The Influence of pH and Salinity on Heavy Metal Contaminants Released into Stormwater from Pipe and Tank Materials

Olga Ogburn[1], Robert Pitt[1], and Shirley Clark[2]

[1] Dept. of Civil, Construct., and Env. Eng., The University of Alabama. E-mail: rpitt@eng.ua.edu

[2] Env.Engineering Program, Penn State Harrisburg, Middletown, PA. Email: seclark@psu.edu

ABSTRACT

The objective of this study was to investigate the effects of pH, salinity, and time of contact on leaching of metals from different pipe, gutter, and storage tank materials. The release of heavy metals from eight pipe and gutter materials was examined during static leaching tests. During the first phase, the materials were submerged into containers with buffered (pH 5 and 8) roof runoff and stormwater. During the second phase, the samples were submerged into natural bay and river waters. Water samples from each leaching container were periodically collected and analyzed over a three month period for a wide range of metallic contaminants, pH, conductivity, and toxicity (using Microtox screening methods), plus periodic samples were collected to describe the basic chemical characteristics of the water. Lead releases were detected only in the galvanized steel material samples. Copper concentrations in containers with the copper materials increased with decreased pH. The greatest copper concentrations were detected under bay water conditions (high salinity). Galvanized materials were the greatest source of zinc. During the first day of exposure, high zinc releases from galvanized steel materials were observed at lower pH conditions. During short periods of exposures, lower zinc concentrations were leached from the galvanized steel materials in river water samples compared to the bay water samples; however, during long period exposures, zinc releases in the bay water samples were exceeded by those in the river water samples. Phase and Pourbaix diagrams are used to determine the predominant

forms of species and to compare maximum observed concentrations in the sampled waters with theoretical equilibrium and saturation concentrations.

KEYWORDS: stormwater, zinc, copper, lead, pH, salinity.

MATERIALS AND METHODS

Stormwater drainage materials undergo degradation when exposed to the environment and release contaminants into stormwater (Clark et al. 2007; Clark et al. 2008; Burton and Pitt 2002). These pollutants are transported to surface and groundwaters (US EPA 2007; Burton and Pitt 2002). Long term-leaching laboratory studies were conducted using eight new gutter and pipe materials. 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 was adjusted to pH values of 5 and 8 using buffer chemicals added to the runoff water ($Na_2HPO_4 * 2H_2O$ and KH_2PO_4). These initial buffered water test solutions therefore had high phosphate concentrations and high conductivity values. Each section of gutter and pipe material was placed into 16 L plastic buckets or 80 L containers (for the concrete materials). 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 were used. Vinyl, aluminum, copper, and galvanized steel gutters purchased from a local building material supplier were utilized in the study. The pipe materials included concrete, PVC, HDPE, and galvanized corrugated steel.

Each specimen of pipe and gutter material was submerged into containers with pH values of 5 and 8 during first series of tests; the gutter materials were submerged in the buffered roof

runoff and the pipe materials were submerged in the buffered parking lot runoff. For the second series of tests, new specimens of the same samples were submerged into containers having un-buffered bay and river waters.

The gutter and pipe sections utilized in the two pH tests were nearly identical. The specimens examined in the natural water tests were also identical. All the gutter and pipe sections used were 30.5 cm long, except for the concrete pipe specimens, which were 15.3 cm long in the first testing stage, and in the second testing stage, a section of the 15.3 cm long section pipe was utilized. The cross-sectional dimensions of vinyl, aluminum, and copper gutters were 5 by 8, 8.4 by 5.6, and 10.6 by 7.2 cm, respectively. The diameters of galvanized steel gutters were 15.2 cm. The diameters of concrete, PVC, HDPE, and galvanized steel pipes were 41.2, 15.7, 17.5, 16.4 cm respectively. The approximate weight of vinyl, aluminum, galvanized steel, and copper gutters was 100, 79, 704, and 503 g, respectively. The approximate weight of the PVC, HDPE, and galvanized steel pipe sections was 1,096, 409, and 8,000 g, respectively. The weight of the concrete pipes was approximately 22 kg each in the first series of the tests; in the second series of the experiments, the concrete pipe sections weighed approximately 4.4 kg.

During the first testing stage, the water from the leaching containers was analyzed at time zero (water with adjusted pH without test sections), 0.5 hr, 1 hr, 27 hrs, 1 month, 2 months, and 3 months for total concentrations of zinc, copper, lead, cadmium, and chromium. Total iron and aluminum and filterable concentrations of zinc, copper, lead, and aluminum were analyzed after three months of exposure. Also, samples were analyzed for ammonia nitrogen, total nitrogen, nitrate and COD, and screened for toxicity using Microtox procedure. During the second testing stage, the containers were sampled and analyzed at time zero (natural bay and river waters without pipes), 1 hr, 27 hrs, 1 week, 1 month, 2 months, and 3 months for total concentrations of

zinc, copper, lead, and tested for toxicity. Total iron and aluminum and filterable concentrations of iron were also determined in the samples after 3 months of exposure. pH, conductivity, Eh, alkalinity, total and calcium hardness, chloride, and sulfate analysis were also conducted during the first and second testing stages. To account for different area surfaces of the pipes and water volumes, concentrations in mg/L were converted to mg of constituent per exposed surface area for each sample.

RESULTS

Resulting concentrations for the tests for the different materials and leaching conditions are shown in Figure 1. As expected, the copper materials resulted in very high copper concentrations in the test waters. After the first day of exposure, the copper concentrations were from 1 to more than 6 mg/L, with greater concentrations for pH 5 conditions when compared with the other samples (the buffered pH 8 samples and the bay and river samples). However, after three months of exposure, the copper concentrations from the copper material tests in the bay samples (more than 35 mg/L) exceeded those at controlled pH 5 conditions (more than 5 mg/L).

The greatest release of zinc was from galvanized metal samples, as expected. Higher zinc concentrations were observed at controlled pH 5 conditions (exceeding 14 mg/L) after the first day of exposure, followed by bay samples (more than 8 mg/L). During long exposure periods (after three month), galv. metals submerged in river water resulted in the greatest zinc concentrations (more than 190 mg/L and more than 60 mg/L for galv. gutter and pipe respectively). Samples at pH 5 conditions had the lowest resulting zinc concentrations from the galvanized materials (11 to 14 mg/L).

Lead releases were only observed for the galvanized material samples. Figure 2 shows total lead releases (mg/m^2) in galvanized steel pipe samples at different water conditions during short exposure periods. After three months of exposure, the highest lead concentrations occurred for controlled pH 8 conditions (630 µg/L for steel pipe), followed by controlled pH 5 conditions (250 µg/L), river (60 µg/L), then bay (< 5 µg/L) samples.

One-Way ANOVA on Ranks (Kruskall-Wallis) tests performed for the galv. steel gutter samples showed there were no observed differences for the sample numbers available in the lead releases for the buffered, the bay and the river waters during short exposure times (Table 1). Also there were no observed differences for the sample numbers available in the copper releases for copper gutter samples at different water conditions and for zinc releases in the galv. steel pipe and gutter samples. Tukey tests showed that for the galv. steel pipe samples, there was a significant difference ($p < 0.05$) in the lead releases for bay vs. the river water samples during short exposure periods (Table 2).

Log Concentration – pH (Phase) diagrams can be used to determine equilibrium concentrations of various species present in the water and their total concentrations. These diagrams can also be utilized to show the predominant soluble species in a given pH range (Snoeyink and Jenkins 1980). The Eh – pH (Pourbaix) diagrams also can be used to delineate the predominant areas of the species present (Garrels and Christ 1990, Degremont 1979). Phase and Pourbaix diagrams are being used to determine the predominant species and the total possible saturation concentrations for the heavy metals of interest. To create log Concentration – pH and Eh – pH diagrams, Medusa software is being used. The following example is for a steel pipe sample submerged into bay water after 3 months of exposure. Figure 3 is the phase diagram

created using Medusa. It can be seen that in this water sample (pH = 7) zinc is predominantly in the free ion form (Zn^{2+}). Table 3 shows the predominant forms of zinc species after 3 months of exposure. The total zinc concentration that can that can be dissolved in a solution at pH 7 is 86 mg/L. The total zinc concentration observed in this sample was 79 mg/L, indicating that the maximum solubility for zinc was not reached, but reflected more than 80% of the maximum expected concentration. Figure 4 also confirms that at pH 7 and Eh = -0.18V, free ion Zn^{2+} is the predominant species. This is also critical information as the toxicity of the resulting water is highly dependent on the species present.

CONCLUSIONS

Heavy metals can be released from drainage system materials into the water immediately after the water comes in contact with the materials. This release can continue during long periods of exposure corresponding to storage facilities. 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. The most significant source of lead and zinc were the galvanized steel materials, while the greatest copper concentrations were observed leaching from the copper materials, as expected. Awareness of the amount of the contaminants leaching from the piping materials will facilitate the design of stormwater control equipment to reduce the negative impact on the environment. The information on pipe stormwater quality runoff will enable government officials to make better regulatory policies for industrial and commercial land uses concerning pollution prevention. Manufactures of these materials can also offer coatings or alternative materials having reduced metal releases.

ACKNOWLEDGEMENTS

REFERENCES:

Burton, G. Allen, Jr., Pitt, Robert, E., 2002. *Stormwater Effects Handbook. A Toolbox for Watershed Managers, Scientists, and Engineers*. Lewis Publishers. A CRC Press LLC. ISBN 0-87371-924-7

Clark, Shirley E., Franklin, Kelly A., Hafera, Julia M., Kirby, Jason T., 2007. Roofing as a contributor to urban runoff pollution. *World Environmental and Water Resources Congress 2007: Restoring Our Natural Habitat*. ASCE/EWRI, Tampa, FL, May 15-19, 2007. CD-ROM.

Clark, Shirley E., Steele, Kelly A., Spicher, Julia, Siu, Christina Y.S., Lalor, Melinda M., Pitt, Robert, Kirby, Jason T., 2008, Roofing Materials' Contributions to Stormwater Runoff Pollution. *Journal of Irrigation and Drainage Engineerigng*.Vol.134, No. 5, October 1, 2008.

Garrels, Robert M., Christ, Charles L., 1990. *Solutions, Minerals, and Equilibria*. Jones and Bartlett Publishers, Inc., Boston, MA

Degremont , 1979. *Water Treatment Handbook*. 5th edition. John Willey & Sons, Inc.. New York., 1979. ISBN:0470-26749-6

Snoeyink Vernon L., David Jenkins, 1980.*Water Chemistry*. John Wiley & Sons, Inc. New York. 1980.

US EPA (U.S. Environmental Protection Agency), 2007. *Framework for Metals Risk Assessment*. EPA 120/R-07/001, March 2007. (http://www.epa.gov/raf/metalsframework/index.htm) (Accessed January 8, 2012)
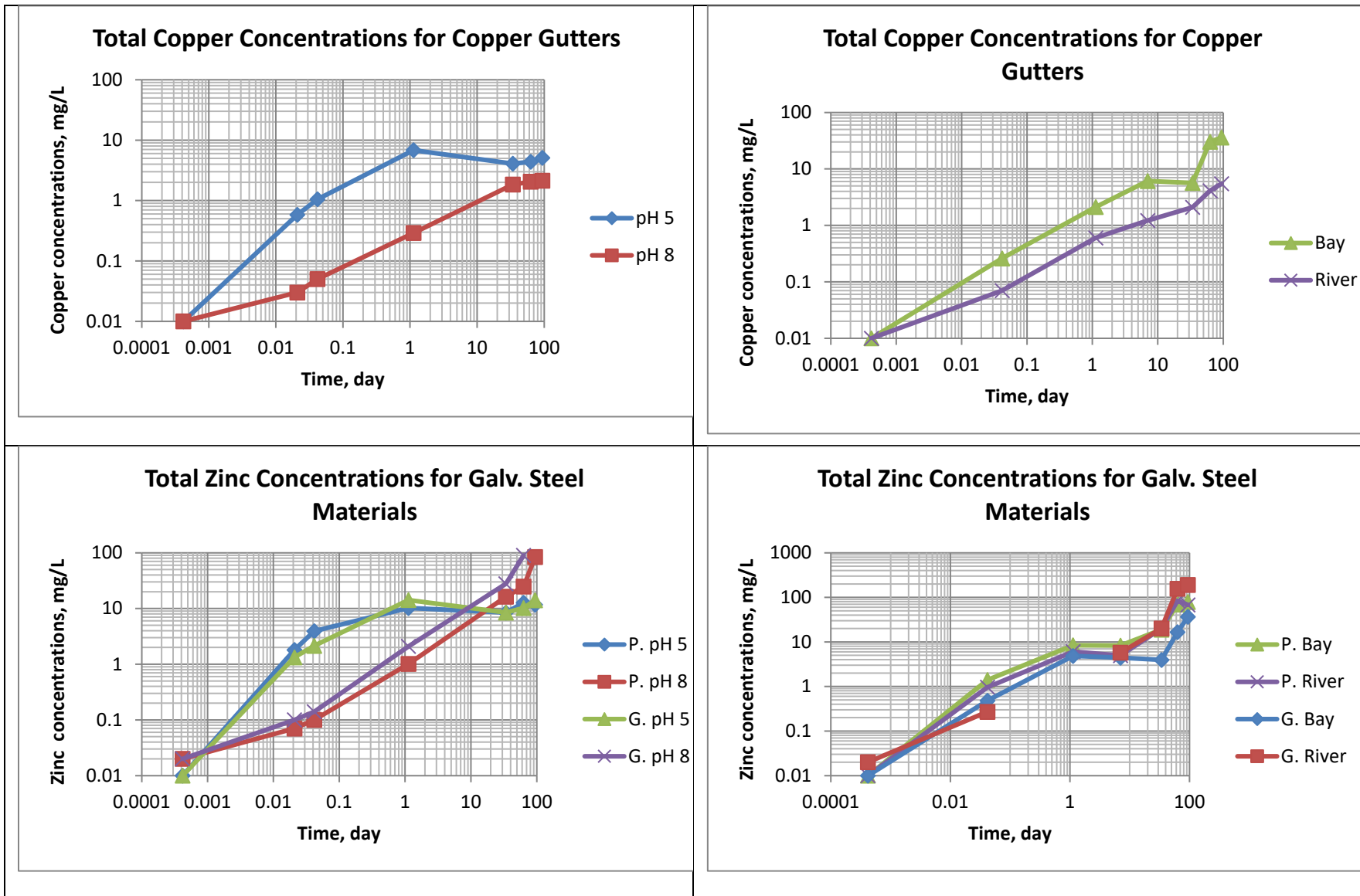
Figure 1. Total metal concentrations leaching from copper and galvanized steel materials.

Table 1. Comparison of Total Metal Releases During Short Exposure Periods for Different Water Conditions. One-Way ANOVA on Ranks (Kruskal-Wallis) Test

Pipe	The null hypothesis of to be drawn from the same population	P-value	There is NO difference between water conditions
Cu in copper gutter sample	not rejected	P = 0.129	yes
Pb in galv. steel pipe sample	rejected	P = 0.024	no
Pb in galv. steel gutter sample	not rejected	P = 0.504	yes
Zn in galv. steel pipe sample	not rejected	P = 0.118	yes
Zn in galv. steel gutter sample	not rejected	P = 0.340	yes

Table 2. Tukey Test for Total Lead Released in Galvanized Steel Pipe Sample During Short Exposure Period

Comparison	Diff. of Ranks	q	p < 0.05?
Bay vs. River	27.000	4.323	Yes
Bay vs. pH 8	13.500	2.162	No
Bay vs. pH 5	13.500	2.162	No
pH 5 vs. River	13.500	2.162	No
pH 5 vs. pH 8	0.000	0.000	No
pH 8 vs. River	13.500	2.162	No

Total Lead Release in Galv. Steel Pipe Samples During Short Exposure Time
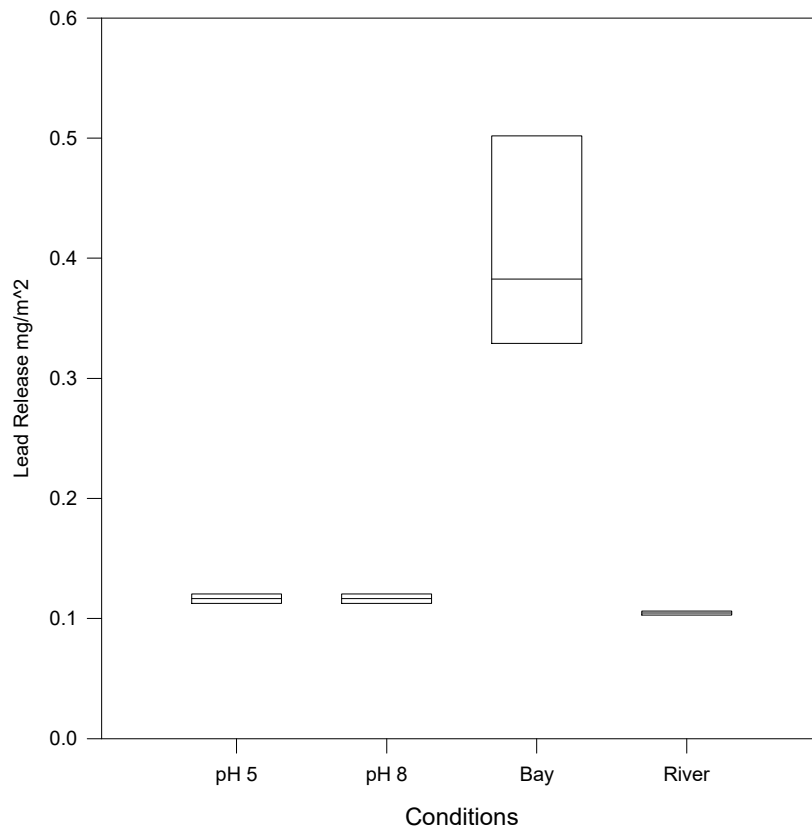

Figure 2. Total lead releases (mg/m^2) in galvanized steel pipe samples at different water conditions.

$[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
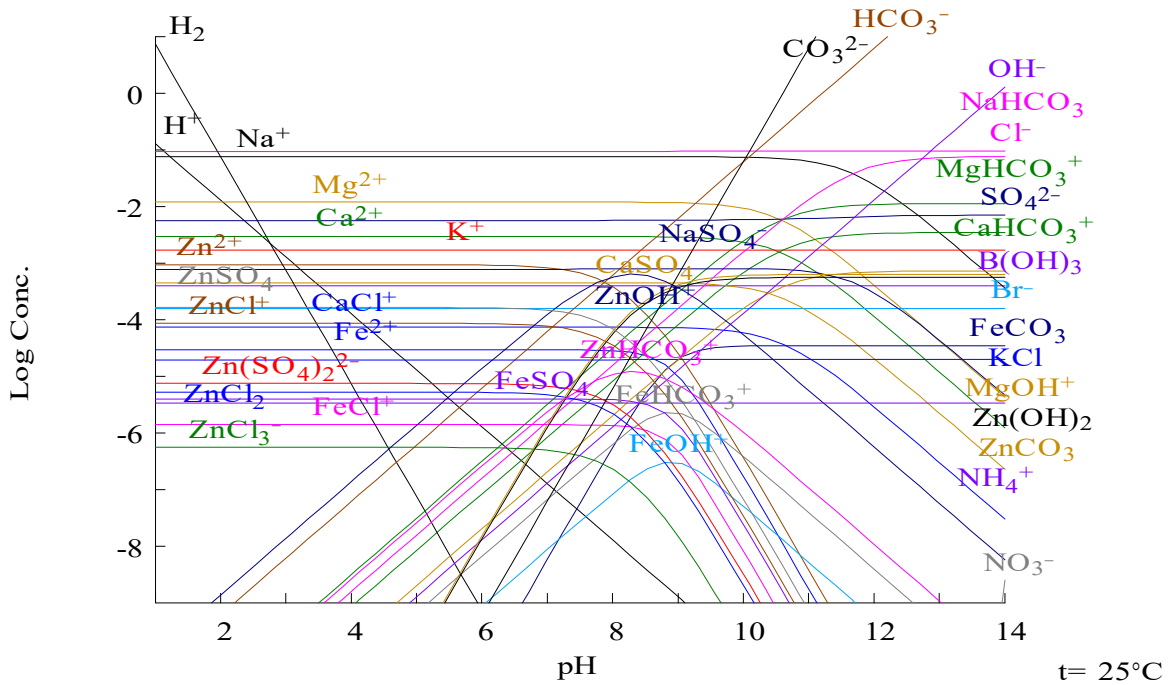
$[NO_3^-]_{TOT} = $ 3.39 μM

Figure 3. Phase diagram for steel pipe sample submerged into Bay Water after three months of exposure.

Table 3. The Predominant Forms of Zinc Species after Three Months of Exposure

Component	Log Concentration (mol/L)	Concentration (mol/L)	Zn Concentration (mg/L)	Cumulative Percentage of Zn
Zn^{2+}	-3.06	8.64E-04	56.48	65.66
ZnOH$^+$	-3.91	1.22E-04	7.96	74.90
ZnSO$_4$	-3.92	1.20E-04	15.39	92.80
ZnCl$^+$	-4.10	8.02E-05	5.24	98.89

$ZnCl_2$	-5.31	4.88E-06	0.32	99.26
$Zn(SO_4)_2^{2-}$	-5.36	4.32E-06	0.28	99.59
$ZnHCO_3^+$	-5.63	2.32E-06	0.15	99.77
$ZnCO_3$	-5.89	1.29E-06	0.08	99.87
$Zn(OH)_2$	-5.94	1.15E-06	0.08	99.95
$ZnCl_3^-$	-6.29	5.15E-07	0.03	99.99

$I = 0.087$ M

$[SO_4^{2-}]_{TOT} = 7.02$ 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

$Log\ P_{CO_2} = -3.50$

$[K^+]_{TOT} = 1.72$ mM

$[Na^+]_{TOT} = 76.60$ mM

$[B(OH)_3]_{TOT} = 0.39$ mM

$[Br^-]_{TOT} = 0.16$ mM
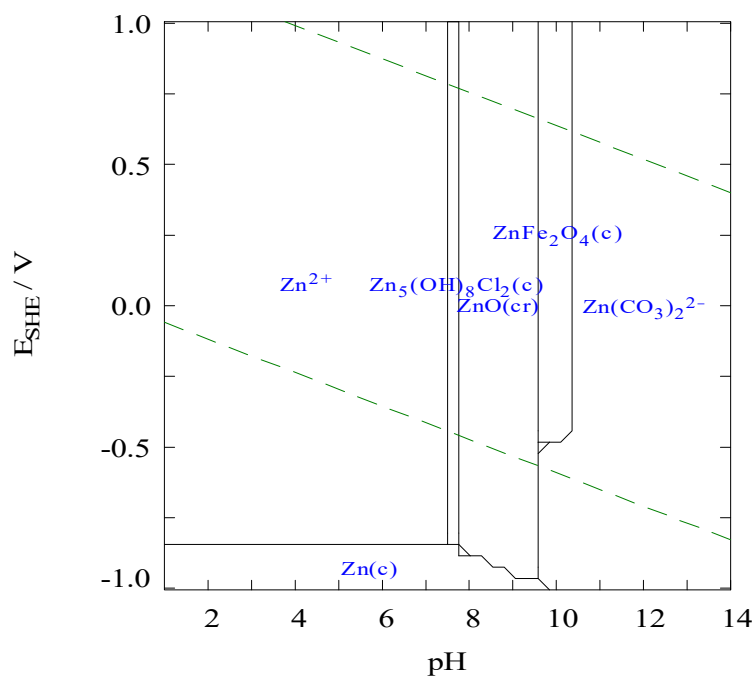
$[NO_3^-]_{TOT} = 3.39$ μM

$t = 25°C$

Figure 4. Pourbaix diagram for steel pipe sample submerged into Bay Water after three months of exposure.