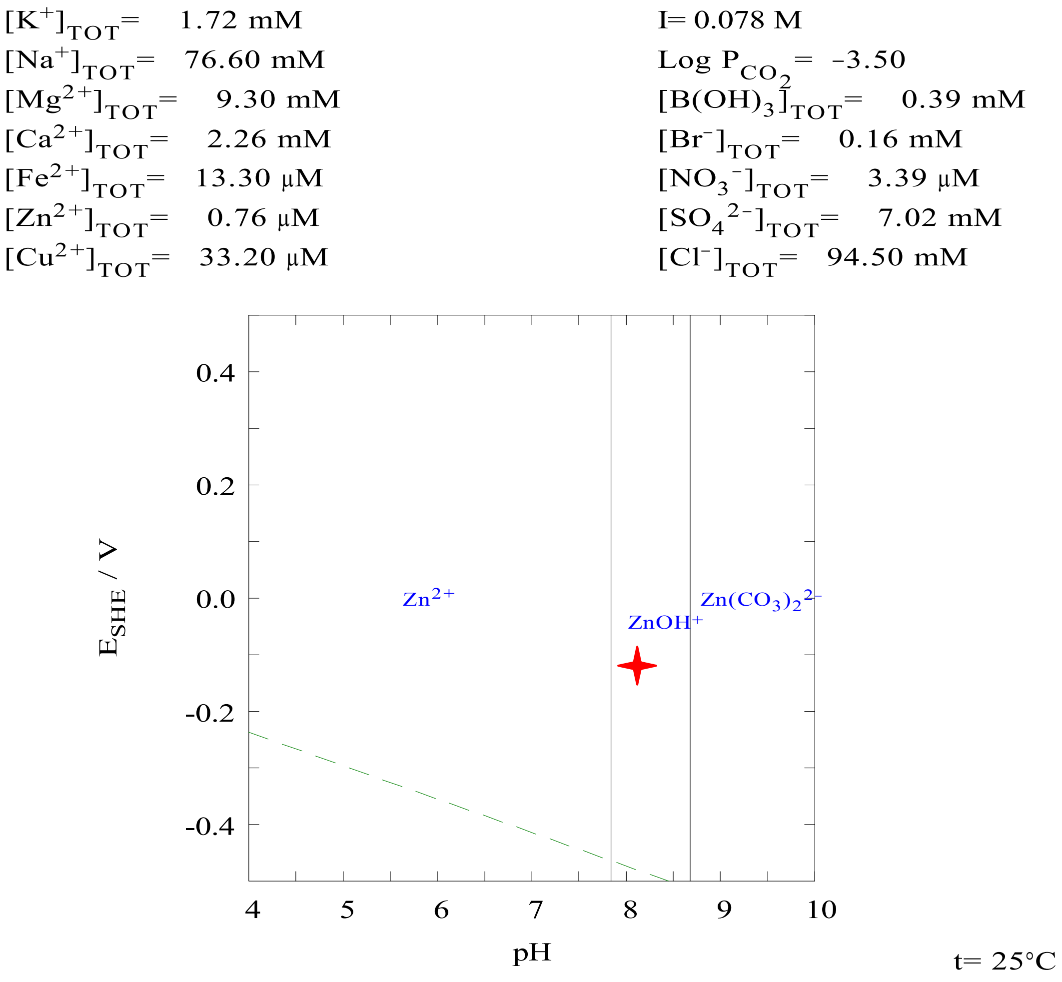


Figure C.322. Pourbaix diagram of zinc for copper gutter section immersed into bay water after one day of exposure. Study area.

Steel Pipe, River Water, After One Day of Exposure

I= 0.008 M

$[K^+]_{TOT}$ = 0.15 mM

$[Na^+]_{TOT}$ = 2.89 mM

$[Mg^{2+}]_{TOT}$ = 0.90 mM

$[Ca^{2+}]_{TOT}$ = 0.57 mM

$[Fe^{2+}]_{TOT}$ = 3.40 µM

$[Zn^{2+}]_{TOT}$ = 92.70 µM

E_H = -0.14 V

Log P_{CO_2} = -3.50

$[B(OH)_3]_{TOT}$ = 52.50 µM

$[Br^-]_{TOT}$ = 2.88 µM

$[NO_3^-]_{TOT}$ = 11.00 µM

$[F^-]_{TOT}$ = 14.70 µM

$[SO_4^{2-}]_{TOT}$ = 1.10 mM

$[Cl^-]_{TOT}$ = 2.51 mM

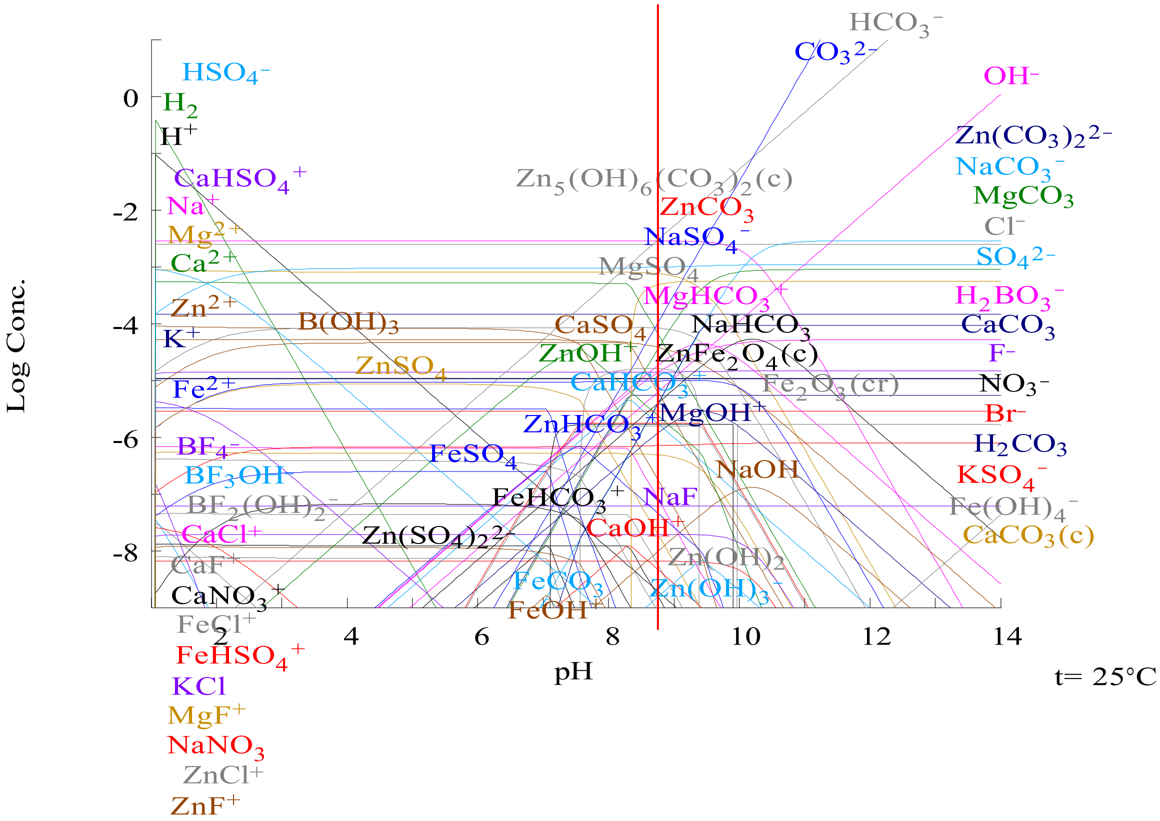


Figure C.323. Phase diagram for steel pipe section immersed into bay river after one day of exposure.

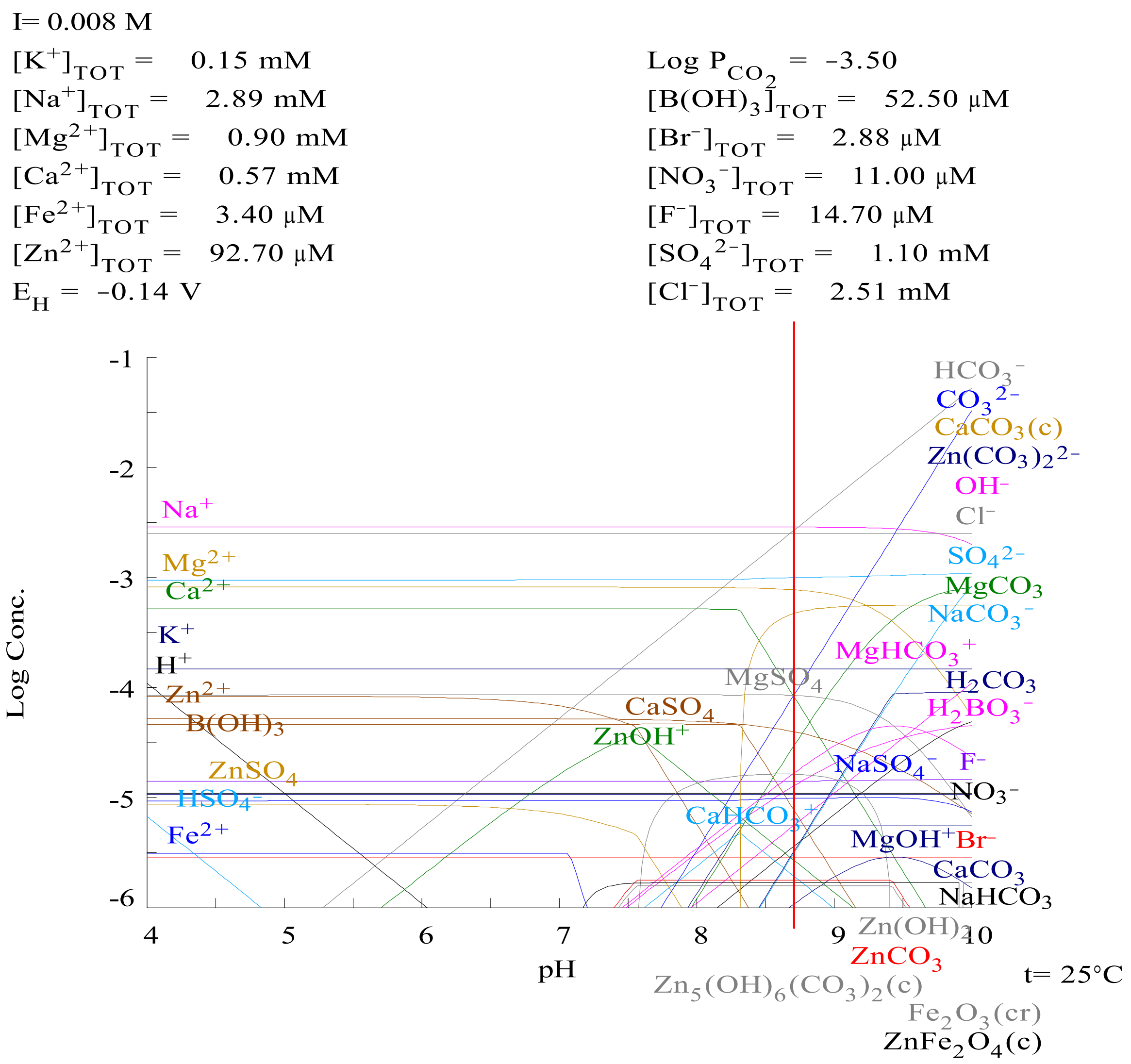
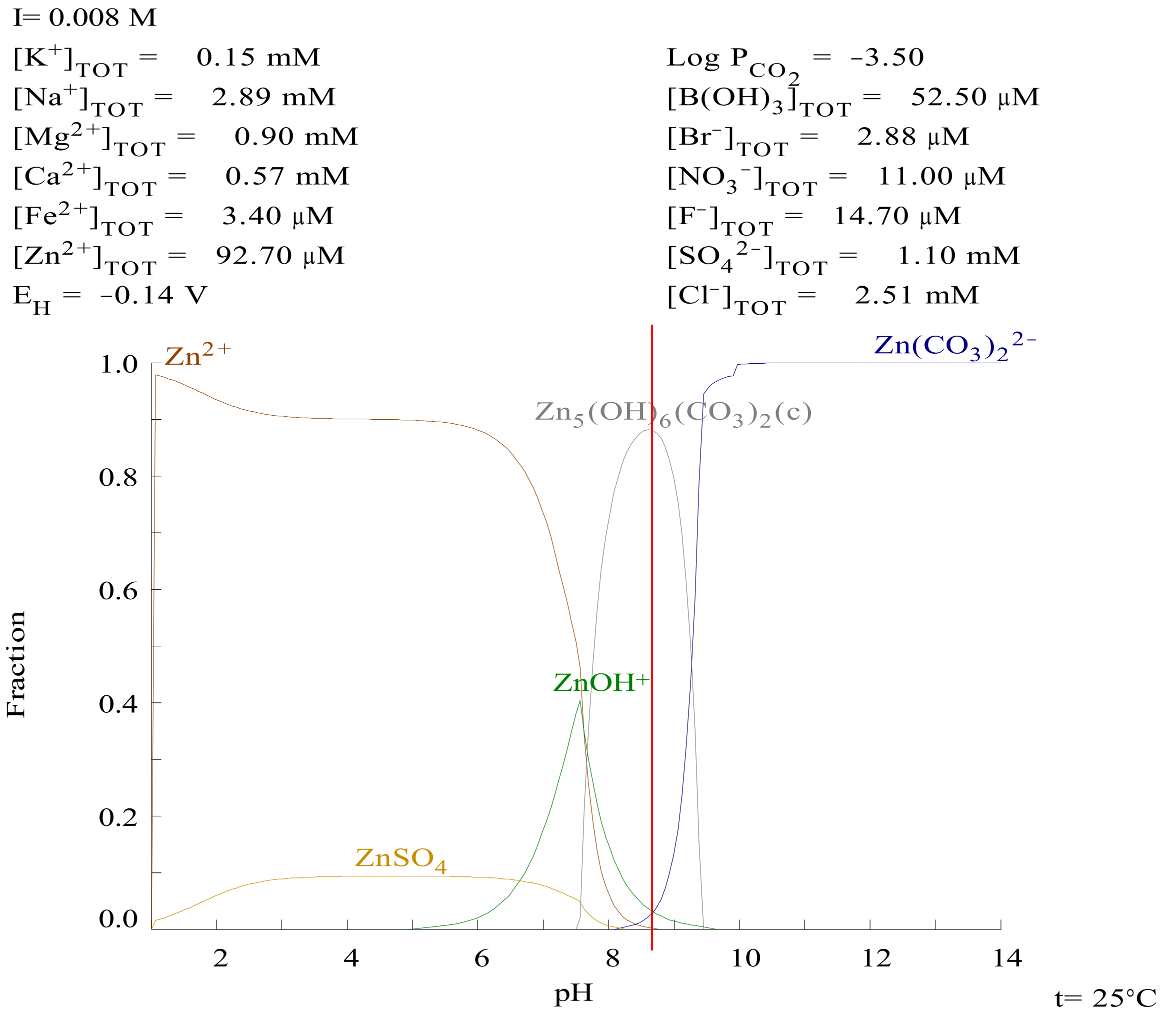


Figure C.324. Phase diagram for steel pipe section immersed into bay river after one day of exposure. Study area.

Table C.76. The predominant species of zinc. Steel pipe section, river water, one day exposure.

Component	Log Concentration (mol/L)	Concentration (mol/L)	Zn as Zn Concentration (mg/L)	Cumulative Percentage of Zn
$Zn_5(OH)_6(CO_3)_2(c)$	-4.79	1.62E-05	5.31E+00	87.59
$Zn(CO3)_2^{2-}$	-5.44	3.66E-06	2.39E-01	91.53
$ZnOH^+$	-5.60	2.53E-06	1.66E-01	94.26
$ZnCO_3$	-5.75	1.77E-06	1.16E-01	96.18
$ZnFe_2O_4(c)$	-5.77	1.70E-06	1.11E-01	98.01
$Zn(OH)_2$	-5.80	1.58E-06	1.03E-01	99.71
Zn^{2+}	-6.71	1.96E-07	1.28E-02	99.92



$I = 0.008$ M

$[K^+]_{TOT}$ = 0.15 mM

$[Na^+]_{TOT}$ = 2.89 mM

$[Mg^{2+}]_{TOT}$ = 0.90 mM

$[Ca^{2+}]_{TOT}$ = 0.57 mM

$[Fe^{2+}]_{TOT}$ = 3.40 μM

$[Zn^{2+}]_{TOT}$ = 92.70 μM

E_H = -0.14 V

Log P_{CO_2} = -3.50

$[B(OH)_3]_{TOT}$ = 52.50 μM

$[Br^-]_{TOT}$ = 2.88 μM

$[NO_3^-]_{TOT}$ = 11.00 μM

$[F^-]_{TOT}$ = 14.70 μM

$[SO_4^{2-}]_{TOT}$ = 1.10 mM

$[Cl^-]_{TOT}$ = 2.51 mM

Figure C.325. Fraction diagram of zinc for steel pipe section immersed into river water after one day of exposure.

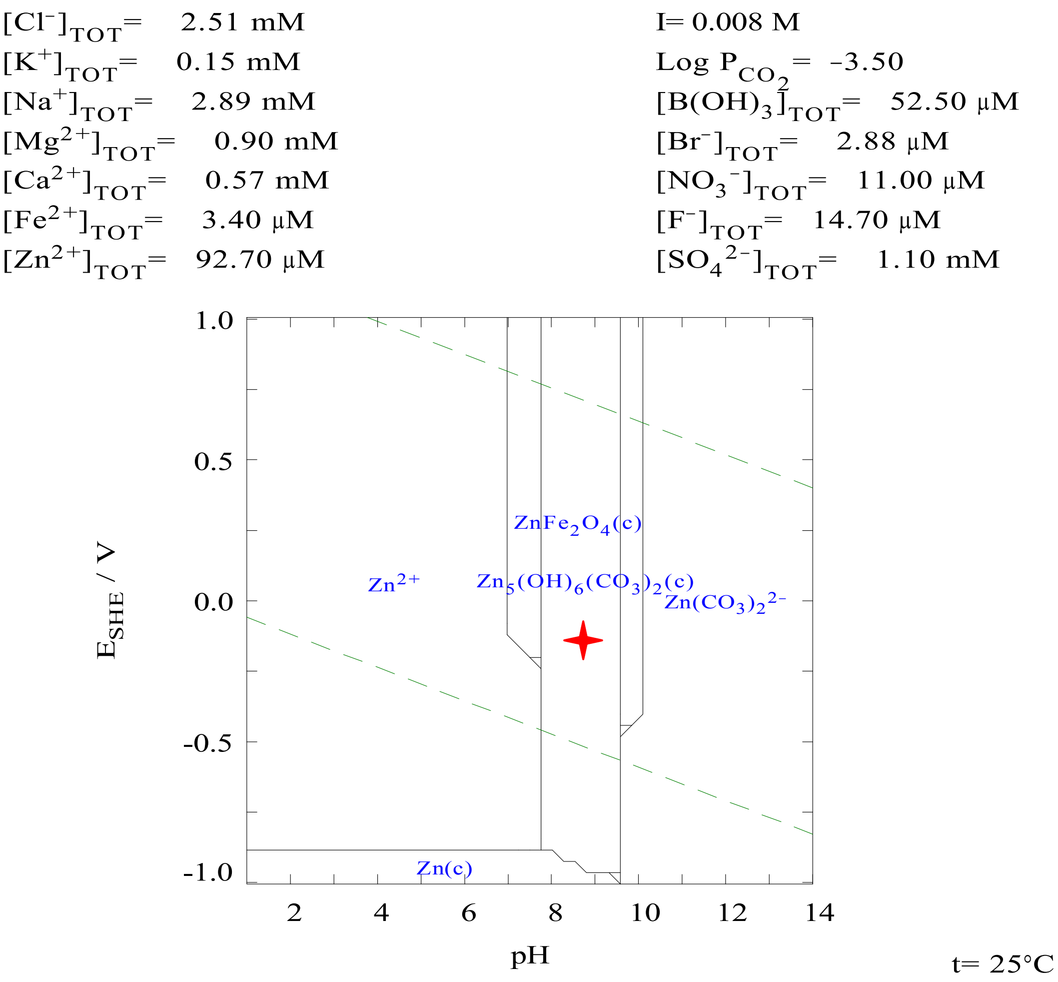


Figure C.326. Pourbaix diagram of zinc for steel pipe section immersed into river water after one day of exposure.

$[Cl^-]_{TOT}=$ 2.51 mM
$[K^+]_{TOT}=$ 0.15 mM
$[Na^+]_{TOT}=$ 2.89 mM
$[Mg^{2+}]_{TOT}=$ 0.90 mM
$[Ca^{2+}]_{TOT}=$ 0.57 mM
$[Fe^{2+}]_{TOT}=$ 3.40 µM
$[Zn^{2+}]_{TOT}=$ 92.70 µM

I= 0.008 M
Log $P_{CO_2}=$ -3.50
$[B(OH)_3]_{TOT}=$ 52.50 µM
$[Br^-]_{TOT}=$ 2.88 µM
$[NO_3^-]_{TOT}=$ 11.00 µM
$[F^-]_{TOT}=$ 14.70 µM
$[SO_4^{2-}]_{TOT}=$ 1.10 mM

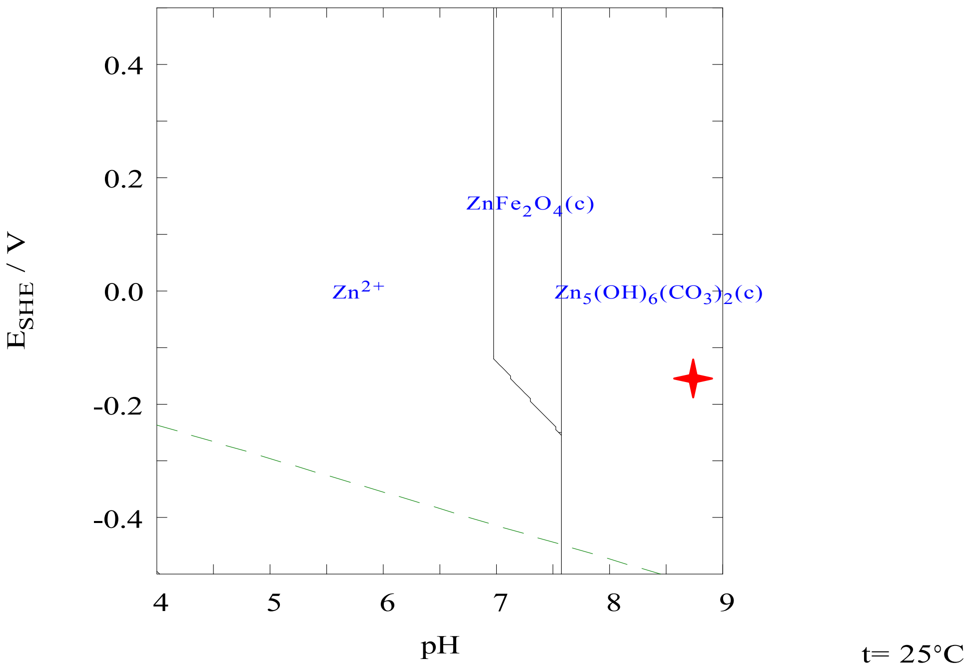


Figure C.327. Pourbaix diagram of zinc for steel pipe section immersed into river water after one day of exposure. Study area.

Steel Gutter, River Water, After One Day of Exposure

I= 0.007 M
$[K^+]_{TOT}$ = 0.15 mM
$[Na^+]_{TOT}$ = 2.89 mM
$[Mg^{2+}]_{TOT}$ = 0.87 mM
$[Ca^{2+}]_{TOT}$ = 0.57 mM
$[Fe^{2+}]_{TOT}$ = 3.40 µM
$[Zn^{2+}]_{TOT}$ = 18.40 µM
E_H = -0.14 V

Log P_{CO_2} = -3.50
$[B(OH)_3]_{TOT}$ = 52.50 µM
$[Br^-]_{TOT}$ = 2.88 µM
$[NO_3{}^-]_{TOT}$ = 11.00 µM
$[F^-]_{TOT}$ = 14.70 µM
$[SO_4{}^{2-}]_{TOT}$ = 1.10 mM
$[Cl^-]_{TOT}$ = 2.51 mM

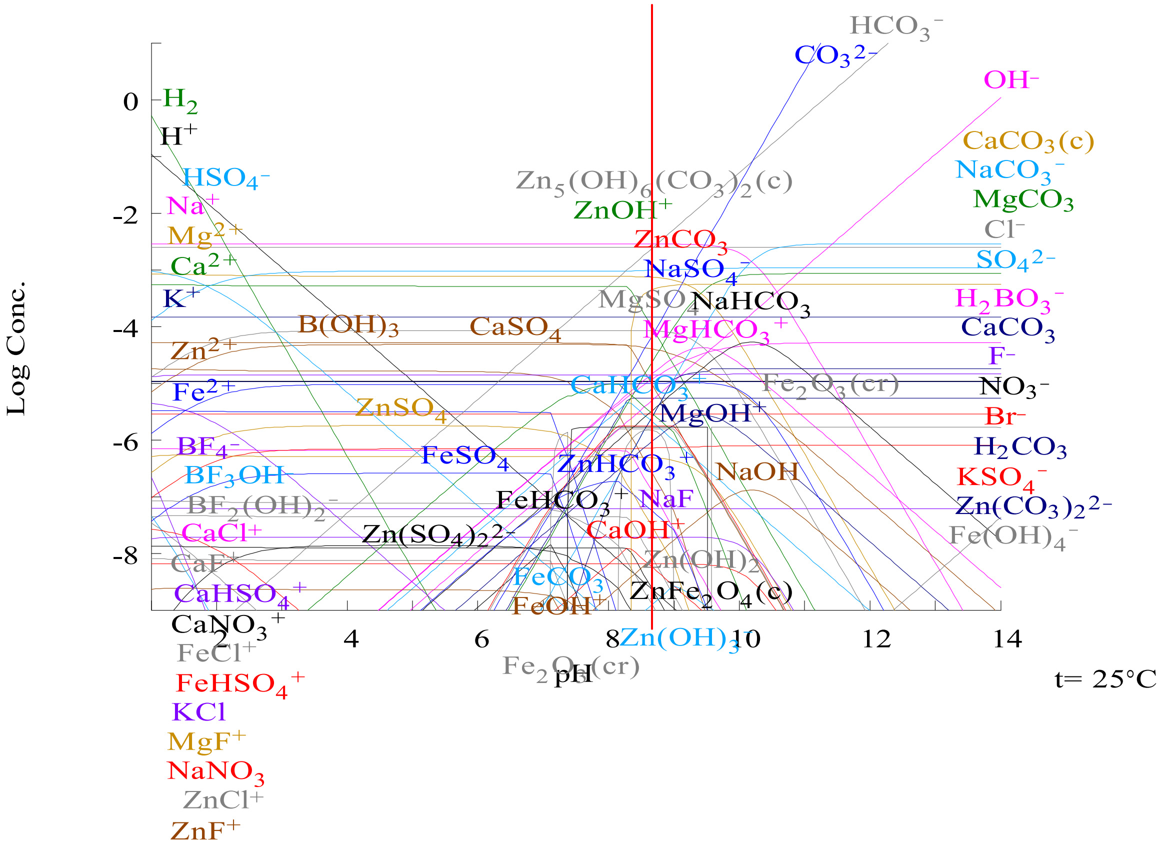


Figure C.328. Phase diagram for steel gutter section immersed into river water after one day of exposure.

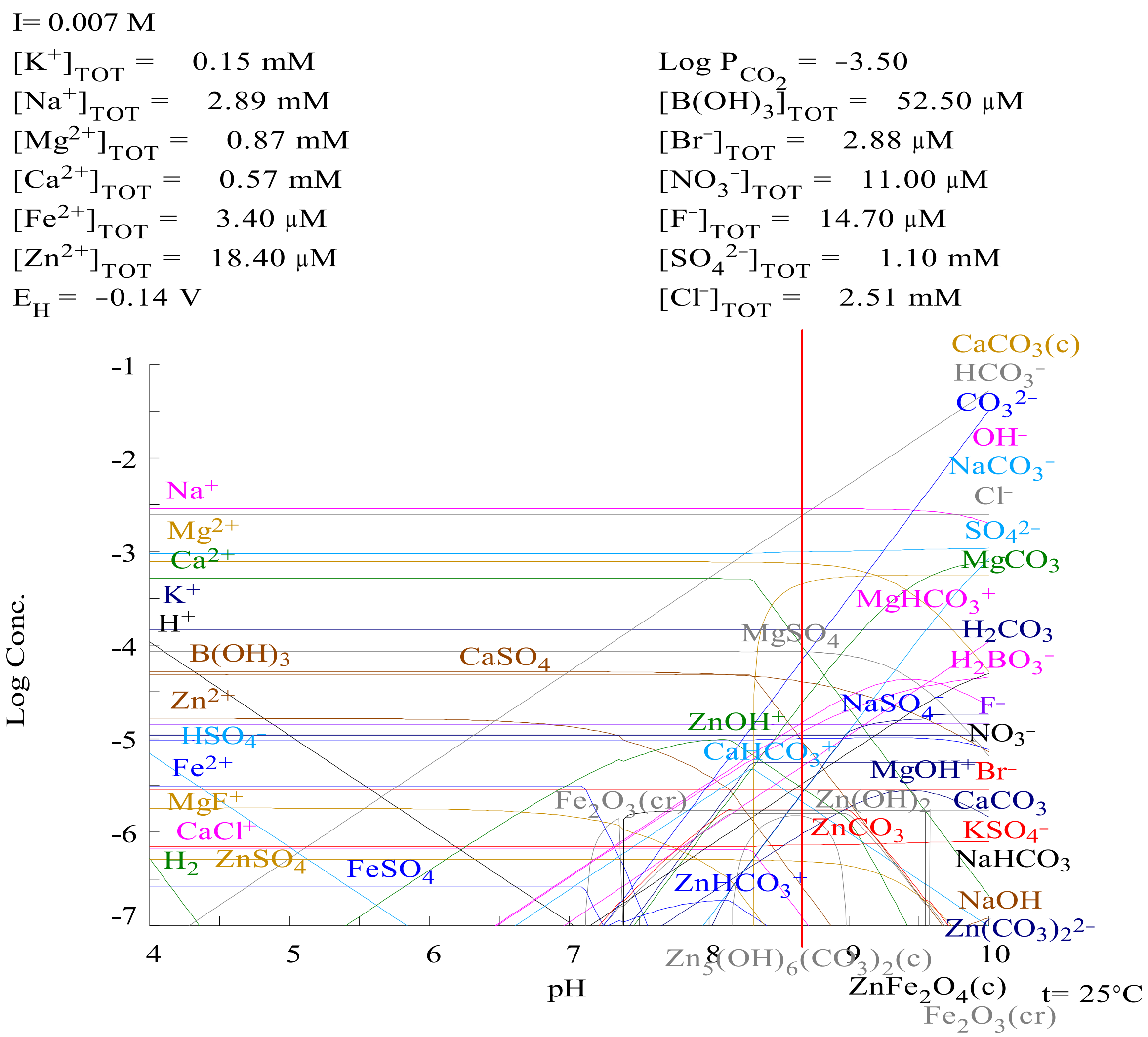


Figure C.329. Phase diagram for steel gutter section immersed into river water after one day of exposure. Study area.

Table C.77. The predominant species of zinc. Steel gutter section, river water, one day exposure.

Component	Log Concentration (mol/L)	Concentration (mol/L)	Zn as Zn Concentration (mg/L)	Cumulative Percentage of Zn
$Zn_5(OH)_6(CO_3)_2(c)$	-5.83	1.49E-06	4.86E-01	40.37
$ZnOH^+$	-5.53	2.92E-06	1.91E-01	56.26
$Zn(CO3)_2^{2-}$	-5.58	2.65E-06	1.74E-01	70.68
$ZnCO_3$	-5.75	1.77E-06	1.16E-01	80.31
$ZnFe_2O_4(c)$	-5.77	1.70E-06	1.11E-01	89.55
$Zn(OH)_2$	-5.80	1.58E-06	1.03E-01	98.12
Zn^{2+}	-6.59	2.58E-07	1.69E-02	99.52
$ZnHCO_3^+$	-7.25	5.57E-08	3.64E-03	99.82
$ZnSO_4$	-7.53	2.96E-08	1.94E-03	99.98

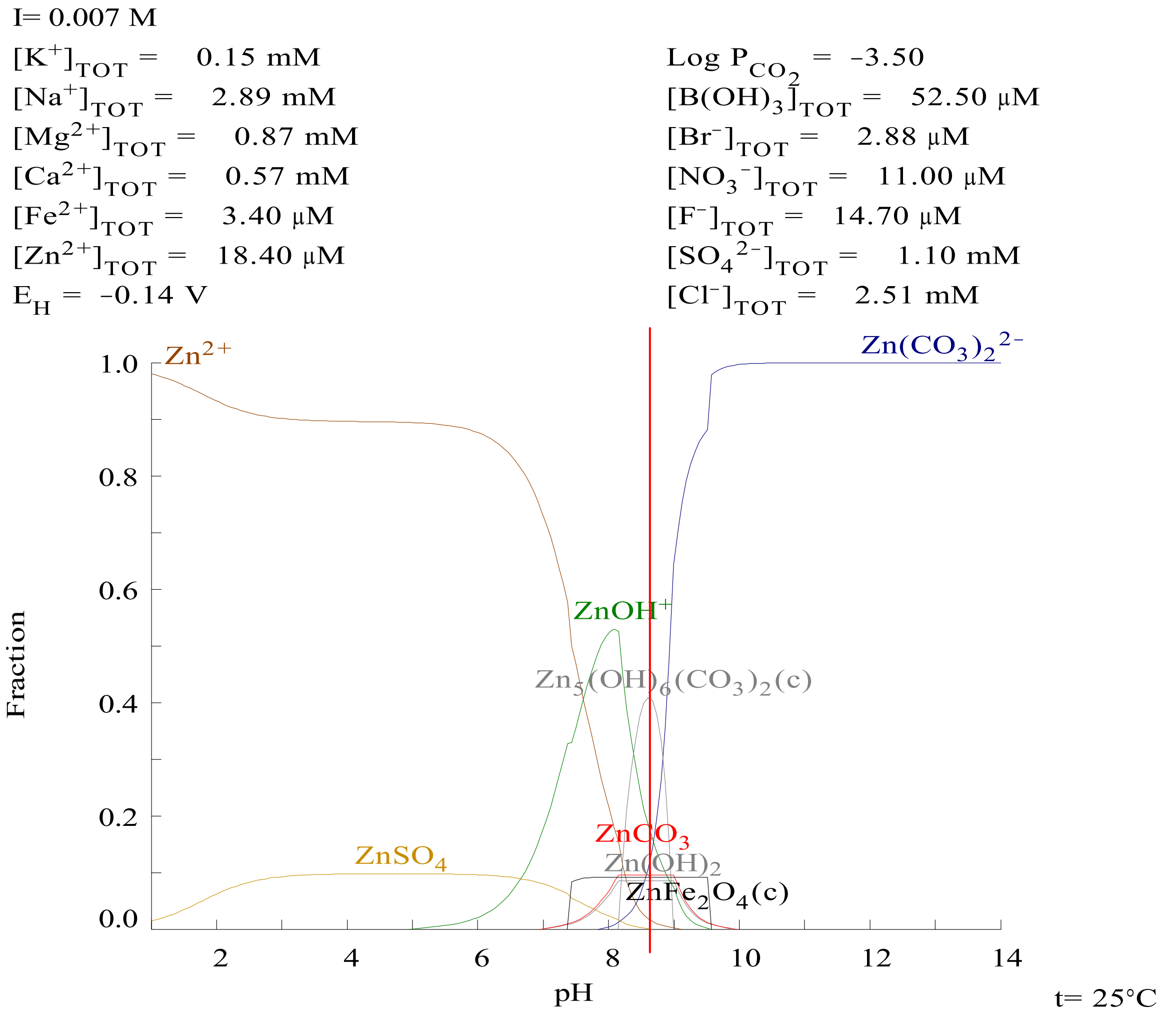


Figure C.330. Fraction diagram of zinc for steel gutter section immersed into river water after one day of exposure.

$[Cl^-]_{TOT}$ = 2.51 mM
$[K^+]_{TOT}$ = 0.15 mM
$[Na^+]_{TOT}$ = 2.89 mM
$[Mg^{2+}]_{TOT}$ = 0.87 mM
$[Ca^{2+}]_{TOT}$ = 0.57 mM
$[Fe^{2+}]_{TOT}$ = 3.40 μM
$[Zn^{2+}]_{TOT}$ = 18.40 μM

I = 0.007 M
Log P_{CO_2} = -3.50
$[B(OH)_3]_{TOT}$ = 52.50 μM
$[Br^-]_{TOT}$ = 2.88 μM
$[NO_3^-]_{TOT}$ = 11.00 μM
$[F^-]_{TOT}$ = 14.70 μM
$[SO_4^{2-}]_{TOT}$ = 1.10 mM

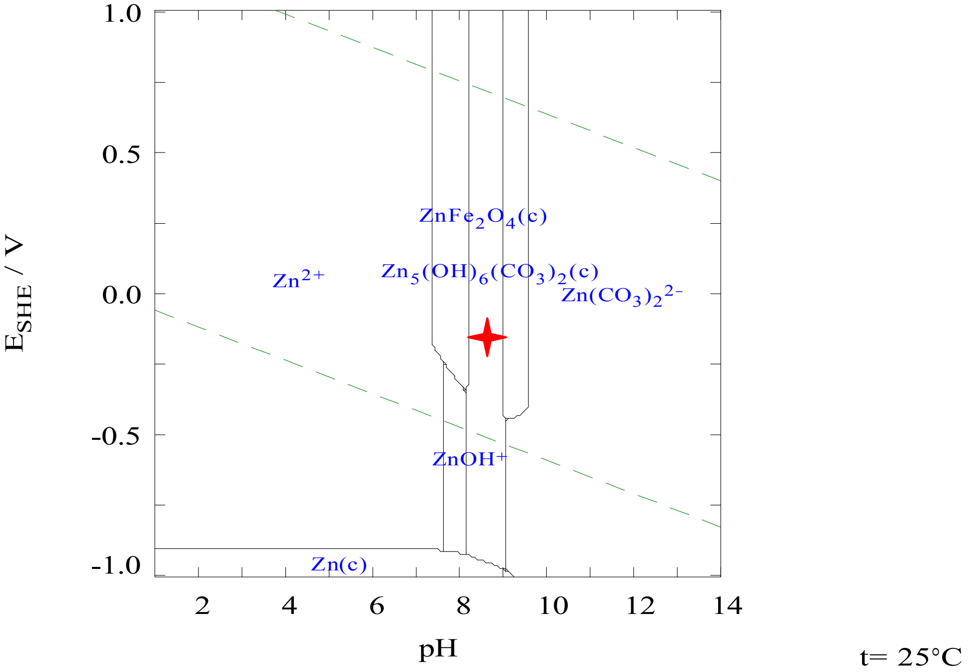


Figure C.331. Pourbaix diagram of zinc for steel gutter section immersed into river water after one day of exposure.

$[Cl^-]_{TOT}$= 2.51 mM
$[K^+]_{TOT}$= 0.15 mM
$[Na^+]_{TOT}$= 2.89 mM
$[Mg^{2+}]_{TOT}$= 0.87 mM
$[Ca^{2+}]_{TOT}$= 0.57 mM
$[Fe^{2+}]_{TOT}$= 3.40 μM
$[Zn^{2+}]_{TOT}$= 18.40 μM

I= 0.007 M
Log P_{CO_2}= -3.50
$[B(OH)_3]_{TOT}$= 52.50 μM
$[Br^-]_{TOT}$= 2.88 μM
$[NO_3^-]_{TOT}$= 11.00 μM
$[F^-]_{TOT}$= 14.70 μM
$[SO_4^{2-}]_{TOT}$= 1.10 mM

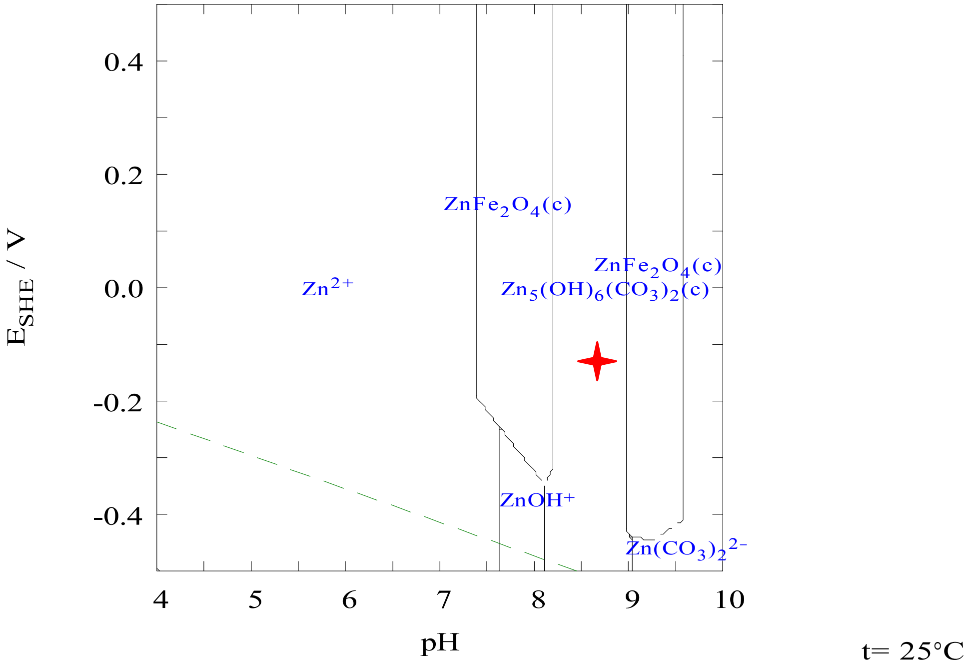


Figure C.332. Pourbaix diagram of zinc for steel gutter section immersed into river water after one day of exposure. Study area.

Copper Gutter, River Water, After One Day of Exposure

I= 0.009 M

$[Na^+]_{TOT}$ = 2.89 mM

$[Mg^{2+}]_{TOT}$ = 1.06 mM

$[Ca^{2+}]_{TOT}$ = 1.02 mM

$[Fe^{2+}]_{TOT}$ = 3.58 µM

$[Zn^{2+}]_{TOT}$ = 0.31 µM

$[Cu^{2+}]_{TOT}$ = 9.44 µM

E_H = -0.10 V

Log P_{CO_2} = -3.50

$[B(OH)_3]_{TOT}$ = 52.50 µM

$[Br^-]_{TOT}$ = 2.88 µM

$[NO_3^-]_{TOT}$ = 11.00 µM

$[SO_4^{2-}]_{TOT}$ = 1.10 mM

$[Cl^-]_{TOT}$ = 2.51 mM

$[K^+]_{TOT}$ = 0.15 mM

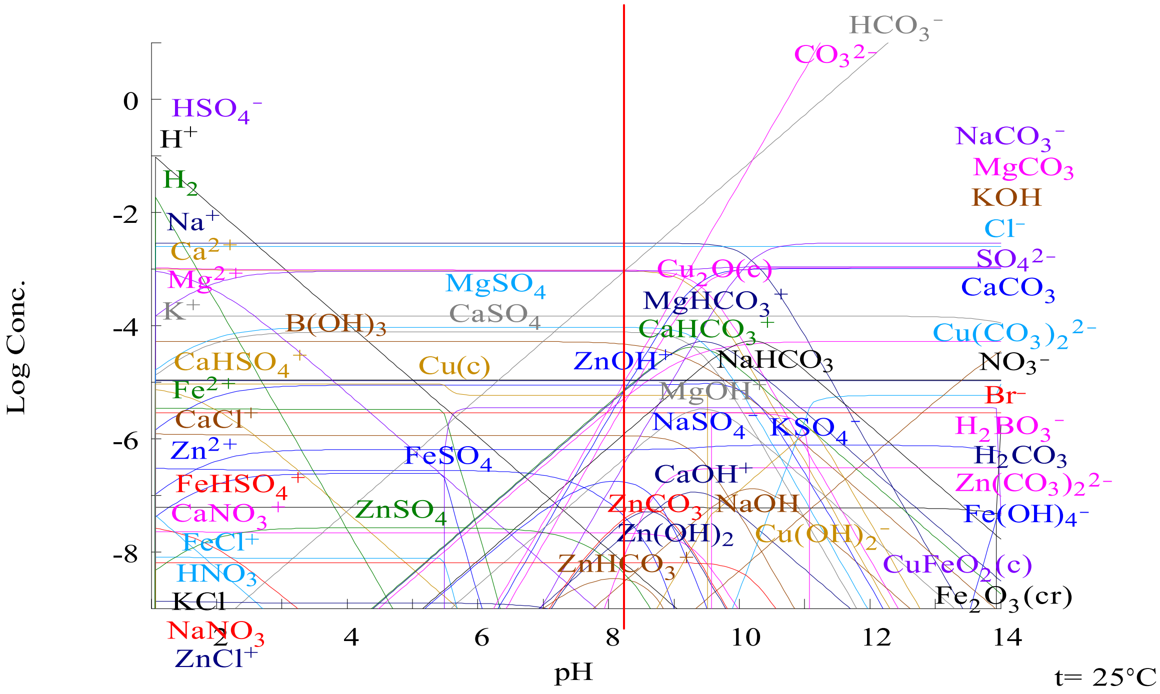


Figure C.333. Phase diagram for copper gutter section immersed into river after one day of exposure.

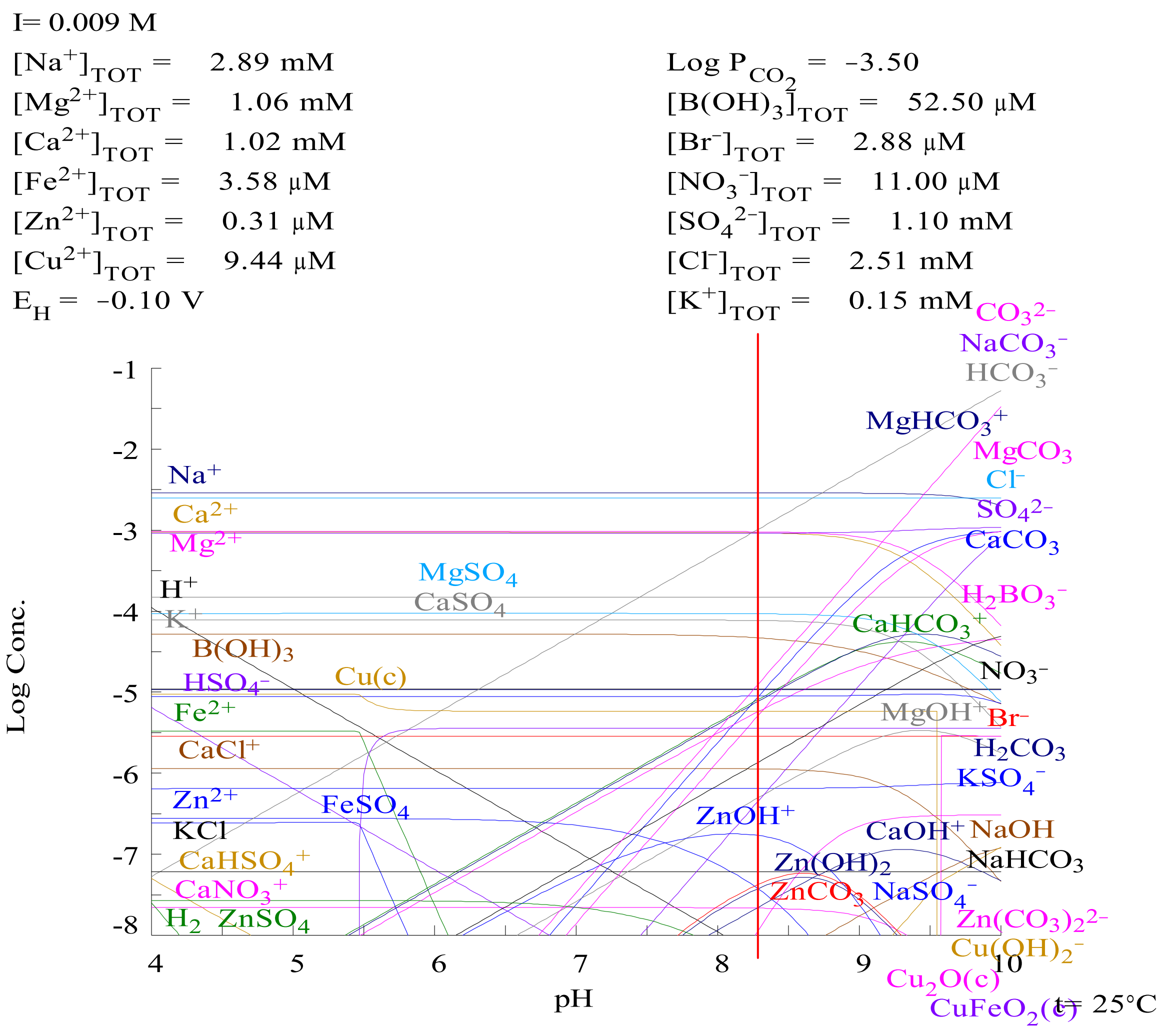


Figure C.334. Phase diagram for copper gutter section immersed into river after one day of exposure. Study area.

Table C.78. The predominant species of copper. Copper gutter section, river water, one day exposure.

Component	Log Concentration (mol/L)	Concentration (mol/L)	Cu as Cu Concentration (mg/L)	Cumulative Percentage of Cu
Cu(c)	-5.23	5.86E-06	3.72E-01	62.07
$CuFeO_2$(c)	-5.45	3.58E-06	2.27E-01	99.997

Table C.79. The predominant species of zinc. Copper gutter section, river water, one day exposure.

Component	Log Concentration (mol/L)	Concentration (mol/L)	Zn as Zn Concentration (mg/L)	Cumulative Percentage of Zn
$ZnOH^+$	-6.77	1.71E-07	1.12E-02	55.76
$ZnCO_3$	-7.38	4.17E-08	2.73E-03	69.39
Zn^{2+}	-7.42	3.82E-08	2.50E-03	81.87
$Zn(OH)_2$	-7.43	3.71E-08	2.43E-03	94.0
$Zn(CO3)_2^{2-}$	-7.97	1.08E-08	7.07E-04	97.53
$ZnSO_4$	-8.43	3.72E-09	2.43E-04	98.75
$ZnHCO_3^+$	-8.49	3.25E-09	2.13E-04	99.81
ZnClOH	-9.43	3.68E-10	2.41E-05	99.93

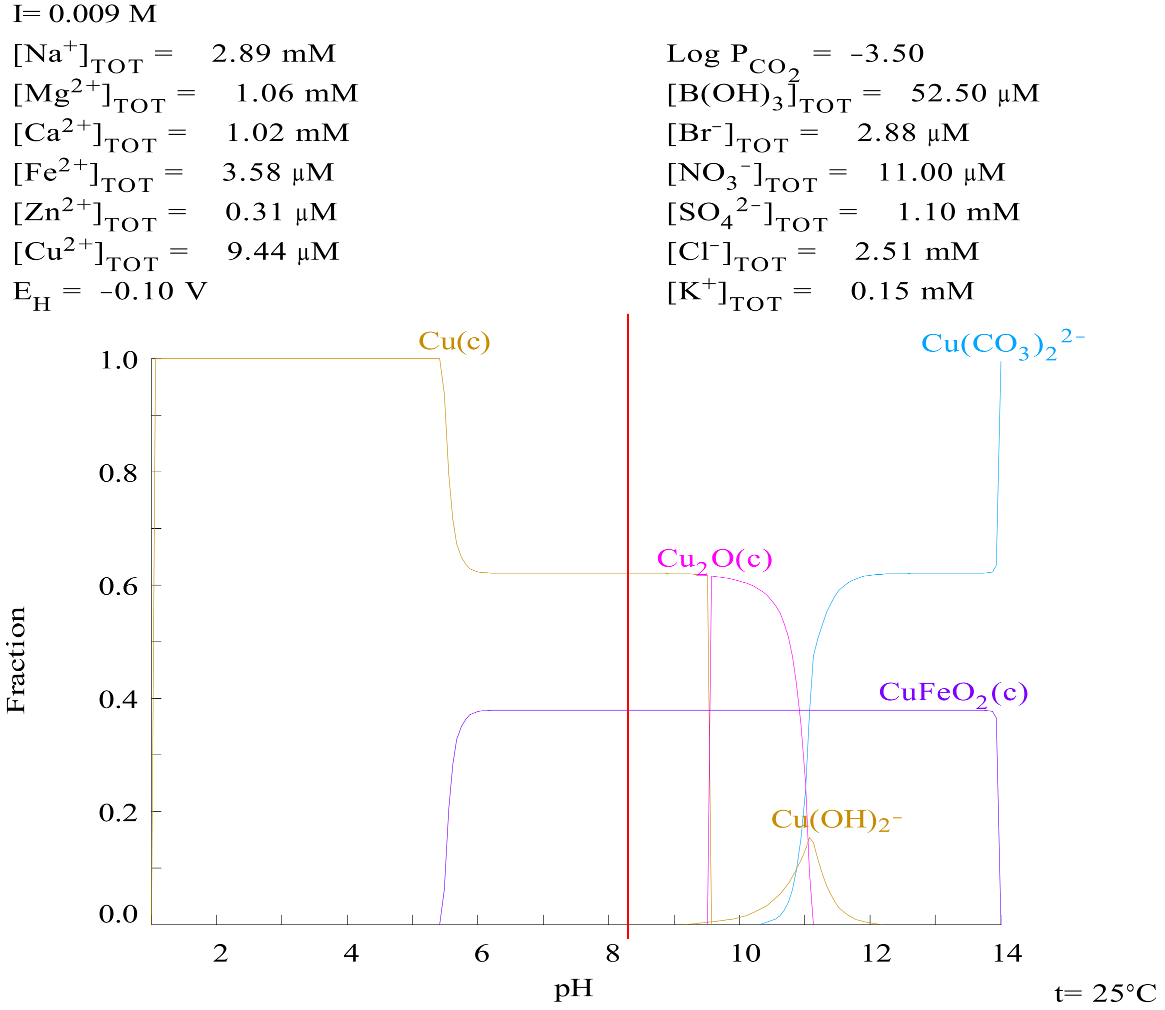


Figure C.335. Fraction diagram of copper for copper gutter section immersed into river water after one day of exposure.

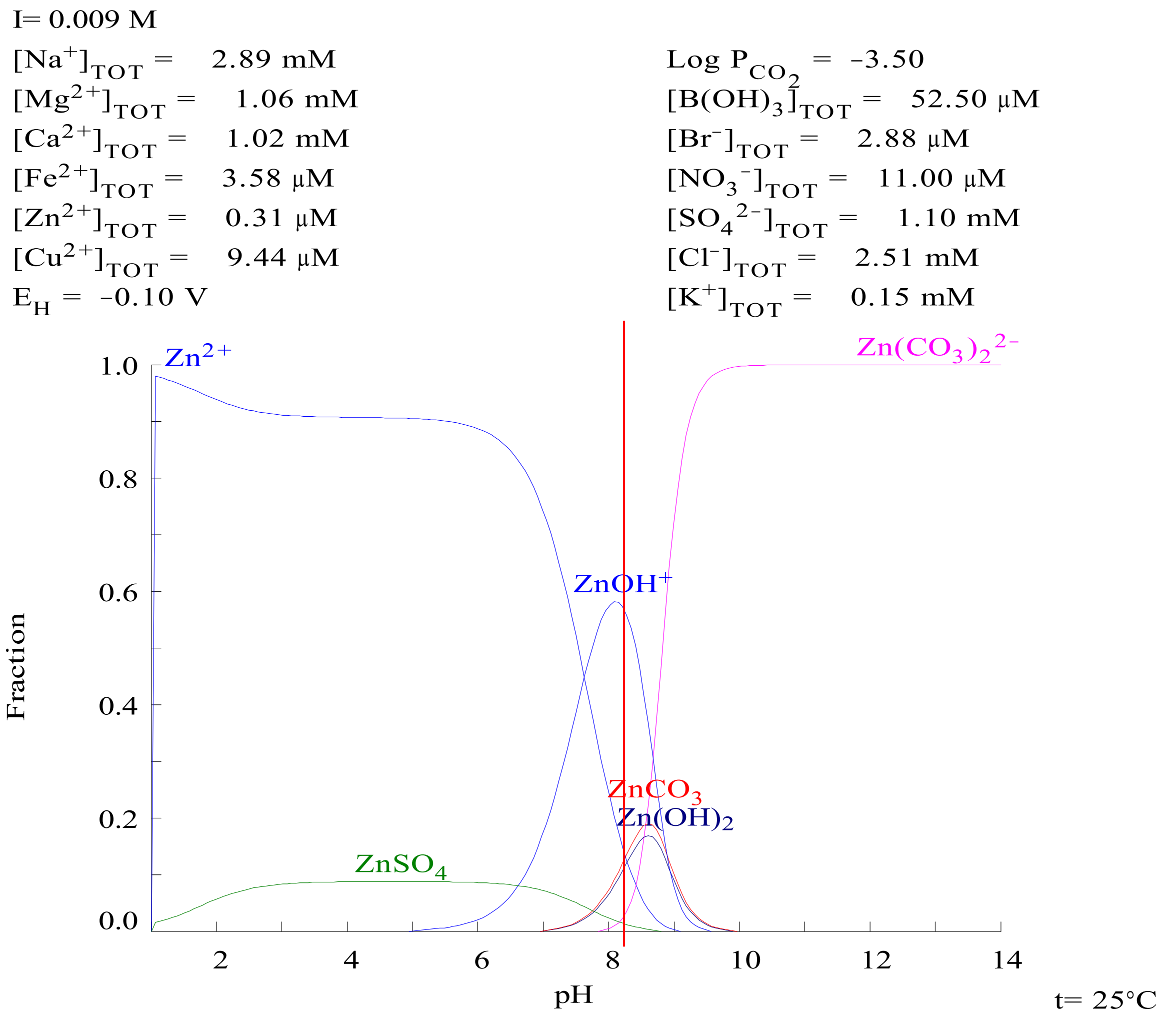


Figure C.336. Fraction diagram of zinc for copper gutter section immersed into river water after one day of exposure.

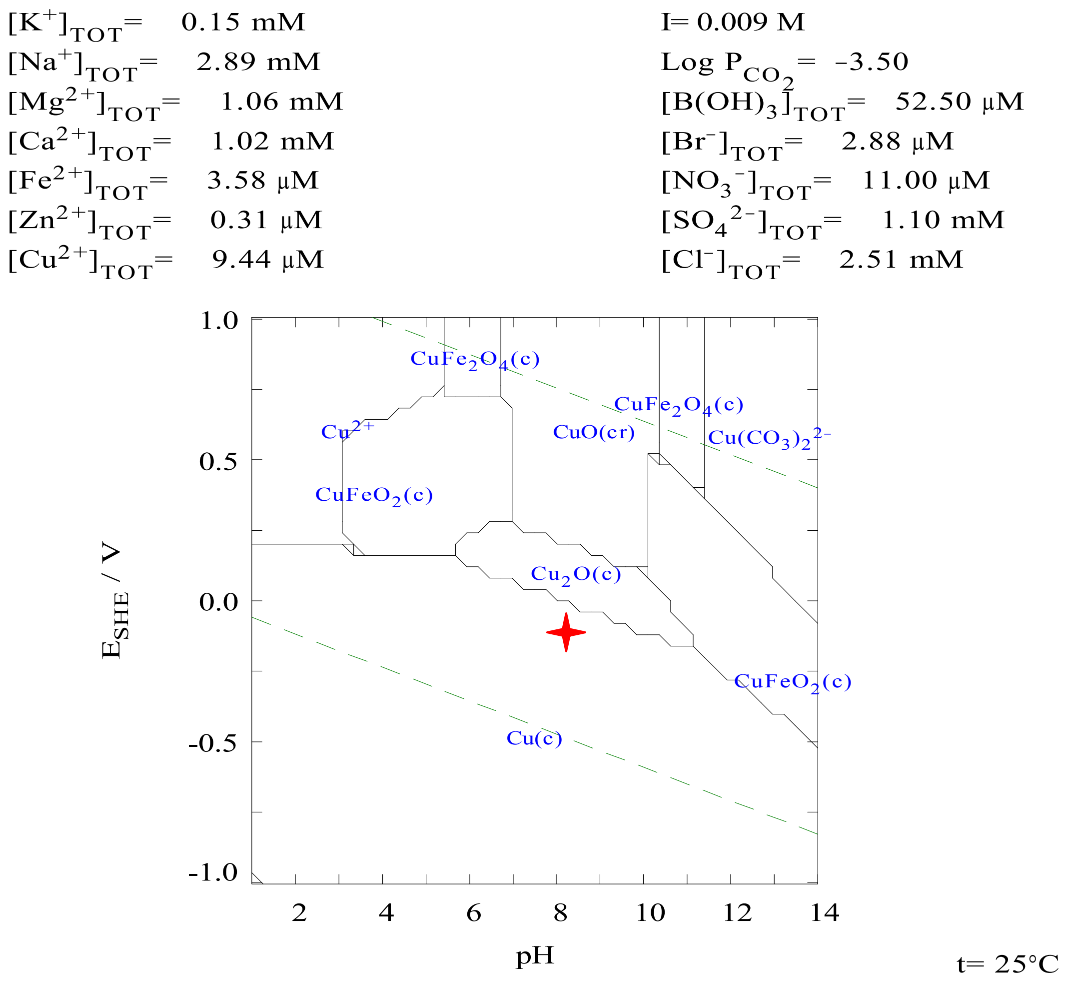


Figure C.337. Pourbaix diagram of copper for copper gutter section immersed into river water after one day of exposure.

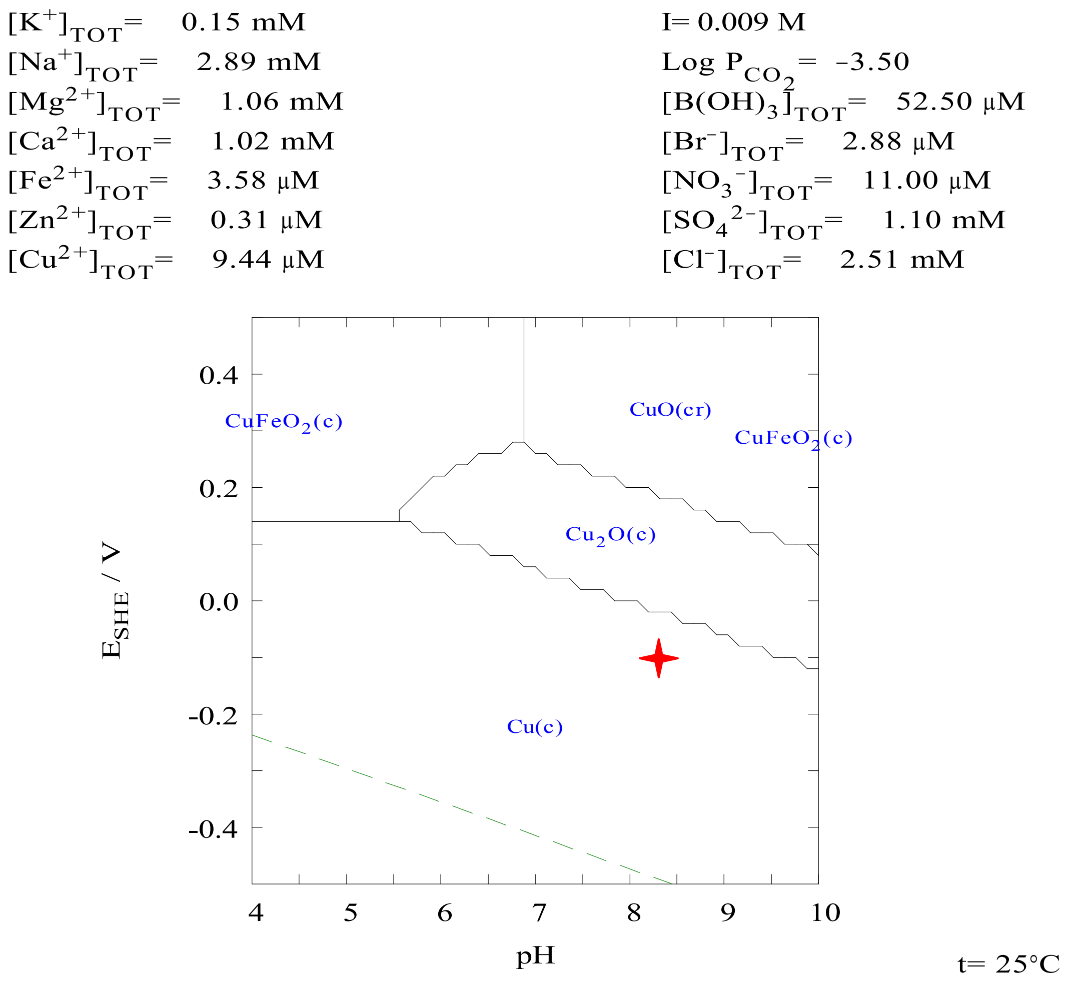


Figure C.338. Pourbaix diagram of copper for copper gutter section immersed into river water after one day of exposure. Study area.

$[K^+]_{TOT}$= 0.15 mM
$[Na^+]_{TOT}$= 2.89 mM
$[Mg^{2+}]_{TOT}$= 1.06 mM
$[Ca^{2+}]_{TOT}$= 1.02 mM
$[Fe^{2+}]_{TOT}$= 3.58 μM
$[Zn^{2+}]_{TOT}$= 0.31 μM
$[Cu^{2+}]_{TOT}$= 9.44 μM

I= 0.007 M
Log P_{CO_2}= -3.50
$[B(OH)_3]_{TOT}$= 52.50 μM
$[Br^-]_{TOT}$= 2.88 μM
$[NO_3^-]_{TOT}$= 11.00 μM
$[SO_4^{2-}]_{TOT}$= 1.10 mM
$[Cl^-]_{TOT}$= 2.51 mM

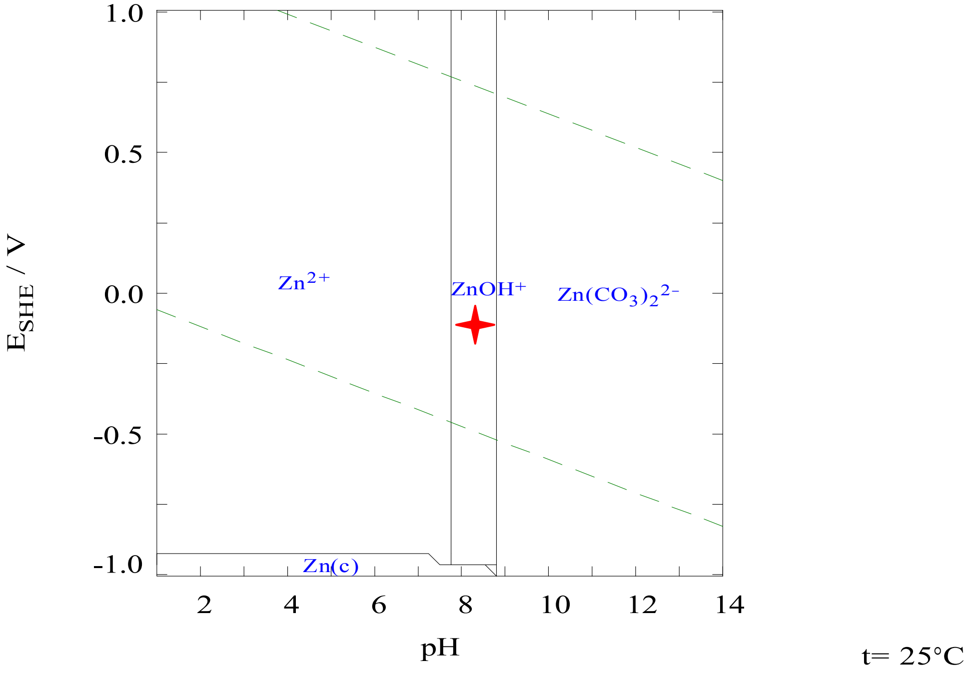


Figure C.339. Pourbaix diagram of zinc for copper gutter section immersed into river water after one day of exposure.

$[K^+]_{TOT}$= 0.15 mM
$[Na^+]_{TOT}$= 2.89 mM
$[Mg^{2+}]_{TOT}$= 1.06 mM
$[Ca^{2+}]_{TOT}$= 1.02 mM
$[Fe^{2+}]_{TOT}$= 3.58 μM
$[Zn^{2+}]_{TOT}$= 0.31 μM
$[Cu^{2+}]_{TOT}$= 9.44 μM

I= 0.009 M
Log P_{CO_2}= -3.50
$[B(OH)_3]_{TOT}$= 52.50 μM
$[Br^-]_{TOT}$= 2.88 μM
$[NO_3^-]_{TOT}$= 11.00 μM
$[SO_4^{2-}]_{TOT}$= 1.10 mM
$[Cl^-]_{TOT}$= 2.51 mM

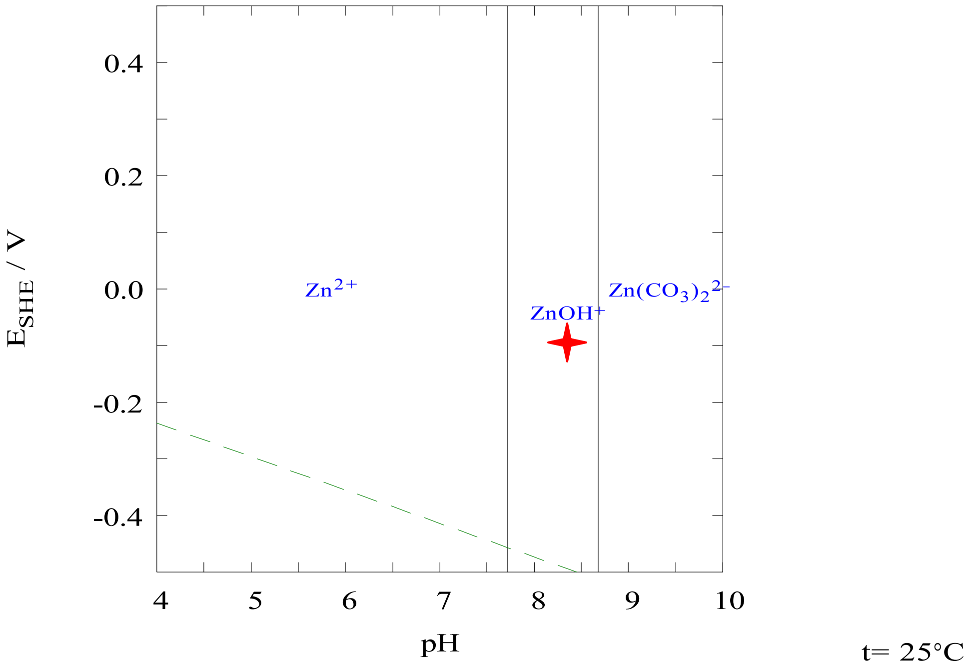


Figure C.340. Pourbaix diagram of zinc for copper gutter section immersed into river water after one day of exposure. Study area.

APPENDIX D: LANGELIER INDEX

Ionic strength was calculated using the formula (Snoeyink and Jenkins, 1980; Klyachko, 1971):

$\mu = 0.5\ \Sigma\ (C_iZ_i^2)$

Where,

Ci = concentration of ionic species i, mol/L

Zi = charge of species i

The Activity coefficients in aqueous solutions were calculated using both the DeBye-Huckel equation and theMaclinnes assumption.

The DeBye-Huckel equation can be used for ionic strength of less than approximately 0.1 (Snoeyink and Jenkins, 1980, Truesdell and Jones, 1974):

$-\log \gamma_i = A\ Z_i^2\ \mu^{1/2} / (1 + B\ \alpha_i \mu^{1/2})$

Where,

A = a constant that relates to the solvent

B = a constant that relates to the solvent

A = 0.509 at 25 °C (Snoeyink and Jenkins, 1980)

B = $0.328*10^8$ at 25 °C (Snoeyink and Jenkins, 1980)

α_i = the quantity dependent upon the “effective diameter” of the ion in solution (Garrels and Christ, 1990). For Ca^{2+}, α_i = 6.00E-08; for HCO_3^-, α_i = 4.00E-08 (Garrels and Christ, 1990).

Also, activity coefficients in aqueous solutions were calculated using theMaclinnes assumption, which offers information of the behavior of single-ion activities at higher concentrations (Truesdell and Jones, 1974):

$\log\gamma_i = - A Z_i^2 \mu^{1/2} / (1 + B \alpha_i \mu^{1/2}) + b_i \mu$

Where,

A, B, α_i are the same as in the DeBye-Huckel equation.

b_i = an adjustable parameter for concentrated solutions. For Ca^{2+}, $b_i = 0.165$; for HCO_3^-, $b_i = 0$ (Truesdell and Jones, 1974).

APPENDIX E: TOXICITY DATA

Table E.1. Toxicity effect of eight different NaCl additions to a composite of three stormwater samples.

NaCl (g) added per 10 mL composite sample	Toxicity Effect, %			
	at 5 min	at 15 min	at 25 min	at 45 min
0.1	68.90	73.80	81.14	86.28
0.1	67.07	71.08	75.75	81.71
Ave.	67.99	72.44	78.45	84.00
St. Dev.	1.29	1.92	3.81	3.23
COV	0.019	0.027	0.049	0.038
0.2	41.46	44.88	46.11	46.04
0.2	33.23	35.84	37.13	35.98
Ave.	37.35	40.36	41.62	41.01
St. Dev.	5.82	6.39	6.35	7.11
COV	0.156	0.158	0.153	0.173
0.3	25.00	25.90	28.14	25.00
0.3	26.83	27.71	29.04	25.91
Ave.	25.92	26.81	28.59	25.46
St. Dev.	1.29	1.28	0.64	0.64
COV	0.050	0.048	0.022	0.025
0.4	35.98	38.55	48.80	56.10
0.4	38.72	44.88	54.19	60.67
Ave.	37.35	41.72	51.50	58.39
St. Dev.	1.94	4.48	3.81	3.23
COV	0.052	0.107	0.074	0.055
0.5	51.52	53.92	54.19	54.27
0.5	52.44	54.82	57.78	57.01
Ave.	51.98	54.37	55.99	55.64
St. Dev.	0.65	0.64	2.54	1.94
COV	0.013	0.012	0.045	0.035
0.6	67.99	69.28	71.26	72.56
0.6	67.07	68.37	73.95	78.05
Ave.	67.53	68.83	72.61	75.31
St. Dev.	0.65	0.64	1.90	3.88
COV	0.010	0.009	0.026	0.052
0.7	79.88	80.12	81.14	82.62
0.7	79.88	80.12	82.04	82.62
Ave.	79.88	80.12	81.59	82.62
St. Dev.	0.00	0.00	0.64	0.00

COV	0.000	0.000	0.008	0.000
0.8	88.11	88.25	90.12	90.85
0.8	89.94	90.96	92.81	94.51
Ave.	89.03	89.61	91.47	92.68
St. Dev.	1.29	1.92	1.90	2.59
COV	0.015	0.021	0.021	0.028

Table E.2. Toxicity effect of different $ZnSO_4$ concentrations.

ZnSO4, mg/L	Toxicity Effect, %			
	at 5 min	at 15 min	at 25 min	at 45 min
0.1	-0.68	5.69	6.76	2.53
0.1	-0.68	8.70	11.82	13.36
Ave.	-0.68	7.20	9.29	7.95
St. Dev.	0.00	2.13	3.58	7.66
COV	0.000	0.296	0.385	0.964
0.2	-3.77	10.70	21.96	30.69
0.2	-4.79	14.72	23.99	30.69
Ave.	-4.28	12.71	22.98	30.69
St. Dev.	0.72	2.84	1.44	0.00
COV				
0.4	14.73	47.83	64.53	79.42
0.4	13.70	46.82	62.50	78.34
Ave.	14.22	47.33	63.52	78.88
St. Dev.	0.73	0.71	1.44	0.76
COV	0.051	0.015	0.023	0.010
0.6	13.70	44.82	64.53	81.59
0.6	10.62	44.82	64.53	81.59
Ave.	12.16	44.82	64.53	81.59
St. Dev.	2.18	0.00	0.00	0.00
COV	0.179	0.000	0.000	0.000
0.8	23.97	52.84	67.57	83.75
0.8	33.22	58.86	71.62	85.92
Ave.	28.60	55.85	69.60	84.84
St. Dev.	6.54	4.26	2.86	1.53
COV	0.229	0.076	0.041	0.018
1	36.30	59.87	70.61	83.75
1	38.36	60.87	70.61	84.84
Ave.	37.33	60.37	70.61	84.30
St. Dev.	1.46	0.71	0.00	0.77
COV	0.039	0.012	0.000	0.009

Table E.3. Toxicity effect of different phenol concentrations.

Phenol, mg/L	Toxicity Effect, %			
	at 5 min	at 15 min	at 25 min	at 45 min
0.2	-9.93	-13.38	-13.51	-12.64
0.2	-10.96	-16.39	-16.55	-20.22
Ave.	-10.45	-14.89	-15.03	-16.43
St. Dev.	0.73	2.13	2.15	5.36
COV	-0.070	-0.143	-0.143	-0.326
3	12.67	10.70	7.77	7.94
3	13.70	10.70	8.78	9.03
Ave.	13.19	10.70	8.28	8.49
St. Dev.	0.73	0.00	0.71	0.77
COV	0.055	0.000	0.086	0.091
6	25.00	23.75	25.00	23.10
6	23.97	21.74	20.95	20.94
Ave.	24.49	22.75	22.98	22.02
St. Dev.	0.73	1.42	2.86	1.53
COV	0.030	0.062	0.125	0.069
9	29.11	26.76	27.03	27.44
9	32.19	31.77	35.14	38.27
Ave.	30.65	29.27	31.09	32.86
St. Dev.	2.18	3.54	5.73	7.66
COV	0.071	0.121	0.184	0.233
15	12.67	9.70	13.85	16.61
15	6.51	3.68	4.73	5.78
Ave.	9.59	6.69	9.29	11.20
St. Dev.	4.36	4.26	6.45	7.66
COV	0.454	0.636	0.694	0.684

Table E.4. Toxicity effect of different samples. pH 5 water. Time zero

Sample	Toxicity Effect, %			
	at 5 min	at 15 min	at 25 min	at 45 min
P. Concrete	92.28	95.59	95.47	97.62
P. Concrete	92.28	94.49	95.47	97.62
Ave.	92.28	95.04	95.47	97.62
St. Dev.	0.00	0.78	0.00	0.00
COV	0.000	0.008	0.000	0.000
P. PVC	94.21	97.79	98.87	100.00
P. PVC	94.21	97.79	97.74	100.00
Ave.	94.21	97.79	98.30	100.00
St. Dev.	0.00	0.00	0.80	0.00
COV	0.000	0.000	0.008	0.000
P. HDPE	95.18	97.79	98.87	100.00
P. HDPE	94.21	96.69	97.74	98.81
Ave.	94.69	97.24	98.30	99.40
St. Dev.	0.68	0.78	0.80	0.84
COV	0.007	0.008	0.008	0.008
P. Steel	94.21	96.69	97.74	100.00
P. Steel	95.18	97.79	97.74	100.00
Ave.	94.69	97.24	97.74	100.00
St. Dev.	0.68	0.78	0.00	0.00
COV	0.007	0.008	0.000	0.000
G. Vinyl	94.21	96.69	97.74	98.81
G. Vinyl	96.14	97.79	98.87	100.00
Ave.	95.18	97.24	98.30	99.40
St. Dev.	1.36	0.78	0.80	0.84
COV	0.014	0.008	0.008	0.008
G. Aluminum	96.14	98.90	98.87	100.00
G. Aluminum	96.14	97.79	98.87	100.00
Ave.	96.14	98.35	98.87	100.00
St. Dev.	0.00	0.78	0.00	0.00
COV	0.000	0.008	0.000	0.000
G. Steel	96.14	97.79	98.87	100.00
G. Steel	96.14	97.79	98.87	100.00
Ave.	96.14	97.79	98.87	100.00
St. Dev.	0.00	0.00	0.00	0.00
COV	0.000	0.000	0.000	0.000
G. Copper	95.18	96.69	97.74	98.81
G. Copper	95.18	96.69	97.74	98.81
Ave.	95.18	96.69	97.74	98.81
St. Dev.	0.00	0.00	0.00	0.00
COV	0.000	0.000	0.000	0.000

Table E.5. Toxicity effect of different samples. pH 5 water. 0.5 hour of exposure

Sample	Toxicity Effect, %			
	at 5 min	at 15 min	at 25 min	at 45 min
P. Concrete	90.35	91.18	92.08	95.24
P. Concrete	90.35	91.18	93.21	95.24
Ave.	90.35	91.18	92.64	95.24
St. Dev.	0.00	0.00	0.80	0.00
COV	0.000	0.000	0.009	0.000
P. PVC	95.18	96.69	97.74	98.81
P. PVC	96.14	97.79	98.87	100.00
Ave.	95.66	97.24	98.30	99.40
St. Dev.	0.68	0.78	0.80	0.84
COV	0.007	0.008	0.008	0.008
P. HDPE	95.18	96.69	97.74	98.81
P. HDPE	95.18	96.69	97.74	98.81
Ave.	95.18	96.69	97.74	98.81
St. Dev.	0.00	0.00	0.00	0.00
COV	0.000	0.000	0.000	0.000
P. Steel	99.00	100.00	100.00	98.03
P. Steel	100.00	100.00	99.01	98.03
Ave.	99.50	100.00	99.50	98.03
St. Dev.	0.71	0.00	0.70	0.00
COV	0.007	0.000	0.007	0.000
G. Vinyl	94.00	97.05	99.01	98.03
G. Vinyl	93.00	96.07	99.01	99.01
Ave.	93.50	96.56	99.01	98.52
St. Dev.	0.71	0.70	0.00	0.70
COV	0.008	0.007	0.000	0.007
G. Aluminum	95.00	98.03	100.00	98.03
G. Aluminum	96.00	99.02	100.00	97.04
Ave.	95.50	98.52	100.00	97.53
St. Dev.	0.71	0.70	0.00	0.70
COV	0.007	0.007	0.000	0.007
G. Steel	97.00	99.02	100.00	98.03
G. Steel	96.00	99.02	100.00	98.03
Ave.	96.50	99.02	100.00	98.03
St. Dev.	0.71	0.00	0.00	0.00
COV	0.007	0.000	0.000	0.000
G. Copper	96.00	100.00	99.01	97.04
G. Copper	96.00	100.00	99.01	97.04
Ave.	96.00	100.00	99.01	97.04
St. Dev.	0.00	0.00	0.00	0.00
COV	0.000	0.000	0.000	0.000

Table E.6. Toxicity effect of different samples. pH 5 water. One hour of exposure

Sample	Toxicity Effect, %			
	at 5 min	at 15 min	at 25 min	at 45 min
P. Concrete	82.00	84.26	86.09	91.12
P. Concrete	80.00	82.30	85.10	89.14
Ave.	81.00	83.28	85.60	90.13
St. Dev.	1.41	1.39	0.70	1.40
COV	0.017	0.017	0.008	0.015
P. PVC	86.00	90.16	91.06	99.01
P. PVC	89.00	92.13	96.03	100.00
Ave.	87.50	91.15	93.54	99.51
St. Dev.	2.12	1.39	3.51	0.70
COV	0.024	0.015	0.038	0.007
P. HDPE	92.00	94.10	97.02	100.00
P. HDPE	92.00	96.07	98.01	99.01
Ave.	92.00	95.08	97.52	99.51
St. Dev.	0.00	1.39	0.70	0.70
COV	0.000	0.015	0.007	0.007
P. Steel	98.00	99.02	100.00	98.03
P. Steel	98.00	100.00	100.00	98.03
Ave.	98.00	99.51	100.00	98.03
St. Dev.	0.00	0.70	0.00	0.00
COV	0.000	0.007	0.000	0.000
G. Vinyl	93.00	96.07	99.01	99.01
G. Vinyl	93.00	96.07	99.01	98.03
Ave.	93.00	96.07	99.01	98.52
St. Dev.	0.00	0.00	0.00	0.70
COV	0.000	0.000	0.000	0.007
G. Aluminum	94.00	98.03	100.00	98.03
G. Aluminum	95.00	98.03	100.00	98.03
Ave.	94.50	98.03	100.00	98.03
St. Dev.	0.71	0.00	0.00	0.00
COV	0.007	0.000	0.000	0.000
G. Steel	93.88	96.67	97.69	98.79
G. Steel	93.88	96.67	97.69	100.00
Ave.	93.88	96.67	97.69	99.40
St. Dev.	0.00	0.00	0.00	0.86
COV	0.000	0.000	0.000	0.009
G. Copper	95.92	97.78	100.00	100.00
G. Copper	95.92	97.78	100.00	100.00
Ave.	95.92	97.78	100.00	100.00
St. Dev.	0.00	0.00	0.00	0.00
COV	0.000	0.000	0.000	0.000

Table E.7. Toxicity effect of different samples. pH 5 water. 27 hours of exposure

Sample	Toxicity Effect, %			
	at 5 min	at 15 min	at 25 min	at 45 min
P. Concrete	59.18	57.78	58.46	60.08
P. Concrete	61.22	60.00	59.62	62.50
Ave.	60.20	58.89	59.04	61.29
St. Dev.	1.44	1.57	0.82	1.71
COV	0.024	0.027	0.014	0.028
P. PVC	89.80	92.22	94.23	96.37
P. PVC	88.78	92.22	94.23	96.37
Ave.	89.29	92.22	94.23	96.37
St. Dev.	0.72	0.00	0.00	0.00
COV	0.008	0.000	0.000	0.000
P. HDPE	92.86	95.56	97.69	98.79
P. HDPE	93.88	96.67	97.69	98.79
Ave.	93.37	96.11	97.69	98.79
St. Dev.	0.72	0.79	0.00	0.00
COV	0.008	0.008	0.000	0.000
P. Steel	80.61	82.22	83.85	87.90
P. Steel	81.63	82.22	85.00	87.90
Ave.	81.12	82.22	84.42	87.90
St. Dev.	0.72	0.00	0.82	0.00
COV	0.009	0.000	0.010	0.000
G. Vinyl	93.88	96.67	97.69	98.79
G. Vinyl	94.90	96.67	97.69	98.79
Ave.	94.39	96.67	97.69	98.79
St. Dev.	0.72	0.00	0.00	0.00
COV	0.008	0.000	0.000	0.000
G. Aluminum	94.90	97.78	98.85	100.00
G. Aluminum	95.92	97.78	98.85	100.00
Ave.	95.41	97.78	98.85	100.00
St. Dev.	0.72	0.00	0.00	0.00
COV	0.008	0.000	0.000	0.000
G. Steel	85.71	86.67	89.62	92.74
G. Steel	84.69	87.78	89.62	91.53
Ave.	85.20	87.22	89.62	92.14
St. Dev.	0.72	0.79	0.00	0.86
COV	0.008	0.009	0.000	0.009
G. Copper	95.92	97.78	100.00	100.00
G. Copper	95.92	98.89	100.00	100.00
Ave.	95.92	98.33	100.00	100.00
St. Dev.	0.00	0.79	0.00	0.00
COV	0.000	0.008	0.000	0.000

Table E.8. Toxicity effect of different samples. pH 5 water. One month of exposure

Sample	Toxicity Effect, %			
	at 5 min	at 15 min	at 25 min	at 45 min
P. Concrete	14.15	-2.60	-7.76	-8.33
P. Concrete	10.46	-5.95	-11.43	-16.67
Ave.	12.31	-4.28	-9.59	-12.50
St. Dev.	2.61	2.37	2.60	5.89
COV	0.212	-0.553	-0.271	-0.471
P. PVC	78.77	82.16	86.53	90.28
P. PVC	78.77	83.27	87.76	90.28
Ave.	78.77	82.71	87.14	90.28
St. Dev.	0.00	0.79	0.87	0.00
COV	0.000	0.010	0.010	0.000
P. HDPE	89.85	93.31	96.33	98.61
P. HDPE	88.00	92.19	95.10	98.61
Ave.	88.92	92.75	95.71	98.61
St. Dev.	1.31	0.79	0.87	0.00
COV	0.015	0.009	0.009	0.000
P. Steel	41.85	34.20	32.65	37.50
P. Steel	42.77	30.86	30.20	36.11
Ave.	42.31	32.53	31.43	36.81
St. Dev.	0.65	2.37	1.73	0.98
COV	0.015	0.073	0.055	0.027
G. Vinyl	88.92	93.31	96.33	98.61
G. Vinyl	89.85	93.31	96.33	98.61
Ave.	89.38	93.31	96.33	98.61
St. Dev.	0.65	0.00	0.00	0.00
COV	0.007	0.000	0.000	0.000
G. Aluminum	88.92	92.19	96.33	98.61
G. Aluminum	88.92	93.31	96.33	98.61
Ave.	88.92	92.75	96.33	98.61
St. Dev.	0.00	0.79	0.00	0.00
COV	0.000	0.009	0.000	0.000
G. Steel	62.15	60.97	62.04	66.67
G. Steel	59.38	57.62	58.37	63.89
Ave.	60.77	59.29	60.20	65.28
St. Dev.	1.96	2.37	2.60	1.96
COV	0.032	0.040	0.043	0.030
G. Copper	84.31	87.73	92.65	98.61
G. Copper	83.38	85.50	90.20	95.83
Ave.	83.85	86.62	91.43	97.22
St. Dev.	0.65	1.58	1.73	1.96
COV	0.008	0.018	0.019	0.020

Table E.9. Toxicity effect of different samples. pH 5 water. Two months of exposure

Sample	Toxicity Effect, %			
	at 5 min	at 15 min	at 25 min	at 45 min
P. Concrete	11.44	0.44	-8.17	-13.09
P. Concrete	18.08	4.37	-3.85	-6.81
Ave.	14.76	2.40	-6.01	-9.95
St. Dev.	4.70	2.78	3.06	4.44
COV	0.318	1.157	-0.509	-0.447
P. PVC	83.39	86.90	89.90	93.72
P. PVC	81.18	85.59	89.90	92.15
Ave.	82.29	86.24	89.90	92.93
St. Dev.	1.57	0.93	0.00	1.11
COV	0.019	0.011	0.000	0.012
P. HDPE	91.14	94.76	97.12	100.00
P. HDPE	91.14	94.76	97.12	100.00
Ave.	91.14	94.76	97.12	100.00
St. Dev.	0.00	0.00	0.00	0.00
COV	0.000	0.000	0.000	0.000
P. Steel	54.61	47.60	45.19	48.17
P. Steel	54.61	46.29	43.75	46.60
Ave.	54.61	46.94	44.47	47.38
St. Dev.	0.00	0.93	1.02	1.11
COV	0.000	0.020	0.023	0.023
G. Vinyl	94.46	97.38	98.56	100.00
G. Vinyl	94.46	97.38	98.56	100.00
Ave.	94.46	97.38	98.56	100.00
St. Dev.	0.00	0.00	0.00	0.00
COV	0.000	0.000	0.000	0.000
G. Aluminum	94.46	97.38	98.56	100.00
G. Aluminum	93.36	97.38	98.56	100.00
Ave.	93.91	97.38	98.56	100.00
St. Dev.	0.78	0.00	0.00	0.00
COV	0.008	0.000	0.000	0.000
G. Steel	73.43	72.49	71.15	73.30
G. Steel	72.32	71.18	71.15	73.30
Ave.	72.88	71.83	71.15	73.30
St. Dev.	0.78	0.93	0.00	0.00
COV	0.011	0.013	0.000	0.000
G. Copper	88.93	92.14	95.67	98.43
G. Copper	90.04	93.45	95.67	98.43
Ave.	89.48	92.79	95.67	98.43
St. Dev.	0.78	0.93	0.00	0.00
COV	0.009	0.010	0.000	0.000

Table E.10. Toxicity effect of different samples. pH 5 water. Three months of exposure

Sample	Toxicity Effect, %			
	at 5 min	at 15 min	at 25 min	at 45 min
P. Concrete	12.94	1.54	-6.53	-9.31
P. Concrete	15.03	1.54	-5.31	-6.88
Ave.	13.99	1.54	-5.92	-8.10
St. Dev.	1.48	0.00	0.87	1.72
COV	0.106	0.000	-0.146	-0.212
P. PVC	80.07	84.94	88.98	92.71
P. PVC	79.02	83.78	87.76	92.71
Ave.	79.55	84.36	88.37	92.71
St. Dev.	0.74	0.82	0.87	0.00
COV	0.009	0.010	0.010	0.000
P. HDPE	89.51	95.37	97.55	100.00
P. HDPE	87.41	94.21	97.55	98.79
Ave.	88.46	94.79	97.55	99.39
St. Dev.	1.48	0.82	0.00	0.86
COV	0.017	0.009	0.000	0.009
P. Steel	30.77	23.55	24.08	34.41
P. Steel	26.57	18.92	17.96	31.98
Ave.	28.67	21.24	21.02	33.20
St. Dev.	2.97	3.28	4.33	1.72
COV	0.103	0.154	0.206	0.052
G. Vinyl	89.51	95.37	98.78	100.00
G. Vinyl	91.61	97.68	98.78	100.00
Ave.	90.56	96.53	98.78	100.00
St. Dev.	1.48	1.64	0.00	0.00
COV	0.016	0.017	0.000	0.000
G. Aluminum	91.61	96.53	98.78	100.00
G. Aluminum	92.66	96.53	98.78	100.00
Ave.	92.13	96.53	98.78	100.00
St. Dev.	0.74	0.00	0.00	0.00
COV	0.008	0.000	0.000	0.000
G. Steel	59.09	58.30	57.14	63.56
G. Steel	67.48	65.25	64.49	67.21
Ave.	63.29	61.78	60.82	65.38
St. Dev.	5.93	4.91	5.20	2.58
COV	0.094	0.080	0.085	0.039
G. Copper	84.27	89.58	93.88	97.57
G. Copper	84.27	89.58	93.88	97.57
Ave.	84.27	89.58	93.88	97.57
St. Dev.	0.00	0.00	0.00	0.00
COV	0.000	0.000	0.000	0.000

Table E.11. Toxicity effect of different samples. pH 8 water. Time zero

Sample	Toxicity Effect, %			
	at 5 min	at 15 min	at 25 min	at 45 min
P. Concrete	-14.29	-17.78	-23.46	-19.76
P. Concrete	-10.20	-22.22	-23.46	-24.60
Ave.	-12.24	-20.00	-23.46	-22.18
St. Dev.	2.89	3.14	0.00	3.42
COV	-0.236	-0.157	0.000	-0.154
P. PVC	-17.10	-17.24	-9.40	0.76
P. PVC	-15.99	-19.54	-10.53	-0.38
Ave.	-16.54	-18.39	-9.96	0.19
St. Dev.	0.79	1.63	0.80	0.81
COV	-0.048	-0.088	-0.080	4.243
P. HDPE	-40.52	-42.53	-40.98	-41.44
P. HDPE	-40.52	-45.98	-40.98	-43.73
Ave.	-40.52	-44.25	-40.98	-42.59
St. Dev.	0.00	2.44	0.00	1.61
COV	0.000	-0.055	0.000	-0.038
P. Steel	-33.83	-40.23	-38.72	-34.60
P. Steel	-33.83	-36.78	-31.95	-31.18
Ave.	-33.83	-38.51	-35.34	-32.89
St. Dev.	0.00	2.44	4.78	2.42
COV	0.000	-0.063	-0.135	-0.074
G. Vinyl	-33.83	-37.93	-34.21	-34.60
G. Vinyl	-32.71	-37.93	-34.21	-34.60
Ave.	-33.27	-37.93	-34.21	-34.60
St. Dev.	0.79	0.00	0.00	0.00
COV	-0.024	0.000	0.000	0.000
G. Aluminum	-38.29	-44.83	-38.72	-39.16
G. Aluminum	-33.83	-40.23	-37.59	-34.60
Ave.	-36.06	-42.53	-38.16	-36.88
St. Dev.	3.15	3.25	0.80	3.23
COV	-0.087	-0.076	-0.021	-0.087
G. Steel	-39.41	-39.08	-39.85	-34.60
G. Steel	-31.60	-34.48	-31.95	-32.32
Ave.	-35.50	-36.78	-35.90	-33.46
St. Dev.	5.52	3.25	5.58	1.61
COV	-0.155	-0.088	-0.155	-0.048
G. Copper	-40.52	-43.68	-36.47	-35.74
G. Copper	-40.52	-44.83	-39.85	-36.88
Ave.	-40.52	-44.25	-38.16	-36.31
St. Dev.	0.00	0.81	2.39	0.81
COV	0.000	-0.018	-0.063	-0.022

Table E.12. Toxicity effect of different samples. pH 8 water. 0.5 hour of exposure

Sample	Toxicity Effect, %			
	at 5 min	at 15 min	at 25 min	at 45 min
P. Concrete	-32.71	-34.48	-30.83	-30.04
P. Concrete	-31.60	-35.63	-27.44	-27.76
Ave.	-32.16	-35.06	-29.14	-28.90
St. Dev.	0.79	0.81	2.39	1.61
COV	-0.025	-0.023	-0.082	-0.056
P. PVC	-2.65	-18.99	-26.90	-25.00
P. PVC	-1.59	-20.25	-25.52	-25.00
Ave.	-2.12	-19.62	-26.21	-25.00
St. Dev.	0.75	0.90	0.98	0.00
COV	-0.354	-0.046	-0.037	0.000
P. HDPE	-12.17	-32.91	-44.83	-47.06
P. HDPE	-15.34	-37.97	-48.97	-50.00
Ave.	-13.76	-35.44	-46.90	-48.53
St. Dev.	2.24	3.58	2.93	2.08
COV	-0.163	-0.101	-0.062	-0.043
P. Steel	-11.11	-35.44	-48.97	-48.53
P. Steel	-10.05	-30.38	-40.69	-42.65
Ave.	-10.58	-32.91	-44.83	-45.59
St. Dev.	0.75	3.58	5.85	4.16
COV	-0.071	-0.109	-0.131	-0.091
G. Vinyl	-12.17	-32.91	-44.83	-48.53
G. Vinyl	-14.29	-35.44	-44.83	-50.00
Ave.	-13.23	-34.18	-44.83	-49.26
St. Dev.	1.50	1.79	0.00	1.04
COV	-0.113	-0.052	0.000	-0.021
G. Aluminum	-13.23	-36.71	-47.59	-51.47
G. Aluminum	-13.23	-36.71	-46.21	-48.53
Ave.	-13.23	-36.71	-46.90	-50.00
St. Dev.	0.00	0.00	0.98	2.08
COV	0.000	0.000	-0.021	-0.042
G. Steel	-8.99	-26.58	-36.55	-38.24
G. Steel	-19.58	-36.71	-37.93	-42.65
Ave.	-14.29	-31.65	-37.24	-40.44
St. Dev.	7.48	7.16	0.98	3.12
COV	-0.524	-0.226	-0.026	-0.077
G. Copper	-0.53	-20.25	-26.90	-30.88
G. Copper	-11.11	-34.18	-42.07	-44.12
Ave.	-5.82	-27.22	-34.48	-37.50
St. Dev.	7.48	9.85	10.73	9.36
COV	-1.286	-0.362	-0.311	-0.250

Table E.13. Toxicity effect of different samples. pH 8 water. One hour of exposure

Sample	Toxicity Effect, %			
	at 5 min	at 15 min	at 25 min	at 45 min
P. Concrete	-36.06	-41.38	-33.08	-34.60
P. Concrete	-37.17	-41.38	-31.95	-35.74
Ave.	-36.62	-41.38	-32.52	-35.17
St. Dev.	0.79	0.00	0.80	0.81
COV	-0.022	0.000	-0.025	-0.023
P. PVC	-2.65	-18.99	-28.28	-25.00
P. PVC	-1.59	-16.46	-21.38	-14.71
Ave.	-2.12	-17.72	-24.83	-19.85
St. Dev.	0.75	1.79	4.88	7.28
COV	-0.354	-0.101	-0.196	-0.367
P. HDPE	-11.11	-32.91	-42.07	-47.06
P. HDPE	-15.34	-36.71	-44.83	-47.06
Ave.	-13.23	-34.81	-43.45	-47.06
St. Dev.	2.99	2.69	1.95	0.00
COV	-0.226	-0.077	-0.045	0.000
P. Steel	-6.88	-30.38	-37.93	-41.18
P. Steel	-13.23	-31.65	-42.07	-45.59
Ave.	-10.05	-31.01	-40.00	-43.38
St. Dev.	4.49	0.90	2.93	3.12
COV	-0.447	-0.029	-0.073	-0.072
G. Vinyl	-11.11	-32.91	-40.69	-45.59
G. Vinyl	-16.40	-37.97	-48.97	-47.06
Ave.	-13.76	-35.44	-44.83	-46.32
St. Dev.	3.74	3.58	5.85	1.04
COV	-0.272	-0.101	-0.131	-0.022
G. Aluminum	19.35	13.98	9.89	7.95
G. Aluminum	19.35	15.05	10.99	10.23
Ave.	19.35	14.52	10.44	9.09
St. Dev.	0.00	0.76	0.78	1.61
COV	0.000	0.052	0.074	0.177
G. Steel	21.51	17.20	13.19	13.64
G. Steel	19.35	12.90	8.79	9.09
Ave.	20.43	15.05	10.99	11.36
St. Dev.	1.52	3.04	3.11	3.21
COV	0.074	0.202	0.283	0.283
G. Copper	27.96	26.88	26.37	25.00
G. Copper	29.03	25.81	25.27	25.00
Ave.	28.49	26.34	25.82	25.00
St. Dev.	0.76	0.76	0.78	0.00
COV	0.027	0.029	0.030	0.000

Table E.14. Toxicity effect of different samples. pH 8 water. 27 hours of exposure

Sample	Toxicity Effect, %			
	at 5 min	at 15 min	at 25 min	at 45 min
P. Concrete	-33.83	-40.23	-33.08	-33.46
P. Concrete	-37.17	-43.68	-36.47	-32.32
Ave.	-35.50	-41.95	-34.77	-32.89
St. Dev.	2.37	2.44	2.39	0.81
COV	-0.067	-0.058	-0.069	-0.025
P. PVC	31.18	29.03	29.67	32.95
P. PVC	30.11	27.96	29.67	35.23
Ave.	30.65	28.49	29.67	34.09
St. Dev.	0.76	0.76	0.00	1.61
COV	0.025	0.027	0.000	0.047
P. HDPE	16.13	9.68	8.79	6.82
P. HDPE	18.28	13.98	12.09	9.09
Ave.	17.20	11.83	10.44	7.95
St. Dev.	1.52	3.04	2.33	1.61
COV	0.088	0.257	0.223	0.202
P. Steel	20.43	17.20	13.19	9.09
P. Steel	18.28	13.98	12.09	10.23
Ave.	19.35	15.59	12.64	9.66
St. Dev.	1.52	2.28	0.78	0.80
COV	0.079	0.146	0.061	0.083
G. Vinyl	15.05	11.83	7.69	7.95
G. Vinyl	15.05	9.68	6.59	5.68
Ave.	15.05	10.75	7.14	6.82
St. Dev.	0.00	1.52	0.78	1.61
COV	0.000	0.141	0.109	0.236
G. Aluminum	13.98	11.83	8.79	5.68
G. Aluminum	15.05	13.98	9.89	7.95
Ave.	14.52	12.90	9.34	6.82
St. Dev.	0.76	1.52	0.78	1.61
COV	0.052	0.118	0.083	0.236
G. Steel	17.20	15.05	10.99	11.36
G. Steel	19.35	15.05	12.09	11.36
Ave.	18.28	15.05	11.54	11.36
St. Dev.	1.52	0.00	0.78	0.00
COV	0.083	0.000	0.067	0.000
G. Copper	44.09	45.16	49.45	54.55
G. Copper	46.24	48.39	50.55	55.68
Ave.	45.16	46.77	50.00	55.11
St. Dev.	1.52	2.28	0.78	0.80
COV	0.034	0.049	0.016	0.015

Table E.15. Toxicity effect of different samples. pH 8 water. One month of exposure

Sample	Toxicity Effect, %			
	at 5 min	at 15 min	at 25 min	at 45 min
P. Concrete	4.00	-12.64	-20.00	-27.78
P. Concrete	5.85	-9.29	-17.55	-29.17
Ave.	4.92	-10.97	-18.78	-28.47
St. Dev.	1.31	2.37	1.73	0.98
COV	0.265	-0.216	-0.092	-0.034
P. PVC	12.83	3.43	-0.93	-3.66
P. PVC	7.17	-4.29	-6.54	-9.95
Ave.	10.00	-0.43	-3.74	-6.81
St. Dev.	4.00	5.46	3.97	4.44
COV	0.400	-12.728	-1.061	-0.653
P. HDPE	-7.55	-22.32	-33.18	-44.50
P. HDPE	-6.42	-24.89	-37.38	-44.50
Ave.	-6.98	-23.61	-35.28	-44.50
St. Dev.	0.80	1.82	2.97	0.00
COV	-0.115	-0.077	-0.084	0.000
P. Steel	13.96	3.43	-0.93	-8.38
P. Steel	15.09	7.30	0.47	-2.09
Ave.	14.53	5.36	-0.23	-5.24
St. Dev.	0.80	2.73	0.99	4.44
COV	0.055	0.509	-4.243	-0.849
G. Vinyl	-6.42	-17.17	-24.77	-35.08
G. Vinyl	0.38	-12.02	-23.36	-33.51
Ave.	-3.02	-14.59	-24.07	-34.29
St. Dev.	4.80	3.64	0.99	1.11
COV	-1.591	-0.250	-0.041	-0.032
G. Aluminum	-9.81	-23.61	-35.98	-49.21
G. Aluminum	-8.68	-27.47	-37.38	-47.64
Ave.	-9.25	-25.54	-36.68	-48.43
St. Dev.	0.80	2.73	0.99	1.11
COV	-0.087	-0.107	-0.027	-0.023
G. Steel	13.96	2.15	-3.74	-8.38
G. Steel	18.49	9.87	4.67	-3.66
Ave.	16.23	6.01	0.47	-6.02
St. Dev.	3.20	5.46	5.95	3.33
COV	0.197	0.909	12.728	-0.553
G. Copper	33.21	27.90	25.70	21.47
G. Copper	26.42	25.32	18.69	16.75
Ave.	29.81	26.61	22.20	19.11
St. Dev.	4.80	1.82	4.96	3.33
COV	0.161	0.068	0.223	0.174

Table E.16. Toxicity effect of different samples. pH 8 water. Two months of exposure

Sample	Toxicity Effect, %			
	at 5 min	at 15 min	at 25 min	at 45 min
P. Concrete	12.55	-0.87	-8.17	-8.38
P. Concrete	12.55	-0.87	-6.73	-8.38
Ave.	12.55	-0.87	-7.45	-8.38
St. Dev.	0.00	0.00	1.02	0.00
COV	0.000	0.000	-0.137	0.000
P. PVC	4.74	-11.35	-20.00	-21.54
P. PVC	3.65	-13.97	-20.00	-23.08
Ave.	4.20	-12.66	-20.00	-22.31
St. Dev.	0.77	1.85	0.00	1.09
COV	0.184	-0.146	0.000	-0.049
P. HDPE	-6.20	-29.69	-37.14	-46.15
P. HDPE	-8.39	-29.69	-40.00	-44.62
Ave.	-7.30	-29.69	-38.57	-45.38
St. Dev.	1.55	0.00	2.02	1.09
COV	-0.212	0.000	-0.052	-0.024
P. Steel	9.12	-6.11	-14.29	-15.38
P. Steel	8.03	-10.04	-17.14	-21.54
Ave.	8.58	-8.08	-15.71	-18.46
St. Dev.	0.77	2.78	2.02	4.35
COV	0.090	-0.344	-0.129	-0.236
G. Vinyl	-2.92	-23.14	-34.29	-41.54
G. Vinyl	-9.49	-29.69	-40.00	-47.69
Ave.	-6.20	-26.42	-37.14	-44.62
St. Dev.	4.65	4.63	4.04	4.35
COV	-0.749	-0.175	-0.109	-0.098
G. Aluminum	-13.87	-37.55	-48.57	-56.92
G. Aluminum	-11.68	-33.62	-42.86	-49.23
Ave.	-12.77	-35.59	-45.71	-53.08
St. Dev.	1.55	2.78	4.04	5.44
COV	-0.121	-0.078	-0.088	-0.102
G. Steel	12.41	-3.49	-11.43	-13.85
G. Steel	9.12	-8.73	-14.29	-18.46
Ave.	10.77	-6.11	-12.86	-16.15
St. Dev.	2.32	3.71	2.02	3.26
COV	0.216	-0.606	-0.157	-0.202
G. Copper	43.07	41.05	41.43	46.15
G. Copper	46.35	42.36	42.86	47.69
Ave.	44.71	41.70	42.14	46.92
St. Dev.	2.32	0.93	1.01	1.09
COV	0.052	0.022	0.024	0.023

Table E.17. Toxicity Effect of different samples. pH 8 water. Three months of exposure

Sample	Toxicity Effect, %			
	at 5 min	at 15 min	at 25 min	at 45 min
P. Concrete	15.03	7.34	5.71	6.48
P. Concrete	13.99	6.18	3.27	7.69
Ave.	14.51	6.76	4.49	7.09
St. Dev.	0.74	0.82	1.73	0.86
COV	0.051	0.121	0.386	0.121
P. PVC	14.29	1.68	-10.23	-15.15
P. PVC	12.14	-0.84	-14.42	-18.18
Ave.	13.21	0.42	-12.33	-16.67
St. Dev.	1.52	1.78	2.96	2.14
COV	0.115	4.243	-0.240	-0.129
P. HDPE	-3.93	-22.27	-36.74	-48.48
P. HDPE	-3.93	-23.53	-38.14	-48.48
Ave.	-3.93	-22.90	-37.44	-48.48
St. Dev.	0.00	0.89	0.99	0.00
COV	0.000	-0.039	-0.026	0.000
P. Steel	10.00	-7.14	-15.81	-22.73
P. Steel	6.79	-5.88	-18.60	-25.76
Ave.	8.39	-6.51	-17.21	-24.24
St. Dev.	2.27	0.89	1.97	2.14
COV	0.271	-0.137	-0.115	-0.088
G. Vinyl	-11.43	-34.87	-46.51	-56.06
G. Vinyl	-12.50	-33.61	-46.51	-56.06
Ave.	-11.96	-34.24	-46.51	-56.06
St. Dev.	0.76	0.89	0.00	0.00
COV	-0.063	-0.026	0.000	0.000
G. Aluminum	-9.29	-32.35	-45.12	-56.06
G. Aluminum	-11.43	-33.61	-45.12	-59.09
Ave.	-10.36	-32.98	-45.12	-57.58
St. Dev.	1.52	0.89	0.00	2.14
COV	-0.146	-0.027	0.000	-0.037
G. Steel	11.07	-7.14	-14.42	-19.70
G. Steel	10.00	-9.66	-17.21	-21.21
Ave.	10.54	-8.40	-15.81	-20.45
St. Dev.	0.76	1.78	1.97	1.07
COV	0.072	-0.212	-0.125	-0.052
G. Copper	32.50	29.41	26.05	33.33
G. Copper	30.36	28.15	24.65	28.79
Ave.	31.43	28.78	25.35	31.06
St. Dev.	1.52	0.89	0.99	3.21
COV	0.048	0.031	0.039	0.103

Table E.18. Toxicity effect of different samples. Bay water. Time zero

Sample	Toxicity Effect, %			
	at 5 min	at 15 min	at 25 min	at 45 min
P. Concrete	-23.723	-31.169	-40.094	-52.308
P. Concrete	-24.818	-32.468	-38.679	-52.308
Ave.	-24.27	-31.818	-39.387	-52.308
St. Dev.	0.77	0.92	1.00	0.00
COV	-0.032	-0.029	-0.025	0.000
P. PVC	-18.248	-29.87	-34.434	-43.077
P. PVC	-16.058	-28.571	-33.019	-41.538
Ave.	-17.153	-29.221	-33.726	-42.308
St. Dev.	1.55	0.92	1.00	1.09
COV	-0.090	-0.031	-0.030	-0.026
P. HDPE	-19.343	-33.766	-40.094	-44.615
P. HDPE	-19.343	-35.065	-42.925	-46.154
Ave.	-19.343	-34.416	-41.509	-45.385
St. Dev.	0.00	0.92	2.00	1.09
COV	0.000	-0.027	-0.048	-0.024
P. Steel	-19.343	-28.571	-37.264	-38.462
P. Steel	-20.438	-28.571	-37.264	-40
Ave.	-19.891	-28.571	-37.264	-39.231
St. Dev.	0.77	0.00	0.00	1.09
COV	-0.039	0.000	0.000	-0.028
G. Vinyl	-18.248	-31.169	-31.604	-46.154
G. Vinyl	-19.343	-32.468	-33.019	-46.154
Ave.	-18.796	-31.818	-32.311	-46.154
St. Dev.	0.77	0.92	1.00	0.00
COV	-0.041	-0.029	-0.031	0.000
G. Aluminum	-19.343	-33.766	-44.34	-46.154
G. Aluminum	-18.248	-32.468	-44.34	-44.615
Ave.	-18.796	-33.117	-44.34	-45.385
St. Dev.	0.77	0.92	0.00	1.09
COV	-0.041	-0.028	0.000	-0.024
G. Steel	-12.774	-27.273	-35.849	-46.154
G. Steel	-13.869	-27.273	-37.264	-47.692
Ave.	-13.321	-27.273	-36.557	-46.923
St. Dev.	0.77	0.00	1.00	1.09
COV	-0.058	0.000	-0.027	-0.023
G. Copper	-17.153	-29.87	-41.509	-46.154
G. Copper	-16.058	-31.169	-40.094	-46.154
Ave.	-16.606	-30.519	-40.802	-46.154
St. Dev.	0.77	0.92	1.00	0.00
COV	-0.047	-0.030	-0.025	0.000

Table E.19. Toxicity effect of different samples. Bay water. One hour.

Sample	Toxicity Effect, %			
	at 5 min	at 15 min	at 25 min	at 45 min
P. Concrete	-32.13	-48.12	-54.05	-55.77
P. Concrete	-34.30	-49.37	-56.76	-55.77
Ave.	-33.21	-48.74	-55.41	-55.77
St. Dev.	1.53	0.89	1.91	0.00
COV	-0.046	-0.018	-0.034	0.000
P. PVC	-26.71	-41.84	-48.65	-51.44
P. PVC	-28.88	-43.10	-47.30	-51.44
Ave.	-27.80	-42.47	-47.97	-51.44
St. Dev.	1.53	0.89	0.96	0.00
COV	-0.055	-0.021	-0.020	0.000
P. HDPE	-31.05	-45.61	-52.70	-52.88
P. HDPE	-32.13	-46.86	-54.05	-52.88
Ave.	-31.59	-46.23	-53.38	-52.88
St. Dev.	0.77	0.89	0.96	0.00
COV	-0.024	-0.019	-0.018	0.000
P. Steel	-13.72	-14.23	-1.35	33.65
P. Steel	-12.64	-11.72	0.00	35.10
Ave.	-13.18	-12.97	-0.68	34.38
St. Dev.	0.77	1.78	0.96	1.02
COV	-0.058	-0.137	-1.414	0.030
G. Vinyl	-29.96	-44.35	-52.70	-54.33
G. Vinyl	-27.80	-43.10	-54.05	-55.77
Ave.	-28.88	-43.72	-53.38	-55.05
St. Dev.	1.53	0.89	0.96	1.02
COV	-0.053	-0.020	-0.018	-0.019
G. Aluminum	-31.05	-45.61	-51.35	-52.88
G. Aluminum	-31.05	-46.86	-50.00	-52.88
Ave.	-31.05	-46.23	-50.68	-52.88
St. Dev.	0.00	0.89	0.96	0.00
COV	0.000	-0.019	-0.019	0.000
G. Steel	-24.55	-36.82	-41.89	-31.25
G. Steel	-24.55	-36.82	-43.24	-31.25
Ave.	-24.55	-36.82	-42.57	-31.25
St. Dev.	0.00	0.00	0.96	0.00
COV	0.000	0.000	-0.022	0.000
G. Copper	43.68	48.54	56.76	68.27
G. Copper	42.60	47.28	54.05	66.83
Ave.	43.14	47.91	55.41	67.55
St. Dev.	0.77	0.89	1.91	1.02
COV	0.018	0.019	0.034	0.015

Table E.20. Toxicity effect of different samples. Bay water. 27 hours

Sample	Toxicity Effect, %			
	at 5 min	at 15 min	at 25 min	at 45 min
P. Concrete	-34.84	-54.39	-62.16	-65.37
P. Concrete	-33.80	-55.65	-62.16	-66.83
Ave.	-34.32	-55.02	-62.16	-66.10
St. Dev.	0.74	0.89	0.00	1.03
COV	-0.022	-0.016	0.000	-0.016
P. PVC	-44.25	-65.69	-68.92	-77.07
P. PVC	-45.30	-65.69	-70.27	-77.07
Ave.	-44.77	-65.69	-69.59	-77.07
St. Dev.	0.74	0.00	0.96	0.00
COV	-0.017	0.000	-0.014	0.000
P. HDPE	-40.07	-60.67	-67.57	-71.22
P. HDPE	-37.98	-59.41	-66.22	-71.22
Ave.	-39.02	-60.04	-66.89	-71.22
St. Dev.	1.48	0.89	0.96	0.00
COV	-0.038	-0.015	-0.014	0.000
P. Steel	32.06	54.81	75.68	94.15
P. Steel	32.06	52.30	75.68	92.68
Ave.	32.06	53.56	75.68	93.41
St. Dev.	0.00	1.78	0.00	1.03
COV	0.000	0.033	0.000	0.011
G. Vinyl	-40.07	-61.92	-63.51	-68.29
G. Vinyl	-41.11	-61.92	-64.86	-69.76
Ave.	-40.59	-61.92	-64.19	-69.02
St. Dev.	0.74	0.00	0.96	1.03
COV	-0.018	0.000	-0.015	-0.015
G. Aluminum	-37.98	-59.41	-63.51	-69.76
G. Aluminum	-40.07	-60.67	-64.86	-71.22
Ave.	-39.02	-60.04	-64.19	-70.49
St. Dev.	1.48	0.89	0.96	1.03
COV	-0.038	-0.015	-0.015	-0.015
G. Steel	20.56	39.75	66.22	89.76
G. Steel	18.47	39.75	64.86	89.76
Ave.	19.51	39.75	65.54	89.76
St. Dev.	1.48	0.00	0.96	0.00
COV	0.076	0.000	0.015	0.000
G. Copper	96.86	100.00	100.00	100.00
G. Copper	96.86	100.00	100.00	100.00
Ave.	96.86	100.00	100.00	100.00
St. Dev.	0.00	0.00	0.00	0.00
COV	0.000	0.000	0.000	0.000

Table E.21. Toxicity effect of different samples. Bay water. One week

Sample	Toxicity Effect, %			
	at 5 min	at 15 min	at 25 min	at 45 min
P. Concrete	-19.34	-45.35	-68.05	-82.89
P. Concrete	-20.44	-46.51	-69.29	-82.89
Ave.	-19.89	-45.93	-68.67	-82.89
St. Dev.	0.77	0.82	0.88	0.00
COV	-0.039	-0.018	-0.013	0.000
P. PVC	-28.10	-56.98	-74.27	-82.89
P. PVC	-27.01	-55.81	-74.27	-82.89
Ave.	-27.55	-56.40	-74.27	-82.89
St. Dev.	0.77	0.82	0.00	0.00
COV	-0.028	-0.015	0.000	0.000
P. HDPE	-22.63	-50.00	-74.27	-82.89
P. HDPE	-23.72	-51.16	-74.27	-82.89
Ave.	-23.18	-50.58	-74.27	-82.89
St. Dev.	0.77	0.82	0.00	0.00
COV	-0.033	-0.016	0.000	0.000
P. Steel	31.02	56.98	77.59	92.11
P. Steel	33.21	58.14	77.59	92.11
Ave.	32.12	57.56	77.59	92.11
St. Dev.	1.55	0.82	0.00	0.00
COV	0.048	0.014	0.000	0.000
G. Vinyl	-24.82	-54.65	-74.27	-84.21
G. Vinyl	-25.91	-55.81	-74.27	-84.21
Ave.	-25.36	-55.23	-74.27	-84.21
St. Dev.	0.77	0.82	0.00	0.00
COV	-0.031	-0.015	0.000	0.000
G. Aluminum	-28.10	-50.00	-74.27	-84.21
G. Aluminum	-30.29	-51.16	-74.27	-84.21
Ave.	-29.20	-50.58	-74.27	-84.21
St. Dev.	1.55	0.82	0.00	0.00
COV	-0.053	-0.016	0.000	0.000
G. Steel	45.26	63.95	80.08	90.79
G. Steel	46.35	65.12	80.08	90.79
Ave.	45.80	64.53	80.08	90.79
St. Dev.	0.77	0.82	0.00	0.00
COV	0.017	0.013	0.000	0.000
G. Copper	100.00	100.00	100.00	100.00
G. Copper	100.00	100.00	100.00	100.00
Ave.	100.00	100.00	100.00	100.00
St. Dev.	0.00	0.00	0.00	0.00
COV	0.000	0.000	0.000	0.000

Table E.22. Toxicity effect of different samples. Bay water. One month

Sample	Toxicity Effect, %			
	at 5 min	at 15 min	at 25 min	at 45 min
P. Concrete	-12.63	-30.19	-40.96	-46.84
P. Concrete	-12.63	-27.92	-39.76	-45.57
Ave.	-12.63	-29.06	-40.36	-46.20
St. Dev.	0.00	1.60	0.85	0.90
COV	0.000	-0.055	-0.021	-0.019
P. PVC	-24.21	-40.38	-45.78	-50.63
P. PVC	-26.32	-40.38	-44.58	-51.90
Ave.	-25.26	-40.38	-45.18	-51.27
St. Dev.	1.49	0.00	0.85	0.90
COV	-0.059	0.000	-0.019	-0.017
P. HDPE	-22.11	-34.72	-45.78	-51.90
P. HDPE	-21.05	-33.58	-46.99	-51.90
Ave.	-21.58	-34.15	-46.39	-51.90
St. Dev.	0.74	0.80	0.85	0.00
COV	-0.034	-0.023	-0.018	0.000
P. Steel	72.63	90.94	93.98	97.47
P. Steel	73.68	92.08	95.18	98.73
Ave.	73.16	91.51	94.58	98.10
St. Dev.	0.74	0.80	0.85	0.90
COV	0.010	0.009	0.009	0.009
G. Vinyl	-25.26	-35.85	-48.19	-54.43
G. Vinyl	-25.26	-36.98	-46.99	-53.16
Ave.	-25.26	-36.42	-47.59	-53.80
St. Dev.	0.00	0.80	0.85	0.90
COV	0.000	-0.022	-0.018	-0.017
G. Aluminum	-21.05	-33.58	-43.37	-50.63
G. Aluminum	-23.16	-35.85	-44.58	-49.37
Ave.	-22.11	-34.72	-43.98	-50.00
St. Dev.	1.49	1.60	0.85	0.90
COV	-0.067	-0.046	-0.019	-0.018
G. Steel	46.32	66.04	81.93	89.87
G. Steel	45.26	64.91	80.72	89.87
Ave.	45.79	65.47	81.33	89.87
St. Dev.	0.74	0.80	0.85	0.00
COV	0.016	0.012	0.010	0.000
G. Copper	93.68	100.00	100.00	100.00
G. Copper	92.63	98.87	100.00	100.00
Ave.	93.16	99.43	100.00	100.00
St. Dev.	0.74	0.80	0.00	0.00
COV	0.008	0.008	0.000	0.000

Table E.23. Toxicity effect of different samples. Bay water. Two months

Sample	Toxicity Effect, %			
	at 5 min	at 15 min	at 25 min	at 45 min
P. Concrete	-22.18	-30.89	-39.59	-46.81
P. Concrete	-23.27	-33.20	-40.82	-48.09
Ave.	-22.73	-32.05	-40.20	-47.45
St. Dev.	0.77	1.64	0.87	0.90
COV	-0.034	-0.051	-0.022	-0.019
P. PVC	-23.27	-41.31	-46.94	-50.64
P. PVC	-24.36	-41.31	-45.71	-50.64
Ave.	-23.82	-41.31	-46.33	-50.64
St. Dev.	0.77	0.00	0.87	0.00
COV	-0.032	0.000	-0.019	0.000
P. HDPE	-22.18	-33.20	-43.27	-51.91
P. HDPE	-21.09	-32.05	-43.27	-51.91
Ave.	-21.64	-32.63	-43.27	-51.91
St. Dev.	0.77	0.82	0.00	0.00
COV	-0.036	-0.025	0.000	0.000
P. Steel	88.00	95.37	97.55	98.72
P. Steel	86.91	94.21	96.33	98.72
Ave.	87.45	94.79	96.94	98.72
St. Dev.	0.77	0.82	0.87	0.00
COV	0.009	0.009	0.009	0.000
G. Vinyl	-22.18	-40.15	-43.27	-50.64
G. Vinyl	-23.27	-39.00	-43.27	-50.64
Ave.	-22.73	-39.58	-43.27	-50.64
St. Dev.	0.77	0.82	0.00	0.00
COV	-0.034	-0.021	0.000	0.000
G. Aluminum	-21.09	-39.00	-40.82	-42.98
G. Aluminum	-20.00	-39.00	-42.04	-42.98
Ave.	-20.55	-39.00	-41.43	-42.98
St. Dev.	0.77	0.00	0.87	0.00
COV	-0.038	0.000	-0.021	0.000
G. Steel	45.45	66.41	80.41	91.06
G. Steel	44.36	65.25	80.41	89.79
Ave.	44.91	65.83	80.41	90.43
St. Dev.	0.77	0.82	0.00	0.90
COV	0.017	0.012	0.000	0.010
G. Copper	100.00	100.00	100.00	100.00
G. Copper	100.00	100.00	100.00	100.00
Ave.	100.00	100.00	100.00	100.00
St. Dev.	0.00	0.00	0.00	0.00
COV	0.000	0.000	0.000	0.000

Table E.24. Toxicity effect of different samples. Bay water. Three months

Sample	Toxicity Effect, %			
	at 5 min	at 15 min	at 25 min	at 45 min
P. Concrete	1.06	-15.47	-27.16	-32.62
P. Concrete	3.19	-13.21	-28.40	-36.48
Ave.	2.13	-14.34	-27.78	-34.55
St. Dev.	1.50	1.60	0.87	2.73
COV	0.707	-0.112	-0.031	-0.079
P. PVC	-12.77	-18.87	-27.16	-28.76
P. PVC	-10.64	-15.47	-24.69	-31.33
Ave.	-11.70	-17.17	-25.93	-30.04
St. Dev.	1.50	2.40	1.75	1.82
COV	-0.129	-0.140	-0.067	-0.061
P. HDPE	-10.64	-16.60	-24.69	-28.76
P. HDPE	-10.64	-16.60	-25.93	-27.47
Ave.	-10.64	-16.60	-25.31	-28.11
St. Dev.	0.00	0.00	0.87	0.91
COV	0.000	0.000	-0.034	-0.032
P. Steel	100.00	100.00	100.00	100.00
P. Steel	95.74	98.87	100.00	100.00
Ave.	97.87	99.43	100.00	100.00
St. Dev.	3.01	0.80	0.00	0.00
COV	0.031	0.008	0.000	0.000
G. Vinyl	-6.38	-12.08	-20.99	-26.18
G. Vinyl	-5.32	-10.94	-19.75	-26.18
Ave.	-5.85	-11.51	-20.37	-26.18
St. Dev.	0.75	0.80	0.87	0.00
COV	-0.129	-0.070	-0.043	0.000
G. Aluminum	-6.38	-12.08	-20.99	-24.89
G. Aluminum	-7.45	-13.21	-23.46	-26.18
Ave.	-6.91	-12.64	-22.22	-25.54
St. Dev.	0.75	0.80	1.75	0.91
COV	-0.109	-0.063	-0.079	-0.036
G. Steel	100.00	100.00	100.00	100.00
G. Steel	96.81	97.74	97.53	100.00
Ave.	98.40	98.87	98.77	100.00
St. Dev.	2.26	1.60	1.75	0.00
COV	0.023	0.016	0.018	0.000
G. Copper	100.00	100.00	100.00	100.00
G. Copper	100.00	100.00	100.00	100.00
Ave.	100.00	100.00	100.00	100.00
St. Dev.	0.00	0.00	0.00	0.00
COV	0.000	0.000	0.000	0.000

Table E.25. Toxicity effect of different samples. River water. Time zero

Sample	Toxicity Effect, %			
	at 5 min	at 15 min	at 25 min	at 45 min
P. Concrete	-6.69	-10.66	-9.21	-8.96
P. Concrete	-7.75	-11.89	-10.53	-8.96
Ave.	-7.22	-11.27	-9.87	-8.96
St. Dev.	0.75	0.87	0.93	0.00
COV	-0.103	-0.077	-0.094	0.000
P. PVC	-9.86	-11.89	-11.84	-8.96
P. PVC	-7.75	-11.89	-10.53	-8.96
Ave.	-8.80	-11.89	-11.18	-8.96
St. Dev.	1.49	0.00	0.93	0.00
COV	-0.170	0.000	-0.083	0.000
P. HDPE	-7.75	-11.89	-9.21	-7.55
P. HDPE	-6.69	-10.66	-9.21	-6.13
Ave.	-7.22	-11.27	-9.21	-6.84
St. Dev.	0.75	0.87	0.00	1.00
COV	-0.103	-0.077	0.000	-0.146
P. Steel	-7.75	-13.11	-10.53	-8.96
P. Steel	-9.86	-13.11	-11.84	-10.38
Ave.	-8.80	-13.11	-11.18	-9.67
St. Dev.	1.49	0.00	0.93	1.00
COV	-0.170	0.000	-0.083	-0.103
G. Vinyl	-5.63	-9.43	-9.21	-6.13
G. Vinyl	-5.63	-10.66	-9.21	-7.55
Ave.	-5.63	-10.04	-9.21	-6.84
St. Dev.	0.00	0.87	0.00	1.00
COV	0.000	-0.087	0.000	-0.146
G. Aluminum	-5.63	-11.89	-9.21	-6.13
G. Aluminum	-3.52	-10.66	-7.89	-4.72
Ave.	-4.58	-11.27	-8.55	-5.42
St. Dev.	1.49	0.87	0.93	1.00
COV	-0.326	-0.077	-0.109	-0.184
G. Steel	-9.86	-14.34	-13.16	-23.11
G. Steel	-9.86	-16.80	-14.47	-24.53
Ave.	-9.86	-15.57	-13.82	-23.82
St. Dev.	0.00	1.74	0.93	1.00
COV	0.000	-0.112	-0.067	-0.042
G. Copper	-9.86	-16.80	-11.84	-8.96
G. Copper	-8.80	-14.34	-13.16	-8.96
Ave.	-9.33	-15.57	-12.50	-8.96
St. Dev.	0.75	1.74	0.93	0.00
COV	-0.080	-0.112	-0.074	0.000

Table E.26. Toxicity effect of different samples. River water. One hour

Sample	Toxicity Effect, %			
	at 5 min	at 15 min	at 25 min	at 45 min
P. Concrete	-21.25	-24.44	-26.25	-32.39
P. Concrete	-19.16	-23.33	-26.25	-31.17
Ave.	-20.21	-23.89	-26.25	-31.78
St. Dev.	1.48	0.79	0.00	0.86
COV	-0.073	-0.033	0.000	-0.027
P. PVC	-8.71	-12.22	-15.83	-19.03
P. PVC	-9.76	-12.22	-15.83	-20.24
Ave.	-9.23	-12.22	-15.83	-19.64
St. Dev.	0.74	0.00	0.00	0.86
COV	-0.080	0.000	0.000	-0.044
P. HDPE	-13.94	-18.89	-22.78	-23.89
P. HDPE	-14.98	-16.67	-20.46	-22.67
Ave.	-14.46	-17.78	-21.62	-23.28
St. Dev.	0.74	1.57	1.64	0.86
COV	-0.051	-0.088	-0.076	-0.037
P. Steel	-6.62	-4.44	0.39	10.12
P. Steel	-8.71	-4.44	-0.77	8.91
Ave.	-7.67	-4.44	-0.19	9.51
St. Dev.	1.48	0.00	0.82	0.86
COV	-0.193	0.000	-4.243	0.090
G. Vinyl	-16.03	-17.78	-21.62	-25.10
G. Vinyl	-17.07	-20.00	-22.78	-26.32
Ave.	-16.55	-18.89	-22.20	-25.71
St. Dev.	0.74	1.57	0.82	0.86
COV	-0.045	-0.083	-0.037	-0.033
G. Aluminum	-17.07	-20.00	-22.78	-27.53
G. Aluminum	-16.03	-18.89	-22.78	-26.32
Ave.	-16.55	-19.44	-22.78	-26.92
St. Dev.	0.74	0.79	0.00	0.86
COV	-0.045	-0.040	0.000	-0.032
G. Steel	-13.94	-15.56	-16.99	-17.81
G. Steel	-12.89	-15.56	-15.83	-17.81
Ave.	-13.41	-15.56	-16.41	-17.81
St. Dev.	0.74	0.00	0.82	0.00
COV	-0.055	0.000	-0.050	0.000
G. Copper	-1.39	7.78	13.13	16.19
G. Copper	-3.48	8.89	14.29	17.41
Ave.	-2.44	8.33	13.71	16.80
St. Dev.	1.48	0.79	0.82	0.86
COV	-0.606	0.094	0.060	0.051

Table E.27. Toxicity effect of different samples. River water. 27 hours

Sample	Toxicity Effect, %			
	at 5 min	at 15 min	at 25 min	at 45 min
P. Concrete	-23.78	-30.77	-33.46	-38.74
P. Concrete	-25.87	-29.67	-32.32	-38.74
Ave.	-24.83	-30.22	-32.89	-38.74
St. Dev.	1.48	0.78	0.81	0.00
COV	-0.060	-0.026	-0.025	0.000
P. PVC	-24.83	-26.37	-28.90	-30.43
P. PVC	-23.78	-25.27	-30.04	-31.62
Ave.	-24.30	-25.82	-29.47	-31.03
St. Dev.	0.74	0.78	0.81	0.84
COV	-0.031	-0.030	-0.027	-0.027
P. HDPE	-20.63	-27.47	-26.62	-33.99
P. HDPE	-22.73	-28.57	-27.76	-35.18
Ave.	-21.68	-28.02	-27.19	-34.58
St. Dev.	1.48	0.78	0.81	0.84
COV	-0.068	-0.028	-0.030	-0.024
P. Steel	8.74	26.37	42.97	76.28
P. Steel	9.79	26.37	42.97	76.28
Ave.	9.27	26.37	42.97	76.28
St. Dev.	0.74	0.00	0.00	0.00
COV	0.080	0.000	0.000	0.000
G. Vinyl	-22.73	-25.27	-27.76	-29.25
G. Vinyl	-23.78	-24.18	-26.62	-28.06
Ave.	-23.25	-24.73	-27.19	-28.66
St. Dev.	0.74	0.78	0.81	0.84
COV	-0.032	-0.031	-0.030	-0.029
G. Aluminum	-29.02	-31.87	-30.04	-33.99
G. Aluminum	-27.97	-29.67	-31.18	-35.18
Ave.	-28.50	-30.77	-30.61	-34.58
St. Dev.	0.74	1.55	0.81	0.84
COV	-0.026	-0.051	-0.026	-0.024
G. Steel	23.43	51.65	73.76	78.66
G. Steel	22.38	50.55	72.62	77.47
Ave.	22.90	51.10	73.19	78.06
St. Dev.	0.74	0.78	0.81	0.84
COV	0.032	0.015	0.011	0.011
G. Copper	62.24	74.73	81.75	94.07
G. Copper	61.19	72.53	81.75	92.89
Ave.	61.71	73.63	81.75	93.48
St. Dev.	0.74	1.55	0.00	0.84
COV	0.012	0.021	0.000	0.009

Table E.28. Toxicity effect of different samples. River water. One week

Sample	Toxicity Effect, %			
	at 5 min	at 15 min	at 25 min	at 45 min
P. Concrete	-3.19	-17.99	-20.00	-23.08
P. Concrete	-2.13	-16.74	-20.00	-23.08
Ave.	-2.66	-17.36	-20.00	-23.08
St. Dev.	0.75	0.89	0.00	0.00
COV	-0.283	-0.051	0.000	0.000
P. PVC	-14.89	-20.50	-20.00	-20.00
P. PVC	-13.83	-19.25	-18.60	-18.46
Ave.	-14.36	-19.87	-19.30	-19.23
St. Dev.	0.75	0.89	0.99	1.09
COV	-0.052	-0.045	-0.051	-0.057
P. HDPE	-4.26	-14.23	-14.42	-18.46
P. HDPE	-5.32	-15.48	-15.81	-20.00
Ave.	-4.79	-14.85	-15.12	-19.23
St. Dev.	0.75	0.89	0.99	1.09
COV	-0.157	-0.060	-0.065	-0.057
P. Steel	7.45	14.64	30.23	61.54
P. Steel	7.45	15.90	30.23	60.00
Ave.	7.45	15.27	30.23	60.77
St. Dev.	0.00	0.89	0.00	1.09
COV	0.000	0.058	0.000	0.018
G. Vinyl	-10.64	-17.99	-20.00	-23.08
G. Vinyl	-12.77	-16.74	-21.40	-21.54
Ave.	-11.70	-17.36	-20.70	-22.31
St. Dev.	1.50	0.89	0.99	1.09
COV	-0.129	-0.051	-0.048	-0.049
G. Aluminum	-17.02	-23.01	-29.77	-30.77
G. Aluminum	-15.96	-21.76	-28.37	-29.23
Ave.	-16.49	-22.38	-29.07	-30.00
St. Dev.	0.75	0.89	0.99	1.09
COV	-0.046	-0.040	-0.034	-0.036
G. Steel	24.47	47.28	69.30	76.92
G. Steel	26.60	48.54	70.70	76.92
Ave.	25.53	47.91	70.00	76.92
St. Dev.	1.50	0.89	0.99	0.00
COV	0.059	0.019	0.014	0.000
G. Copper	100.00	100.00	100.00	100.00
G. Copper	100.00	100.00	100.00	100.00
Ave.	100.00	100.00	100.00	100.00
St. Dev.	0.00	0.00	0.00	0.00
COV	0.000	0.000	0.000	0.000

Table E.29. Toxicity effect of different samples. River water. One month

Sample	Toxicity Effect, %			
	at 5 min	at 15 min	at 25 min	at 45 min
P. Concrete	-2.89	-17.62	-20.00	-17.26
P. Concrete	-1.81	-16.30	-18.57	-17.26
Ave.	-2.35	-16.96	-19.29	-17.26
St. Dev.	0.77	0.93	1.01	0.00
COV	-0.326	-0.055	-0.052	0.000
P. PVC	-5.05	-14.98	-22.86	-20.30
P. PVC	-6.14	-17.62	-20.00	-18.78
Ave.	-5.60	-16.30	-21.43	-19.54
St. Dev.	0.77	1.87	2.02	1.08
COV	-0.137	-0.115	-0.094	-0.055
P. HDPE	-1.81	-9.69	-8.57	-12.69
P. HDPE	-0.72	-9.69	-7.14	-11.17
Ave.	-1.26	-9.69	-7.86	-11.93
St. Dev.	0.77	0.00	1.01	1.08
COV	-0.606	0.000	-0.129	-0.090
P. Steel	16.61	23.35	40.00	69.54
P. Steel	15.52	22.03	40.00	68.02
Ave.	16.06	22.69	40.00	68.78
St. Dev.	0.77	0.93	0.00	1.08
COV	0.048	0.041	0.000	0.016
G. Vinyl	-8.30	-18.94	-15.71	-14.21
G. Vinyl	-7.22	-17.62	-17.14	-15.74
Ave.	-7.76	-18.28	-16.43	-14.97
St. Dev.	0.77	0.93	1.01	1.08
COV	-0.099	-0.051	-0.061	-0.072
G. Aluminum	-11.55	-22.91	-15.71	-18.78
G. Aluminum	-12.64	-24.23	-17.14	-18.78
Ave.	-12.09	-23.57	-16.43	-18.78
St. Dev.	0.77	0.93	1.01	0.00
COV	-0.063	-0.040	-0.061	0.000
G. Steel	30.69	45.81	72.86	80.20
G. Steel	31.77	47.14	72.86	78.68
Ave.	31.23	46.48	72.86	79.44
St. Dev.	0.77	0.93	0.00	1.08
COV	0.025	0.020	0.000	0.014
G. Copper	100.00	100.00	100.00	100.00
G. Copper	98.92	100.00	100.00	100.00
Ave.	99.46	100.00	100.00	100.00
St. Dev.	0.77	0.00	0.00	0.00
COV	0.008	0.000	0.000	0.000

Table E.30. Toxicity effect of different samples. River water. Two months

Sample	Toxicity Effect, %			
	at 5 min	at 15 min	at 25 min	at 45 min
P. Concrete	-7.53	-21.49	-25.23	-27.32
P. Concrete	-8.60	-22.73	-25.23	-27.32
Ave.	-8.06	-22.11	-25.23	-27.32
St. Dev.	0.76	0.88	0.00	0.00
COV	-0.094	-0.040	0.000	0.000
P. PVC	-9.68	-16.53	-21.10	-24.39
P. PVC	-10.75	-17.77	-22.48	-24.39
Ave.	-10.22	-17.15	-21.79	-24.39
St. Dev.	0.76	0.88	0.97	0.00
COV	-0.074	-0.051	-0.045	0.000
P. HDPE	-8.60	-12.81	-18.35	-20.00
P. HDPE	-7.53	-11.57	-19.72	-20.00
Ave.	-8.06	-12.19	-19.04	-20.00
St. Dev.	0.76	0.88	0.97	0.00
COV	-0.094	-0.072	-0.051	0.000
P. Steel	33.33	65.29	86.24	97.07
P. Steel	32.26	64.05	84.86	95.61
Ave.	32.80	64.67	85.55	96.34
St. Dev.	0.76	0.88	0.97	1.03
COV	0.023	0.014	0.011	0.011
G. Vinyl	-7.53	-12.81	-15.60	-17.07
G. Vinyl	-6.45	-11.57	-14.22	-15.61
Ave.	-6.99	-12.19	-14.91	-16.34
St. Dev.	0.76	0.88	0.97	1.03
COV	-0.109	-0.072	-0.065	-0.063
G. Aluminum	-12.90	-19.01	-23.85	-27.32
G. Aluminum	-13.98	-20.25	-25.23	-27.32
Ave.	-13.44	-19.63	-24.54	-27.32
St. Dev.	0.76	0.88	0.97	0.00
COV	-0.057	-0.045	-0.040	0.000
G. Steel	96.77	98.76	100.00	100.00
G. Steel	96.77	98.76	100.00	100.00
Ave.	96.77	98.76	100.00	100.00
St. Dev.	0.00	0.00	0.00	0.00
COV	0.000	0.000	0.000	0.000
G. Copper	100.00	100.00	100.00	100.00
G. Copper	100.00	100.00	100.00	100.00
Ave.	100.00	100.00	100.00	100.00
St. Dev.	0.00	0.00	0.00	0.00
COV	0.000	0.000	0.000	0.000

Table E.31. Toxicity effect of different samples. River water. Three months

Sample	Toxicity Effect, %			
	at 5 min	at 15 min	at 25 min	at 45 min
P. Concrete	-1.10	-15.58	-21.13	-22.45
P. Concrete	-3.30	-18.18	-23.94	-25.51
Ave.	-2.20	-16.88	-22.54	-23.98
St. Dev.	1.55	1.84	1.99	2.16
COV	-0.707	-0.109	-0.088	-0.090
P. PVC	-6.59	-15.58	-15.49	-16.33
P. PVC	-4.40	-14.29	-15.49	-16.33
Ave.	-5.49	-14.94	-15.49	-16.33
St. Dev.	1.55	0.92	0.00	0.00
COV	-0.283	-0.061	0.000	0.000
P. HDPE	-7.69	-16.88	-19.72	-22.45
P. HDPE	-9.89	-18.18	-18.31	-25.51
Ave.	-8.79	-17.53	-19.01	-23.98
St. Dev.	1.55	0.92	1.00	2.16
COV	-0.177	-0.052	-0.052	-0.090
P. Steel	34.07	63.64	84.51	96.94
P. Steel	34.07	62.34	80.28	95.41
Ave.	34.07	62.99	82.39	96.17
St. Dev.	0.00	0.92	2.99	1.08
COV	0.000	0.015	0.036	0.011
G. Vinyl	1.10	-10.39	-12.68	-14.80
G. Vinyl	-2.20	-12.99	-14.08	-17.86
Ave.	-0.55	-11.69	-13.38	-16.33
St. Dev.	2.33	1.84	1.00	2.16
COV	-4.243	-0.157	-0.074	-0.133
G. Aluminum	-10.99	-19.48	-22.54	-19.39
G. Aluminum	-12.09	-19.48	-25.35	-22.45
Ave.	-11.54	-19.48	-23.94	-20.92
St. Dev.	0.78	0.00	1.99	2.16
COV	-0.067	0.000	-0.083	-0.103
G. Steel	94.51	98.70	100.00	100.00
G. Steel	95.60	98.70	100.00	100.00
Ave.	95.05	98.70	100.00	100.00
St. Dev.	0.78	0.00	0.00	0.00
COV	0.008	0.000	0.000	0.000
G. Copper	100.00	100.00	100.00	100.00
G. Copper	100.00	100.00	100.00	100.00
Ave.	100.00	100.00	100.00	100.00
St. Dev.	0.00	0.00	0.00	0.00
COV	0.000	0.000	0.000	0.000

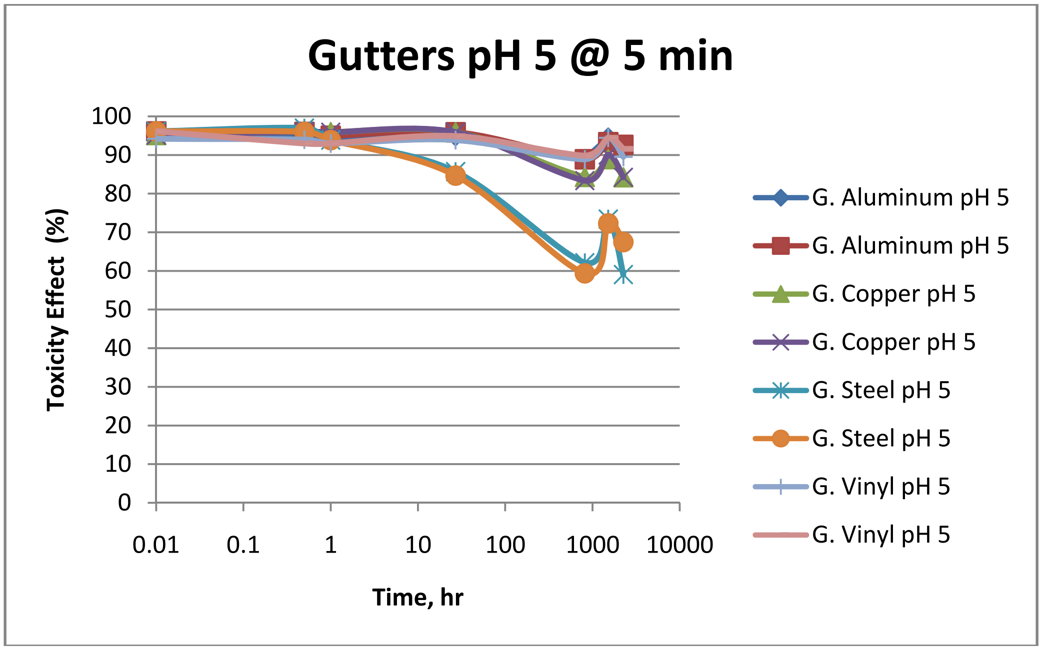


Figure E.1.1 Toxicity effect in samples with gutter materials under pH 5 conditions at 5 min.

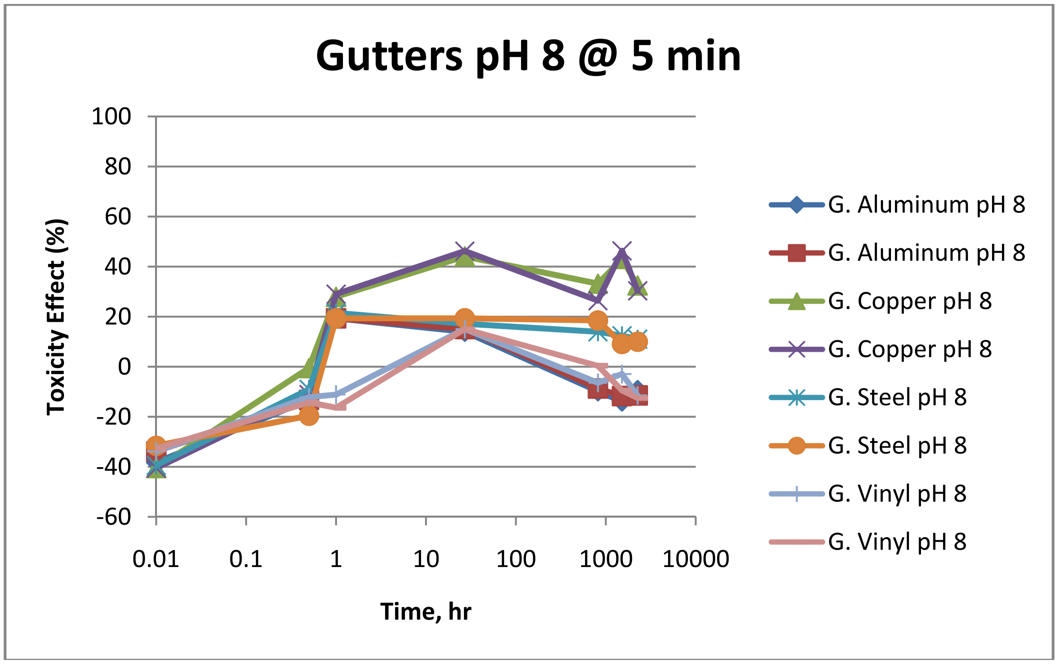


Figure E.1.2 Toxicity effect in samples with gutter materials under pH 8 conditions at 5 min.

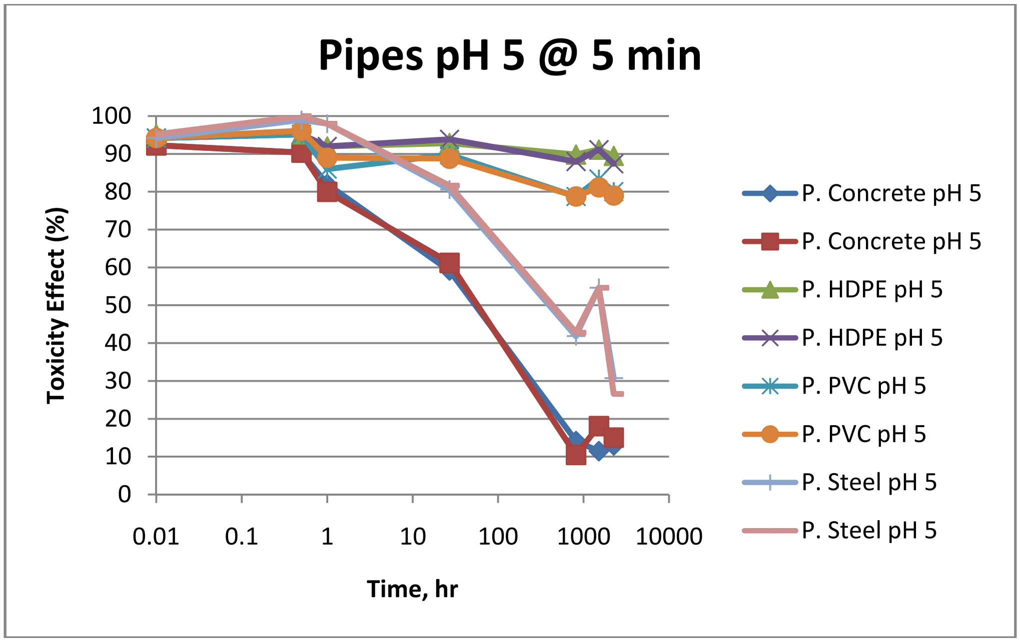


Figure E.1.3 Toxicity effect in samples with pipe materials under pH 5 conditions at 5 min.

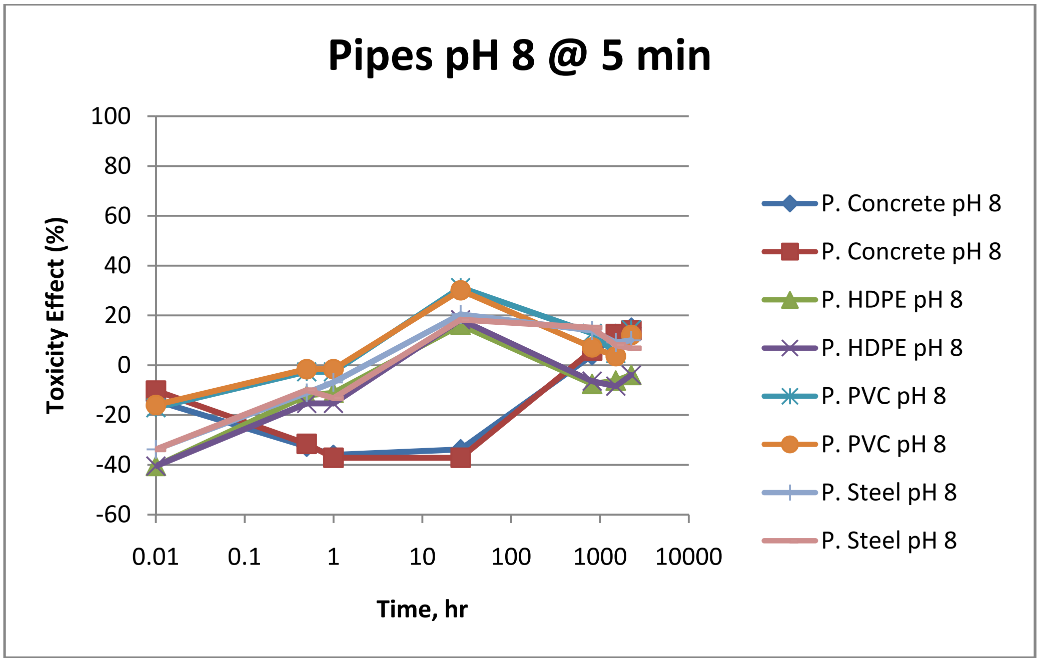


Figure E.1.4 Toxicity effect in samples with pipe materials under pH 8 conditions at 5 min.

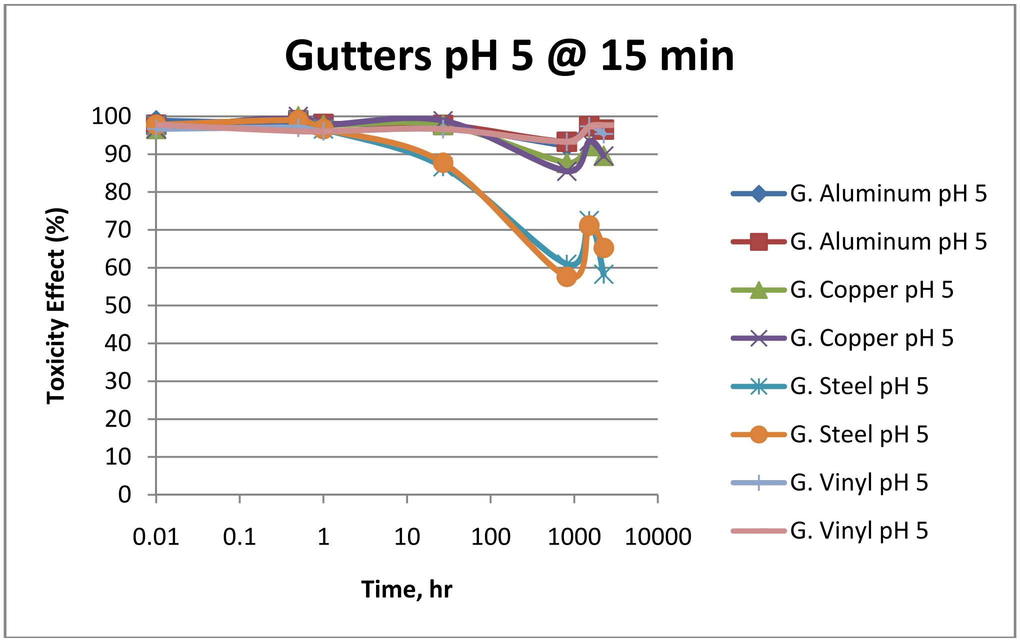


Figure E.1.5 Toxicity effect in samples with gutter materials under pH 5 conditions at 15 min.

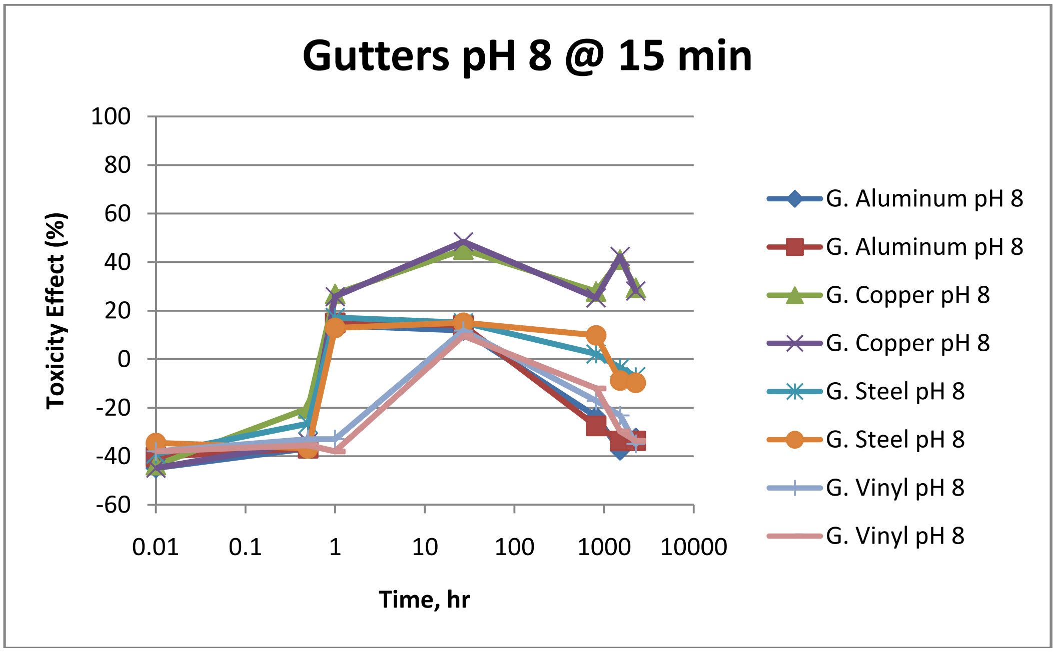


Figure E.1.6 Toxicity effect in samples with gutter materials under pH 8 conditions at 15 min.

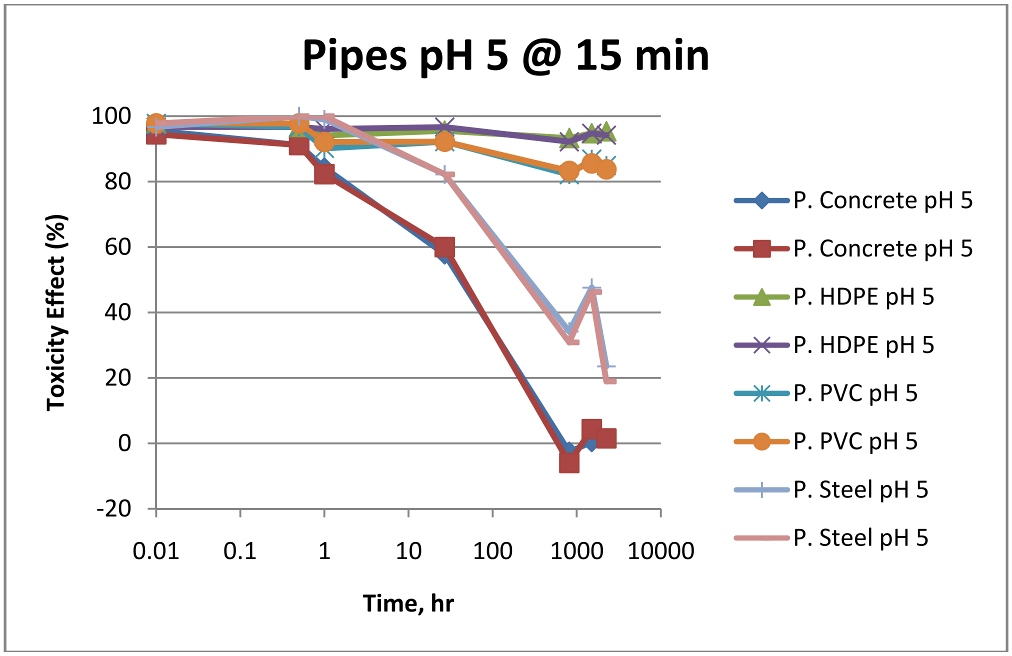


Figure E.1.7 Toxicity effect in samples with pipe materials under pH 5 conditions at 15 min.

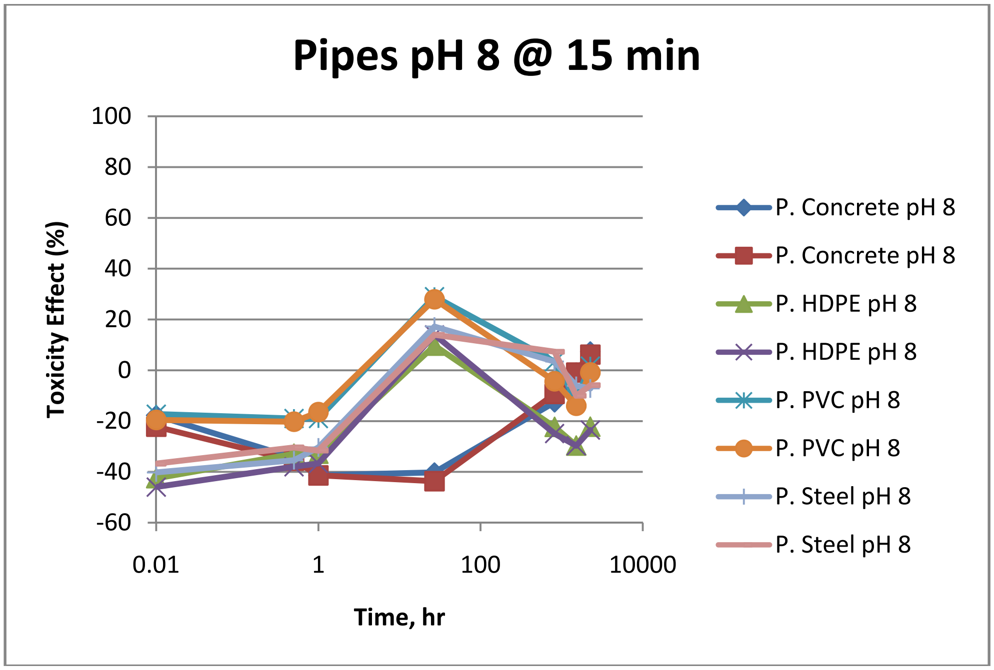


Figure E.1.8 Toxicity effect in samples with pipe materials under pH 8 conditions at 15 min.

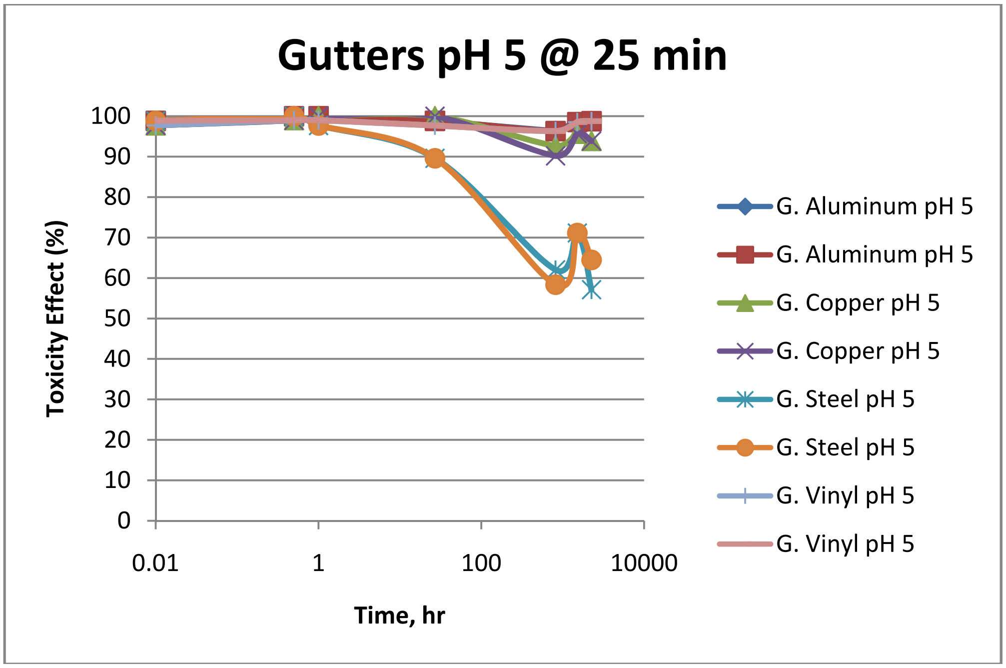


Figure E.1.9 Toxicity effect in samples with gutter materials under pH 5 conditions at 25 min.

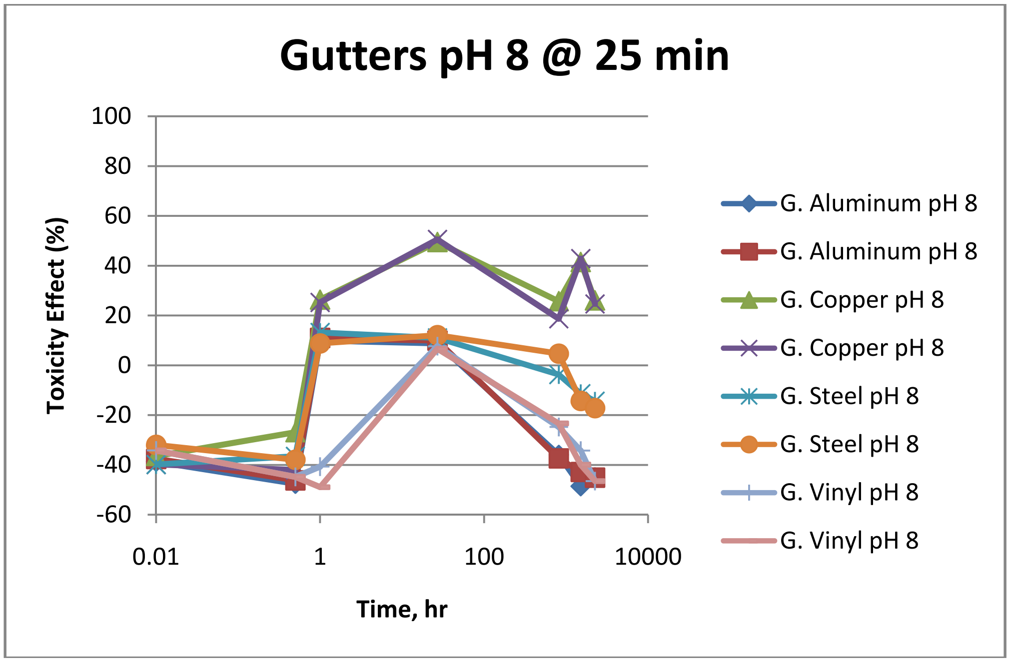


Figure E.1.10 Toxicity effect in samples with gutter materials under pH 8 conditions at 25 min.

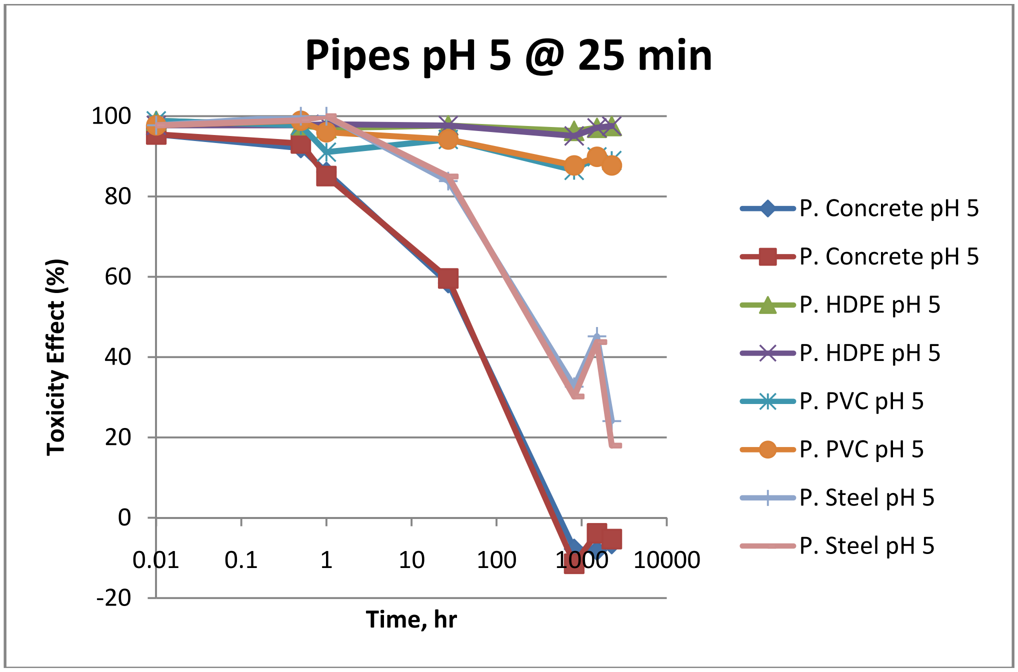


Figure E.1.11 Toxicity effect in samples with pipe materials under pH 5 conditions at 25 min.

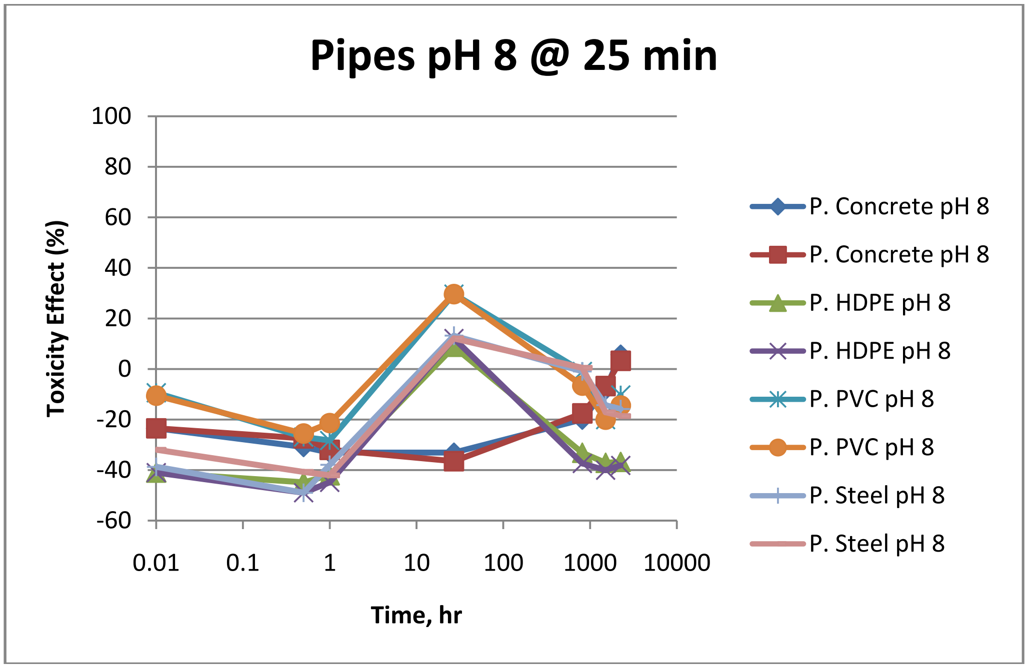


Figure E.1.12 Toxicity effect in samples with pipe materials under pH 8 conditions at 25 min.

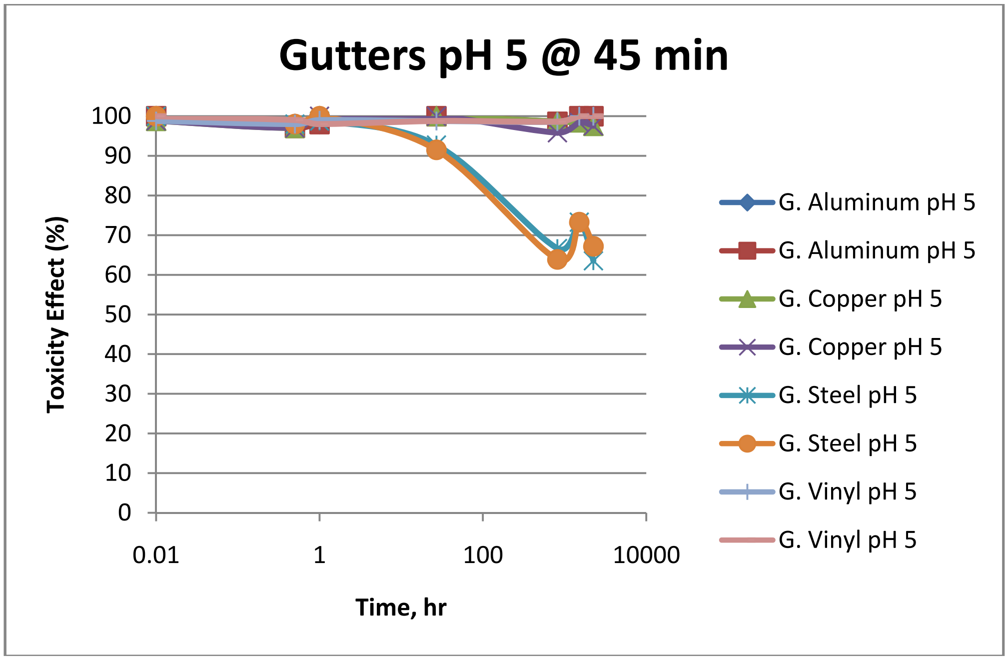


Figure E.1.13 Toxicity effect in samples with gutter materials under pH 5 conditions at 45 min.

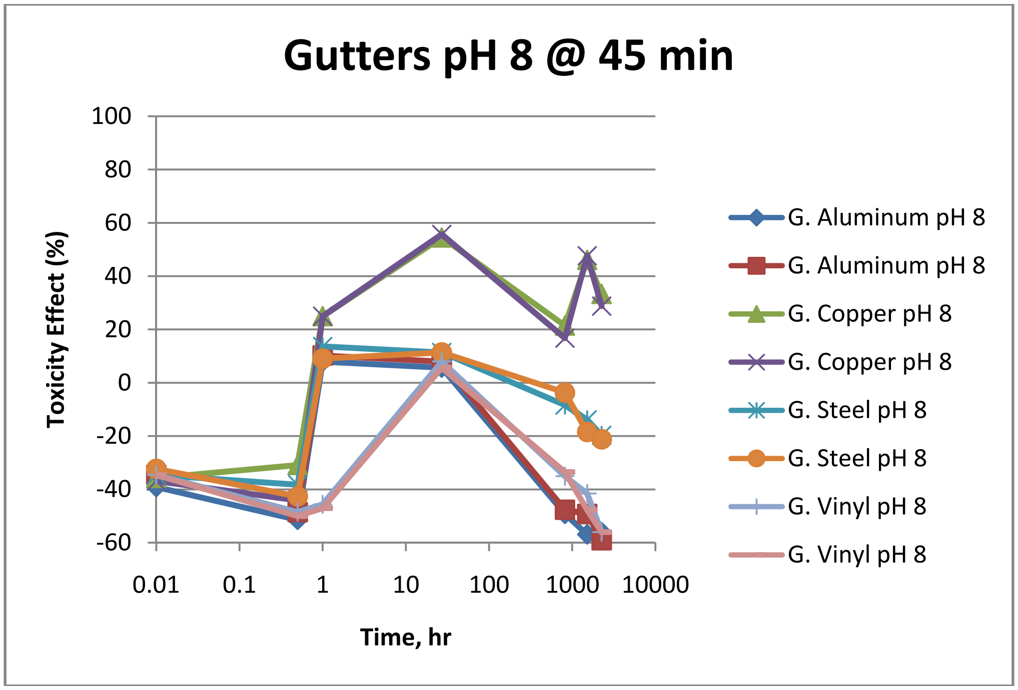


Figure E.1.14 Toxicity effect in samples with gutter materials under pH 8 conditions at 45 min.

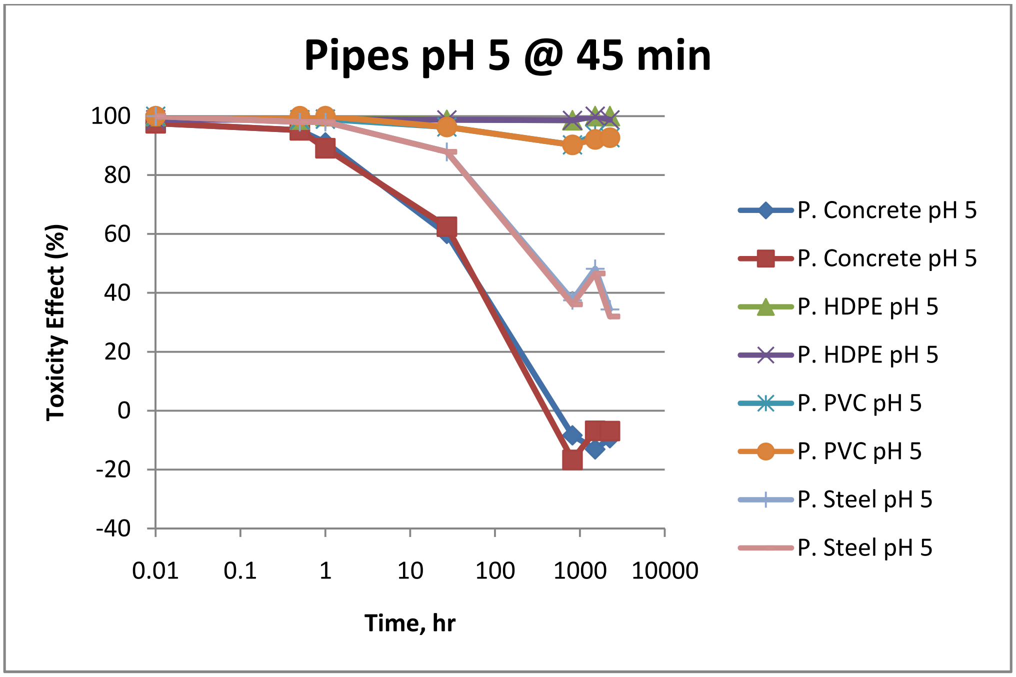
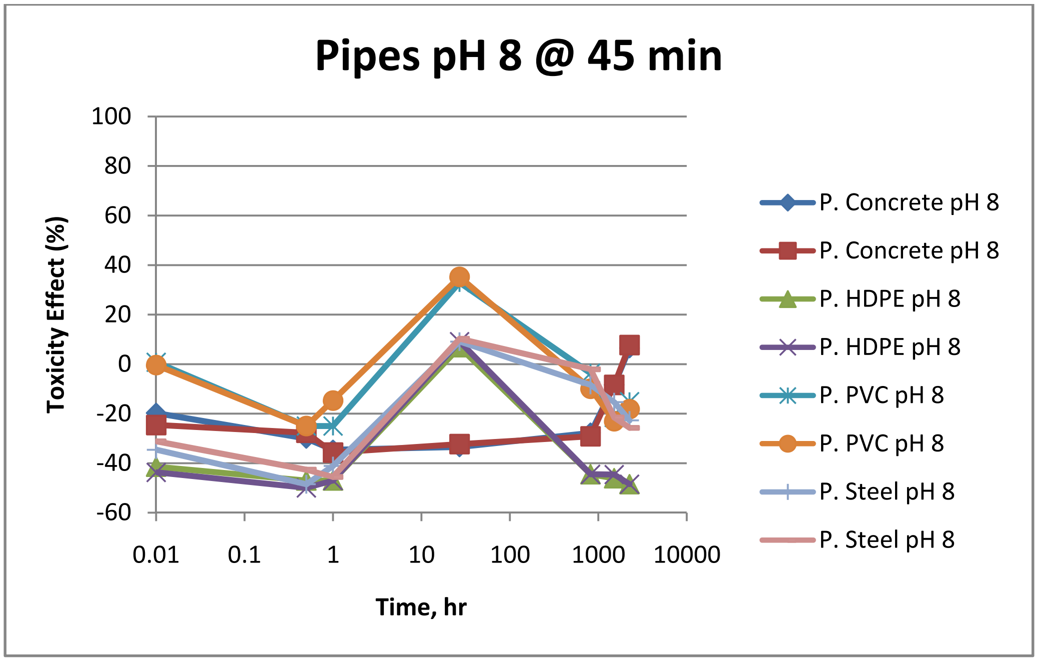


Figure E.1.15 Toxicity effect in samples with pipe materials under pH 5 conditions at 45 min.



FigureE.1.16 Toxicity effect in samples with pipe materials under pH 8 conditions at 45 min.

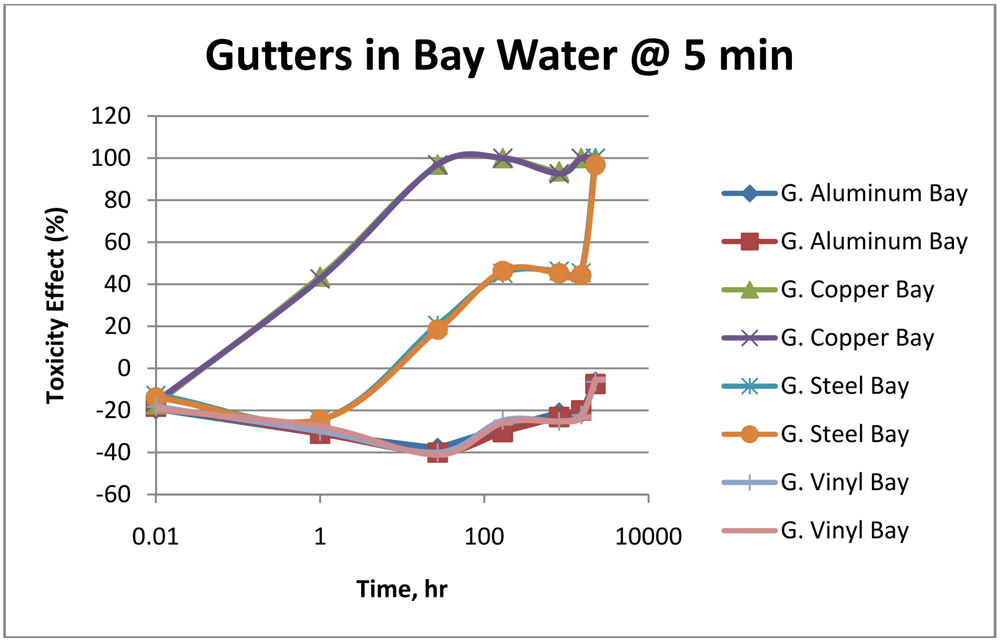


Figure E.2.1 Toxicity effect in samples with gutter materials. Bay water.At 5 min.

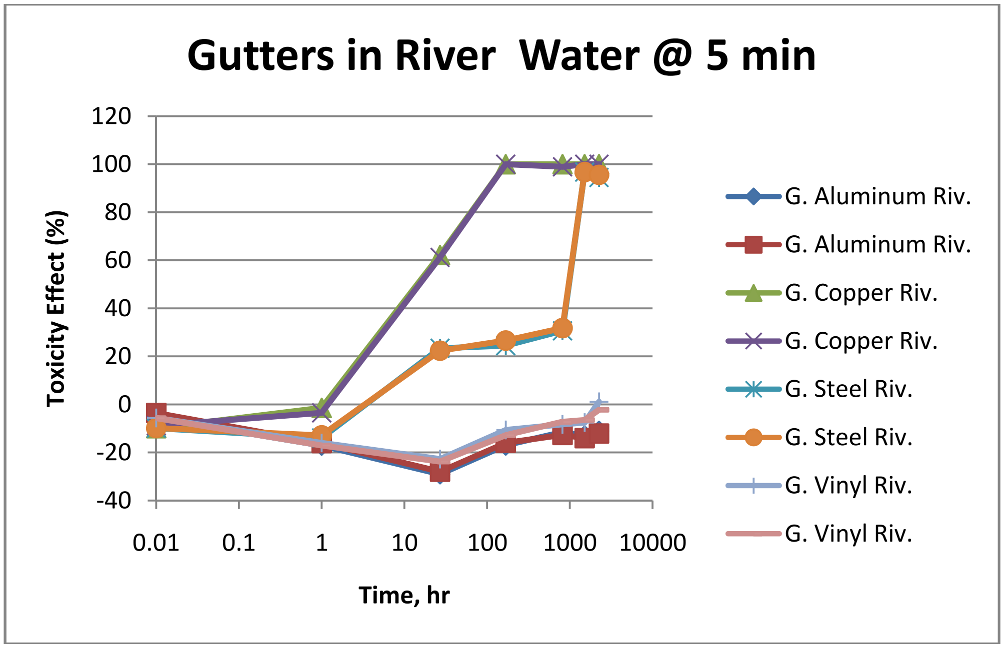


Figure E.2.2 Toxicity effect in samples with gutter materials. River water. At 5 min.

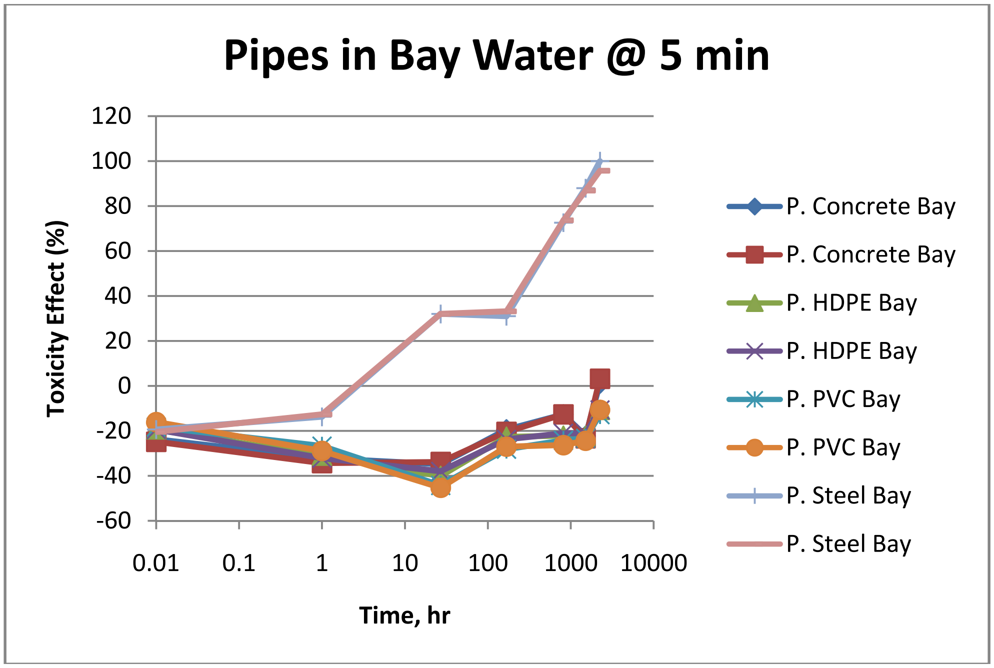


Figure E.2.3 Toxicity effect in samples with pipe materials. Bay water. At 5 min.

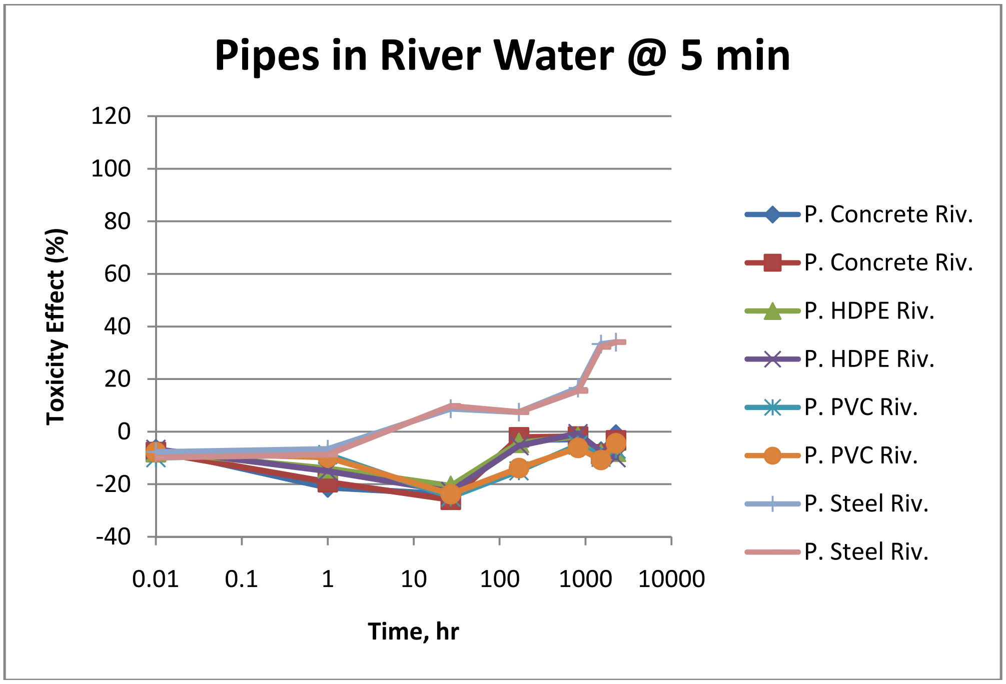


Figure E.2.4 Toxicity effect in samples with pipe materials. River water. At 5 min.

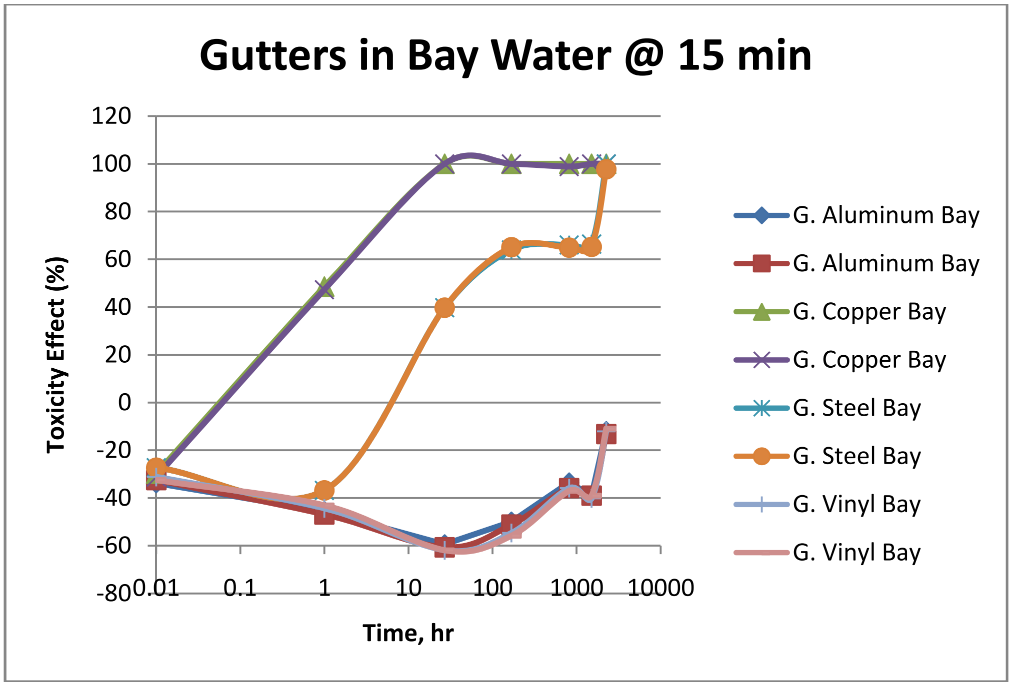


Figure E.2.5 Toxicity effect in samples with gutter materials. Bay water. At 15 min.

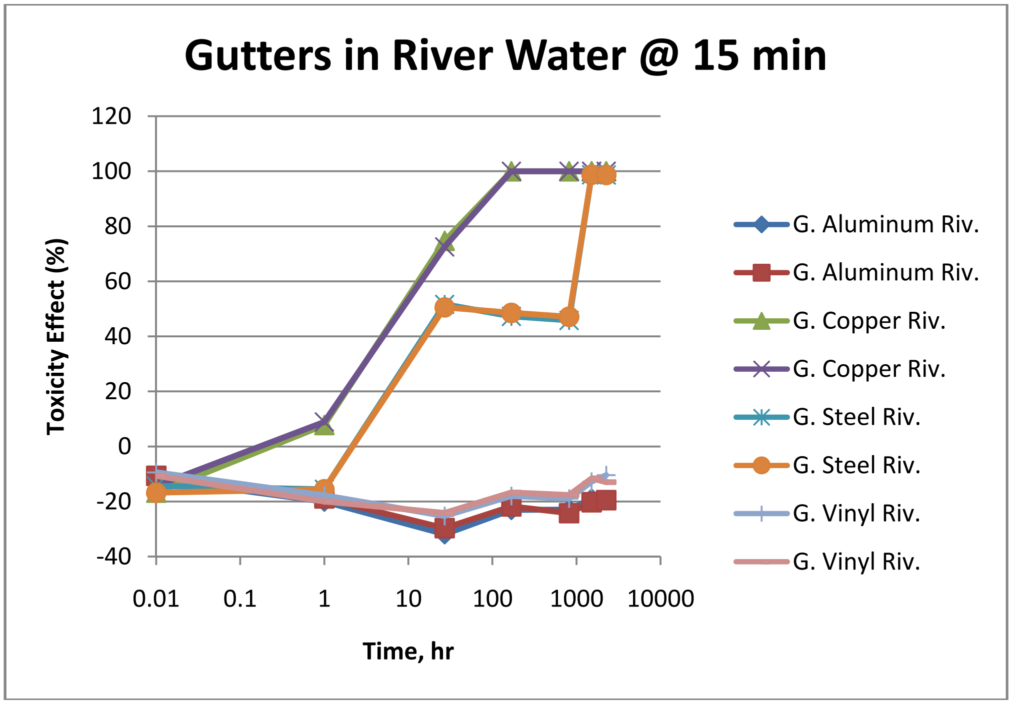


Figure E.2.6 Toxicity effect in samples with gutter materials. River water. At 15 min.

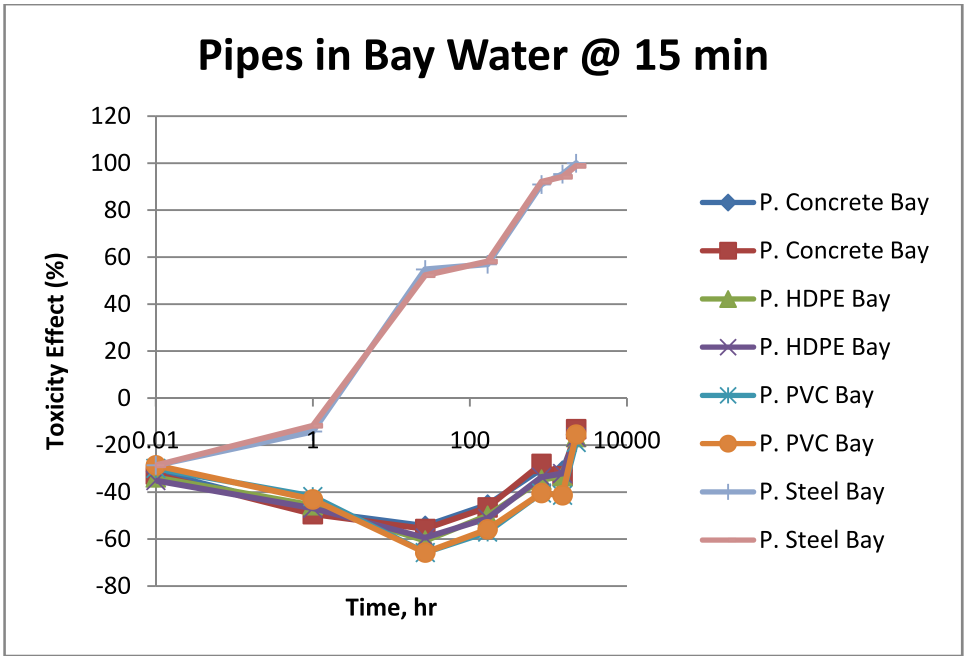


Figure E.2.7 Toxicity effect in samples with pipe materials. Bay water. At 15 min.

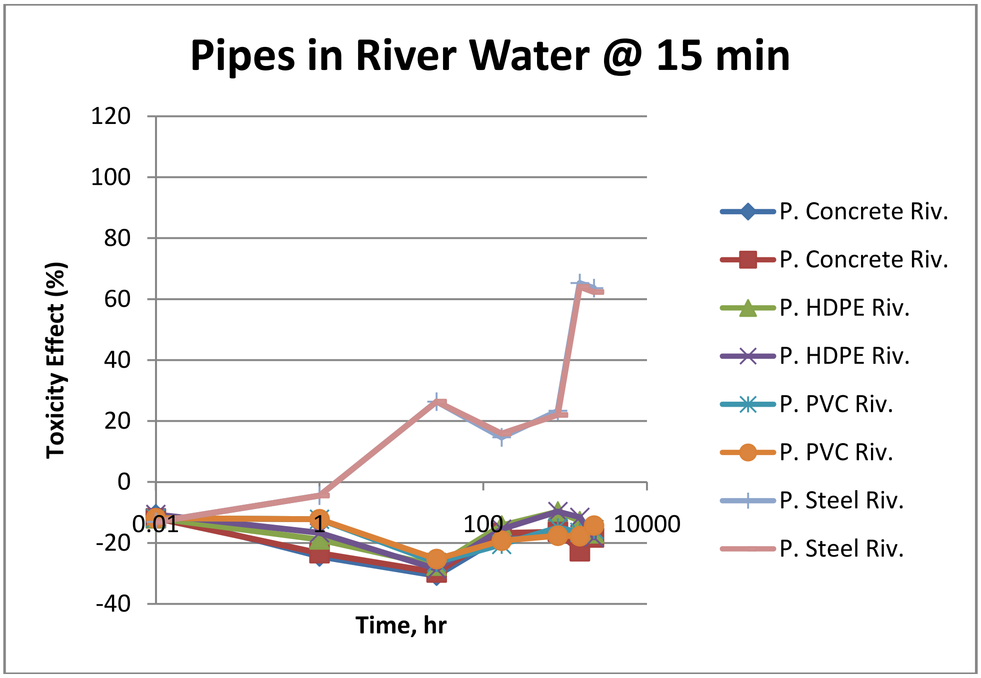


Figure E.2.8 Toxicity effect in samples with pipe materials. River water. At 15 min.

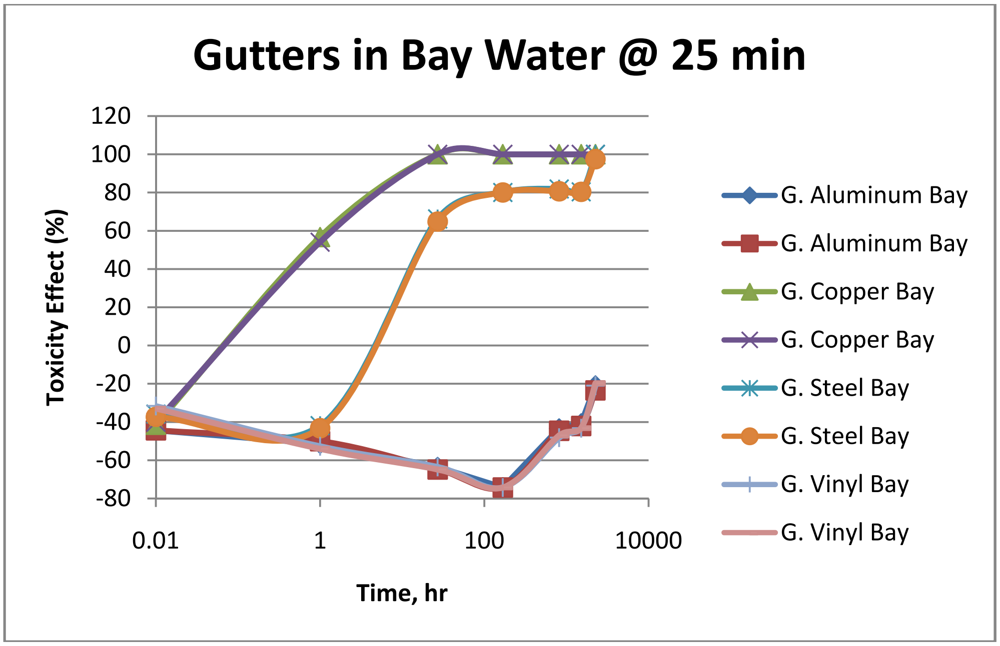


Figure E.2.9 Toxicity effect in samples with gutter materials. Bay water. At 25 min.

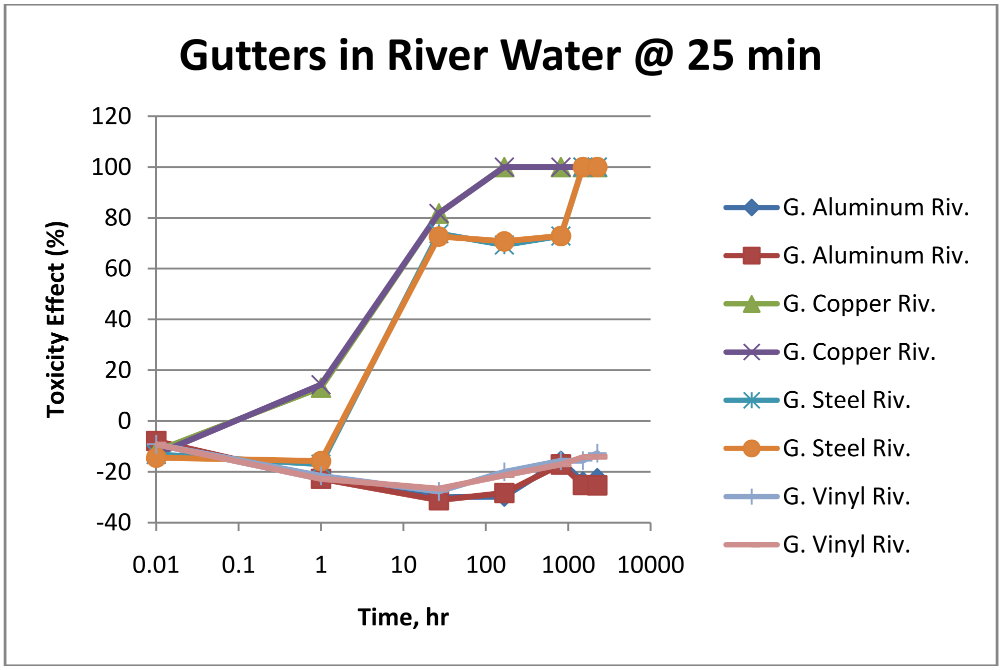


Figure E.2.10 Toxicity effect in samples with gutter materials. River water. At 25 min.

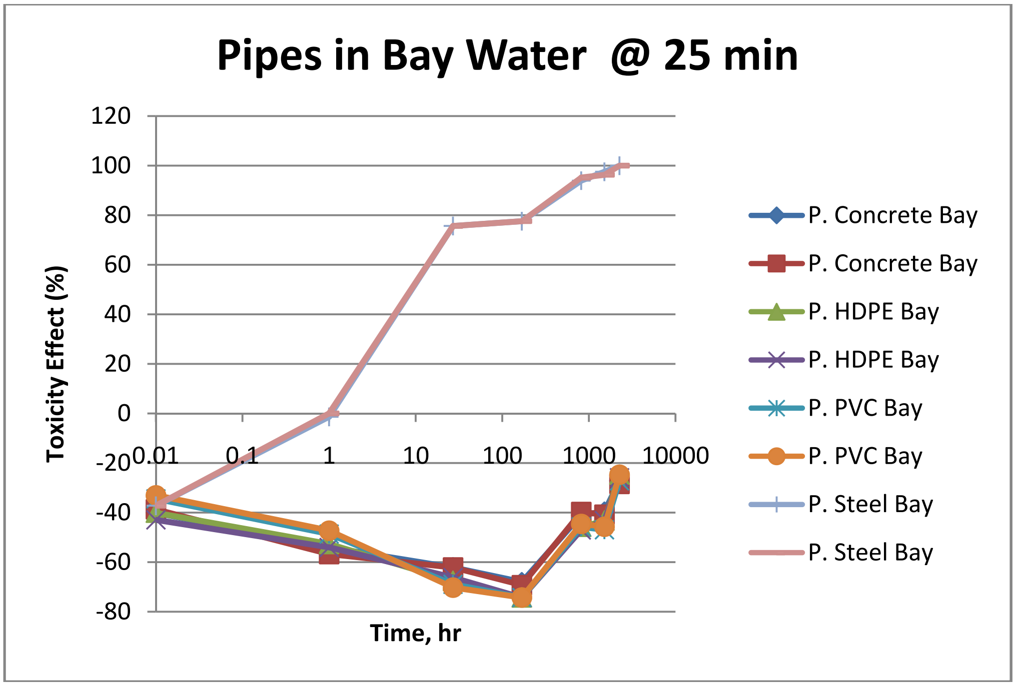


Figure E.2.11 Toxicity effect in samples with pipe materials. Bay water. At 25 min.

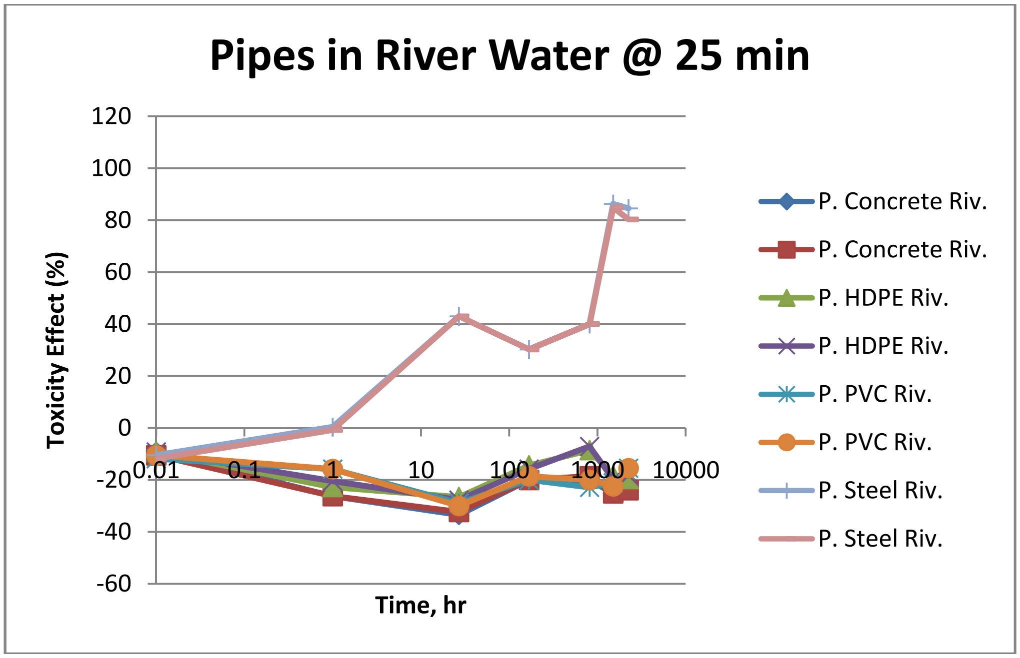


Figure E.2.12 Toxicity effect in samples with pipe materials. River water. At 25 min.

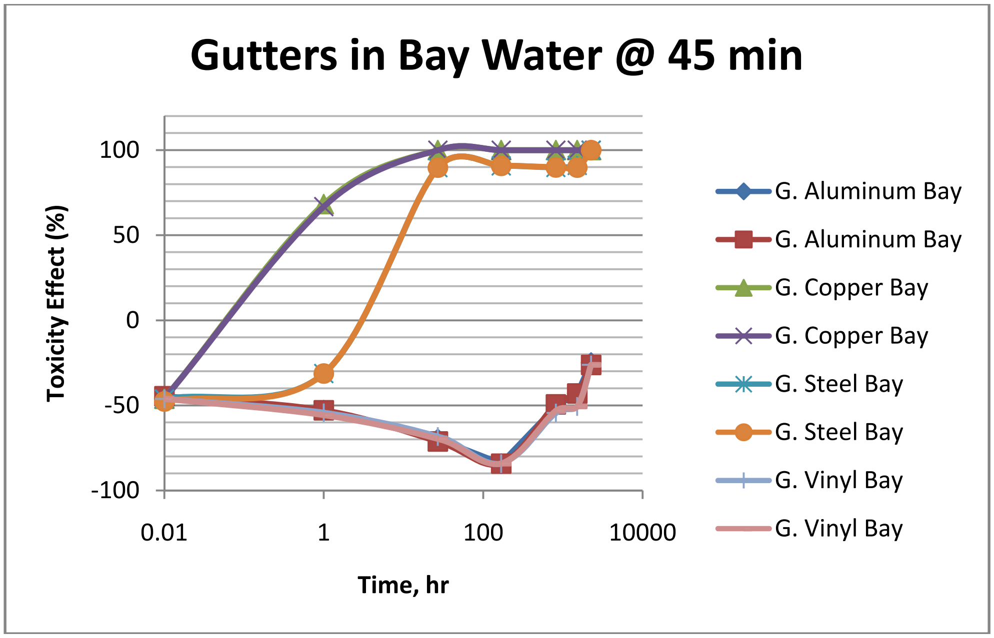


Figure E.2.13 Toxicity effect in samples with gutter materials. Bay water. At 45 min.

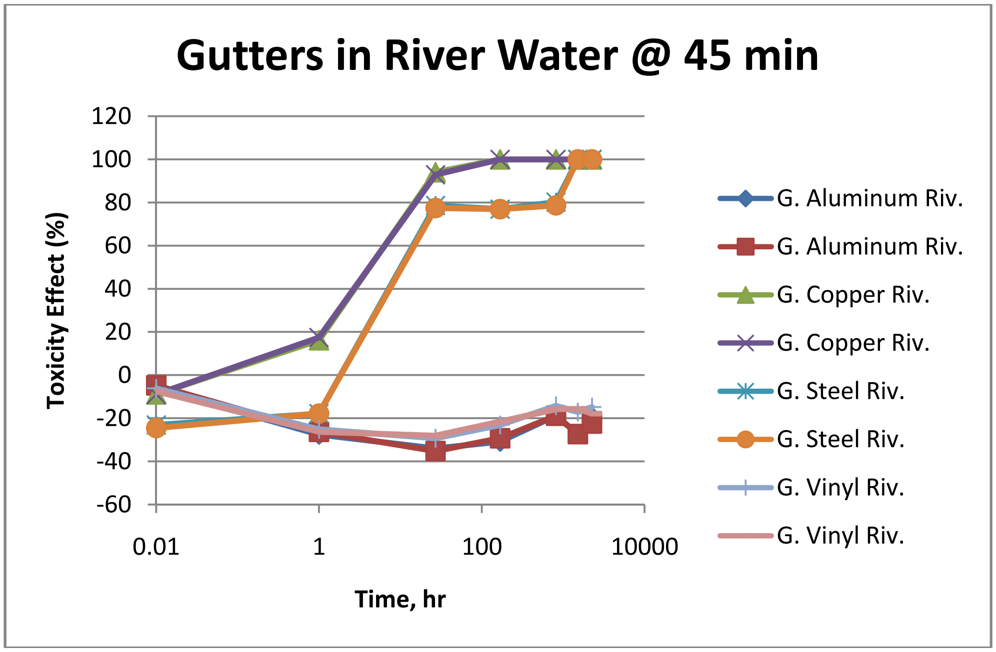


Figure E.2.14 Toxicity effect in samples with gutter materials. River water. At 45 min.

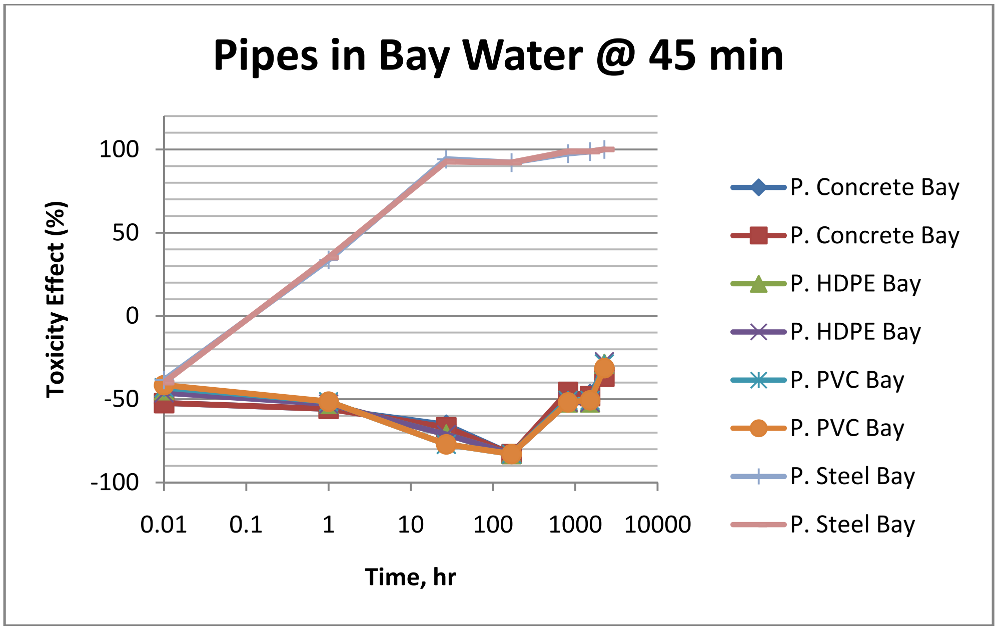


Figure E.2.15 Toxicity effect in samples with pipe materials. Bay water. At 45 min.

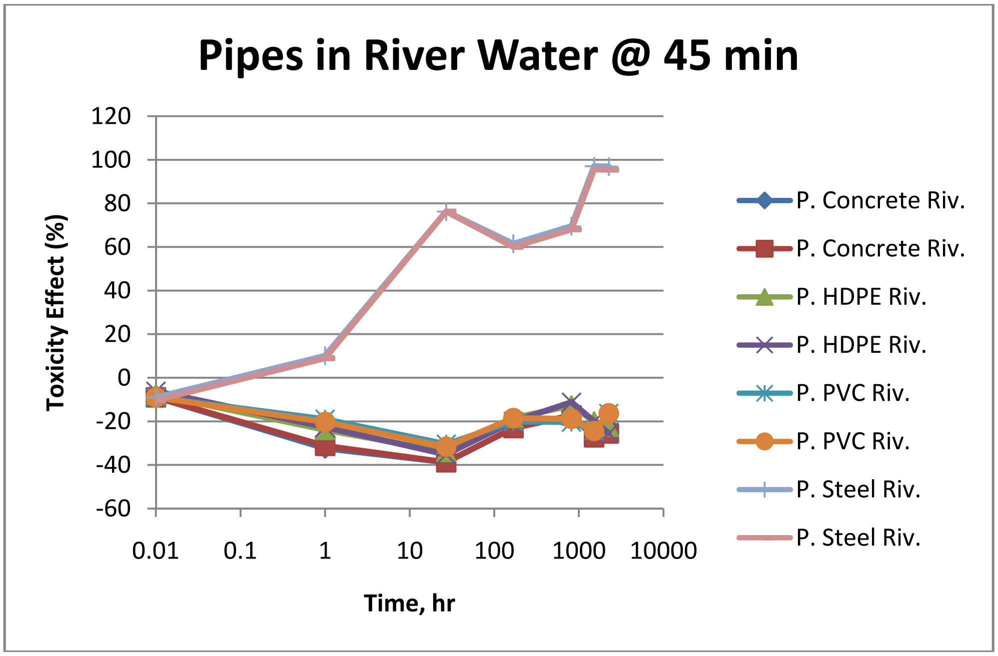


Figure E.2.16 Toxicity effect in samples with pipe materials. River water. At 45 min.

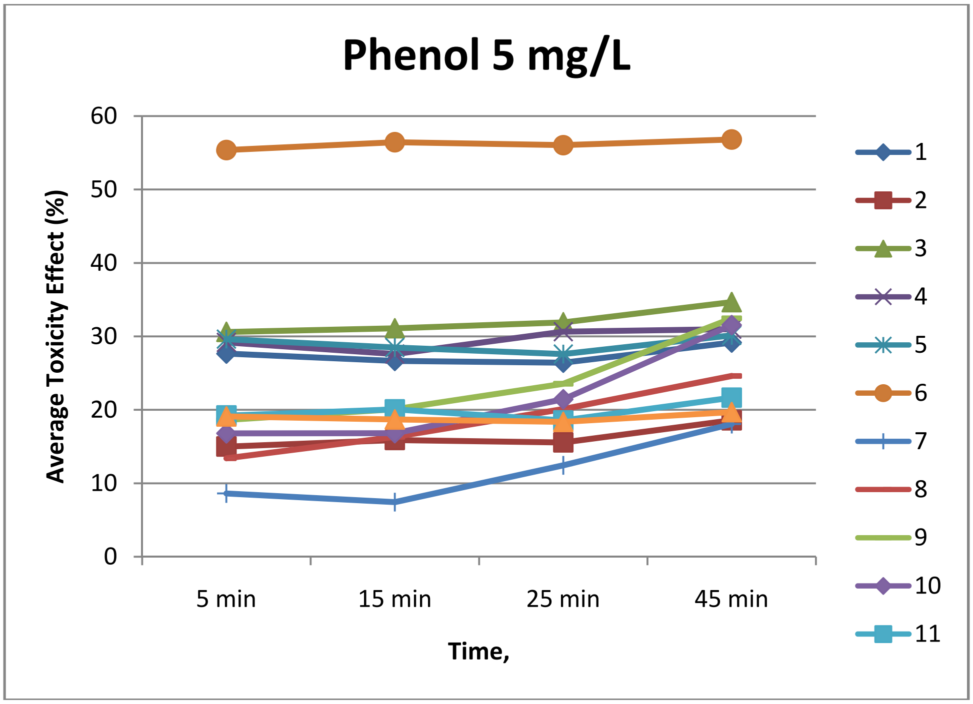


Figure E.3.1. Average toxicity effect of 5 mg/L of phenol. Controlled pH conditions. (Each point is an average of 2 replicates.)

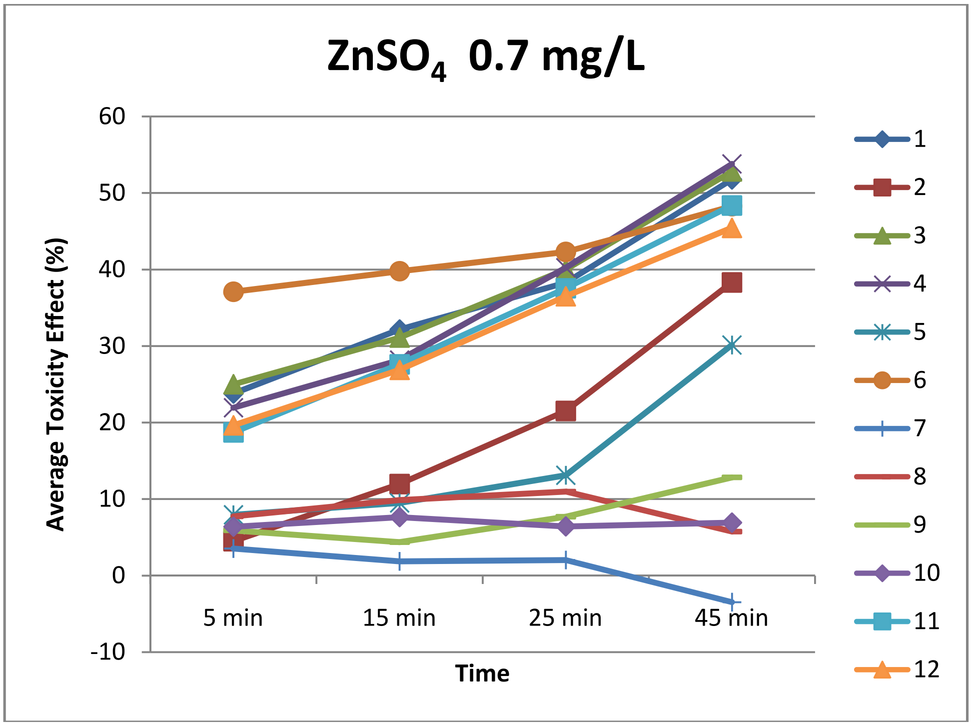


Figure E.3.2. Average toxicity effect of 0.7 mg/L of $ZnSO_4$. Controlled pH conditions. (Each point is an average of 2 replicates.)

Table E.32. Toxicity effect of phenol on Microtox acute test bacteria with each batch of the water samples at 15 min. Controlled pH tests. Controlled pH tests.

Analysis #	Phenol Conc., (mg/L)	Average Toxicity Effect, %
1	5	26.66
2	5	15.91
3	5	31.11
4	5	27.59
5	5	28.48
6	5	56.45
7	5	7.44
8	5	16.31
9	5	20.09
10	5	16.82
11	5	20.08
12	5	18.95
Average		23.82
St. Dev.		12.25
COV		0.514

Table E.33. Toxicity effect of $ZnSO_4$ on Microtox acute test bacteria with each batch of the water samples at 15 min. Controlled pH tests.

Analysis #	$ZnSO_4$, (mg/L)	Average Toxicity Effect, %
1	0.7	32.17
2	0.7	11.97
3	0.7	31.11
4	0.7	28.17
5	0.7	9.50
6	0.7	39.79
7	0.7	1.86
8	0.7	9.88
9	0.7	4.37
10	0.7	7.65
11	0.7	27.61
12	0.7	26.89
Average		19.24
St. Dev.		12.90
COV		0.671

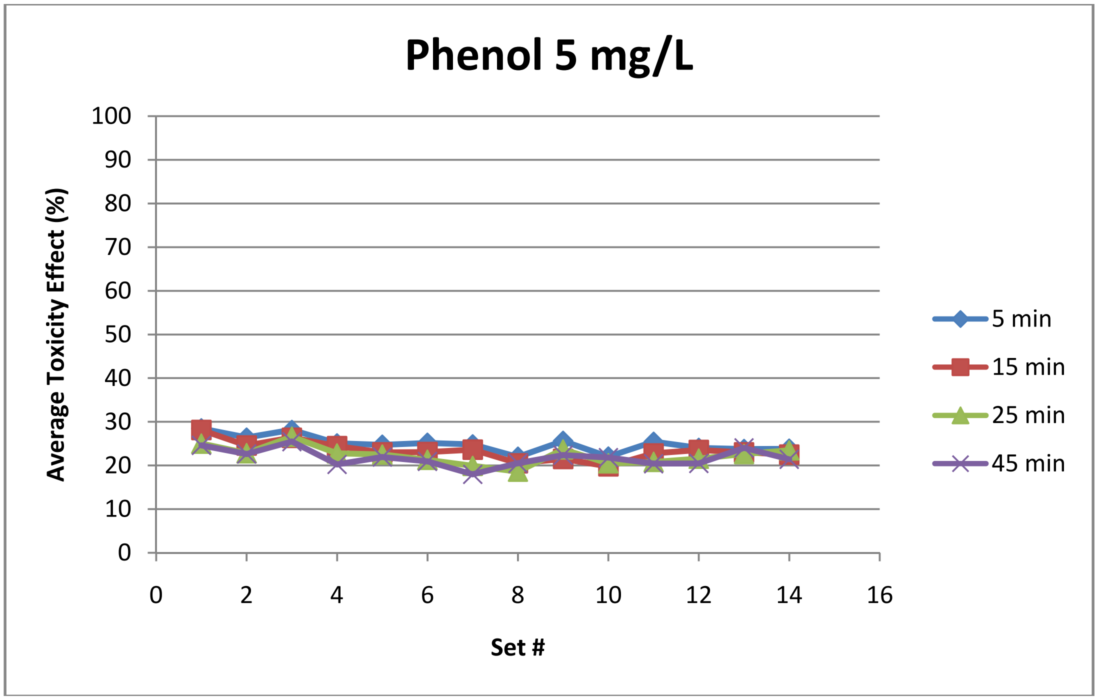


Figure E.3.3. Average toxicity effect of 5 mg/L of phenol. Natural pH conditions. (Each point is an average of 3 replicates.)

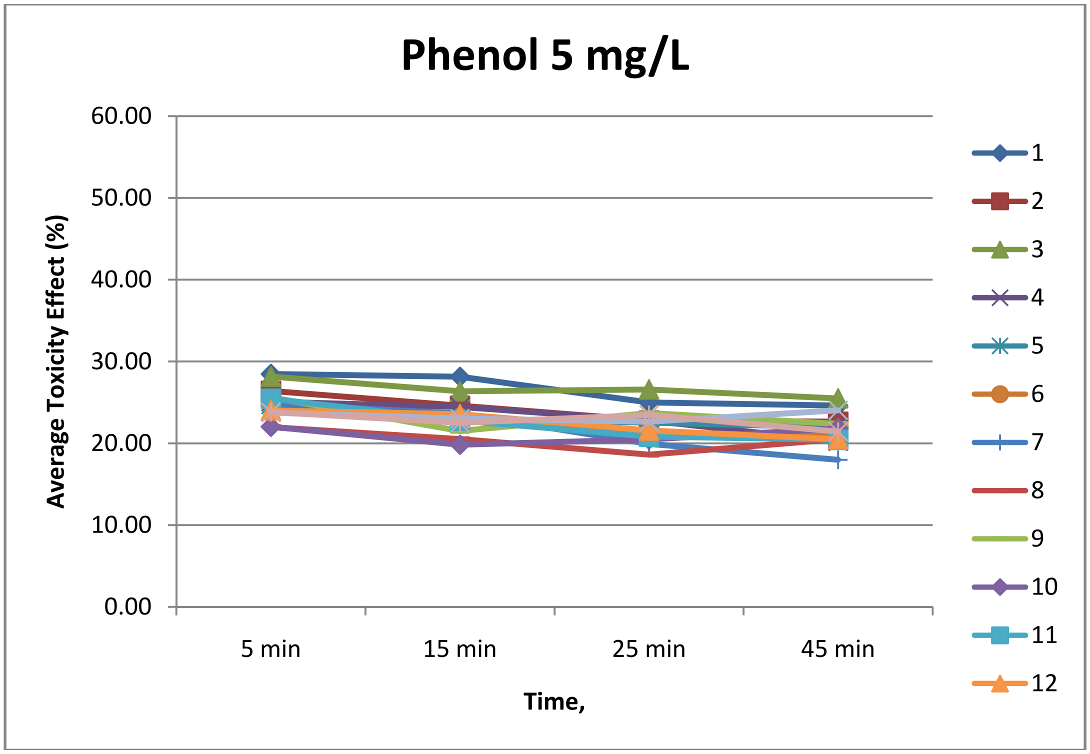


Figure E.3.4. Average toxicity effect of 5 mg/L of phenol. Natural pH Conditions. (Each point is an average of 3 replicates.)

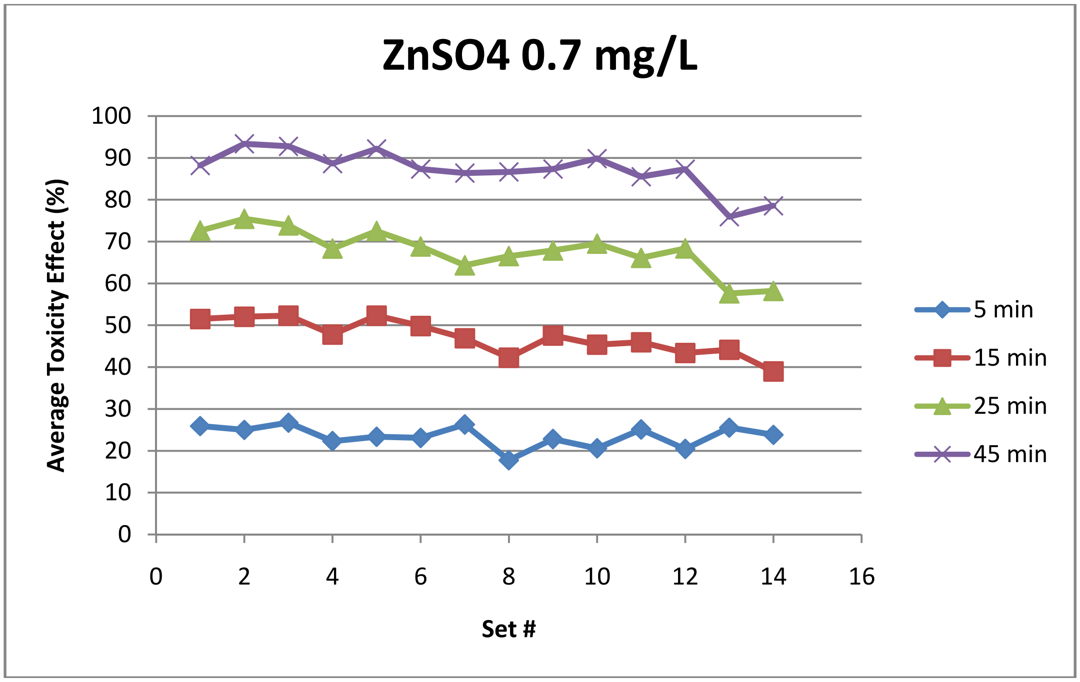


Figure E.3.5. Average toxicity effect of 0.7 mg/L of $ZnSO_4$. Controlled pH conditions. (Each point is an average of 3 replicates.)

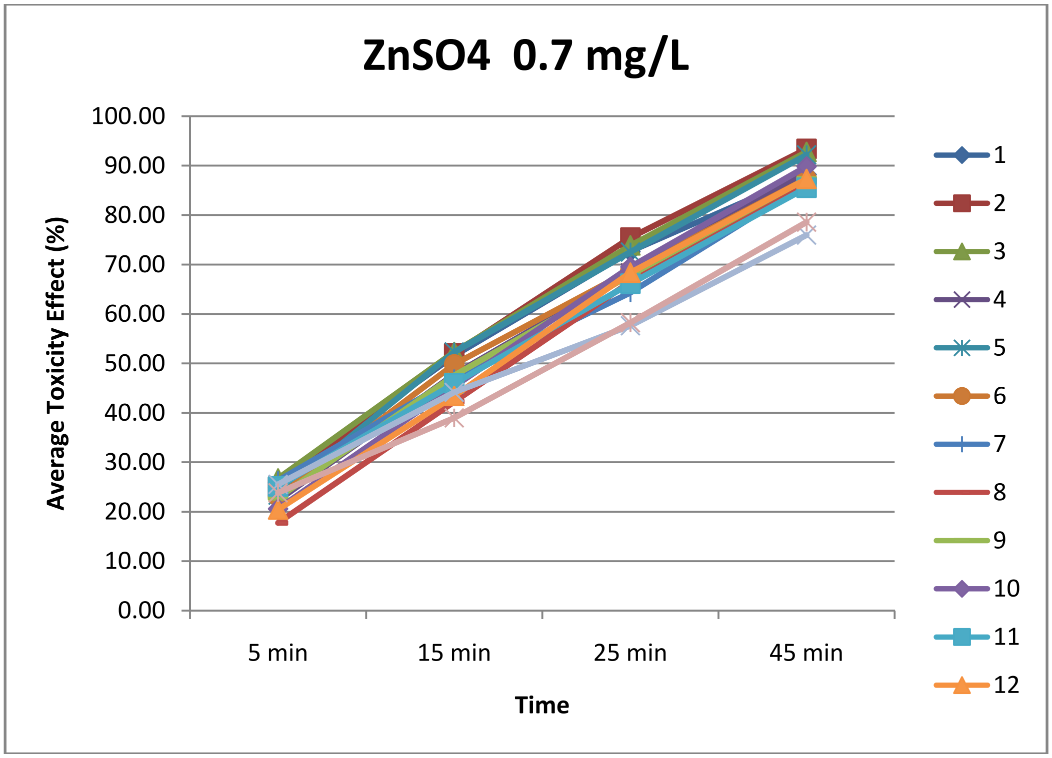


Figure E.3.6. Average toxicity effect of 0.7 mg/L of $ZnSO_4$. Natural pH conditions. (Each point is an average of 3 replicates.)

Table E.34. Toxicity effect of phenol on Microtox acute test bacteria with each batch of the water samples at 15 min. Natural pH tests.

Analysis #	Phenol Conc., (mg/L)	Average Toxicity Effect, %
1	5	28.14
2	5	24.59
3	5	26.36
4	5	24.44
5	5	23.01
6	5	23.08
7	5	23.64
8	5	20.50
9	5	21.51
10	5	19.82
11	5	22.78
12	5	23.55
13		23.02
14		22.51
Average		23.35
St. Dev.		2.15
COV		0.092

Table E.35. Toxicity effect of $ZnSO_4$ on Microtox acute test bacteria with each batch of the water samples at 15 min. Natural pH tests.

Analysis #	$ZnSO_4$, (mg/L)	Average Toxicity Effect, %
1	0.7	51.52
2	0.7	52.05
3	0.7	52.30
4	0.7	47.78
5	0.7	52.30
6	0.7	49.82
7	0.7	46.90
8	0.7	42.26
9	0.7	47.55
10	0.7	45.37
11	0.7	45.95
12	0.7	43.39
Average		44.15
St. Dev.		38.96
COV		47.16

APPENDIX F: 2^3 FACTORIAL ANALYSIS RESULTS

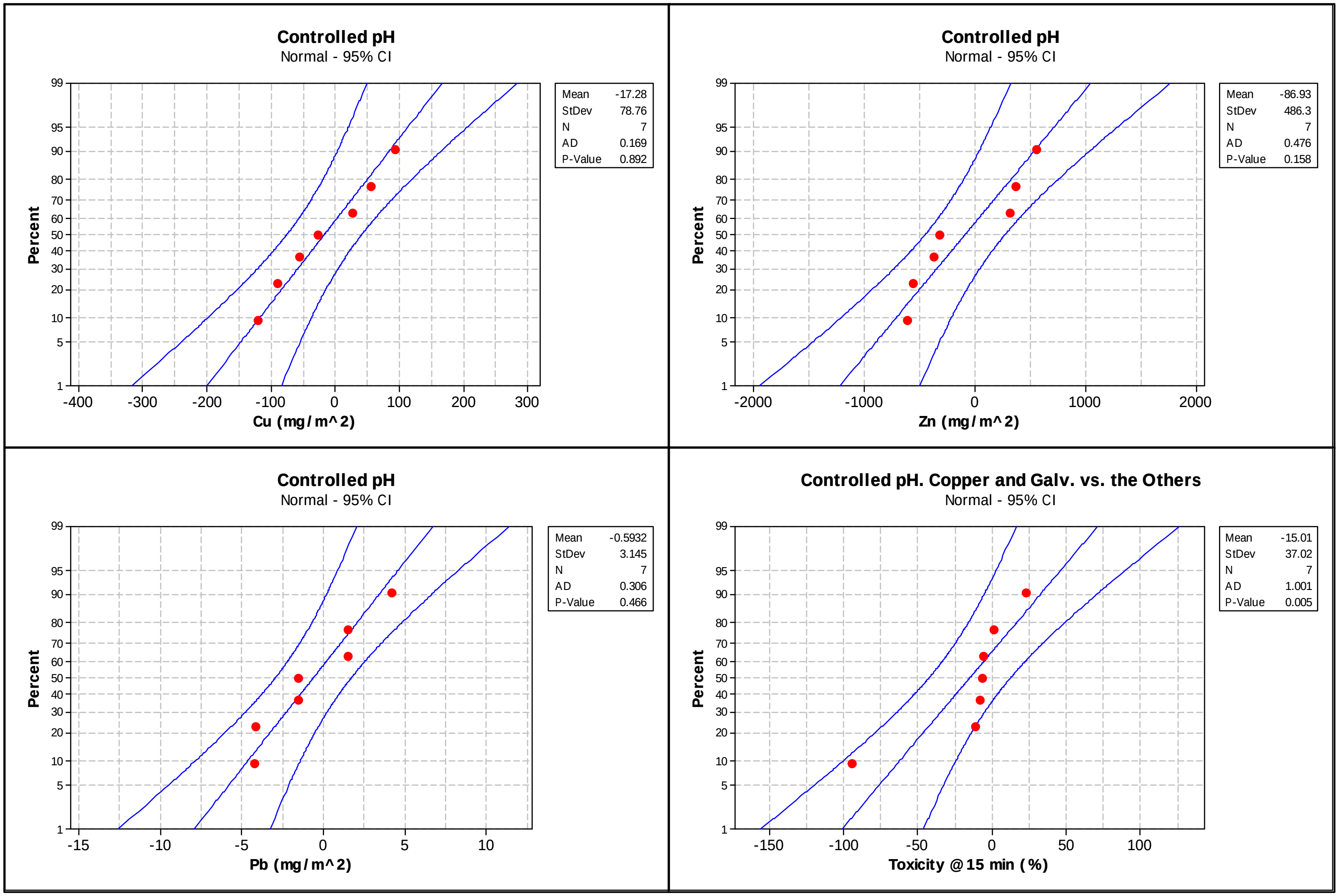


Figure F.1. Normal probability plots of the 3^2 Factorial Analysis effects and their interactions.

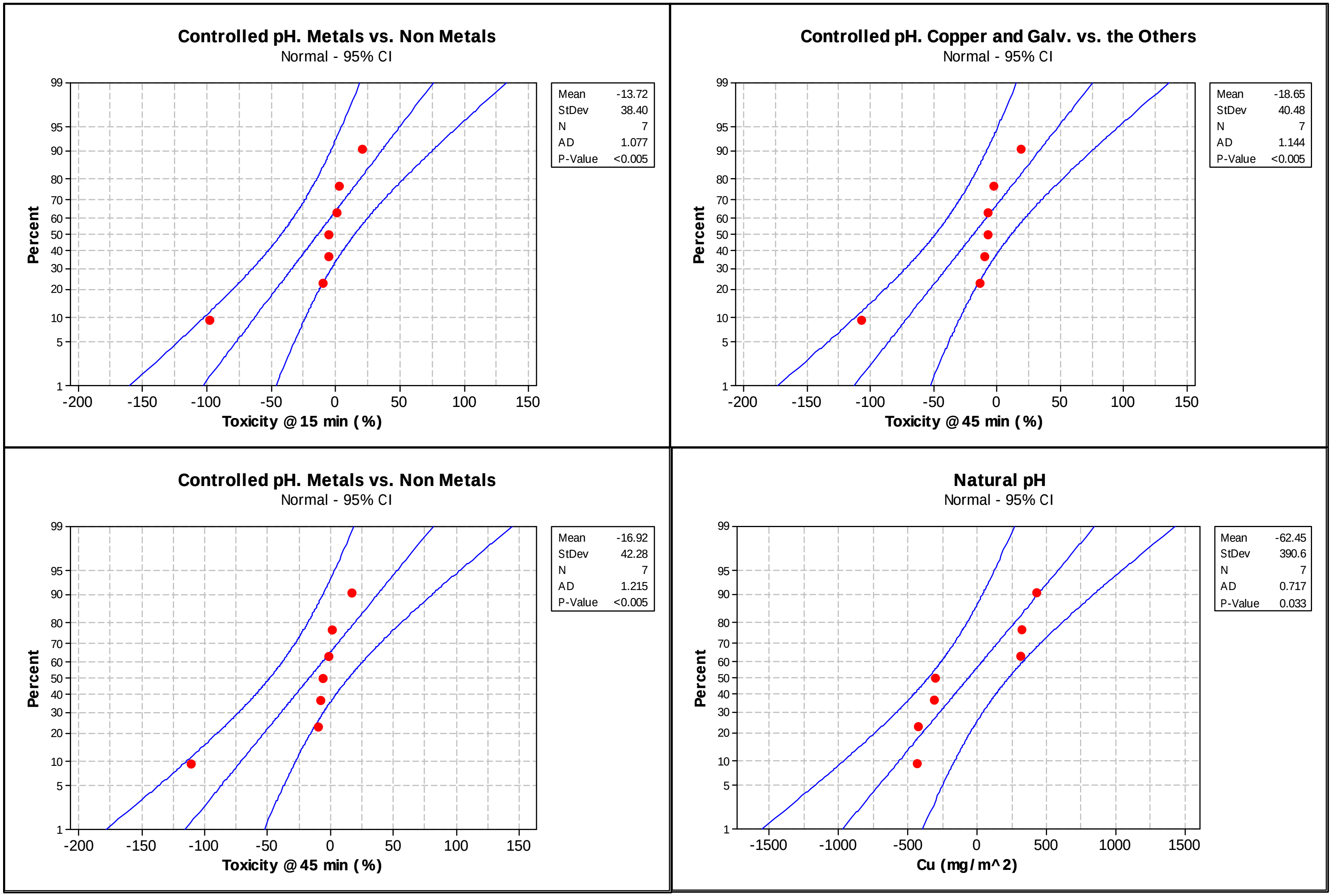


Figure F.1. - *Continued*

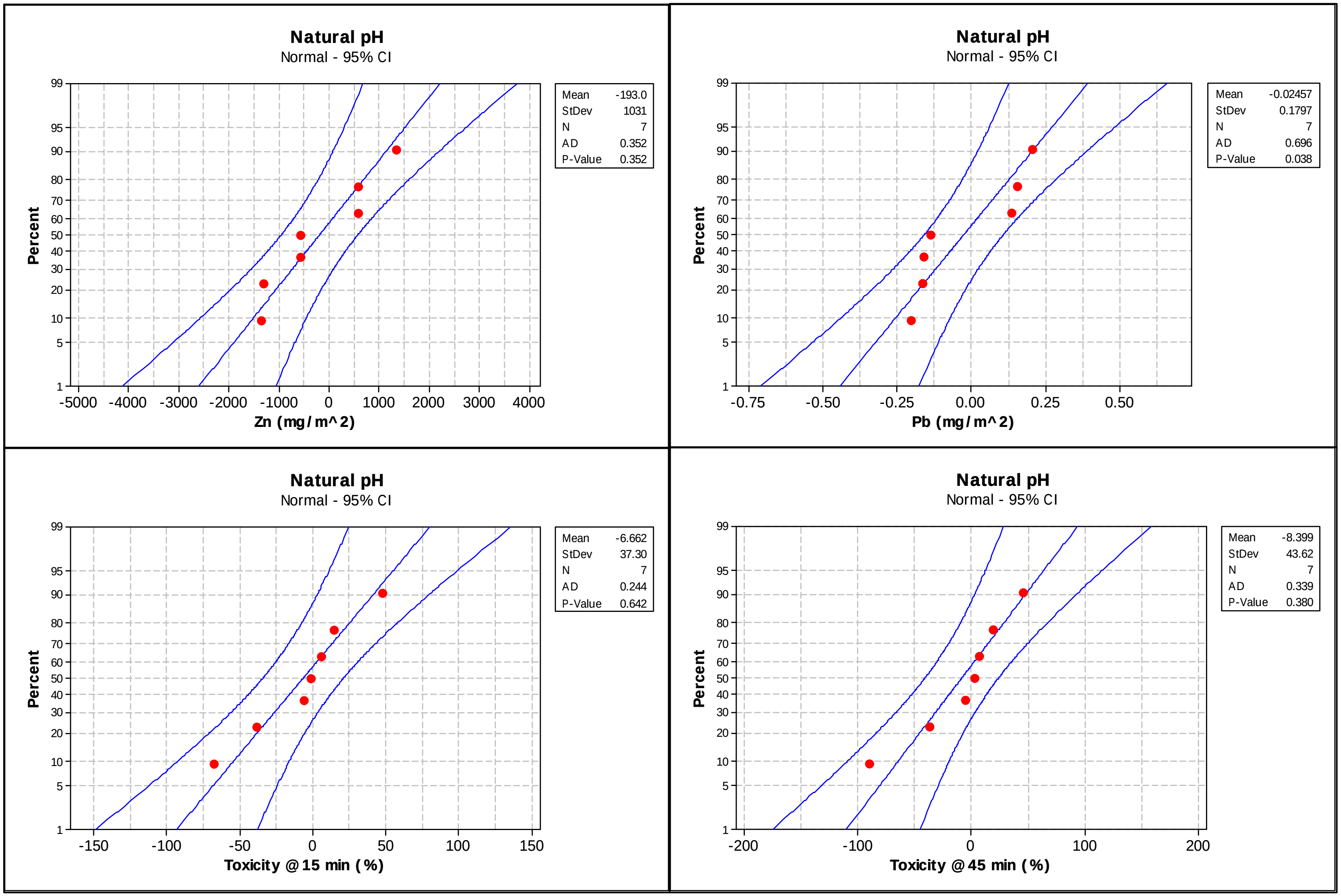

Natural pH
Normal - 95% CI

Figure F.1. - *Continued*

Table F.1. 2^3 Factorial Analysis. Standard Error of an Effect. Controlled pH Tests

Constituent	3^2 Factorial	Estimate of Variance, S^2	Variance of an Effect, V(eff.)	Standard Error of Main Effects and Interactions, SE (eff.)	Average Effect and Standard Error of Average Effect
Cu	pH: 5 vs. 8 M: Cop vs. the rest T: Short vs. Long	25.15	1.26	1.12	62.31 ± 11.85
Zn	pH: 5 vs. 8 M: Galv. vs. the rest T: Short vs. Long	170655.90	8532.79	92.37	308.83 ± 72.51
Pb	pH: 5 vs. 8 M: Galv. vs. the rest T: Short vs. Long	12.58	0.63	0.79	2.27 ± 0.47
Tox. 15 min	pH: 5 vs. 8 M: Cop, Galv. vs. the rest T: Short vs. Long	502.52	12.56	3.54	34.97 ± 4.18
Tox. 45 min	pH: 5 vs. 8 M: Cop, Galv. vs. the rest T: Short vs. Long	693.03	17.33	4.16	31.41 ± 4.68

Footnote: M = Material, T = Time

Table F.2. 2^3 Factorial Analysis. Standard Error of an Effect. Natural pH Tests

Constituent	3^2 Factorial	Estimate of Variance, S^2	Variance of an Effect, V(eff.)	Standard Error of Main Effects and Interactions, SE (eff.)	Average Effect and Standard Error of Average Effect
Cu	Cond.: High vs. Low M: Cop vs. the rest T: Short vs. Long	35332.64	2279.53	47.74	219.19 ± 65.91
Zn	Cond.: High vs. Low M: Galv. vs. the rest T: Short vs. Long	1000637.20	62539.82	250.08	677.84 ± 172.20
Pb	Cond.: High vs. Low M: Galv. vs. the rest T: Short vs. Long	0.07	4.68E-03	6.84E-02	0.26 ± 0.03
Tox. 15 min	Cond.: High vs. Low M: Cop.& Galv. vs. the rest T: Short vs. Long	243.00	7.59	2.76	6.74 ± 4.40
Tox. 45 min	Cond.: High vs. Low M: Cop.& Galv. vs. the rest T: Short vs. Long	148.41	4.64	2.15	9.44 ± 5.16

Footnote: M = Material, T = Time

Table F.3. 2^3 Factorial Analysis. Effects and Their Interactions. Controlled pH Tests

Constituent	3^2 Factorial	pH Effect	Material Effect	Time Effect	(pH x Material) Interaction	(pH x Time) Interaction	(Material x Time) Interaction	(pH x Material x Time) Interaction
Cu	pH: 5 vs. 8 M: Cop vs. the rest T: Short vs. Long	-55.82	-121.94	92.21	55.63	-27.05	-90.93	26.92
Zn	pH: 5 vs. 8 M: Galv. vs. the rest T: Short vs. Long	317.45	-612.94	557.88	-316.34	371.80	-555.24	-371.10
Pb	pH: 5 vs. 8 M: Galv. vs. the rest T: Short vs. Long	1.52	-4.13	4.21	-1.52	1.52	-4.22	-1.52
Tox. 15 min	pH: 5 vs. 8 M: Cop, Galv. vs. the rest T: Short vs. Long	-94.89	-8.35	-6.09	-11.84	22.29	0.88	-7.06
Tox. 45 min	pH: 5 vs. 8 M: Cop, Galv. vs. the rest T: Short vs. Long	-107.32	-10.02	-7.22	-13.45	18.58	-3.40	-7.73

Footnote: M = Material, T = Time

Table F.4. 2^3 Factorial Analysis. Effects and Their Interactions Natural pH Tests

Constituent	**3^2 Factorial**	**Cond. Effect**	**Material Effect**	**Time Effect**	**(Cond. x Material) Interaction**	**(Cond. x Time) Interaction**	**(Material x Time) Interaction**	**(Cond. x Material x Time) Interaction**
Cu	Cond.: High vs. Low M: Cop vs. the rest T: Short vs. Long	-314.45	-437.08	426.68	314.45	-308.10	-426.73	308.10
Zn	Cond.: High vs. Low M: Galv. vs. the rest T: Short vs. Long	572.22	-1351.92	1321.46	-573.42	579.93	-1318.62	-580.54
Pb	Cond.: High vs. Low M: Galv. vs. the rest T: Short vs. Long	0.14	-0.16	0.15	-0.14	0.21	-0.16	-0.21
Tox. 15 min	Cond.: High vs. Low M: Cop.& Galv. vs. the rest T: Short vs. Long	5.63	-68.12	47.71	13.99	-6.26	-38.42	-1.16
Tox. 45 min	Cond.: High vs. Low M: Cop.& Galv. vs. the rest T: Short vs. Long	6.54	-89.76	45.21	18.92	2.83	-37.03	-5.51

Footnote: M = Material, T = Time

Table F.5. 2^3 Factorial Analysis. Table of Contrasts. Copper Releases. Controlled pH Tests

Case	Mean	pH	M (Material)	T (Time)	pH x M	pH x T	M x T	pH x M x T
1	+	5 (-)	G.Copper (-)	Sh (-)	+	+	+	-
2	+	8 (+)	G.Copper (-)	Sh (-)	-	-	+	+
3	+	5 (-)	the rest (+)	Sh (-)	-	+	-	+
4	+	8 (+)	the rest (+)	Sh (-)	+	-	-	-
5	+	5 (-)	G.Copper (-)	Lon (+)	+	-	-	+
6	+	8 (+)	G.Copper (-)	Lon (+)	-	+	-	-
7	+	5 (-)	the rest (+)	Lon (+)	-	-	+	-
8	+	8 (+)	the rest (+)	Lon (+)	+	+	+	+

Table F.6. 2^3 Factorial Analysis. Table of Contrasts. Copper Releases. Natural pH Tests

Case	Mean	Cond	M (Material)	T (Time)	Cond x M	Cond x T	M x T	Cond x M x T
1	+	B (-)	G.Copper (-)	Sh (-)	+	+	+	-
2	+	R (+)	G.Copper (-)	Sh (-)	-	-	+	+
3	+	B (-)	the rest (+)	Sh (-)	-	+	-	+
4	+	R (+)	the rest (+)	Sh (-)	+	-	-	-
5	+	B (-)	G.Copper (-)	Lon (+)	+	-	-	+
6	+	R (+)	G.Copper (-)	Lon (+)	-	+	-	-
7	+	B (-)	the rest (+)	Lon (+)	-	-	+	-
8	+	R (+)	the rest (+)	Lon (+)	+	+	+	+

Table F.7. 2^3 Factorial Analysis. Table of Contrasts. Zinc Releases. Controlled pH Tests

Case	Mean	pH	M (Material)	T (Time)	pH x M	pH x T	M x T	pH x M x T
1	+	5 (-)	P., G.Galv (-)	Sh (-)	+	+	+	-
2	+	8 (+)	P., G.Galv (-)	Sh (-)	-	-	+	+
3	+	5 (-)	the rest (+)	Sh (-)	-	+	-	+
4	+	8 (+)	the rest (+)	Sh (-)	+	-	-	-
5	+	5 (-)	P., G.Galv (-)	Lon (+)	+	-	-	+
6	+	8 (+)	P., G.Galv (-)	Lon (+)	-	+	-	-
7	+	5 (-)	the rest (+)	Lon (+)	-	-	+	-
8	+	8 (+)	the rest (+)	Lon (+)	+	+	+	+

Table F.8. 2^3 Factorial Analysis. Table of Contrasts. Zinc Releases. Natural pH Tests

Case	Mean	Cond	M (Material)	T (Time)	Cond x M	Cond x T	M x T	Cond x M x T
1	+	B (-)	P., G.Galv (-)	Sh (-)	+	+	+	-
2	+	R (+)	P., G.Galv (-)	Sh (-)	-	-	+	+
3	+	B (-)	the rest (+)	Sh (-)	-	+	-	+
4	+	R (+)	the rest (+)	Sh (-)	+	-	-	-
5	+	B (-)	P., G.Galv (-)	Lon (+)	+	-	-	+
6	+	R (+)	P., G.Galv (-)	Lon (+)	-	+	-	-
7	+	B (-)	the rest (+)	Lon (+)	-	-	+	-
8	+	R (+)	the rest (+)	Lon (+)	+	+	+	+

Table F.9. 2^3 Factorial Analysis. Table of Contrasts. Lead Releases. Controlled pH Tests

Case	Mean	pH	M (Material)	T (Time)	pH x M	pH x T	M x T	pH x M x T
1	+	5 (-)	G.,P. Galv (-)	Sh (-)	+	+	+	-
2	+	8 (+)	G.,P. Galv (-)	Sh (-)	-	-	+	+
3	+	5 (-)	the rest (+)	Sh (-)	-	+	-	+
4	+	8 (+)	the rest (+)	Sh (-)	+	-	-	-
5	+	5 (-)	G., P. Galv (-)	Lon (+)	+	-	-	+
6	+	8 (+)	G., P. Galv (-)	Lon (+)	-	+	-	-
7	+	5 (-)	the rest (+)	Lon (+)	-	-	+	-
8	+	8 (+)	the rest (+)	Lon (+)	+	+	+	+

Table F.10. 2^3 Factorial Analysis. Table of Contrasts. Lead Releases. Natural pH Tests

Case	Mean	Cond	M (Material)	T (Time)	Cond x M	Cond x T	M x T	Cond x M x T
1	+	B (-)	P., G.Galv (-)	Sh (-)	+	+	+	-
2	+	R (+)	P., G.Galv (-)	Sh (-)	-	-	+	+
3	+	B (-)	the rest (+)	Sh (-)	-	+	-	+
4	+	R (+)	the rest (+)	Sh (-)	+	-	-	-
5	+	B (-)	P., G.Galv (-)	Lon (+)	+	-	-	+
6	+	R (+)	P., G.Galv (-)	Lon (+)	-	+	-	-
7	+	B (-)	the rest (+)	Lon (+)	-	-	+	-
8	+	R (+)	the rest (+)	Lon (+)	+	+	+	+

Table F.11. 2^3 Factorial Analysis. Table of Contrasts. Toxicity at 15 min. Controlled pH Tests

Case	Mean	pH	M (Material)	T (Time)	pH x M	pH x T	M x T	pH x M x T
1	+	5 (-)	Cop,Galv (-)	Sh (-)	+	+	+	-
2	+	8 (+)	Cop,Galv (-)	Sh (-)	-	-	+	+
3	+	5 (-)	the rest (+)	Sh (-)	-	+	-	+
4	+	8 (+)	the rest (+)	Sh (-)	+	-	-	-
5	+	5 (-)	Cop,Galv (-)	Lon (+)	+	-	-	+
6	+	8 (+)	Cop,Galv (-)	Lon (+)	-	+	-	-
7	+	5 (-)	the rest (+)	Lon (+)	-	-	+	-
8	+	8 (+)	the rest (+)	Lon (+)	+	+	+	+

Table F.12. 2^3 Factorial Analysis. Table of Contrasts. Toxicity at 45 min. Controlled pH Tests

Case	Mean	pH	M (Material)	T (Time)	pH x M	pH x T	M x T	pH x M x T
1	+	5 (-)	Cop,Galv (-)	Sh (-)	+	+	+	-
2	+	8 (+)	Cop,Galv (-)	Sh (-)	-	-	+	+
3	+	5 (-)	the rest (+)	Sh (-)	-	+	-	+
4	+	8 (+)	the rest (+)	Sh (-)	+	-	-	-
5	+	5 (-)	Cop,Galv (-)	Lon (+)	+	-	-	+
6	+	8 (+)	Cop,Galv (-)	Lon (+)	-	+	-	-
7	+	5 (-)	the rest (+)	Lon (+)	-	-	+	-
8	+	8 (+)	the rest (+)	Lon (+)	+	+	+	+

Table F.13. 2^3 Factorial Analysis. Table of Contrasts. Toxicity at 15 min. Natural pH Tests

Case	Mean	Cond	M (Material)	T (Time)	Cond x M	Cond x T	M x T	Cond x M x T
1	+	B (-)	Cop,Galv (-)	Sh (-)	+	+	+	-
2	+	R (+)	Cop,Galv (-)	Sh (-)	-	-	+	+
3	+	B (-)	the rest (+)	Sh (-)	-	+	-	+
4	+	R (+)	the rest (+)	Sh (-)	+	-	-	-
5	+	B (-)	Cop,Galv (-)	Lon (+)	+	-	-	+
6	+	R (+)	Cop,Galv (-)	Lon (+)	-	+	-	-
7	+	B (-)	the rest (+)	Lon (+)	-	-	+	-
8	+	R (+)	the rest (+)	Lon (+)	+	+	+	+

Table F.14. 2^3 Factorial Analysis. Table of Contrasts. Toxicity at 45 min. Natural pH Tests

Case	Mean	Cond	M (Material)	T (Time)	Cond x M	Cond x T	M x T	Cond x M x T
1	+	B (-)	Cop,Galv (-)	Sh (-)	+	+	+	-
2	+	R (+)	Cop,Galv (-)	Sh (-)	-	-	+	+
3	+	B (-)	the rest (+)	Sh (-)	-	+	-	+
4	+	R (+)	the rest (+)	Sh (-)	+	-	-	-
5	+	B (-)	Cop,Galv (-)	Lon (+)	+	-	-	+
6	+	R (+)	Cop,Galv (-)	Lon (+)	-	+	-	-
7	+	B (-)	the rest (+)	Lon (+)	-	-	+	-
8	+	R (+)	the rest (+)	Lon (+)	+	+	+	+

APPENDIX G: SPEARMAN CORRELATION MATRICES AND CLUSTER ANALYSES

Table G.1 Spearman correlation matrix for the concrete pipe during the buffered pH tests.

	Pb	Cu	Zn	pH	Cond.	Tox. 5min	Tox. 15min	Tox. 25min	Tox. 45min	Time
Pb*		all ND	0.298	-0.440	-0.240	-0.0424	-0.0424	-0.0565	-0.0707	-1.000
Cu*			0.298	-0.440	-0.240	-0.0424	-0.0424	-0.0565	-0.0707	-1.000
Zn				0.354	0.228	0.0246	0.102	0.0949	0.151	-0.298
pH					**0.825**	-0.611	-0.554	-0.547	-0.512	0.440
Cond.						**-0.769**	**-0.748**	**-0.741**	-0.699	0.240
Tox. 5min							**0.986**	**0.972**	**0.958**	0.0424
Tox. 15min								**0.993**	**0.972**	0.0424
Tox. 25min									**0.986**	0.0565
Tox. 45min										0.0707
Time										

Legend: Cond. = conductivity. Tox.5 min = toxicity after 5 min of bacteria exposure to a sample.
* All lead and copper concentrations were below detection limit.
High spearman correlation coefficients (at or above 0.75) are highlighted in bold.

Table G.2 Spearman correlation matrix for the concrete pipe during the natural pH tests.

	Pb	Cu	Zn	pH	Cond.	Tox. 5min	Tox. 15min	Tox. 25min	Tox. 45min	Time
Pb*		all ND	all ND	-0.135	-0.481	-0.749	-0.650	-0.368	-0.353	-1.000
Cu*			all ND	-0.135	-0.481	-0.749	-0.650	-0.368	-0.353	-1.000
Zn*				-0.135	-0.481	-0.749	-0.650	-0.368	-0.353	-1.000
pH					-0.305	0.270	0.137	0.242	0.249	0.135
Cond.						0.0839	-0.133	-0.524	-0.531	0.481
Tox. 5min							**0.937**	0.685	0.706	0.749
Tox. 15min								**0.832**	**0.846**	0.650
Tox. 25min									**0.993**	0.368
Tox. 45min										0.353
Time										

Legend: Cond. = conductivity. Tox.5 min = toxicity after 5 min of bacteria exposure to a sample.
* All lead, copper, and zinc concentrations were below detection limit.
High spearman correlation coefficients (at or above 0.75) are highlighted in bold.

Table G.3 Spearman correlation matrix for the PVC pipe during the buffered pH tests.

	Pb	Cu	Zn	pH	Cond.	Tox. 5min	Tox. 15min	Tox. 25min	Tox. 45min	Time
Pb*		-0.733	-0.865	-0.378	-0.482	0.0496	0.0424	0.0707	0.113	-1.000
Cu			**0.751**	0.00888	0.148	0.0935	0.0810	0.0599	0.0106	0.733
Zn				0.485	0.637	-0.408	-0.411	-0.442	-0.453	**0.865**
pH					**0.949**	-0.746	-0.741	**-0.755**	**-0.801**	0.378
Cond.						**-0.777**	**-0.775**	**-0.789**	**-0.825**	0.482
Tox. 5 min							**0.998**	**0.991**	**0.960**	-0.0496
Tox. 15min								**0.993**	**0.965**	-0.0424
Tox. 25min									**0.972**	-0.0707
Tox. 45min										-0.113
Time										

Legend: Cond. = conductivity. Tox.5 min = toxicity after 5 min of bacteria exposure to a sample.
* All lead concentrations were below detection limit.
High spearman correlation coefficients (at or above 0.75) are highlighted in bold.

Table G.4 Spearman correlation matrix for the PVC pipe during the natural pH tests.

	Pb	Cu	Zn	pH	Cond.	Tox. 5min	Tox. 15min	Tox. 25min	Tox. 45min	Time
Pb*		all ND	0.285	-0.142	-0.481	-0.509	-0.311	-0.283	-0.368	-1.000
Cu*			0.285	-0.142	-0.481	-0.509	-0.311	-0.283	-0.368	-1.000
Zn				0.275	-0.549	0.158	0.261	0.299	0.218	-0.285
pH					-0.644	0.606	0.553	0.644	0.687	0.142
Cond.						-0.371	-0.503	-0.566	-0.524	0.481
Tox. 5min							**0.951**	**0.902**	**0.902**	0.509
Tox. 15min								**0.944**	**0.888**	0.311
Tox. 25min									**0.972**	0.283
Tox. 45min										0.368
Time										

Legend: Cond. = conductivity. Tox.5 min = toxicity after 5 min of bacteria exposure to a sample.
* All lead and copper concentrations were below detection limit.
High spearman correlation coefficients (at or above 0.75) are highlighted in bold.

Table G.5 Spearman correlation matrix for the HDPE pipe during the buffered pH tests.

	Pb	Cu	Zn	pH	Cond.	Tox. 5min	Tox. 15min	Tox. 25min	Tox. 45min	Time
Pb*		-0.541	-0.537	-0.0141	-0.474	0.0707	0.0283	0.000	-0.0989	-1.000
Cu			0.444	-0.120	0.162	-0.0634	-0.0634	-0.0880	0.0775	0.541
Zn				-0.699	-0.452	0.657	0.678	0.678	**0.762**	0.537
pH					0.746	-0.608	-0.629	-0.678	-0.727	0.0141
Cond.						**-0.792**	**-0.771**	**-0.753**	-0.729	0.474
Tox. 5min							**0.979**	**0.951**	**0.825**	-0.0707
Tox. 15min								**0.986**	**0.832**	-0.0283
Tox. 25min									**0.846**	0.000
Tox. 45min										0.0989
Time										

Legend: Cond. = conductivity. Tox.5 min = toxicity after 5 min of bacteria exposure to a sample.
* All lead concentrations were below detection limit.
High spearman correlation coefficients (at or above 0.75) are highlighted in bold.

Table G.6 Spearman correlation matrix for the HDPE pipe during the natural pH tests.

	Pb	Cu	Zn	pH	Cond.	Tox. 5min	Tox. 15min	Tox. 25min	Tox. 45min	Time
Pb*		all ND	0.114	-0.149	-0.481	-0.523	-0.466	-0.368	-0.269	-1.000
Cu*			0.114	-0.149	-0.481	-0.523	-0.466	-0.368	-0.269	-1.000
Zn				0.482	0.520	-0.471	-0.524	-0.580	-0.576	-0.114
pH					-0.697	**0.774**	0.697	**0.788**	**0.785**	0.149
Cond.						-0.322	-0.385	-0.524	-0.573	0.481
Tox. 5min							**0.951**	**0.937**	**0.937**	0.523
Tox. 15min								**0.944**	**0.951**	0.466
Tox. 25min									**0.972**	0.368
Tox. 45min										0.269
Time										

Legend: Cond. = conductivity. Tox.5 min = toxicity after 5 min of bacteria exposure to a sample.
* All lead and copper concentrations were below detection limit.
High spearman correlation coefficients (at or above 0.75) are highlighted in bold.

Table G.7 Spearman correlation matrix for the galvanized steel pipe during the buffered pH tests.

	Pb	Cu	Zn	pH	Cond.	Tox. 5min	Tox. 15min	Tox. 25min	Tox. 45min	Time
Pb		0.385	0.464	0.109	0.239	-0.148	-0.155	-0.162	-0.155	0.554
Cu			-0.0351	0.0105	0.134	-0.211	-0.218	-0.225	-0.218	-0.171
Zn				0.413	0.406	0.0280	0.0350	0.0350	0.0315	**0.848**
pH					**0.958**	**-0.825**	**-0.811**	**-0.818**	**-0.823**	0.452
Cond.						**-0.818**	**-0.811**	**-0.825**	**-0.823**	0.466
Tox. 5min							**0.993**	**0.993**	**0.998**	-0.127
Tox. 15min								**0.986**	**0.991**	-0.113
Tox. 25min									**0.998**	-0.113
Tox. 45min										-0.120
Time										

Legend: Cond. = conductivity. Tox.5 min = toxicity after 5 min of bacteria exposure to a sample.
High spearman correlation coefficients (at or above 0.75) are highlighted in bold.

Table G.8 Spearman correlation matrix for the galv. steel pipe during the natural pH tests.

	Pb	Zn	pH	Cond.	Tox. 5min	Tox. 15min	Tox. 25min	Tox. 45min	Time
Pb		-0.175	0.413	-0.406	-0.508	-0.462	-0.462	-0.427	-0.496
Zn			-0.0699	0.000	**0.853**	**0.846**	**0.846**	**0.860**	**0.905**
pH				**-0.902**	-0.399	-0.399	-0.399	-0.413	-0.0283
Cond.					0.392	0.399	0.399	0.399	0.000
Tox. 5min						**0.986**	**0.986**	**0.972**	**0.862**
Tox. 15min							**1.000**	**0.986**	**0.820**
Tox. 25min								**0.986**	**0.820**
Tox. 45min									**0.806**
Time									

Legend: Cond. = conductivity. Tox.5 min = toxicity after 5 min of bacteria exposure to a sample.
* All copper concentrations were below detection limit.
High spearman correlation coefficients (at or above 0.75) are highlighted in bold.

Table G.9 Spearman correlation matrix for the vinyl gutter during the buffered pH tests.

	Pb	Cu	Zn	pH	Cond.	Tox. 5min	Tox. 15min	Tox. 25min	Tox. 45min	Time
Pb*		-0.512	-0.0566	-0.0354	-0.474	-0.0565	-0.0424	0.142	-0.199	-1.000
Cu			0.00352	-0.454	-0.0423	0.179	0.214	0.134	0.321	0.512
Zn				0.740	0.621	-0.501	-0.536	-0.626	-0.717	0.0566
pH					**0.754**	-0.711	**-0.781**	**-0.759**	**-0.873**	0.0354
Cond.						-0.718	-0.715	**-0.830**	-0.668	0.474
Tox. 5min							**0.986**	**0.870**	**0.881**	0.0565
Tox. 15min								**0.870**	**0.916**	0.0424
Tox. 25min									**0.827**	-0.142
Tox. 45min										0.199
Time										

Legend: Cond. = conductivity. Tox.5 min = toxicity after 5 min of bacteria exposure to a sample.
* All lead concentrations were below detection limit.
High spearman correlation coefficients (at or above 0.75) are highlighted in bold.

Table G.10 Spearman correlation matrix for the vinyl gutter during the natural pH tests.

	Pb	Cu	Zn	pH	Cond.	Tox. 5min	Tox. 15min	Tox. 25min	Tox. 45min	Time
Pb*		all ND	0.428	-0.135	-0.481	-0.721	-0.622	-0.594	-0.438	-1.000
Cu*			0.428	-0.135	-0.481	-0.721	-0.622	-0.594	-0.438	-1.000
Zn				-0.218	-0.176	-0.381	-0.430	-0.289	-0.243	-0.428
pH					-0.691	0.488	0.467	0.582	0.698	0.135
Cond.						-0.140	-0.182	-0.329	-0.490	0.481
Tox. 5min							**0.958**	**0.951**	**0.874**	0.721
Tox. 15min								**0.930**	**0.839**	0.622
Tox. 25min									**0.958**	0.594
Tox. 45min										0.438
Time										

Legend: Cond. = conductivity. Tox.5 min = toxicity after 5 min of bacteria exposure to a sample.
* All lead and copper concentrations were below detection limit.
High spearman correlation coefficients (at or above 0.75) are highlighted in bold.

Table G.11 Spearman correlation matrix for the Aluminum gutter during the buffered pH tests.

	Pb	Cu	Zn	pH	Cond.	Tox. 5min	Tox. 15min	Tox. 25min	Tox. 45min	Time
Pb*		-0.543	-0.339	-0.0283	-0.466	0.212	0.226	0.205	-0.0285	-1.000
Cu			0.339	-0.0283	0.297	-0.297	-0.283	-0.304	-0.114	0.543
Zn				**0.755**	**0.860**	-0.748	-0.741	-0.767	-0.746	0.339
pH					**0.755**	-0.692	-0.699	-0.711	**-0.873**	0.0283
Cond.						**-0.881**	**-0.895**	**-0.893**	**-0.775**	0.466
Tox. 5min							**0.993**	**0.981**	**0.810**	-0.212
Tox. 15min								**0.991**	**0.789**	-0.226
Tox. 25min									**0.794**	-0.205
Tox. 45min										0.0285
Time										

Legend: Cond. = conductivity. Tox.5 min = toxicity after 5 min of bacteria exposure to a sample.
* All lead concentrations were below detection limit.
High spearman correlation coefficients (at or above 0.75) are highlighted in bold.

Table G.12 Spearman correlation matrix for the Aluminum gutter during the natural pH tests.

	Pb	Cu	Zn	pH	Cond.	Tox. 5min	Tox. 15min	Tox. 25min	Tox. 45min	Time
Pb*		all ND	-0.142	-0.248	-0.495	-0.735	-0.424	-0.410	-0.481	-1.000
Cu*			-0.142	-0.248	-0.495	-0.735	-0.424	-0.410	-0.481	-1.000
Zn				-0.705	**0.806**	-0.438	-0.666	-0.644	-0.606	0.142
pH					-0.614	0.554	0.460	0.516	0.586	0.248
Cond.						-0.0559	-0.294	-0.343	-0.350	0.495
Tox. 5min							**0.874**	**0.888**	**0.909**	0.735
Tox. 15min								**0.881**	**0.860**	0.424
Tox. 25min									**0.979**	0.410
Tox. 45min										0.481
Time										

Legend: Cond. = conductivity. Tox.5 min = toxicity after 5 min of bacteria exposure to a sample.
* All lead and copper concentrations were below detection limit.
High spearman correlation coefficients (at or above 0.75) are highlighted in bold.

Table G.13 Spearman correlation matrix for the galv. steel gutter during the buffered pH tests.

	Pb	Cu	Zn	pH	Cond.	Tox. 5min	Tox. 15min	Tox. 25min	Tox. 45min	Time
Pb		0.307	0.593	0.703	0.695	-0.512	-0.501	-0.488	-0.515	**0.752**
Cu			0.0668	0.535	0.534	-0.517	-0.525	-0.531	-0.539	-0.128
Zn				0.291	0.252	-0.0210	-0.0140	-0.00699	0.000	0.721
pH					**0.991**	**-0.879**	**-0.875**	**-0.869**	**-0.882**	0.460
Cond.						**-0.902**	**-0.897**	**-0.888**	**-0.904**	0.466
Tox. 5min							**0.998**	**0.993**	**0.991**	-0.240
Tox. 15min								**0.998**	**0.993**	-0.234
Tox. 25min									**0.991**	-0.226
Tox. 45min										-0.219
Time										

Legend: Cond. = conductivity. Tox.5 min = toxicity after 5 min of bacteria exposure to a sample.
High spearman correlation coefficients (at or above 0.75) are highlighted in bold.

Table G.14 Spearman correlation matrix for the galv. steel gutter during the natural pH tests.

	Pb	Cu	Zn	pH	Cond.	Tox. 5min	Tox. 15min	Tox. 25min	Tox. 45min	Time
Pb		-0.396	0.592	-0.221	-0.360	0.151	0.151	0.295	0.215	0.396
Cu*			-0.891	0.432	-0.361	-0.905	-0.905	-0.899	-0.868	-1.000
Zn				-0.336	0.0841	**0.769**	0.727	0.739	**0.782**	**0.891**
pH					-0.470	-0.396	-0.459	-0.505	-0.497	-0.432
Cond.						0.406	0.469	0.368	0.508	0.361
Tox. 5min							**0.944**	**0.935**	**0.937**	**0.905**
Tox. 15min								**0.963**	**0.908**	**0.905**
Tox. 25min									**0.917**	**0.899**
Tox. 45min										**0.868**
Time										

Legend: Cond. = conductivity. Tox.5 min = toxicity after 5 min of bacteria exposure to a sample.
* All copper concentrations were below detection limit.
High spearman correlation coefficients (at or above 0.75) are highlighted in bold.

Table G.15 Spearman correlation matrix for the copper gutter during the buffered pH tests.

	Pb	Cu	Zn	pH	Cond.	Tox. 5min	Tox. 15min	Tox. 25min	Tox. 45min	Time
Pb*		-0.707	-0.101	-0.396	-0.474	0.0496	0.0424	0.0920	-0.135	-1.000
Cu			0.648	-0.203	-0.165	0.480	0.503	0.473	0.641	0.707
Zn				**-0.776**	-0.717	**0.824**	**0.829**	**0.799**	**0.777**	0.101
pH					**0.942**	**-0.858**	**-0.853**	**-0.872**	**-0.767**	0.396
Cond.						**-0.784**	**-0.778**	**-0.830**	-0.721	0.474
Tox. 5min							**0.998**	**0.958**	**0.888**	-0.0496
Tox. 15min								**0.956**	**0.886**	-0.0424
Tox. 25min									**0.951**	-0.0920
Tox. 45min										0.135
Time										

Legend: Cond. = conductivity. Tox.5 min = toxicity after 5 min of bacteria exposure to a sample.
* All lead concentrations were below detection limit.
High spearman correlation coefficients (at or above 0.75) are highlighted in bold.

Table G.16 Spearman correlation matrix for the copper gutter during the natural pH tests.

	Pb	Cu	Zn	pH	Cond.	Tox. 5min	Tox. 15min	Tox. 25min	Tox. 45min	Time
Pb*		-0.792	-0.446	-0.0638	-0.489	-0.785	-0.690	-0.742	-0.742	-1.000
Cu			0.522	-0.109	**0.848**	0.724	0.653	**0.762**	**0.762**	**0.792**
Zn				-0.121	0.511	0.439	0.536	0.565	0.565	0.446
pH					-0.503	0.358	0.353	0.322	0.322	0.0638
Cond.						0.404	0.383	0.524	0.524	0.489
Tox. 5min							**0.897**	**0.813**	**0.813**	**0.785**
Tox. 15min								**0.907**	**0.907**	0.690
Tox. 25min									**1.000**	0.742
Tox. 45min										0.742
Time										

Legend: Cond. = conductivity. Tox.5 min = toxicity after 5 min of bacteria exposure to a sample.
* All lead concentrations were below detection limit.
High spearman correlation coefficients (at or above 0.75) are highlighted in bold.

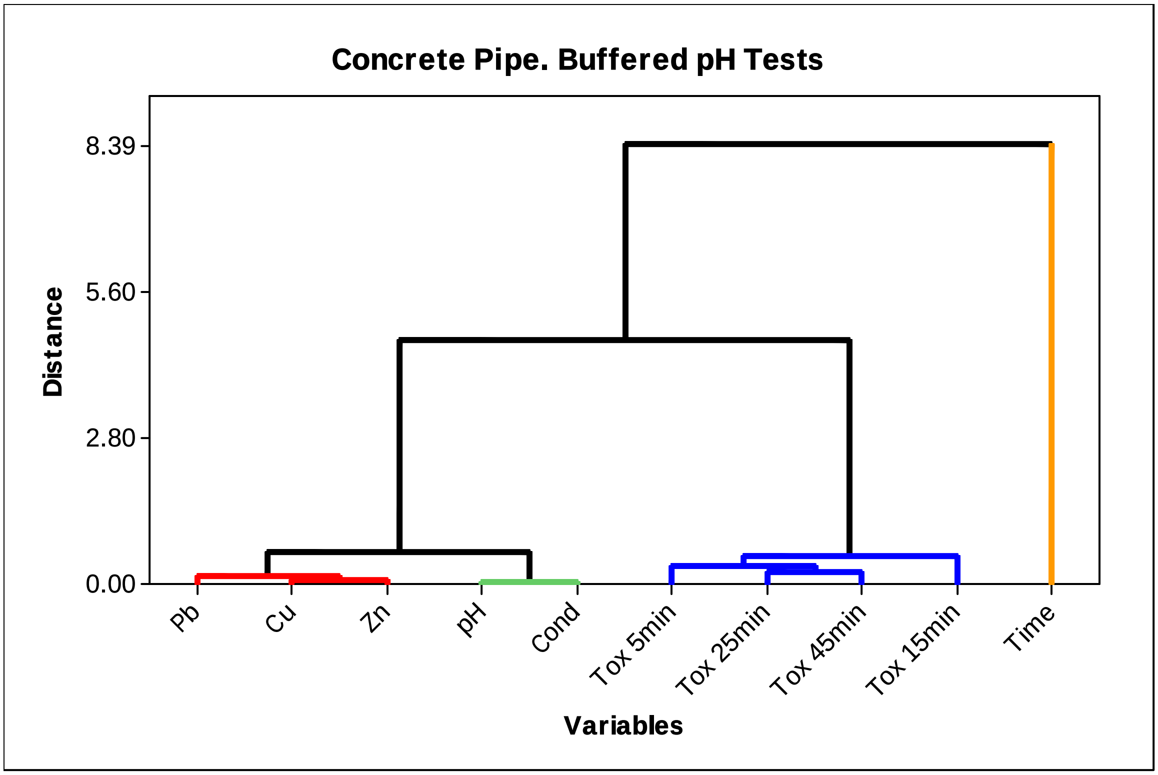


Figure G.1 Dendrogram from cluster analysis for water quality parameters. Concrete pipe. Buffered tests.

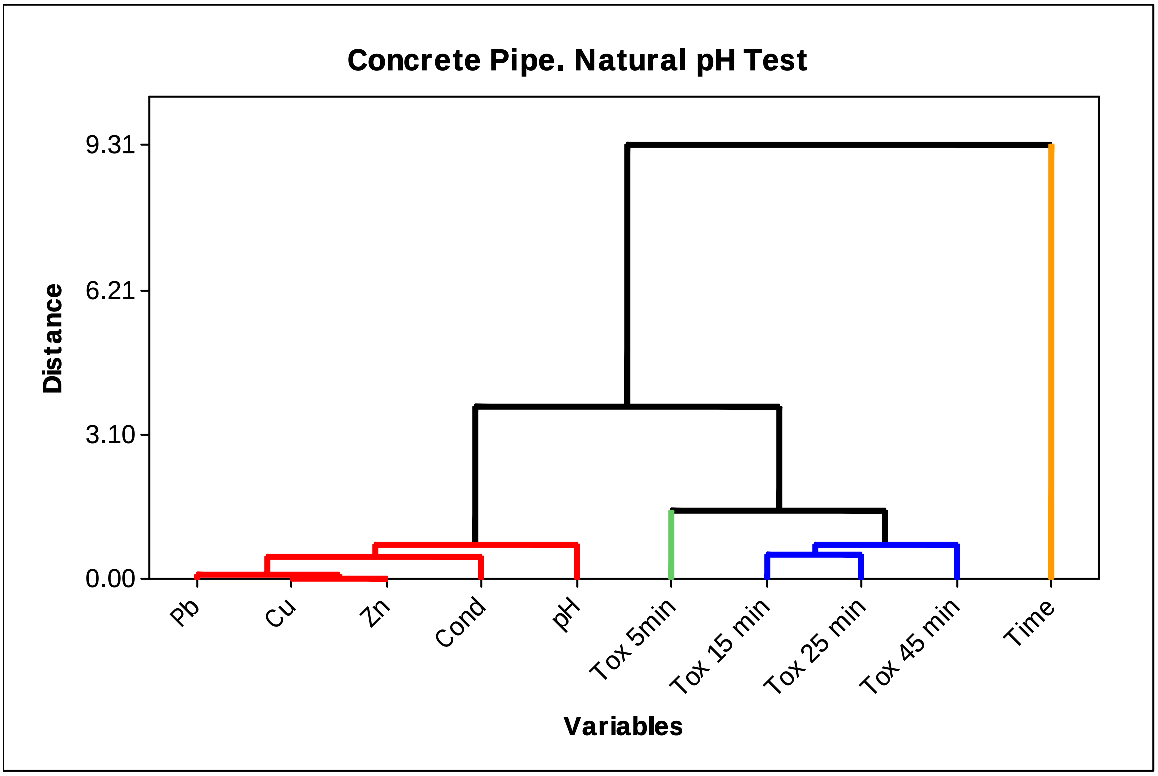


Figure G.2 Dendrogram from cluster analysis for water quality parameters. Concrete pipe. Natural pH tests.

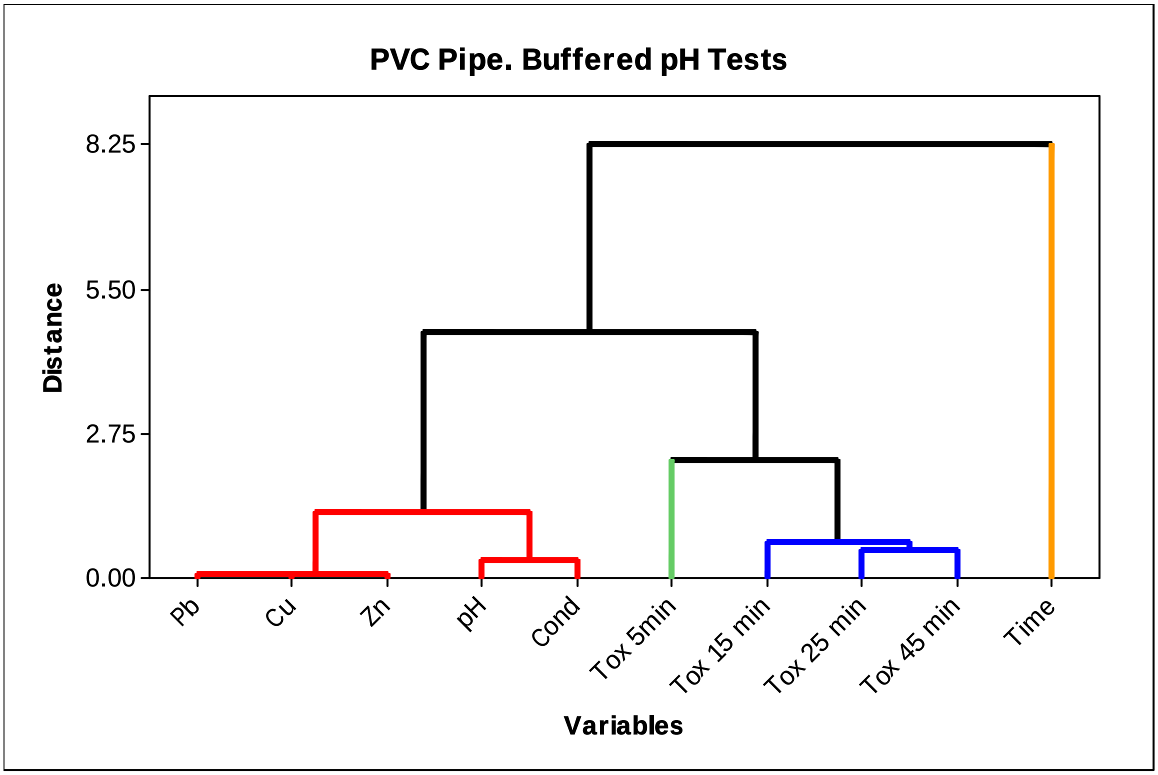


Figure G.3 Dendrogram from cluster analysis for water quality parameters. PVC pipe. Buffered tests.

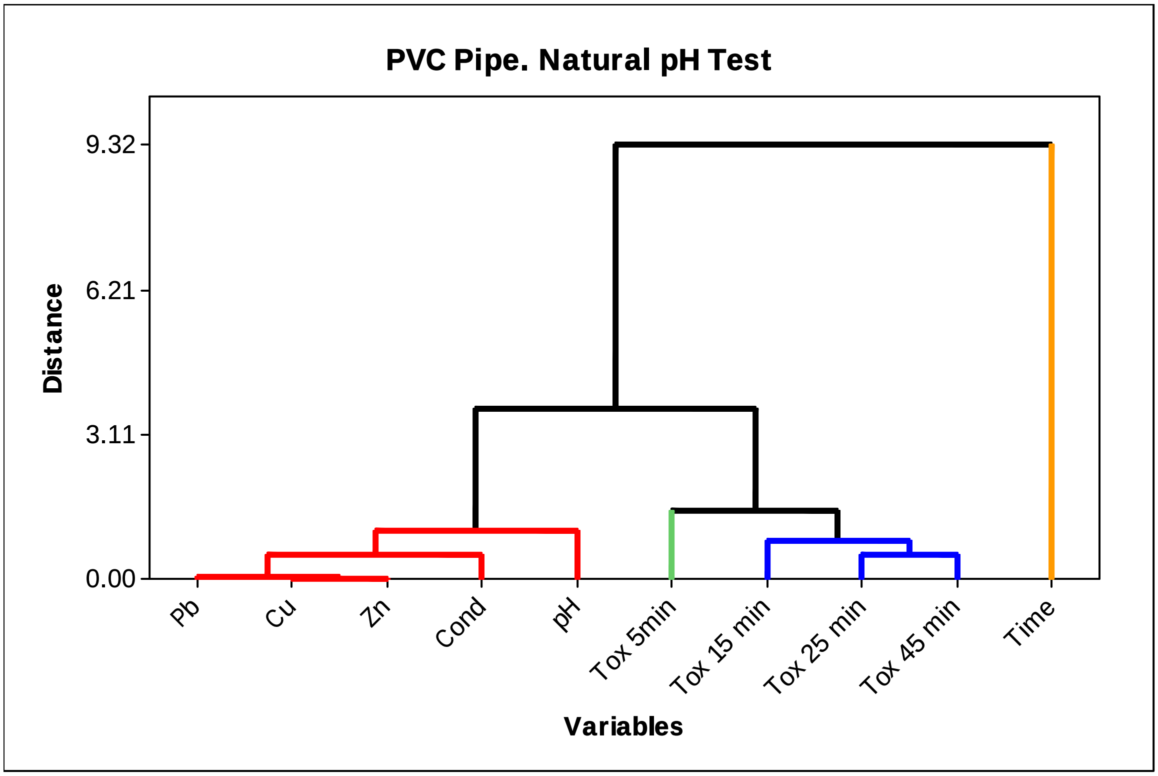


Figure G.4 Dendrogram from cluster analysis for water quality parameters. PVC pipe. Natural pH tests.

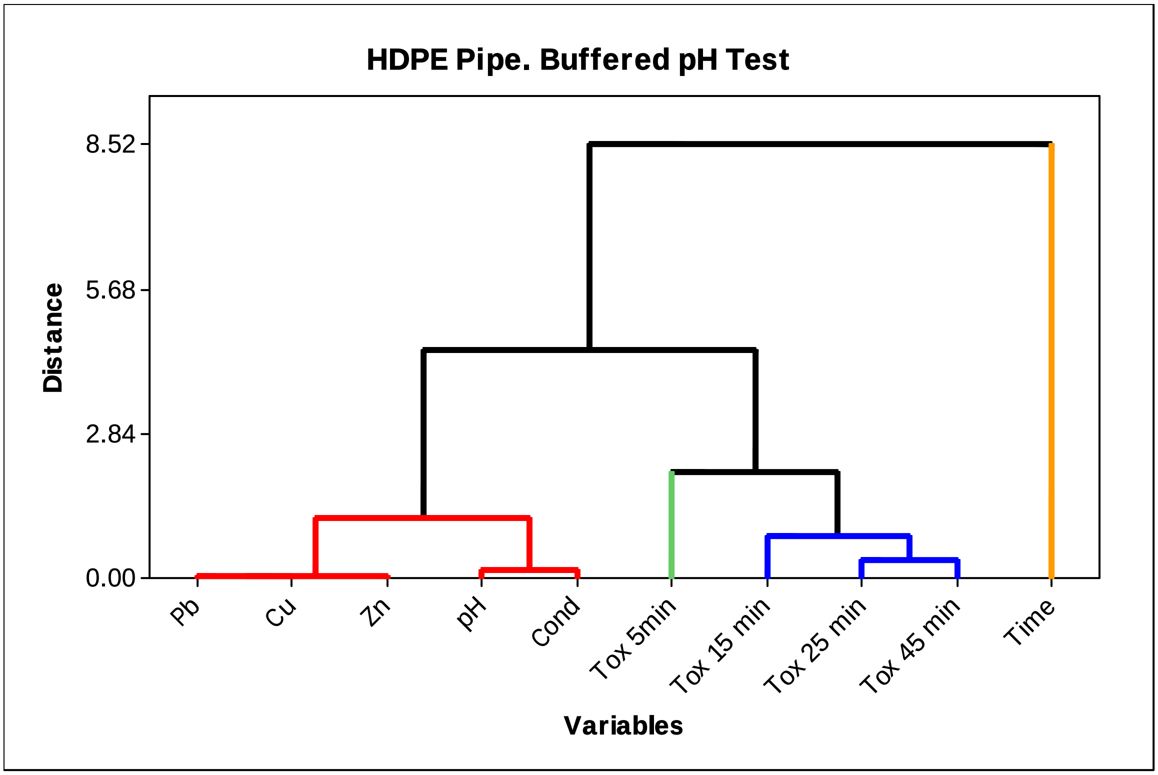


Figure G.5 Dendrogram from cluster analysis for water quality parameters. HDPE pipe. Buffered tests.

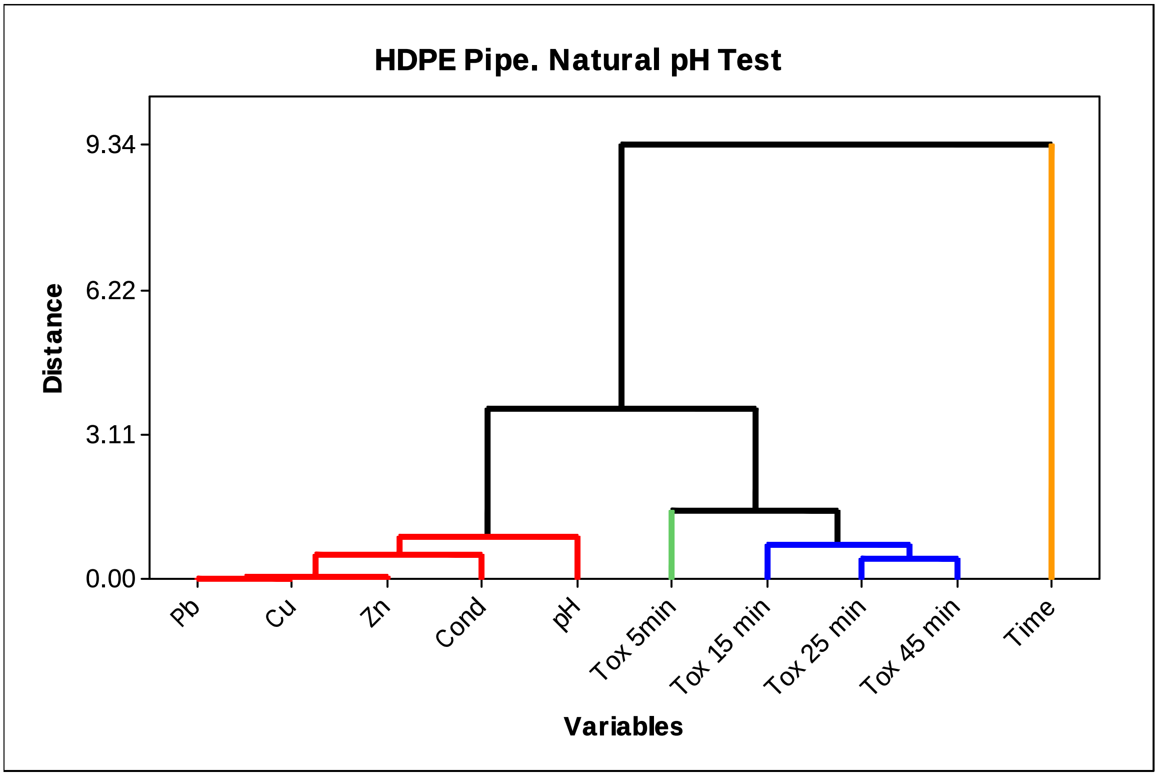


Figure G.6 Dendrogram from cluster analysis for water quality parameters. HDPE pipe. Natural pH tests.

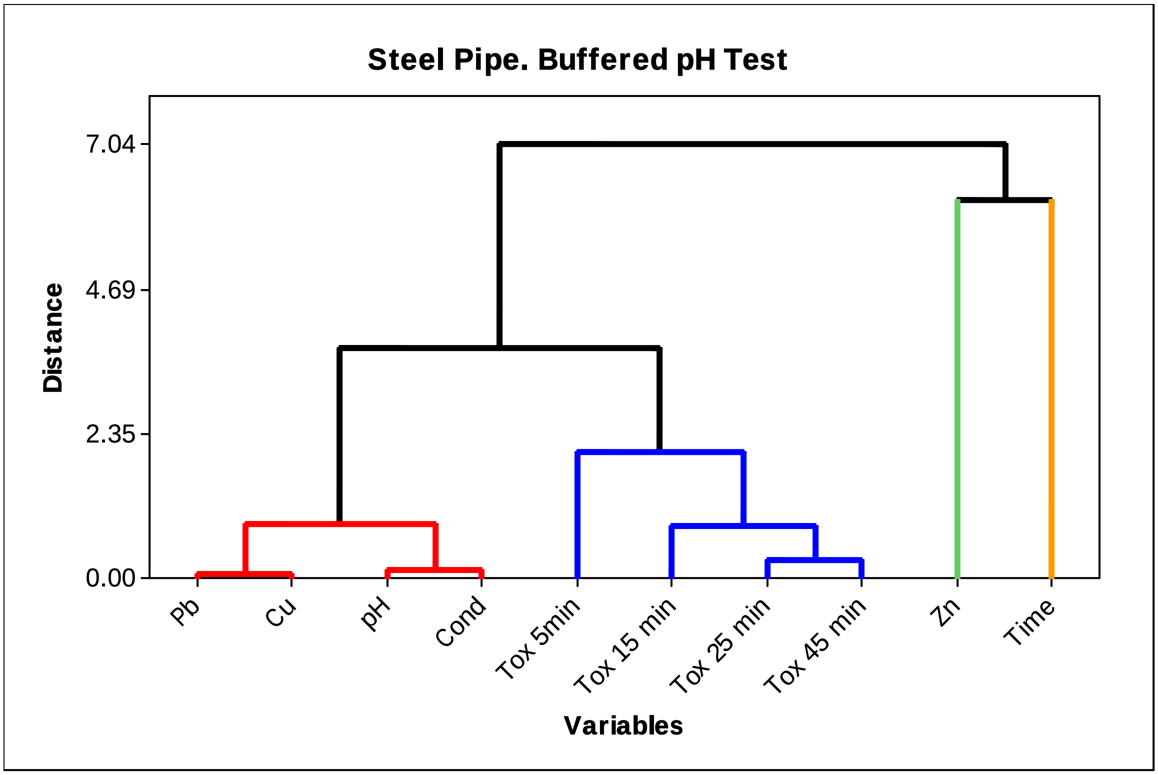


Figure G.7 Dendrogram from cluster analysis for water quality parameters. Galvanized steel pipe. Buffered tests.

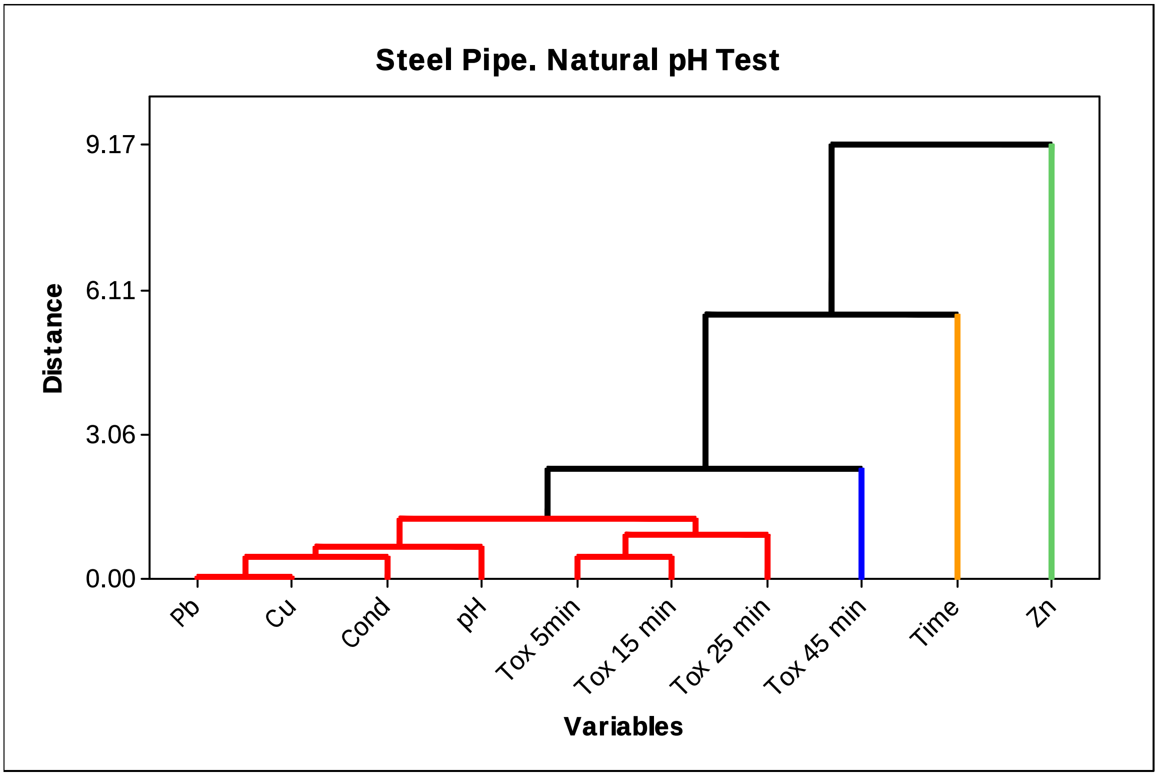


Figure G.8 Dendrogram from cluster analysis for water quality parameters. Galvanized steel pipe. Natural pH tests.

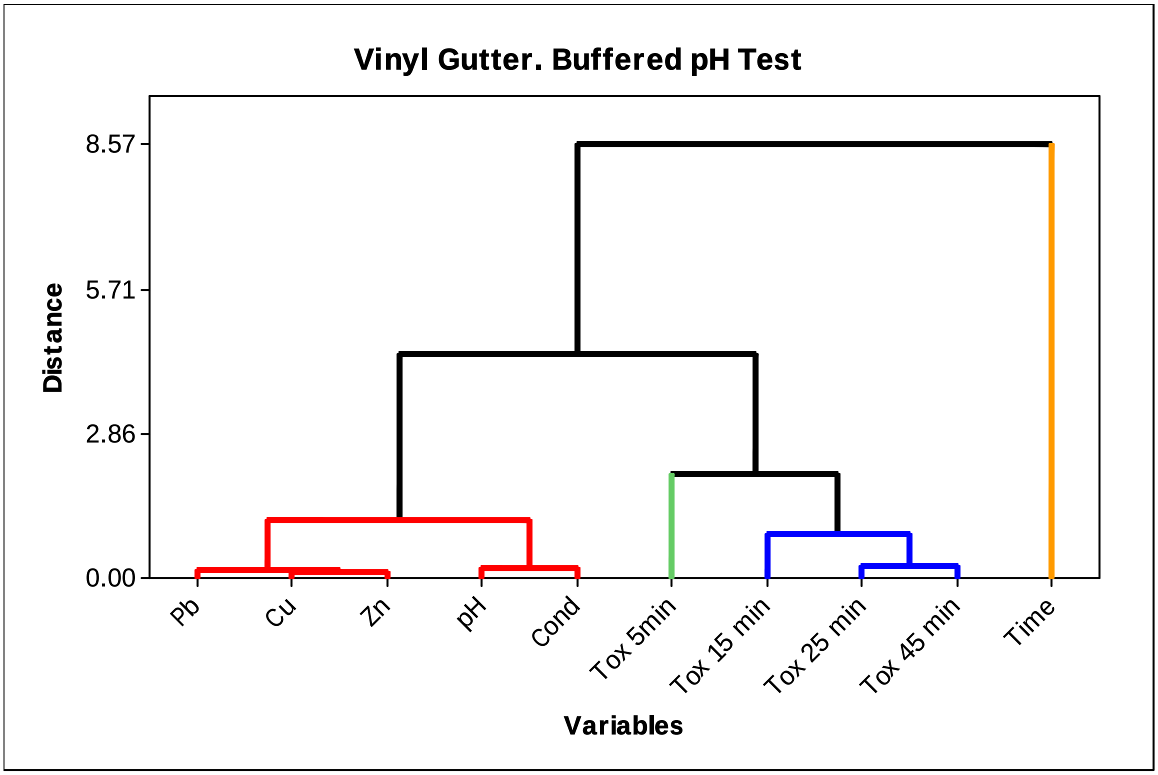


Figure G.9 Dendrogram from cluster analysis for water quality parameters. Vinyl gutter. Buffered tests.

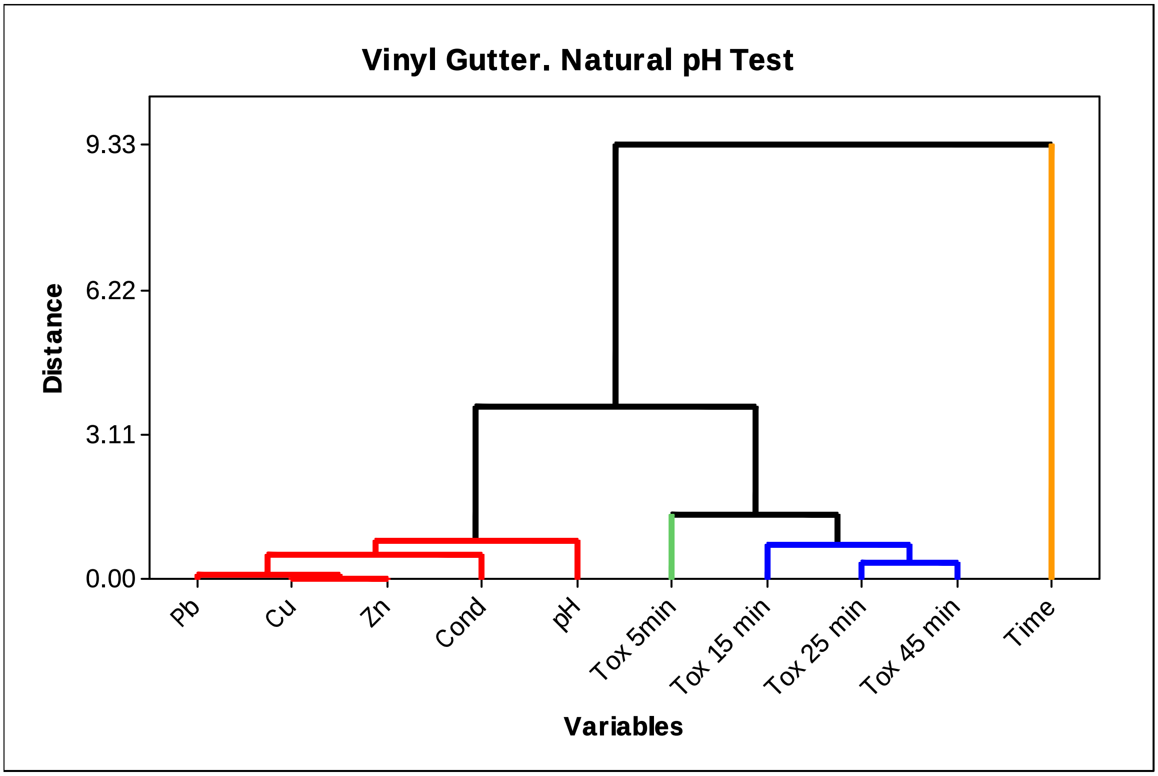


Figure G.10 Dendrogram from cluster analysis for water quality parameters. Vinyl gutter. Natural pH tests.

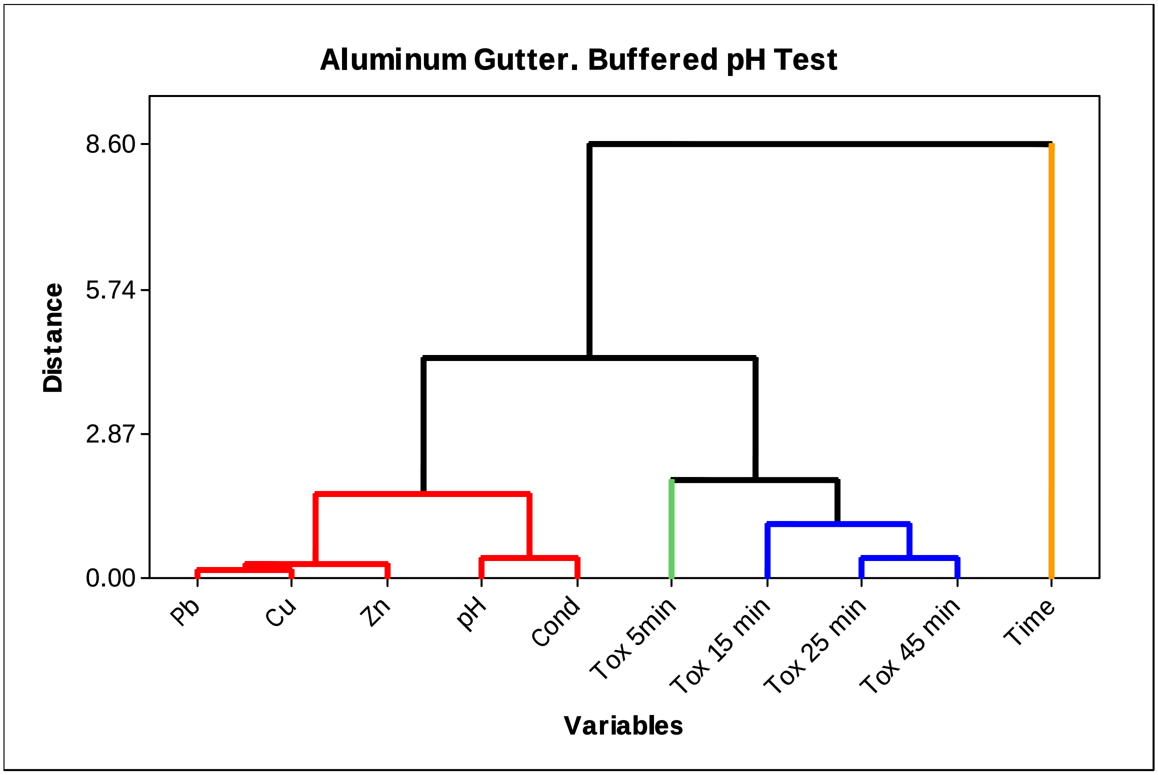


Figure G.11 Dendrogram from cluster analysis for water quality parameters. Aluminum gutter. Buffered tests.

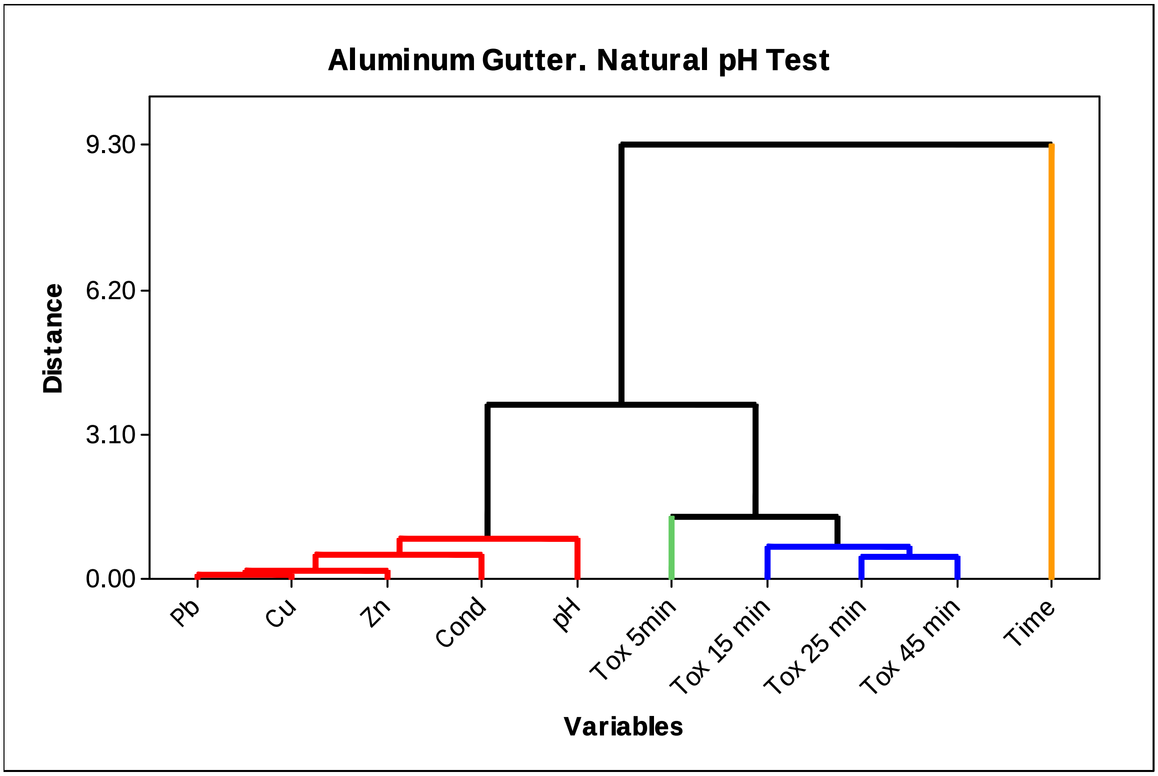


Figure G.12 Dendrogram from cluster analysis for water quality parameters. Aluminum gutter. Natural pH tests.

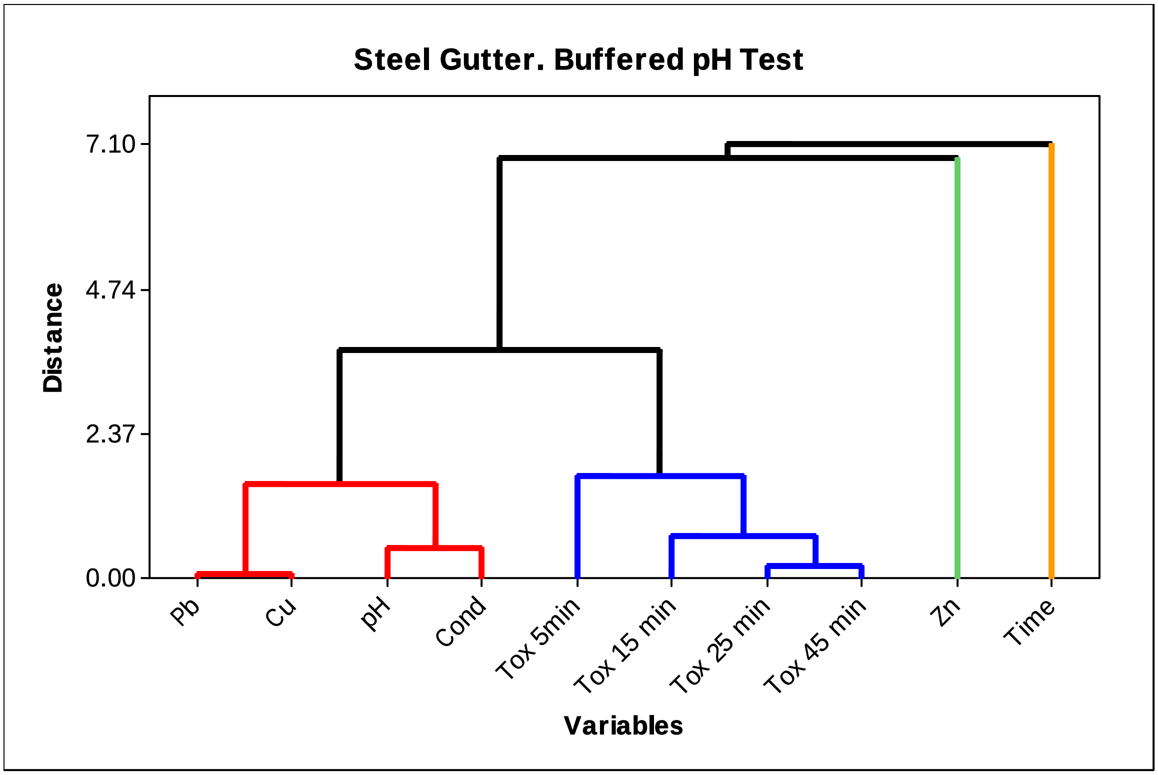


Figure G.13 Dendrogram from cluster analysis for water quality parameters. Galvanized steel gutter. Buffered tests.

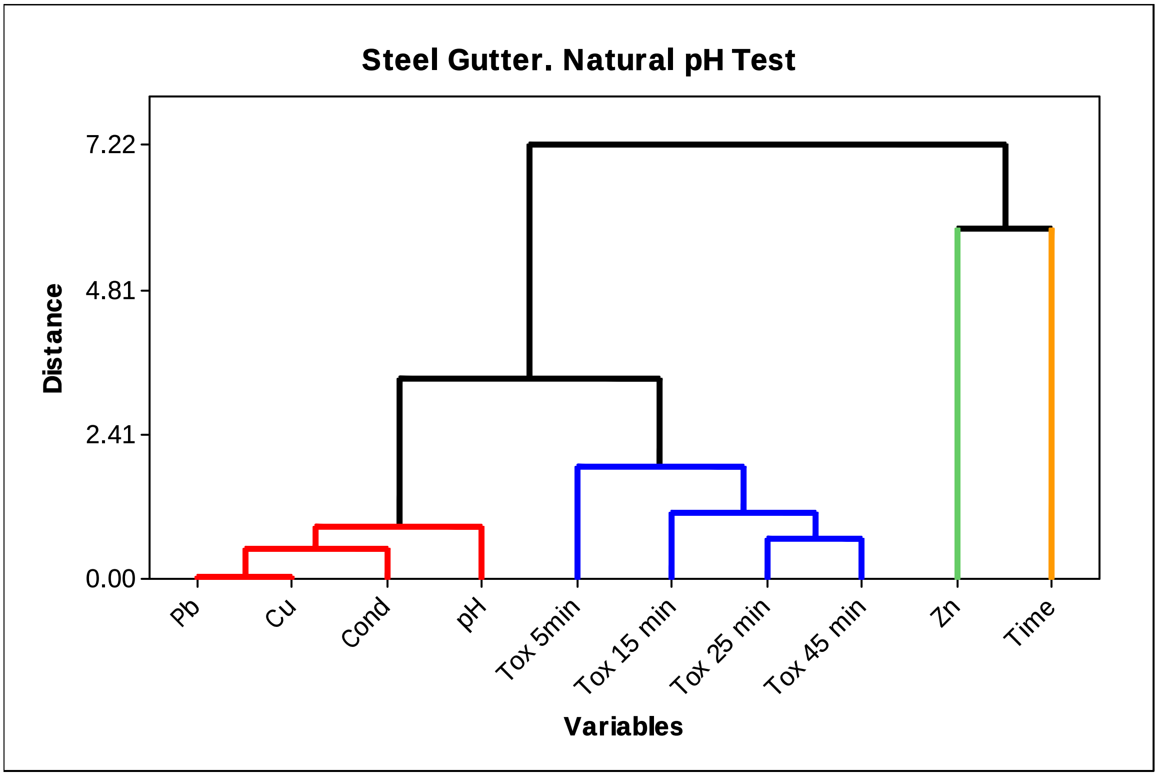


Figure G.14 Dendrogram from cluster analysis for water quality parameters. Galvanized steel gutter. Natural pH tests.

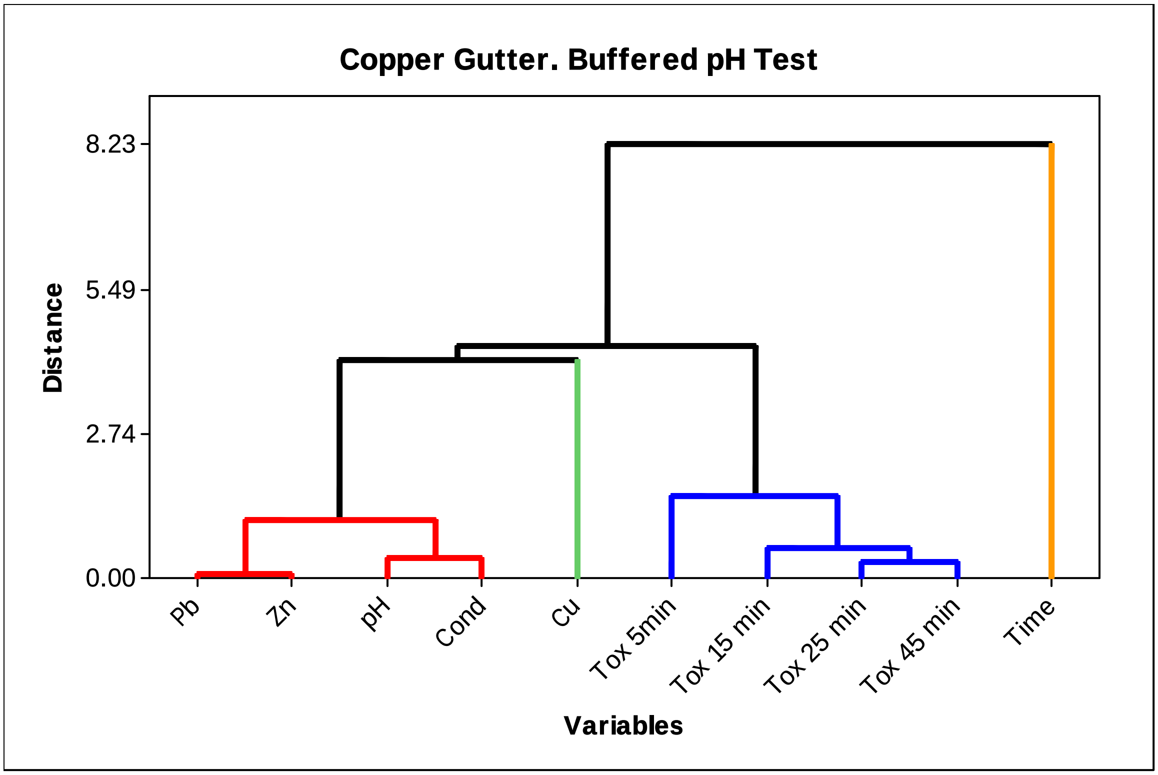


Figure G.15 Dendrogram from cluster analysis for water quality parameters. Copper gutter. Buffered tests.

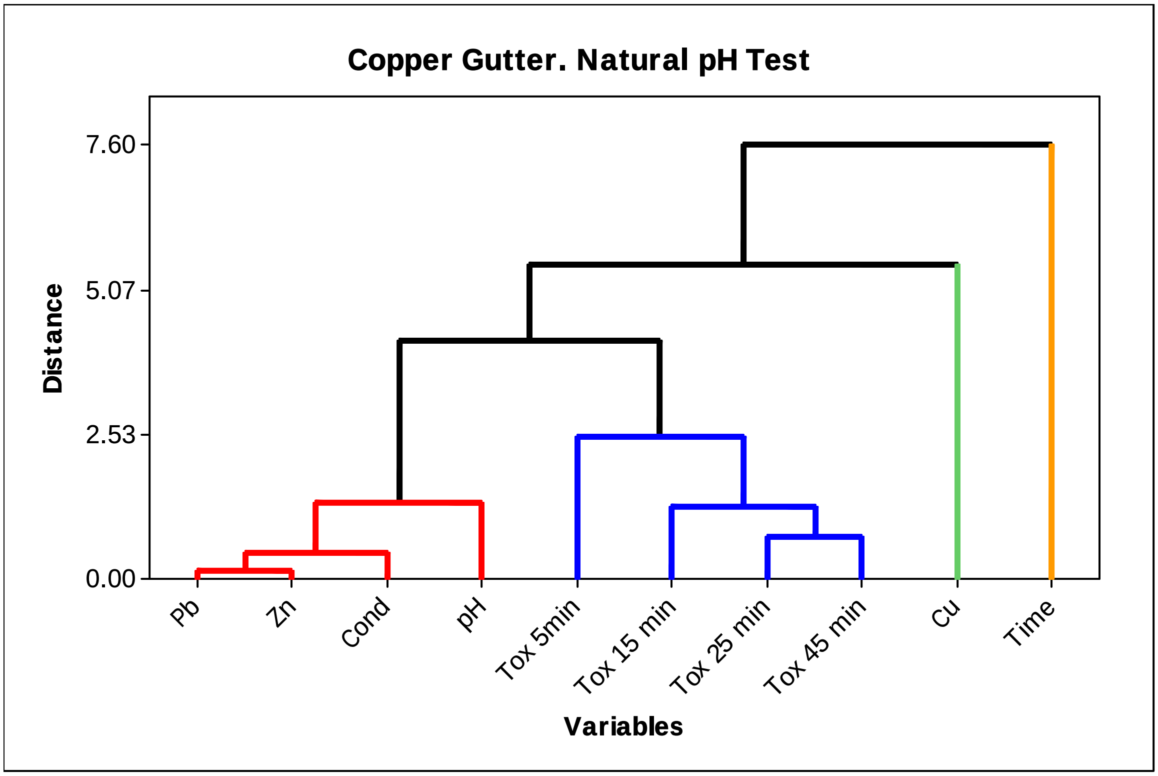


Figure G.16 Dendrogram from cluster analysis for water quality parameters. Copper gutter. Natural pH tests.

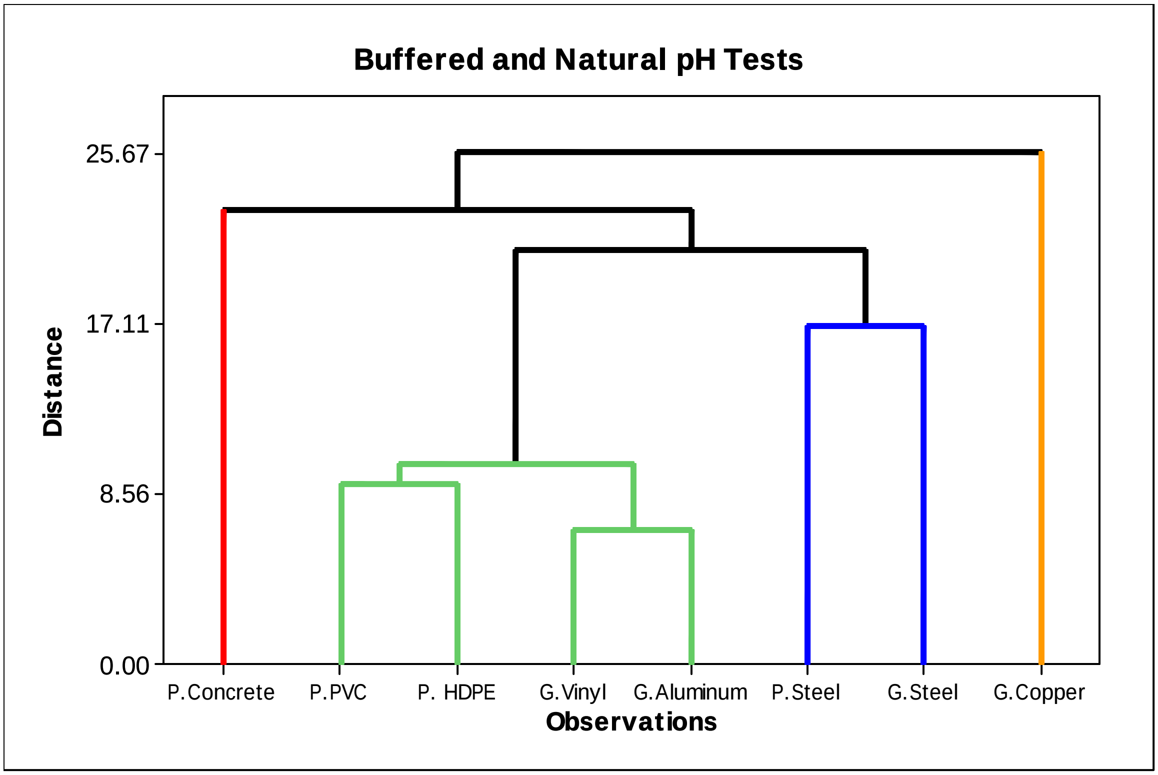


Figure G.17 Dendrogram from cluster analysis for pipe and gutter materials. Buffered and natural pH tests.

APPENDIX H: NUTRIENTS DATA

H.1 Nutrients Method Detection Limit

The Method Detection Limit (MDL) of nitrogen ammonia, total nitrogen, nitrate, and chemical oxygen demand was determined using standards with known concentrations close to the expected MDL. Seven replicates were analyzed. Standard deviation of the replicates was calculated. The MDL is the calculated standard deviation times the coefficient at specified confidence level (Burton and Pitt, 2002). Detection limit is the smallest concentration of a constituent that can be detected above the background noise when a specific procedure is used with a specific confidence (Standard Methods 1992).

H.1.1. Method Detection Limit for Nitrogen Ammonia

To determine the Method Detection Limit (MDL) for ammonia nitrogen, a standard with the concentration of 1 mg/L as N was used. Detection limit of 0.5 mg/L as N was expected. Seven replicates of ammonia nitrogen standard 1 mg/L as N were analyzed. The values observed are shown in the table below.

Table H.1. Observed values for nitrogen ammonia standardwith concentration 1 mg/L as N

Value Observed, mg/L as NH3-N	
0.88	
0.92	
0.92	
0.94	
0.96	
0.97	
0.96	
0.032	**ST DEV**
0.936	**AVERAGE**
0.034	**COV**
0.94	**MEDIAN**

Standard deviation of the seven samples was equal to 0.032 mg/L as N. The MDL is the calculated standard deviation times the t-value from a table of the one-sided t distribution at specified confidence level. The calculated MDLs at different confidence intervals are listed below.

Table H.2. Method detection limits for ammonia nitrogen at specified confidence levels.

MDL	Confidence Level, %
0.099	99
0.061	95
0.045	90

HACH states that standard deviation of ± 0.03 mg/L N for ammonia nitrogen was obtained using 1.5 mg/L as N ammonia nitrogen standard.

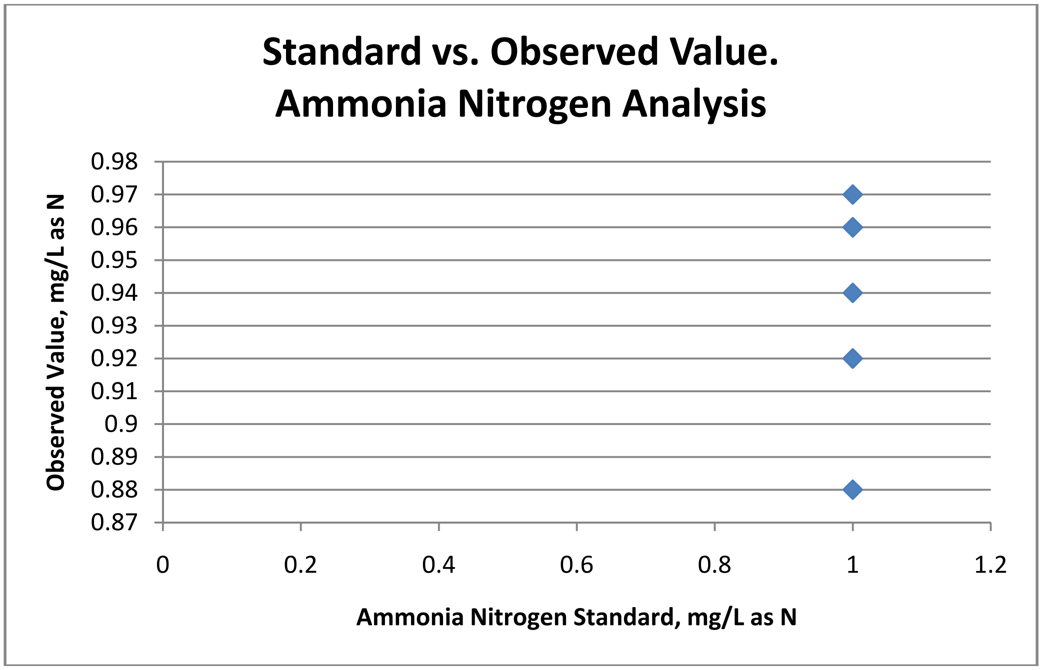


Figure H.1. Observed values vs. standard for ammonia nitrogen analysis.

H.1.2 Method Detection Limit for Total Nitrogen

To determine the Method Detection Limit (MDL) for total nitrogen, ammonia nitrogen standard with the concentration of 1 mg/L as N was used. Detection limit of 0.5 mg/L as N was expected. Seven replicates of nitrogen ammonia standard 1 mg/L as N were analyzed. The values observed are shown in the table below.

Table H.3. Observed values for nitrogen ammonia standard
with concentration 1 mg/L as N

Value Observed, mg/L as NH3-N	
2	
1	
1	
1	
1	
1	
1	
0.378	**ST DEV**
1.143	**AVERAGE**
0.331	**COV**
1	**MEDIAN**

Standard deviation of the seven samples was equal to 0.378 mg/L as N. The MDL is the calculated standard deviation times the coefficient at specified confidence level. The calculated MDLs at different confidence intervals are listed below.

Table H.4. Method detection limits for total nitrogen at specified confidence levels.

MDL	**Confidence Level, %**
1.188	99
0.734	95
0.544	90

HACH states that standard deviation of less than 1 mg/L N for total nitrogen was obtained using 15 mg/L as N ammonia nitrogen standard.

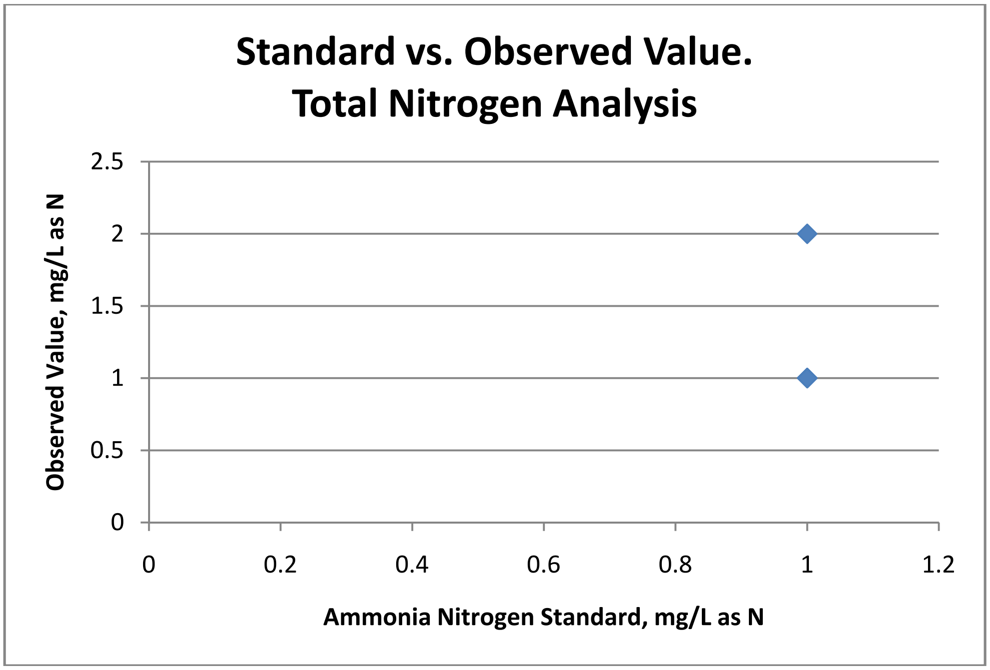


Figure H.2. Observed values vs. standard for total nitrogen analysis.

H.1.3 Method Detection Limit for Nitrate

To determine the Method Detection Limit (MDL) for nitrate, nitrogen-nitrate standard solution with the concentration of 2 mg/L as N was used. Seven replicates of nitrogen-nitrate standard 2 mg/L as N were analyzed. The values observed are shown in the table below.

Table H.5. Observed values for nitrogen nitrate standard
with concentration 2 mg/L as N

Value Observed, mg/L as NO_3^--N	
1.9	
1.9	
1.8	
1.8	
1.8	
1.8	
1.8	
0.049	**ST DEV**
1.829	**AVERAGE**
0.027	**COV**
1.8	**MEDIAN**

Standard deviation of the seven samples was equal to 0.049 mg/L asN. The MDL is the calculated standard deviation times the coefficient at specified confidence level. The calculated MDLs at different confidence intervals are listed below.

Table H.6. Method detection limits for nitrate at specified confidence levels.

MDL	Confidence Level, %
0.153	99
0.095	95
0.070	90

HACH states that standard deviation of 0.03 mg/L N for nitrate analysis was obtained using 1.5 mg/L as N nitrogen nitrate standard.

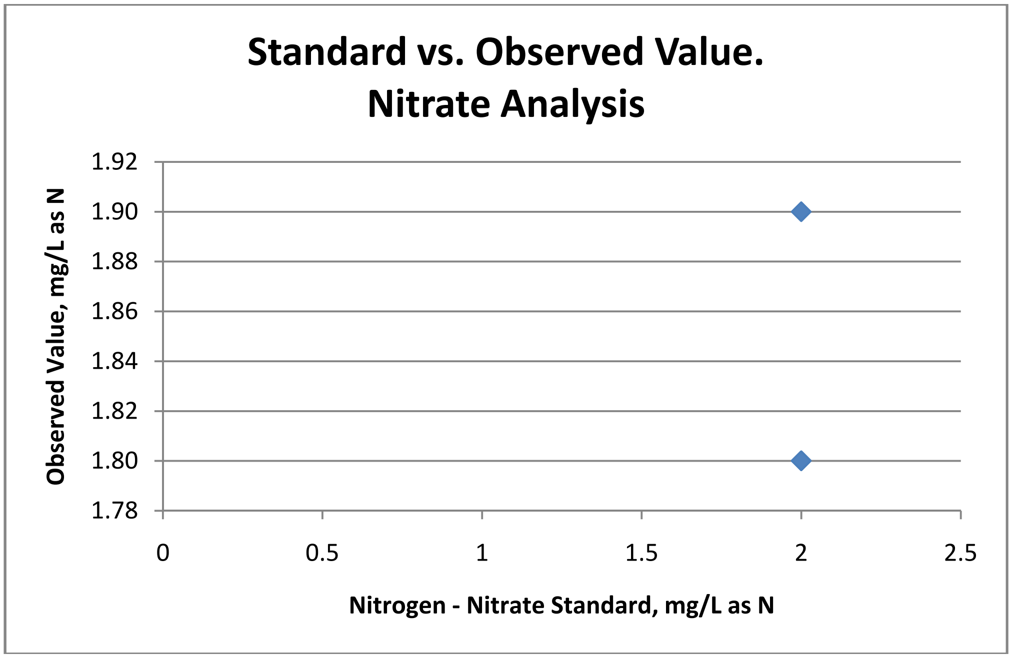


Figure H.3. Observed values vs. standard for nitrate analysis.

H.1.4 Method Detection Limit for Chemical Oxygen Demand

To determine the Method Detection Limit (MDL), Chemical Oxygen Demand (COD) Standard with the concentrations of 1 and 3 mg/L were used. Seven replicates of COD standard of each of 1 and 3 mg/L COD were analyzed. The values observed for standard with the concentration of 1 mg/L are shown in the table below.

Table H.7. Observed values for COD standard
with concentration 1 mg/L COD

Value Observed, mg/L COD	
1	
0	
2	
0	
0	
0	
0	
0.787	**ST DEV**
0.429	**AVERAGE**
1.836	**COV**
0	**MEDIAN**

Standard deviation of the seven samples was equal to 0.787 mg/L COD. The MDL is the calculated standard deviation times the coefficient at specified confidence level. The calculated MDLs at different confidence intervals are listed below.

Table H.8. Method detection limits for COD at specified confidence levels.

MDL	**Confidence Level, %**
2.473	99
1.529	95
1.133	90

The values observed for standard with the concentration of 3 mg/L are shown in the table below.

Table H.9. Observed values for COD standard
with concentration 3 mg/L COD

Value Observed, mg/L as COD	
4	
2	
1	
2	
3	
4	
3	
1.113	**ST DEV**
2.714	**AVERAGE**
0.410	**COV**
3	**MEDIAN**

Standard deviation of the seven samples was equal to 1.113 mg/L COD. The MDL is the calculated standard deviation times the coefficient at specified confidence level. The calculated MDLs at different confidence intervals are listed below.

Table H.10. Method detection limits for COD at specified confidence levels.

MDL	Confidence Level, %
2.473	99
1.529	95
1.133	90

HACH states that standard deviation of ±2.7 mg/L COD for COD analysis was obtained using 100 mg/L COD standard.

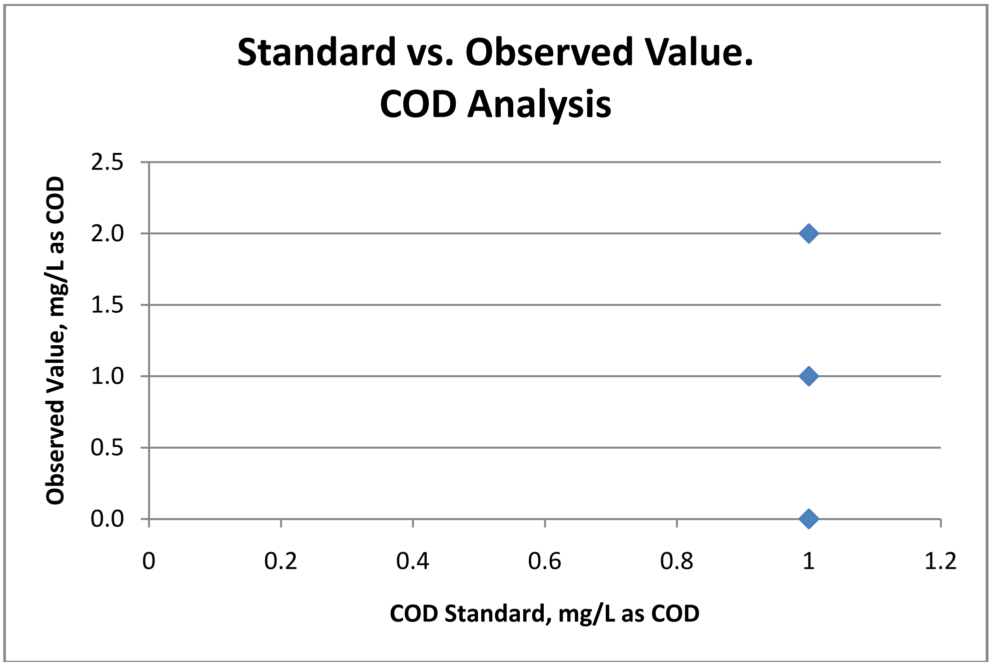


Figure H.4. Observed values vs. standard of 1 mg/L for COD analysis.

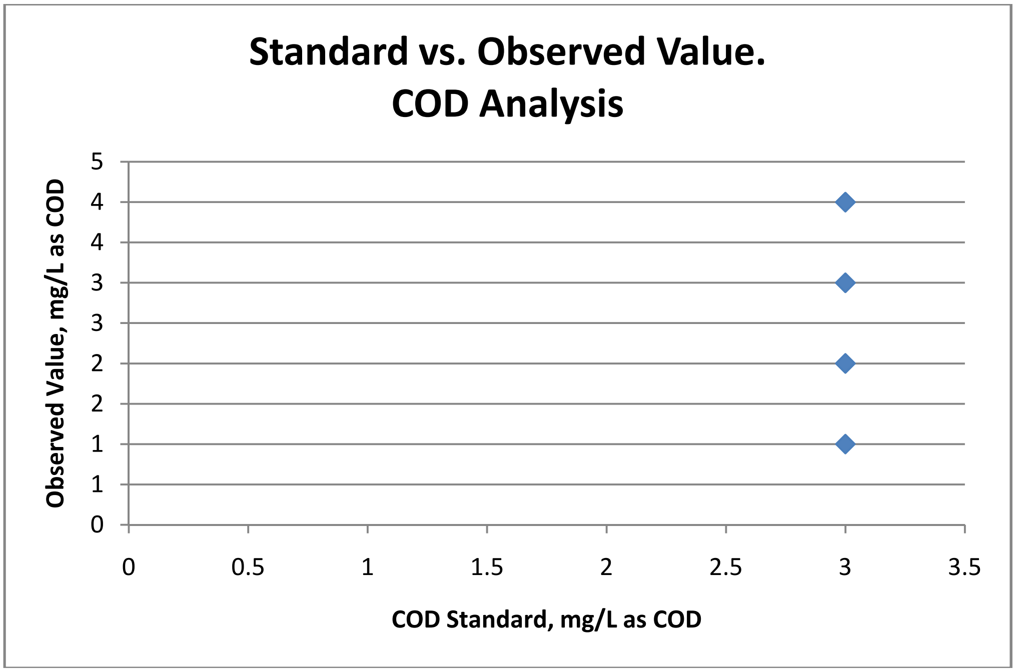


Figure H.5. Observed values vs. standard of 3 mg/L for COD analysis.

H.2 Nitrogen Ammonia Data

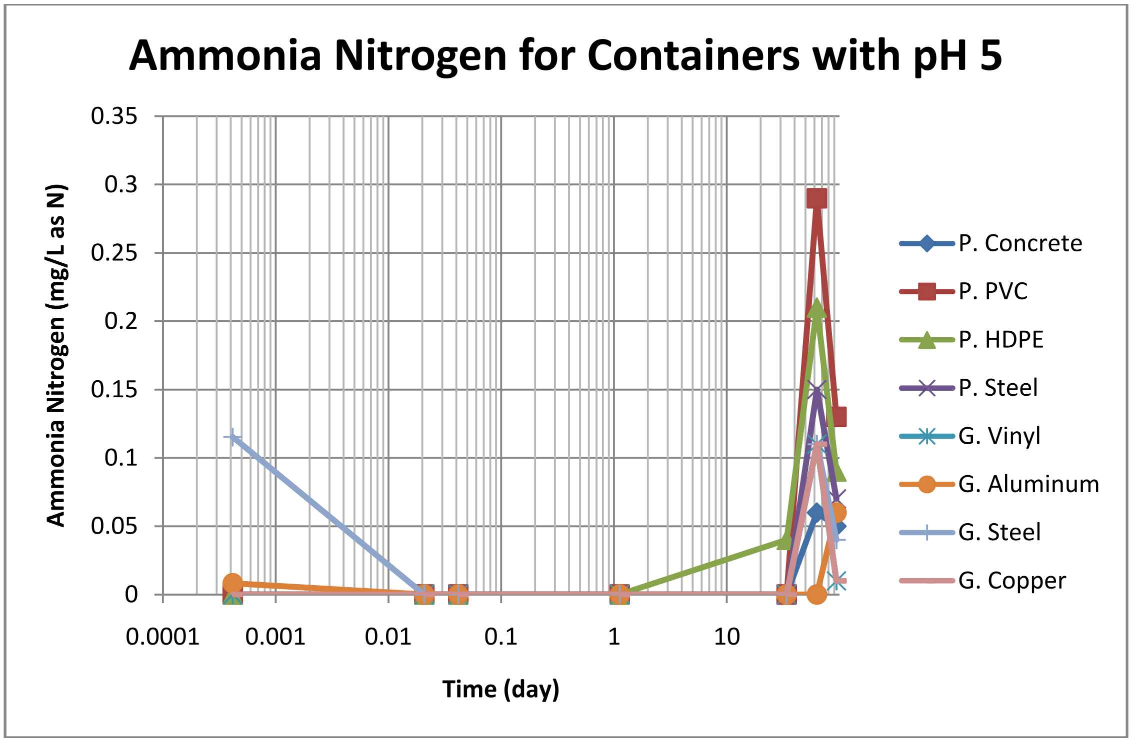


Figure H.6. Ammonia nitrogen concentrations in the containers with pH 5 water.

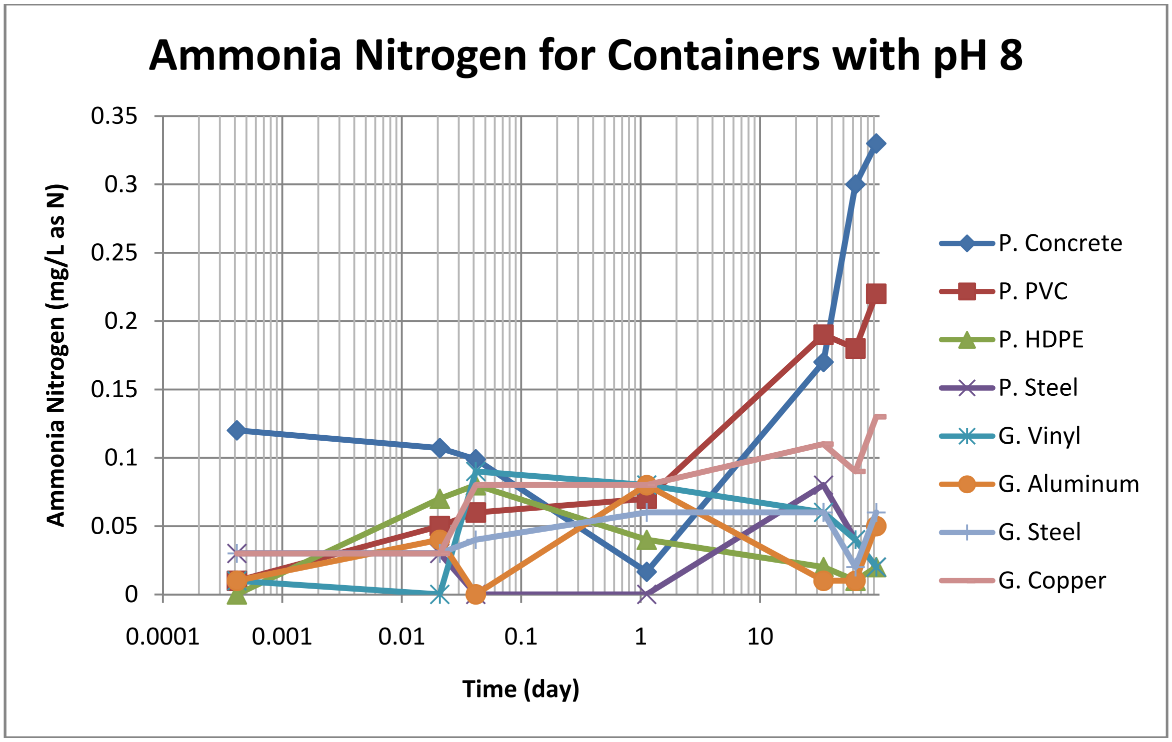


Figure H.7. Ammonia nitrogen concentrations in the containers with pH 8 water.

Table H.11. Ammonia nitrogen concentrations in the containers with pH 5 water.

	Ammonia Nitrogen, mg/L as N for containers with pH 5							
Time, hr	P. Concrete	P. PVC	P. HDPE	P. Steel	G. Vinyl	G. Aluminum	G. Steel	G. Copper
0.01	0.00	0.00	0.00	0.00	0.00	0.01	0.12	0.00
0.5	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
1	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
27	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
816	0.00	0.00	0.04	0.00	0.00	0.00	0.00	0.00
1512	0.06	0.29	0.21	0.15	0.11	0.00	0.11	0.11
2256	0.05	0.13	0.09	0.07	0.01	0.06	0.04	0.01

Table H.12. Ammonia nitrogen concentrations in the containers with pH 8 water.

	Ammonia Nitrogen, mg/L as N for containers with pH 8							
Time, hr	P. Concrete	P. PVC	P. HDPE	P. Steel	G. Vinyl	G. Aluminum	G. Steel	G. Copper
0.01	0.12	0.01	0.00	0.03	0.01	0.01	0.03	0.03
0.5	0.11	0.05	0.07	0.03	0.00	0.04	0.03	0.03
1	0.10	0.06	0.08	0.00	0.09	0.00	0.04	0.08
27	0.02	0.07	0.04	0.00	0.08	0.08	0.06	0.08
816	0.17	0.19	0.02	0.08	0.06	0.01	0.06	0.11
1512	0.30	0.18	0.01	0.04	0.04	0.01	0.02	0.09
2256	0.33	0.22	0.02	0.02	0.02	0.05	0.06	0.13

Table H.13. Ammonia nitrogen analysis with the standards.

Nitrogen Ammonia Standard, mg/L as NH_3-N	Observed Value, mg/L as NH_3-N
20	20
20	19
2	2
24	22
2	3
2	2.15
1.21	1.31
1.21	0.83
1.21	1.45
2.42	2.52
1.21	1.16
2.42	2.44

H.3 Total Nitrogen

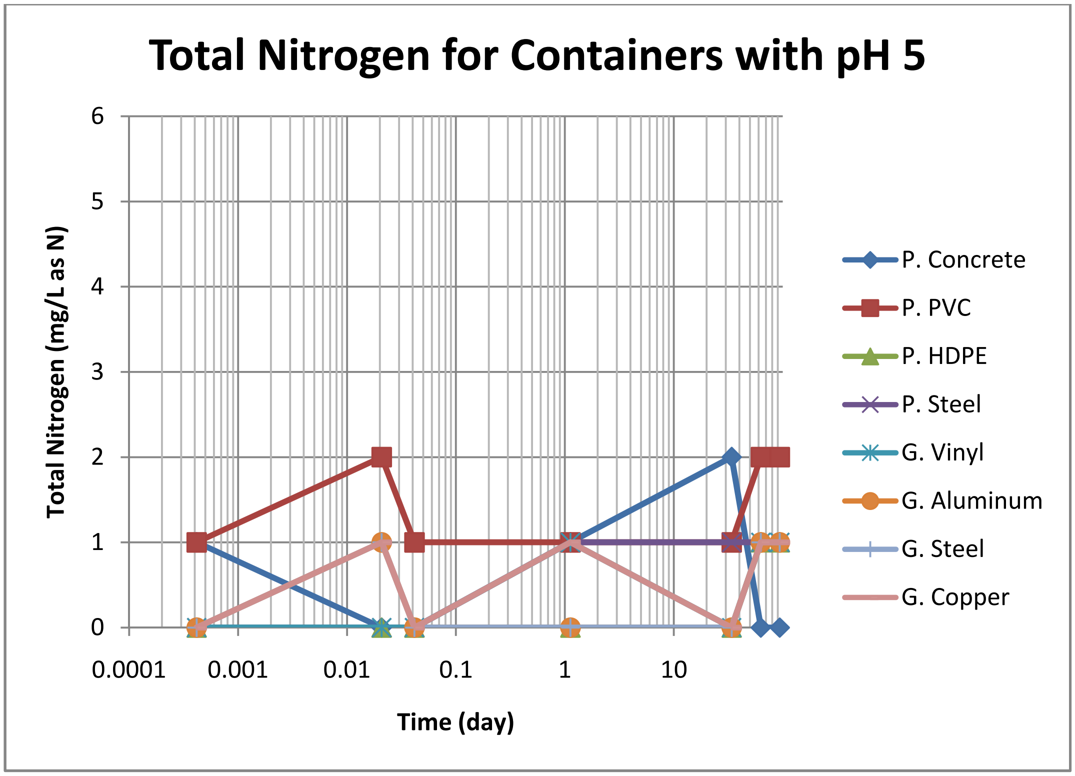


Figure H.8. Total nitrogen concentrations in the containers with pH 5 water.

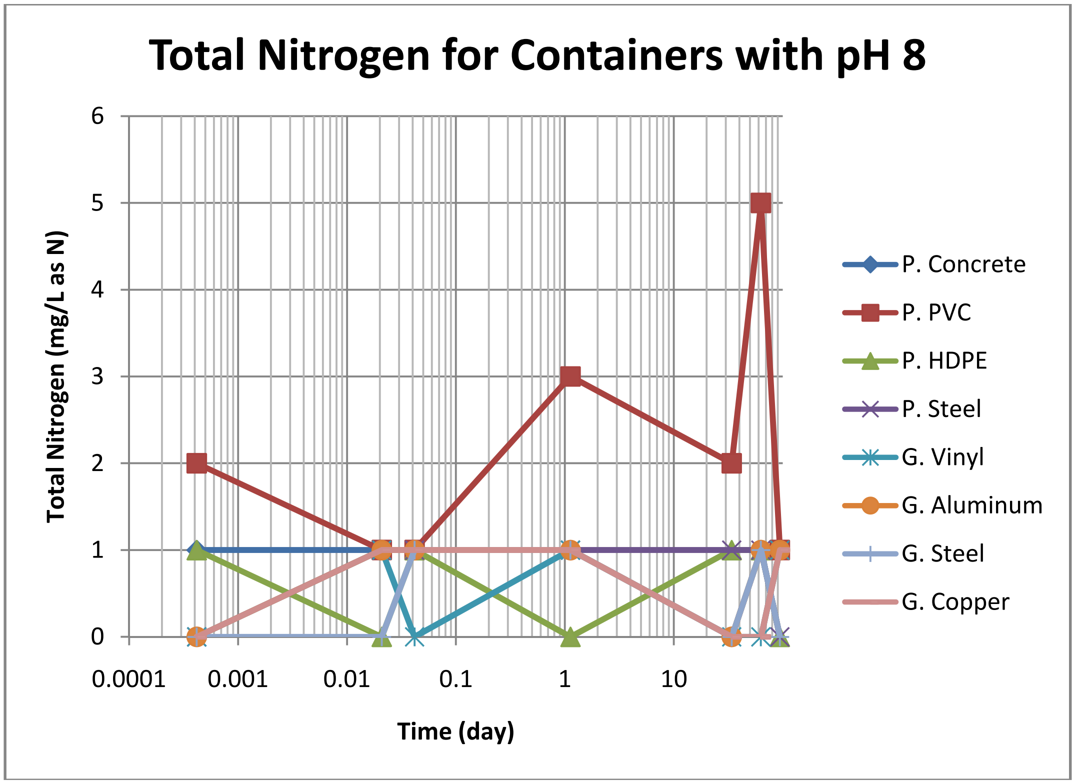


Figure H.9. Total nitrogen concentrations in the containers with pH 8 water.

Table H.14. Total nitrogen concentrations in the containers with pH 5 water.

	Total Nitrogen, mg/L as N for containers with pH 5							
Time, hr	P. Concrete	P. PVC	P. HDPE	P. Steel	G. Vinyl	G. Aluminum	G. Steel	G. Copper
0.01	1	1	0	0	0	0	0	0
0.5	0	2	0	0	0	1	1	1
1	0	1	0	0	0	0	0	0
27	1	1	0	1	1	0	0	1
816	2	1	0	1	0	0	0	0
1512	0	2	1	1	1	1	1	1
2256	0	2	1	1	1	1	1	1

Table H.15. Total nitrogen concentrations in the containers with pH 8 water.

	Total Nitrogen, mg/L as N for containers with pH 8							
Time, hr	P. Concrete	P. PVC	P. HDPE	P. Steel	G. Vinyl	G. Aluminum	G. Steel	G. Copper
0.01	1	2	1	0	0	0	0	0
0.5	1	1	0	1	1	1	0	1
1	1	1	1	1	0	1	1	1
27	1	3	0	1	1	1	1	1
816	0	2	1	1	0	0	0	0
1512	1	5	1	1	0	1	1	0
2256	1	1	0	0	1	1	0	1

Table H.16. Total nitrogen analyses with the standards

Nitrogen Ammonia Standard, mg/L as NH_3- N	Observed Value, mg/L as NH_3-N
17	17
17	16
2	2
20	18
20	20
2	2
2	3
10	9
10	10
10	10
3	3
1	0

H.4 Nitrate

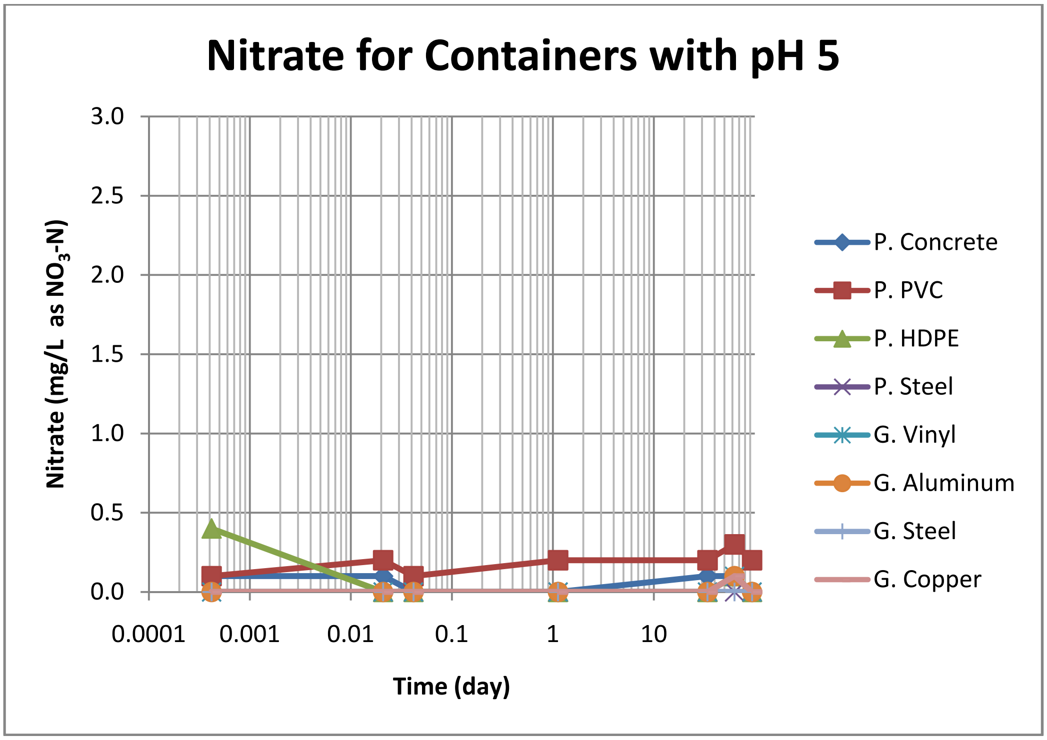


Figure H.10. Nitrate concentrations in the containers with pH 5 water.

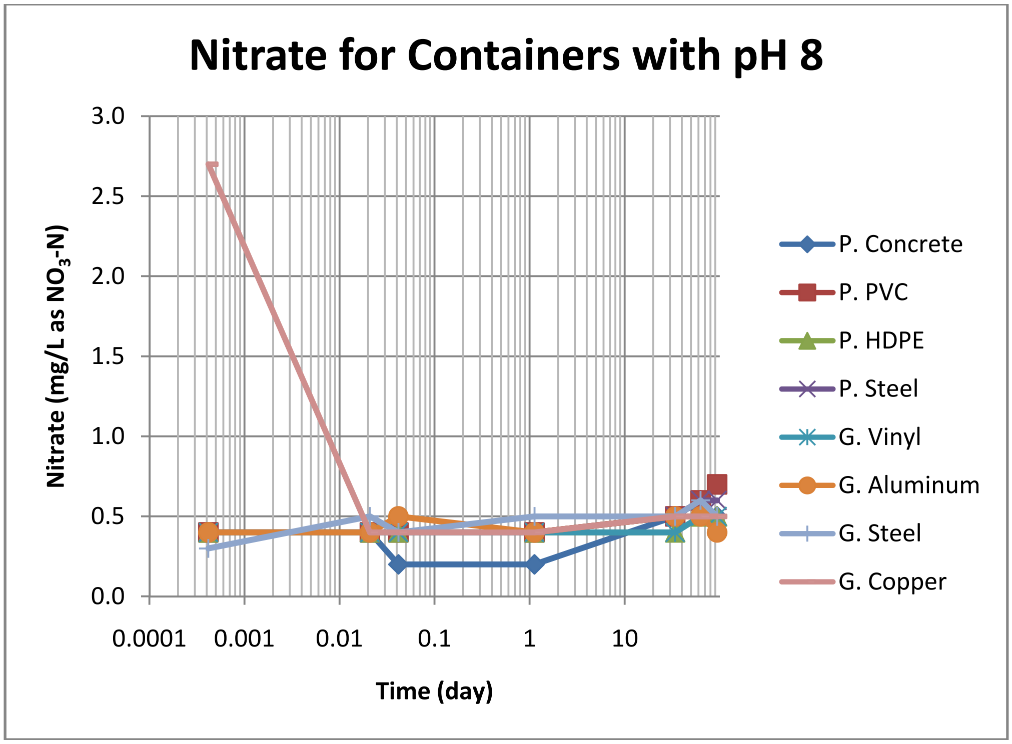


Figure H.11. Nitrate concentrations in the containers with pH 8 water.

Table H.17. Nitrate analyses for the containers with pH 5 water.

	Nitrate, mg/L as N for containers with pH 5							
Time, hr	P. Concrete	P. PVC	P. HDPE	P. Steel	G. Vinyl	G. Aluminum	G. Steel	G. Copper
0.01	0.1	0.1	0.4	0.0	0.0	0.0	0.0	0.0
0.5	0.1	0.2	0.0	0.0	0.0	0.0	0.0	0.0
1	0.0	0.1	0.0	0.0	0.0	0.0	0.0	0.0
27	0.0	0.2	0.0	0.0	0.0	0.0	0.0	0.0
816	0.1	0.2	0.0	0.0	0.0	0.0	0.0	0.0
1512	0.1	0.3	0.1	0.0	0.1	0.1	0.0	0.1
2256	0.0	0.2	0.0	0.0	0.0	0.0	0.0	0.0

Table H.18. Nitrate analyses for the containers with pH 8 water

	Nitrate, mg/L as N for containers with pH 8							
Time, hr	P. Concrete	P. PVC	P. HDPE	P. Steel	G. Vinyl	G. Aluminum	G. Steel	G. Copper
0.01	0.4	0.4	0.4	0.4	0.4	0.4	0.3	2.7
0.5	0.4	0.4	0.4	0.4	0.4	0.4	0.5	0.4
1	0.2	0.4	0.4	0.4	0.4	0.5	0.4	0.4
27	0.2	0.4	0.4	0.4	0.4	0.4	0.5	0.4
816	0.5	0.5	0.4	0.5	0.4	0.5	0.5	0.5
1512	0.6	0.6	0.5	0.6	0.5	0.5	0.6	0.5
2256	0.5	0.7	0.5	0.6	0.5	0.4	0.5	0.5

H.5 COD

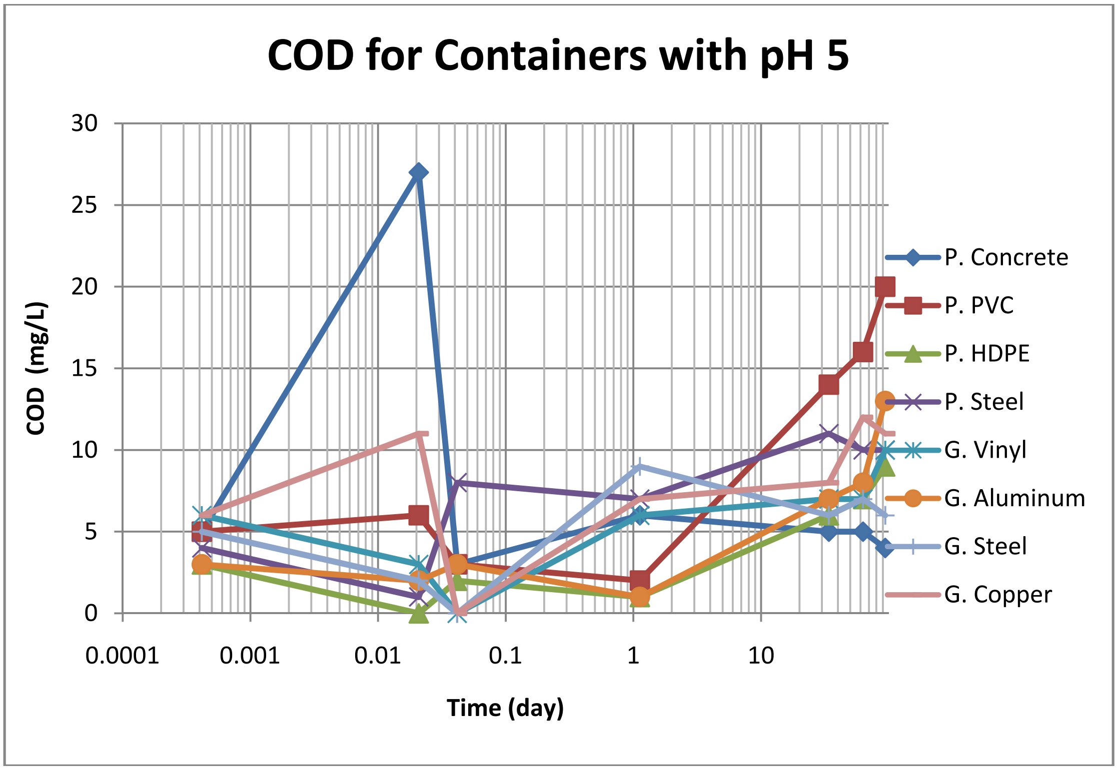


Figure H.12. Chemical oxygen demand in the containers with pH 5 water.

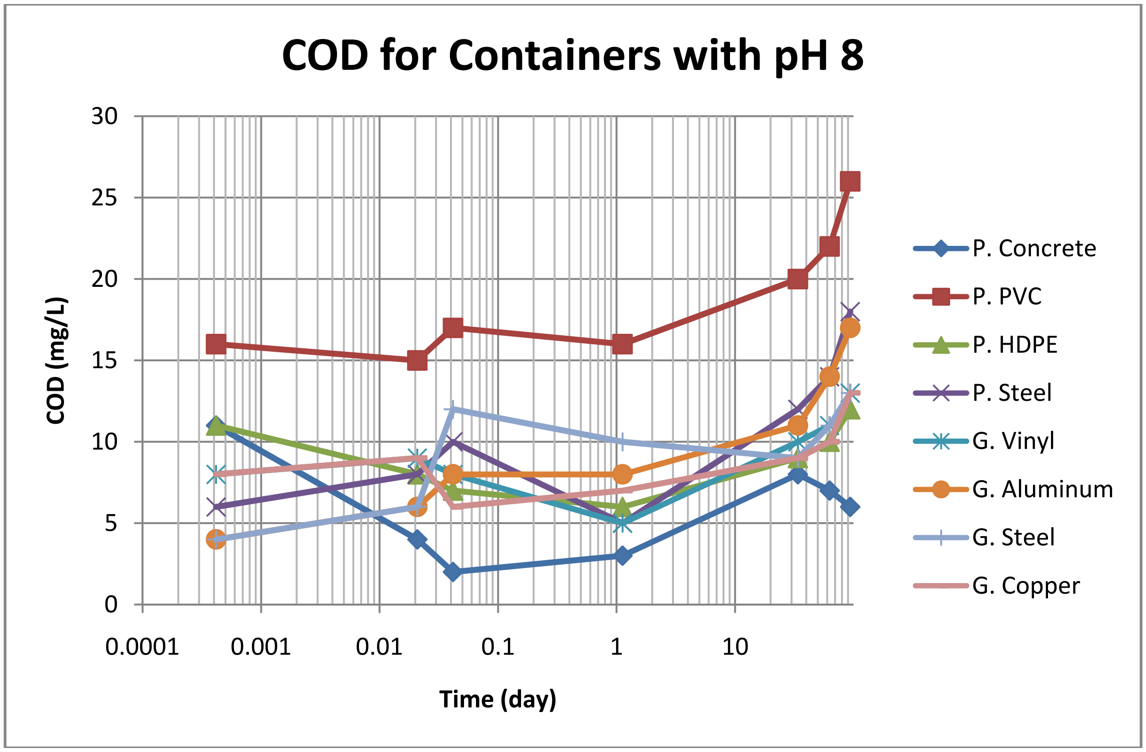


Figure H.13. Chemical oxygen demand in the containers with pH 8 water.

Table H.19. Chemical oxygen demand analyses for the containers with pH 5 water.

	COD, mg/L as COD for containers with pH 5							
Time, hr	P. Concrete	P. PVC	P. HDPE	P. Steel	G. Vinyl	G. Aluminum	G. Steel	G. Copper
0.01	5	5	3	4	6	3	5	6
0.5	27	6	0	1	3	2	2	11
1	3	3	2	8	0	3	0	0
27	6	2	1	7	6	1	9	7
816	5	14	6	11	7	7	6	8
1512	5	16	7	10	7	8	7	12
2256	4	20	9	10	10	13	6	11

Table H.20. Chemical oxygen demand analyses for the containers with pH 8 water.

	COD, mg/L as COD for containers with pH 8							
Time, hr	P. Concrete	P. PVC	P. HDPE	P. Steel	G. Vinyl	G. Aluminum	G. Steel	G. Copper
0.01	11	16	11	6	8	4	4	8
0.5	4	15	8	8	9	6	6	9
1	2	17	7	10	8	8	12	6
27	3	16	6	5	5	8	10	7
816	8	20	9	12	10	11	9	9
1512	7	22	10	14	11	14	11	10
2256	6	26	12	18	13	17	13	13

APPENDIX I: MAJOR IONS DATA

During the buffered tests, the samples were analyzed for alkalinity, total hardness as $CaCO_3$ and calcium hardness as $CaCO_3$, chloride and sulfate after three months of exposure in each bucket. These concentrations were assumed to be constant during the test series. During the natural pH experiments, alkalinity, total hardness as $CaCO_3$ and calcium hardness as $CaCO_3$ were measured at time zero and after three months of exposure; chloride and sulfate concentrations were measured in the source water. The detection limits for the constituents are shown in Table I.10.

Table I.1. Water constituents. Containers with pH 5 water.

	Containers with pH 5							
Constituent, mg/L	**P. Concrete**	**P. PVC**	**P. HDPE**	**P. Steel**	**G. Vinyl**	**G. Aluminum**	**G. Steel**	**G. Copper**
Total Alkalinity	644	190	70	570	72	84	350	210
Total Hardness as $CaCO_3$	37.5	64.1	1.87	2.41	1.13	0.99	1.42	0.45
Calcium Hardness as $CaCO_3$	1.35	60.9	1.37	1.05	0.8	0.5	1.05	< 0.02
Calculated Calcium Ca^{2+}	0.54	24.39	0.55	0.42	0.32	0.20	0.42	4.0E-03
Calculated Magnesium Mg^{2+}	10.42	0.92	0.14	0.39	0.10	0.14	0.11	0.13
Chloride, Cl^-	< 0.02	< 0.02	< 0.02	< 0.02	< 0.02	< 0.02	< 0.02	< 0.02
Sulfate, SO_4^{2-}	8.50	14.30	1.59	5.11	1.35	1.90	2.02	2.65
Calculated sodium Na^+	29.12	29.12	29.12	29.12	29.12	29.12	29.12	29.12
Calculated potassium K^+	2582.04	2582.04	2582.04	2582.04	2582.04	2582.04	2582.04	2582.04
Calculated HPO_4^{2-}	60.79	60.79	60.79	60.79	60.79	60.79	60.79	60.79
Calculated $H_2PO_4^-$	6404.76	6404.76	6404.76	6404.76	6404.76	6404.76	6404.76	6404.76
H^+	4.30E-04	5.94E-03	1.46E-02	1.60E-03	1.49E-02	1.46E-02	3.75E-03	7.47E-03
OH^-	3.99E-04	2.89E-05	1.18E-05	1.07E-04	1.15E-05	1.18E-05	4.58E-05	2.29E-05

Table I.2. Water constituents. Containers with pH 8 water.

	Containers with pH 8							
Constituent, mg/L	**P. Concrete**	**P. PVC**	**P. HDPE**	**P. Steel**	**G. Vinyl**	**G. Aluminum**	**G. Steel**	**G. Copper**
Total Alkalinity	3690	6900	5800	5900	5800	6300	7400	7300
Total Hardness as $CaCO_3$	1.64	7.00	1.23	0.87	0.83	0.25	0.97	0.48
Calcium Hardness as $CaCO_3$	0.65	4.69	0.77	0.37	0.50	< 0.02	0.47	0.15
Calculated Calcium Ca^{2+}	0.26	1.88	0.31	0.15	0.20	4.00E-03	0.19	0.06
Calculated MagnesiumMg^{2+}	0.29	0.67	0.13	0.14	0.10	0.07	0.14	0.10
Chloride, Cl^-	< 0.02	< 0.02	< 0.02	< 0.02	< 0.02	< 0.02	< 0.02	< 0.02
Sulfate, SO_4^{2-}	4.32	16.3	0.53	2.28	0.50	0.76	0.69	2.38
Calculated sodium Na^+	2970.30	2970.30	2970.30	2970.30	2970.30	2970.30	2970.30	2970.30
Calculated potassium K^+	80.81	80.81	80.81	80.81	80.81	80.81	80.81	80.81
Calculated HPO_4^{2-}	6200.27	6200.27	6200.27	6200.27	6200.27	6200.27	6200.27	6200.27
Calculated $H_2PO_4^-$	200.45	200.45	200.45	200.45	200.45	200.45	200.45	200.45
H^+	1.11E-06	3.19E-06	3.42E-06	1.27E-06	3.34E-06	3.19E-06	8.58E-07	1.75E-06
OH^-	1.55E-01	5.38E-02	5.02E-02	1.35E-01	5.14E-02	5.38E-02	2.00E-01	9.79E-02

Table I.3. Water constituents. Containers with bay water. Time zero.

	Containers with Bay Water. Time Zero							
Constituent, mg/L	**P. Concrete**	**P. PVC**	**P. HDPE**	**P. Steel**	**G. Vinyl**	**G. Aluminum**	**G. Steel**	**G. Copper**
Total Alkalinity	70	60	60	60	60	70	60	60
Total Hardness as $CaCO_3$	1160	1090	1110	1010	1100	1110	1010	1010
Calcium Hardness as $CaCO_3$	221	213	209	215	209	226	215	226
Calculated Calcium Ca^{2+}	88.50	85.29	83.69	86.09	83.69	90.50	86.09	90.50
Calculated Magnesium Mg^{2+}	270.68	252.81	259.73	229.17	256.85	254.83	229.17	226.00

Table I.4. Water constituents. Containers with river water. Time zero.

	Containers with River Water. Time Zero							
Constituent, mg/L	**P. Concrete**	**P. PVC**	**P. HDPE**	**P. Steel**	**G. Vinyl**	**G. Aluminum**	**G. Steel**	**G. Copper**
Total Alkalinity	60	90	85	90	90	85	90	85
Total Hardness as $CaCO_3$	136	145	133	133	123	122	130	191
Calcium Hardness as $CaCO_3$	56.7	68.2	62.4	56.7	51.20	51.2	56.7	102
Calculated Calcium Ca^{2+}	22.70	27.31	24.99	22.70	20.50	20.50	22.70	40.84
Calculated MagnesiumMg^{2+}	22.86	22.14	20.35	21.99	20.70	20.41	21.13	25.66

Table I.5. Water constituents. Containers with bay water. After three months of exposure.

	Containers with Bay Water. After Three Months of Exposure							
Constituent, mg/L	**P. Concrete**	**P. PVC**	**P. HDPE**	**P. Steel**	**G. Vinyl**	**G. Aluminum**	**G. Steel**	**G. Copper**
Total Alkalinity	184	80	80	12	92	108	16	100
Total Hardness as $CaCO_3$	1240	1560	1640	1360	1610	1860	1430	1270
Calcium Hardness as $CaCO_3$	332	365	382	347	400	459	432	337
Calculated Calcium Ca^{2+}	132.94	146.16	152.97	138.95	160.17	183.80	172.99	134.95
Calculated MagnesiumMg^{2+}	261.75	344.48	362.64	292.02	348.80	403.86	287.69	268.95
Fluoride F^-	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1
Nitrate NO_3^-	0.21	0.21	0.21	0.21	0.21	0.21	0.21	0.21
Total Phosphorus	< 0.02	< 0.02	< 0.02	< 0.02	< 0.02	< 0.02	< 0.02	< 0.02
Bromide Br^-	12.8	12.8	12.8	12.8	12.8	12.8	12.8	12.8
Manganese Mn	< 0.02	< 0.02	< 0.02	< 0.02	< 0.02	< 0.02	< 0.02	< 0.02
Boron as BO_3^{3-}	4.05	4.05	4.05	4.05	4.05	4.05	4.05	4.05
Silicon Si	< 10	< 10	< 10	< 10	< 10	< 10	< 10	< 10
Sodium Na^+	1760	1760	1760	1760	1760	1760	1760	1760
Potassium K^+	67.3	67.3	67.3	67.3	67.3	67.3	67.3	67.3
Chloride Cl^-	3350	3350	3350	3350	3350	3350	3350	3350
Sulfate SO_4^{2-}	674	674	674	674	674	674	674	674
H^+	4.11E-06	1.27E-05	1.46E-05	1.01E-04	1.08E-05	1.01E-05	1.46E-05	1.33E-05
OH^-	4.17E-02	1.35E-02	1.18E-02	1.70E-03	1.59E-02	1.70E-02	1.18E-02	1.74E-02

Table I.6. Water constituents. Containers with river water. After three months of exposure.

	Containers with River Water. After Three Months of Exposure							
Constituent, mg/L	**P. Concrete**	**P. PVC**	**P. HDPE**	**P. Steel**	**G. Vinyl**	**G. Aluminum**	**G. Steel**	**G. Copper**
Total Alkalinity	156	140	124	56	116	116	16	116
Total Hardness as $CaCO_3$	107	195	177	69.6	171.00	181	171	175
Calcium Hardness as $CaCO_3$	48.4	104	91.6	15.6	91.6	99.9	99.9	99.9
Calculated Calcium Ca^{2+}	19.38	41.64	36.68	6.25	36.68	40.00	40.00	40.00
Calculated MagnesiumMg^{2+}	16.89	26.23	24.62	15.57	22.89	23.38	20.50	21.65
Fluoride F^-	0.28	0.28	0.28	0.28	0.28	0.28	0.28	0.28
Nitrate NO_3^-	0.68	0.68	0.68	0.68	0.68	0.68	0.68	0.68
Total Phosphorus	< 0.02	< 0.02	< 0.02	< 0.02	< 0.02	< 0.02	< 0.02	< 0.02
Bromide Br^-	0.23	0.23	0.23	0.23	0.23	0.23	0.23	0.23
Manganese Mn	< 0.02	< 0.02	< 0.02	< 0.02	< 0.02	< 0.02	< 0.02	< 0.02
Boron as BO_3^{3-}	0.54	0.54	0.54	0.54	0.54	0.54	0.54	0.54
Silicon Si	< 10	< 10	< 10	< 10	< 10	< 10	< 10	< 10
Sodium Na^+	66.4	66.4	66.4	66.4	66.4	66.4	66.4	66.4
Potassium K^+	5.82	5.82	5.82	5.82	5.82	5.82	5.82	5.82
Chloride Cl^-	89.0	89.0	89.0	89.0	89.0	89.0	89.0	89.0
Sulfate SO_4^{2-}	106	106	106	106	106	106	106	106
H^+	1.83E-06	3.75E-06	4.50E-06	1.36E-06	4.94E-06	4.61E-06	1.18E-04	4.94E-06
OH^-	9.35E-02	4.58E-02	3.81E-02	1.26E-01	3.47E-02	3.72E-02	1.45E-03	3.47E-02

Table I.7. Oxidation Reduction Potential. Buffered tests. After three months of exposure.

	Oxidation Reduction Potential (ORP), Volts. Buffered Tests. After Three Months of Exposure.							
Condition	**P. Concrete**	**P. PVC**	**P. HDPE**	**P. Steel**	**G. Vinyl**	**G. Aluminum**	**G. Steel**	**G. Copper**
pH 5	0.158	0.223	0.210	0.174	0.212	0.202	0.19	0.251
pH 8	0.128	0.132	0.132	0.108	0.134	0.138	0.117	0.165

Table I.8. Oxidation Reduction Potential. Bay water.

	Oxidation Reduction Potential (ORP), Volts. Bay Water							
Time, hr	**P. Concrete**	**P. PVC**	**P. HDPE**	**P. Steel**	**G. Vinyl**	**G. Aluminum**	**G. Steel**	**G. Copper**
0.01	-0.125	-0.126	-0.126	-0.126	-0.127	-0.128	-0.128	-0.129
1	-0.121	-0.125	-0.118	-0.119	-0.117	-0.120	-0.116	-0.110
27	-0.146	-0.144	-0.145	-0.146	-0.146	-0.145	-0.147	-0.135
168	-0.207	-0.205	-0.205	-0.203	-0.200	-0.200	-0.202	-0.194
816	-0.190	-0.190	-0.191	-0.182	-0.186	-0.189	-0.190	-0.158
1512	-0.156	-0.159	-0.159	-0.172	-0.173	-0.175	-0.176	-0.119
2256	-0.175	-0.175	-0.178	-0.178	-0.177	-0.180	-0.181	-0.138

Table I.9. Oxidation Reduction Potential. River water.

	Oxidation Reduction Potential (ORP), Volts. River Water							
Time, hr	**P. Concrete**	**P. PVC**	**P. HDPE**	**P. Steel**	**G. Vinyl**	**G. Aluminum**	**G. Steel**	**G. Copper**
0.01	-0.148	-0.145	-0.144	-0.144	-0.145	-0.144	-0.146	-0.147
1	-0.131	-0.132	-0.121	-0.121	-0.116	-0.114	-0.110	-0.139
27	-0.138	-0.138	-0.138	-0.144	-0.139	-0.139	-0.144	-0.105
168	-0.192	-0.194	-0.193	-0.213	-0.196	-0.197	-0.208	-0.172
816	-0.121	-0.121	-0.187	-0.151	-0.130	-0.130	-0.146	-0.73
1512	-0.95	-0.92	-0.108	-0.123	-0.106	-0.107	-0.96	-0.63
2256	-0.120	-0.121	-0.123	-0.128	-0.115	-0.117	-0.097	-0.056

APPENDIX J: QA/QC

J.1. pH Data

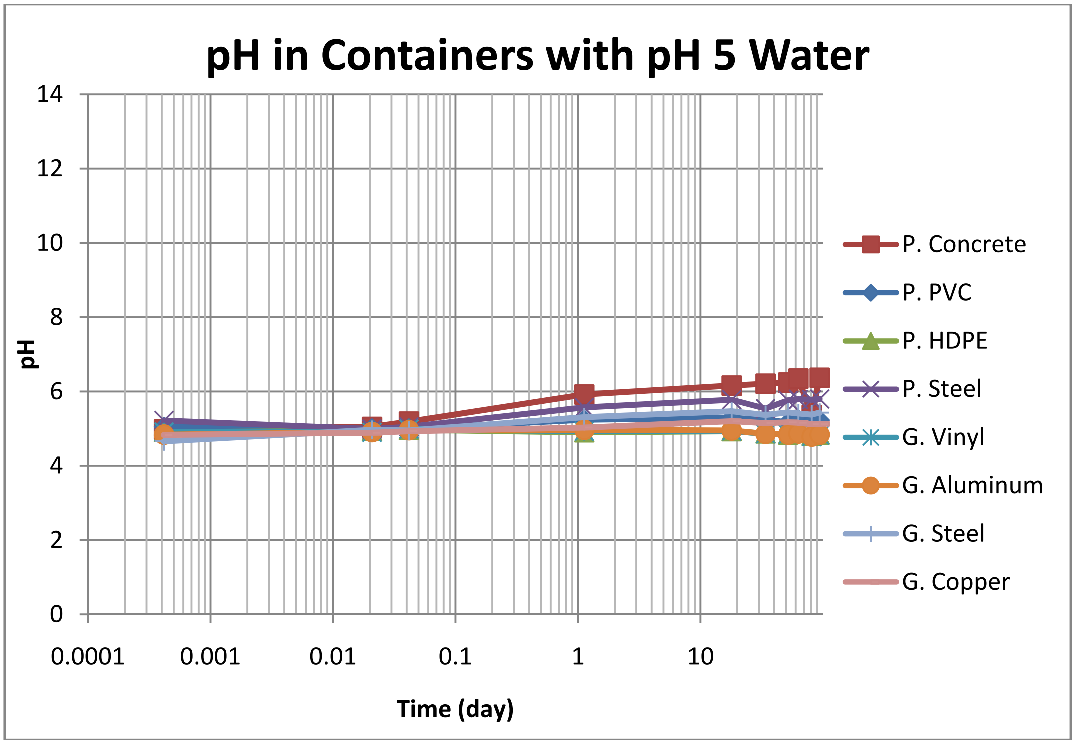


Figure J.1. pH measurements in the containers with pH 5 water.

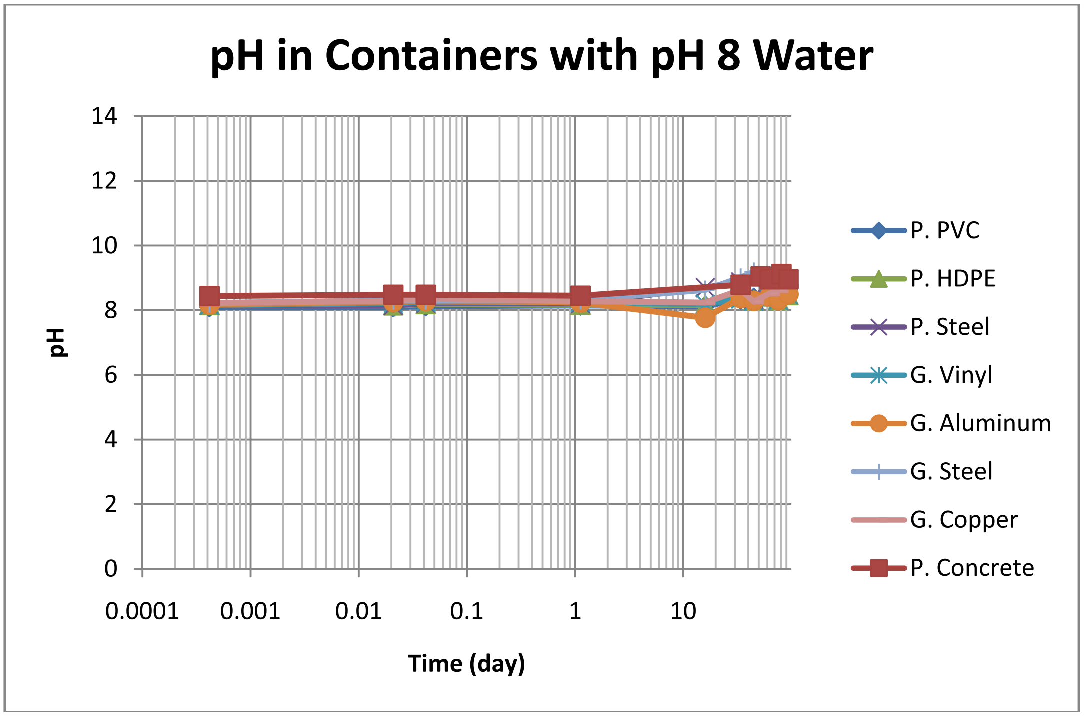


Figure J.2. pH measurements in the containers with pH 8 water.

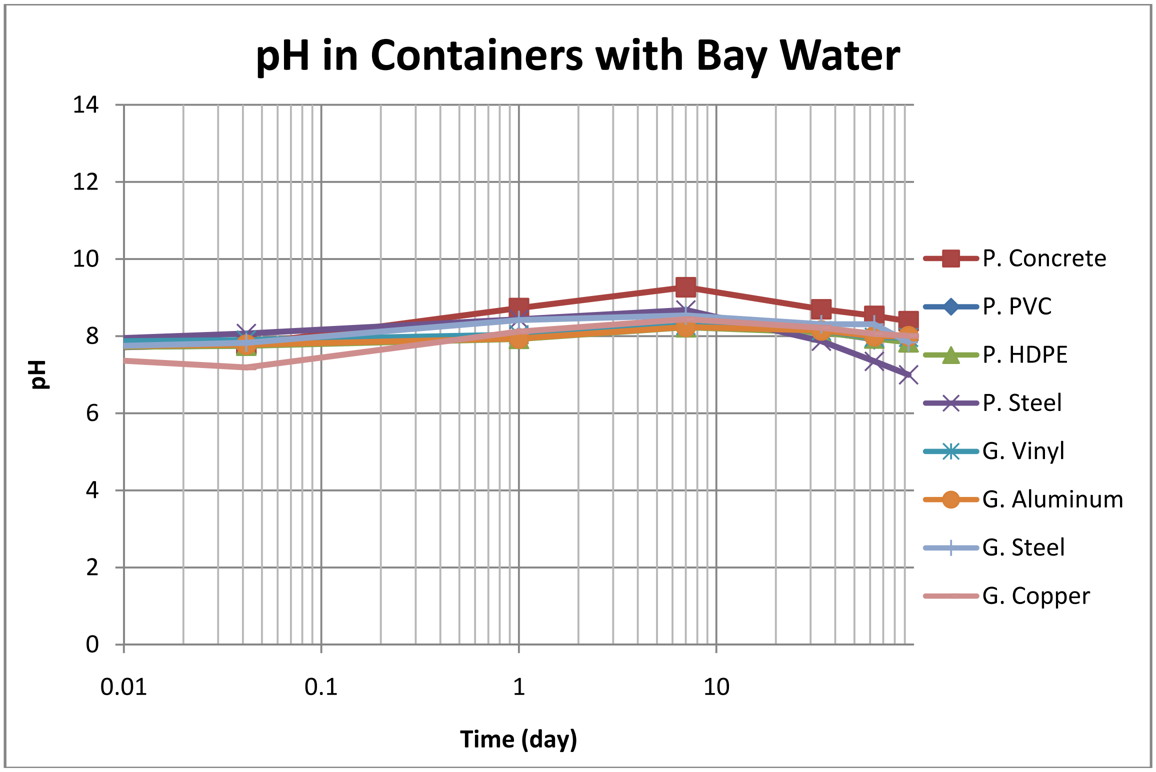


Figure J.3. pH measurements in the containers with bay water.

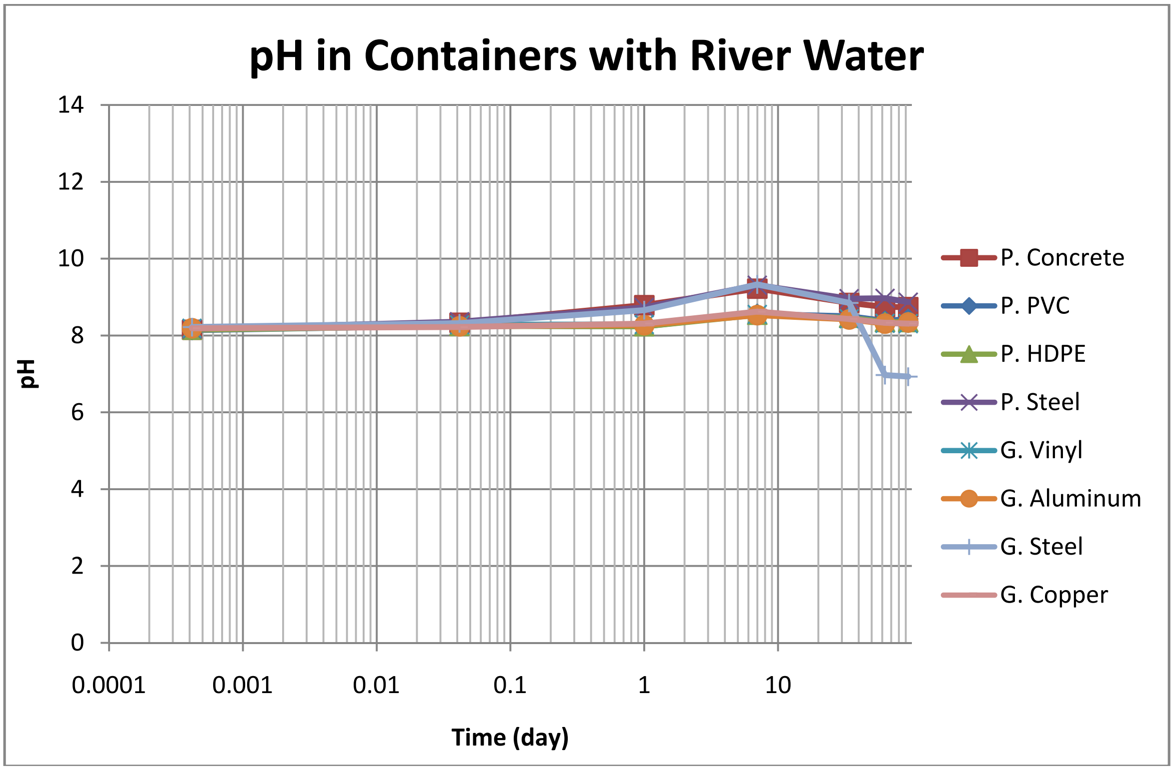


Figure J.4. pH measurements in the containers with river water.

Table J.1. pH in the containers with pH 5 water.

	pH for Containers with pH 5							
Time, hr	**P. Concrete**	**P. PVC**	**P. HDPE**	**P. Steel**	**G. Vinyl**	**G. Aluminum**	**G. Steel**	**G. Copper**
0.01	4.98	5.05	4.91	5.22	4.91	4.84	4.66	4.83
0.5	5.05	5.00	4.94	4.99	4.90	4.91	4.97	4.89
1	5.19	5.00	4.97	5.05	4.99	4.96	4.95	4.93
27	5.92	5.24	4.90	5.57	4.93	4.97	5.31	5.03
816	6.21	5.24	4.87	5.54	4.86	4.86	5.37	5.15
1512	6.35	5.24	4.89	5.79	4.86	4.87	5.41	5.16
2256	6.37	5.23	4.84	5.8	4.83	4.84	5.43	5.13

Table J.2. pH in the containers with pH 8 water.

	pH for Containers with pH 8							
Time, hr	**P. Concrete**	**P. PVC**	**P. HDPE**	**P. Steel**	**G. Vinyl**	**G. Aluminum**	**G. Steel**	**G. Copper**
0.01	8.44	8.10	8.16	8.16	8.16	8.18	8.22	8.23
0.5	8.48	8.10	8.15	8.15	8.22	8.26	8.31	8.29
1	8.48	8.13	8.19	8.22	8.26	8.29	8.31	8.36
27	8.45	8.15	8.17	8.21	8.25	8.24	8.32	8.28
816	8.79	8.34	8.42	8.88	8.35	8.38	9.01	8.63
1512	8.96	8.42	8.43	8.83	8.37	8.42	9.08	8.52
2256	8.96	8.50	8.47	8.90	8.48	8.50	9.07	8.76

Table J.3. pH in the containers with bay water.

	pH for Containers with Bay Water							
Time, hr	**P. Concrete**	**P. PVC**	**P. HDPE**	**P. Steel**	**G. Vinyl**	**G. Aluminum**	**G. Steel**	**G. Copper**
0.01	7.54	7.64	7.67	7.69	7.81	7.67	7.58	7.75
1	7.79	7.76	7.75	8.07	7.90	7.78	7.83	7.19
27	8.73	7.97	7.93	8.44	8.04	7.94	8.42	8.12
168	9.27	8.26	8.23	8.68	8.28	8.24	8.54	8.44
816	8.70	8.12	8.10	7.87	8.14	8.15	8.31	8.22
1512	8.53	7.92	7.94	7.35	7.97	8.00	8.31	8.06
2256	8.39	7.90	7.84	7.00	7.97	8.00	7.84	8.01

Table J.4. pH in the containers with river water.

	pH for Containers with River Water							
Time, hr	**P. Concrete**	**P. PVC**	**P. HDPE**	**P. Steel**	**G. Vinyl**	**G. Aluminum**	**G. Steel**	**G. Copper**
0.01	8.15	8.14	8.15	8.17	8.19	8.19	8.22	8.19
1	8.33	8.26	8.25	8.36	8.28	8.24	8.32	8.22
27	8.79	8.24	8.24	8.73	8.29	8.27	8.66	8.31
168	9.22	8.56	8.54	9.31	8.55	8.53	9.33	8.62
816	8.85	8.50	8.46	8.96	8.44	8.42	8.85	8.43
1512	8.74	8.38	8.35	8.97	8.32	8.31	6.97	8.33
2256	8.74	8.43	8.35	8.87	8.31	8.34	6.93	8.31

J.2 Conductivity Data

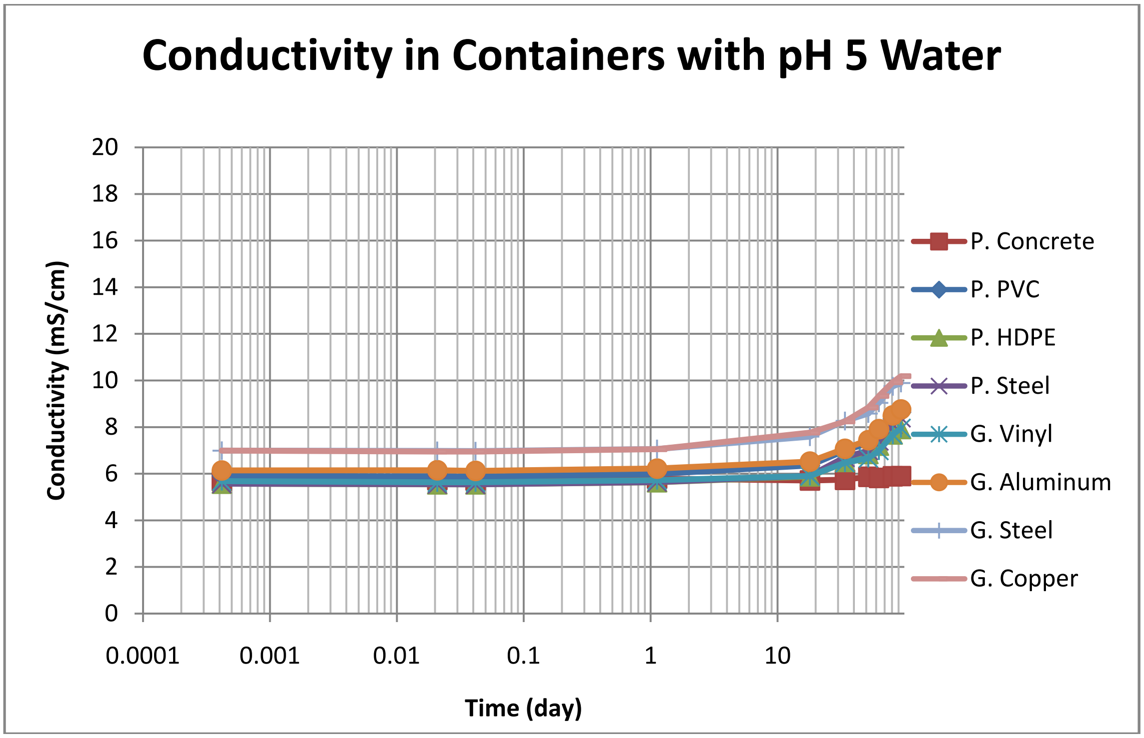


Figure J.5. Conductivity measurements in the containers with pH 5 water.

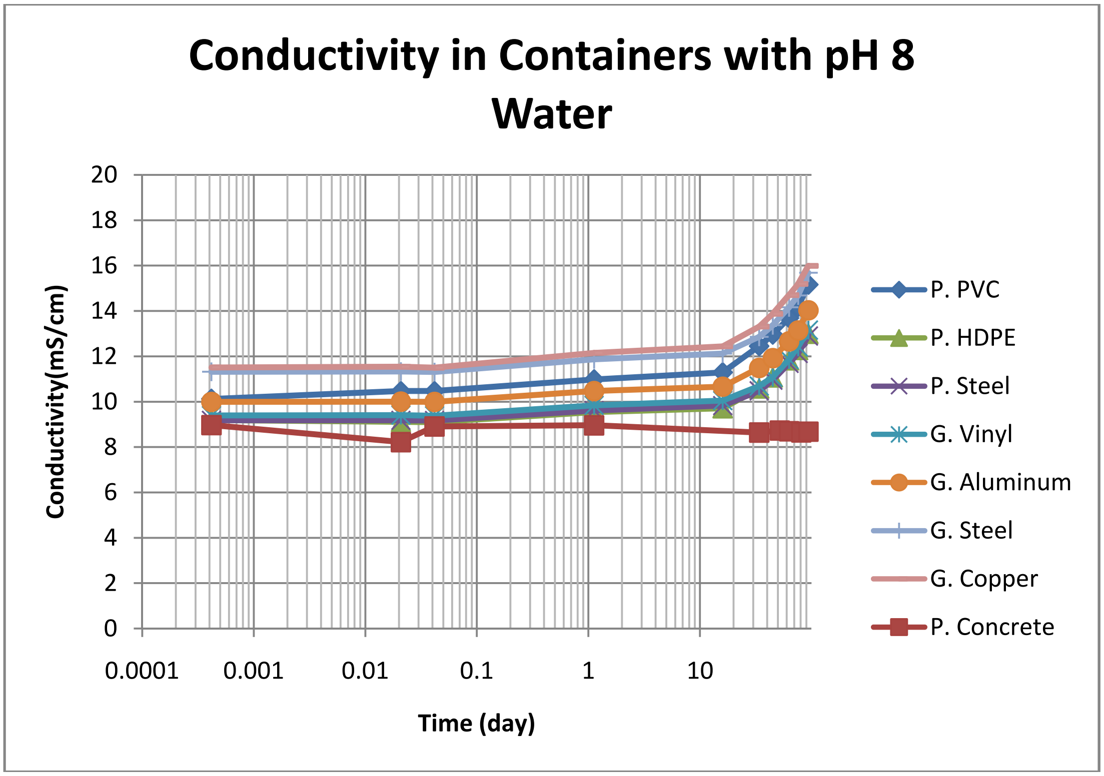


Figure J.6. Conductivity measurements in the containers with pH 8 water.

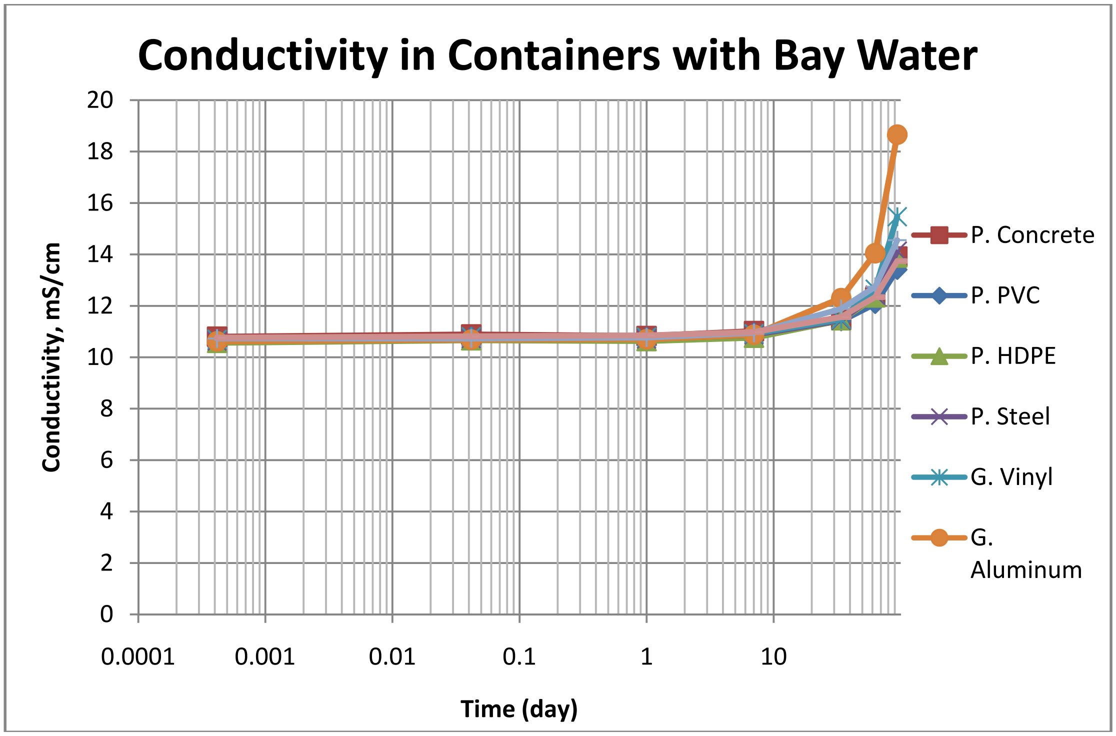


Figure J.7. Conductivity measurements in the containers with bay water.

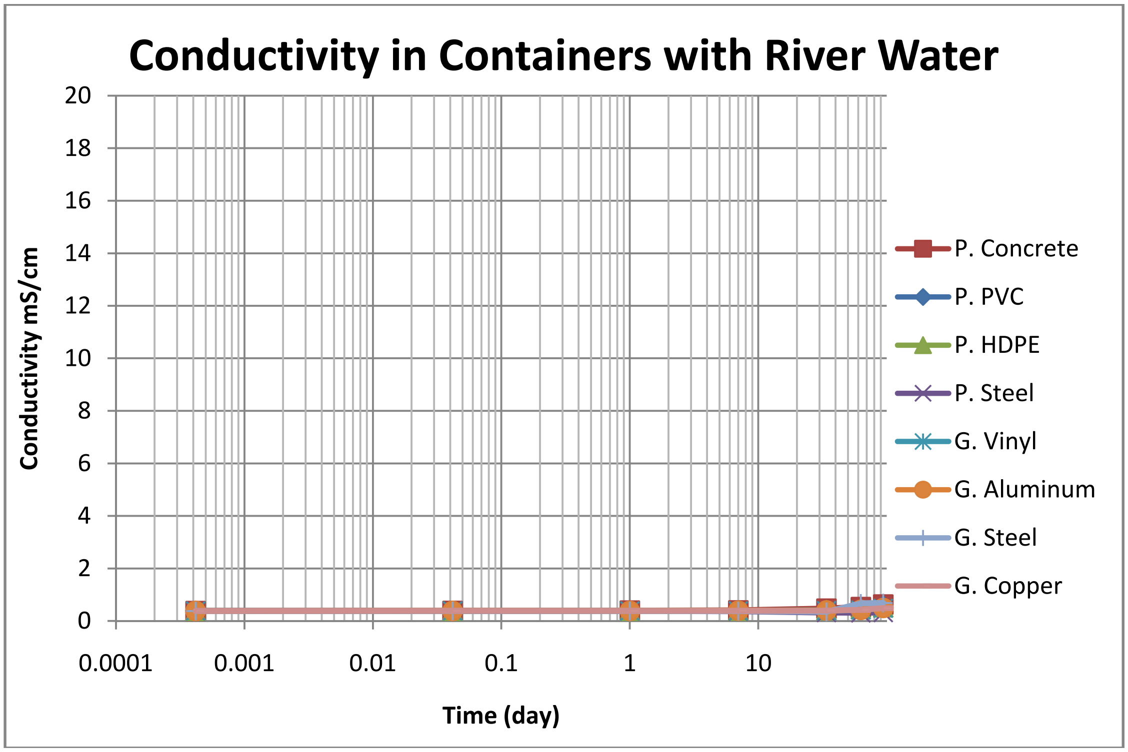


Figure J.8. Conductivity measurements in the containers with river water.

Table J.5. Conductivity in the containers with pH 5 water.

	Conductivity for Containers with pH 5, mS/cm							
Time, hr	**P. Concrete**	**P. PVC**	**P. HDPE**	**P. Steel**	**G. Vinyl**	**G. Aluminum**	**G. Steel**	**G. Copper**
0.01	5.69	5.92	5.57	5.57	5.68	6.14	6.99	6.99
0.5	5.73	5.87	5.54	5.55	5.63	6.15	6.98	6.95
1	5.71	5.87	5.54	5.54	5.63	6.12	6.97	6.95
27	5.79	5.99	5.63	5.64	5.72	6.22	7.06	7.05
816	5.74	6.99	6.50	6.70	6.47	7.07	8.26	8.24
1512	5.82	7.73	7.20	7.40	6.99	7.91	9.04	9.33
2256	5.90	8.63	7.91	8.40	7.95	8.76	9.89	10.18

Table J.6. Conductivity in the containers with pH 8 water.

	Conductivity for Containers with pH 8, mS/cm							
Time, hr	**P. Concrete**	**P. PVC**	**P. HDPE**	**P. Steel**	**G. Vinyl**	**G. Aluminum**	**G. Steel**	**G. Copper**
0.01	8.97	10.12	9.19	9.18	9.39	9.99	11.32	11.51
0.5	8.22	10.47	9.11	9.18	9.41	10.00	11.33	11.54
1	8.91	10.47	9.10	9.17	9.38	9.99	11.31	11.50
27	8.96	10.98	9.54	9.61	9.84	10.47	11.87	12.15
816	8.64	12.45	10.58	10.48	10.69	11.49	12.86	13.31
1512	8.70	13.69	11.82	11.69	11.86	12.66	14.16	14.70
2256	8.68	15.16	12.99	12.90	13.16	14.03	15.68	15.99

Table J.7. Conductivity in the containers with bay water.

	Conductivity for Containers with Bay Water, mS/cm							
Time, hr	**P. Concrete**	**P. PVC**	**P. HDPE**	**P. Steel**	**G. Vinyl**	**G. Aluminum**	**G. Steel**	**G. Copper**
0.01	10.8	10.69	10.56	10.63	10.70	10.62	10.73	10.76
0.5	10.89	10.79	10.66	10.73	10.80	10.69	10.73	10.81
1	10.83	10.78	10.63	10.71	10.79	10.70	10.77	10.85
27	11.02	10.96	10.76	10.87	10.92	10.88	10.95	10.98
816	11.48	11.41	11.44	11.44	11.48	12.30	11.88	11.56
1512	12.34	12.08	12.33	12.42	12.65	14.05	12.74	12.34
2256	13.92	13.41	13.88	14.13	15.47	18.66	14.55	13.74

Table J.8. Conductivity in the containers with river water.

	Conductivity for Containers with River Water, mS/cm							
Time, hr	**P. Concrete**	**P. PVC**	**P. HDPE**	**P. Steel**	**G. Vinyl**	**G. Aluminum**	**G. Steel**	**G. Copper**
0.01	0.381	0.383	0.383	0.382	0.382	0.383	0.382	0.384
0.5	0.388	0.385	0.386	0.385	0.385	0.386	0.384	0.386
1	0.395	0.387	0.387	0.382	0.386	0.388	0.384	0.386
27	0.405	0.393	0.392	0.370	0.390	0.393	0.378	0.389
816	0.472	0.408	0.409	0.323	0.396	0.401	0.349	0.397
1512	0.533	0.449	0.457	0.313	0.418	0.427	0.673	0.423
2256	0.628	0.582	0.522	0.321	0.485	0.498	0.685	0.492

TableJ.9. Ammonia nitrogen analysis with the standards.

Nitrogen Ammonia Standard, mg/L as N	Observed Value, mg/L as N
20	20
20	19
2	2
24	22
2	3
2	2.15
1.21	1.31
1.21	0.83
1.21	1.45
2.42	2.52
1.21	1.16
2.42	2.44

Table J.10. Total nitrogen analyses with the standards

Nitrogen Ammonia Standard, mg/L as N	Observed Value, mg/L as N
17	17
17	16
2	2
20	18
20	20
2	2
2	3
10	9
10	10
10	10
3	3
1	0

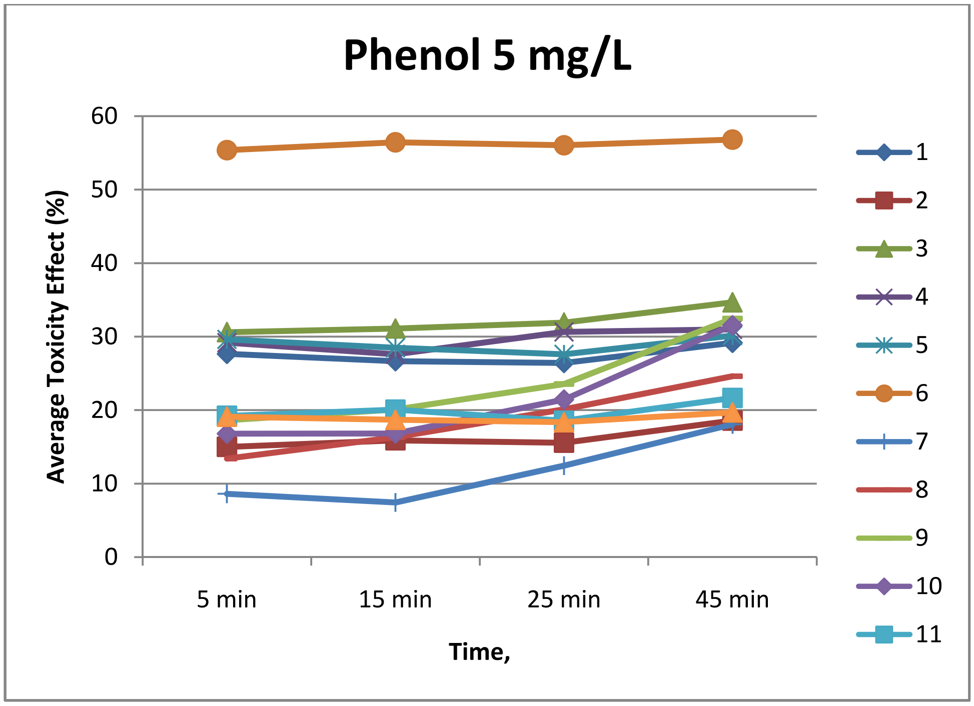


Figure J.9. Average toxicity effect of 5 mg/L of phenol. Controlled pH conditions. (Each point is an average of 2 replicates.)

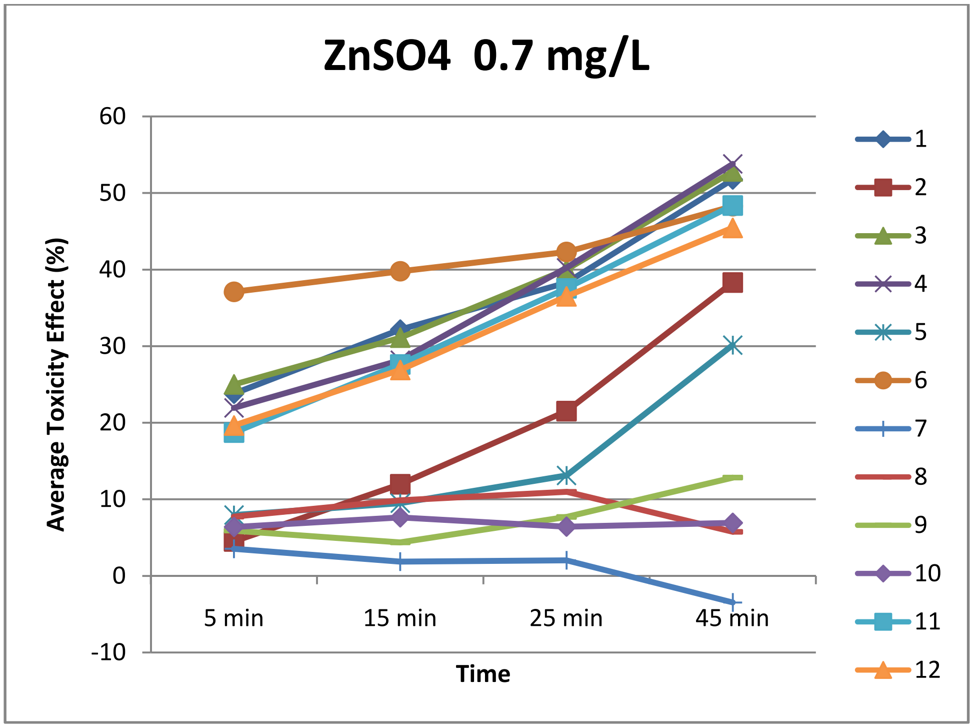


Figure J.10. Average toxicity effect of 0.7 mg/L of $ZnSO_4$. Controlled pH conditions. (Each point is an average of 2 replicates.)

Table J.11. QA/QC of Stillbrook environmental lab analysis. Containers with pH 5 waters.

Batch	Time, hr	Analyte	Assayed	Range	Units	Lab Invoice
1	0	Lead	54.0	45.0-55.0	µg/L	28997
2	0.5	Lead	54.0	45.0-55.0	µg/L	28997
3	1	Lead	54.0	45.0-55.0	µg/L	28998
4	27	Lead	54.0	45.0-55.0	µg/L	28998
5	816	Lead	50.3	45.0-55.0	µg/L	29153
6	1512	Lead	52.2	45.0-55.0	µg/L	29207
7	2256	Lead	49.8	45.0-55.0	µg/L	29280
8	2976	Iron	339.0	314-370	µg/L	29322
9	solid shavings	Lead	49.5	45.0-55.0	µg/L	29452
10	2976*					29323
11	2976*					29324

* not available from commercial lab

Table J.12. QA/QC of Stillbrook environmental lab analysis. Containers with pHº8 waters.

Batch	Time, hr	Analyte	Assayed	Range	Units	Lab Invoice
1	0	Lead	54.0	45.0-55.0	µg/L	28997
2	0.5	Lead	54.0	45.0-55.0	µg/L	28997
3	1	Lead	54.0	45.0-55.0	µg/L	28998
4	27	Lead	54.0	45.0-55.0	µg/L	28998
5	816	Lead	52.2	45.0-55.0	µg/L	29153
6	1512	Lead	49.8	45.0-55.0	µg/L	29207
7	2256	Lead	49.6	45.0-55.0	µg/L	29280
8	2544	Iron	339	314-370	µg/L	29322
9	2544*					29323
10	2544*					29324

* not available from commercial lab

Table J.13. QA/QC of Stillbrook environmental lab analysis. Containers with bay waters.

Batch	Time, hr	Analyte	Assayed	Range	Units	Lab Invoice
1	0	Lead	50.3	45.0-55.0	µg/L	30605
2	0	Iron	197	180-220	µg/L	30772
3	1	Lead	49.2	45.0-55.0	µg/L	30608
4	27	Lead	49.2	45.0-55.0	µg/L	30606
5	168	Lead	49.2	45.0-55.0	µg/L	30607
6	816	Lead	51.9	45.0-55.0	µg/L	30694
7	1512	Lead	51.4	45.0-55.0	µg/L	30773
8	2256	Lead	52.8	45.0-55.0	µg/L	30935
9	2256	Iron	202	180-220	µg/L	30936
10	0	Calcium	75.4	70.1-81.7	mg/L	30610
11	2256	Calcium	73.3	70.2-81.7	mg/L	30934
12	source water	Manganese	45.8	45.0-55.0	µg/L	31134
13	source water	Chloride	56.5	49.7-60.1	mg/L	30937
14	source water	Sulfate	48.4	37.7-51.4	mg/L	30937

Table J.14. QA/QC of Stillbrook environmental lab analysis. Containers with river waters.

Batch	Time, hr	Analyte	Assayed	Range	Units	Lab Invoice
1	0	Lead	50.3	45.0-55.0	µg/L	30605
2	0	Iron	197	180-220	µg/L	30772
3	1	Lead	49.2	45.0-55.0	µg/L	30608
4	27	Lead	49.2	45.0-55.0	µg/L	30606
5	168	Lead	49.2	45.0-55.0	µg/L	30607
6	816	Lead	51.9	45.0-55.0	µg/L	30694
7	1512	Lead	51.4	45.0-55.0	µg/L	30773
8	2256	Lead	52.8	45.0-55.0	µg/L	30935
9	2256	Iron	202	180-220	µg/L	30936
10	0	Calcium	75.4	70.1-81.7	mg/L	30610
11	2256	Calcium	73.3	70.2-81.7	mg/L	30934
12	source water	Manganese	45.8	45.0-55.0	µg/L	31136
13	source water	Chloride	56.5	49.7-60.1	mg/L	30937
14	source water	Sulfate	48.4	37.7-51.4	mg/L	30937