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Contributions of Heavy Metals from Material Exposures to Stormwater

Contents

Introduction

This report section reviews the contributions of selected heavy metals from different materials exposed to rain or runoff. This information is being used to assist in the calibration of WinSLAMM for naval facilities to account for the contributions of these materials exposed at various locations.

The section starts with a review of an extensive literature review that was recently conducted by Olga Ogburn during her PhD research at the University of Alabama. Much of the literature focusses on roofing materials and galvanized metals. Her leaching test results of different pipe and tank materials are also summarized. Washdown tests conducted by SPAWAR personnel during this project are also summarized in this section. An overall summary of these data was also prepared for an overview of the most critical exposed materials and likely concentrations and loss rates.

The treatability of stormwater heavy metals is also briefly discussed based on their characteristics as observed during these tests and from the literature. The most important characteristics affecting treatability include: concentrations, filterable fraction, likely complexation, ionic state, and associations with different particle sizes.

Trace Heavy Metals in Wet Weather Flows

The material in the literature review and leach test sections are summarized from the research conducted by Dr. Olga Ogburn as part of her dissertation research: Ogburn, Olga. Ph.D. *Urban Stormwater Contamination Associated with Gutter and Pipe Material Degradation*. Department of Civil, Construction, and Environmental Engineering at the University of Alabama. 2013. This research was mostly funded by the National Science Foundation (grant no. EPS-0447675). The NSF project included tasks conducted at UA supporting the Center for Optical Sensors and Spectroscopies (COSS) at UAB's Department of Physics by applying emerging technologies to solve current environmental problems.

This research investigated pipe and tank material sources of heavy metals in wet weather flows, to supplement the large amount of available information concerning roof runoff degradation (along with their chemical characteristics and associated treatability). This section shows that many of the heavy metals in stormwater could be related to material selection and that use of proper materials could result in decreased heavy metals in wet weather flows. This section presents the results of a literature review of heavy metal releases from different materials (mostly roofing types) and the results of several controlled leaching tests that examined a variety of roof gutter, piping, and storage tank materials.

Literature Review: Contaminants Associated with Rooftop and Drainage System Materials

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). 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). The following includes summary tables containing observed concentrations from the different monitoring studies associated with material exposure.

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 patina layer (zinc oxides/hydroxides/carbonates) 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). The 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 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). The following table summarizes zinc concentrations or runoff yields from different materials reported by various researchers.

Zinc releases from various sources (Ogburn 2013)

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 City	Gromaire, et al. (2002)

Zinc releases from various sources (Ogburn 2013), continued

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)

Zinc releases from various sources (Ogburn 2013), continued

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)

The largest sources of zinc in stormwater runoff are galvanized materials, such as zinc-based roofing materials, galvanized roof drainage systems, and galvanized pipes. Galvanized materials have a large potential for contributing zinc to runoff during their useful life. Zinc runoff yields were generally observed to increase with the age of the material. Zinc concentrations in runoff from galvanized materials ranged from 100's of µg/L to 10's of mg/L. Zinc concentrations in roof runoff samples frequently exceeded the water quality criteria established by the U.S. EPA and regulatory agencies from other countries.

Copper

Clark, et al. (2008 a and b) monitored runoff from a pilot-scale selection of roofing materials and other materials at the campus of Penn State Harrisburg for 2 years under natural rain conditions. 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).

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). The following table summarizes copper concentrations and runoff yields from different materials reported by various researchers.

Copper Releases from Various Sources (Ogburn 2013)

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)

Copper Releases from Various Sources (Ogburn 2013), continued

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 µg/m^2	Zobrist, et al. (2000)
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)

Copper Releases from Various Sources (Ogburn 2013), continued

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)

As expected, the highest copper runoff rates were noted from exposed copper materials. Copper-based paints can also be a significant source of copper in runoff. Some studies indicated relatively constant copper runoff yields with time during 5 years of exposure. However, other studies found that new copper materials had higher copper runoff yields compared to older copper materials. Galvanized steel, vinyl, and galvalume materials had copper runoff concentrations that were less than 25 µg/L. 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.

Lead

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. 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). The following table summarizes lead concentrations or release rates from different materials reported by various researchers.

Lead Releases from Various Sources (Ogburn 2013)

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	10 μg/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)

Lead Releases from Various Sources (Ogburn 2013), continued

Coated Galvanized Aluminum Roofing Materials			
Kynar®-coated Galvalume® roof	Full-scale Austin, Texas	<0.01 - 0.21 μg/L during first flush; <0.12 μg/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)

Lead Releases from Various Sources (Ogburn 2013), continued

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)

Lead Releases from Various Sources (Ogburn 2013), continued

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

Galvanized steel, PVC and unplasticized PVC, galvalume, and zinc materials can be sources of lead concentration increases in water. Lead concentrations released from galvanized steel and PVC materials increase with increased exposure time, increased pipe age, and pH decreases. Also, exposure to UV-radiation was determined to promote the migration of lead from unplasticized PVC pipes. Additionally, painted materials can be a source of lead in stormwater, with lead releases being higher from older types of paints. 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.

Cadmium

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 generally, the dissolved fraction of cadmium was greater than the particulate fraction for roof runoff. The following table summarizes cadmium concentrations and release rates from different materials reported by various researchers.

Cadmium Releases from Various Sources (Ogburn 2013)

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 hrs.	Mobarakeh, Iran	Before DWDS 0.06 µg/L, after DWDS 0.8 µg/L	Shahmansouri, et al. (2003)

PVC, zinc, tile, tar felt, and galvanized iron materials can all be sources of cadmium in runoff. 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.

Iron

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). 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 were approximatelly100 µg/m of pipe length after 20 hours of stagnation, and reached 375 µg/m of pipe length after 120 hours of stagnation. The following table summarizes iron concentrations and runoff yields from different materials reported by various researchers.

Iron Releases from Various Sources (Ogburn 2013)

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)

Iron Releases from Various Sources (Ogburn 2013), continued

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 contact time	pH = 6	Avg. 1.65 mg/L	Lasheen, et al. (2008)
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)

Iron Releases from Various Sources (Ogburn 2013), continued

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)

PVC, polypropylene, galvanized iron, clay tile, polyester, stainless steel, galvanized iron, and Galvalume® metal materials were found to release iron into runoff water. Exposure time had an effect on iron released from PVC, polypropylene, and galvanized iron materials. Greater iron runoff concentrations were observed for aged PVC, polypropylene, and galvanized iron pipes compared to new materials. As pH decreased, iron concentrations leaching from PVC, polypropylene, and galvanized iron, cast iron, and galvanized steel materials increased. High Cl^-/SO_4^{2-} ratios increased iron concentrations from PVC, polypropylene, and galvanized iron pipes. The mass loss of carbon steel is influenced by the frequency and the amount of rain and is proportional to the chloride deposition rate.

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. The following table summarizes aluminum concentrations from different materials.

Aluminum Releases from Various Sources (Ogburn 2013)

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 12 µg/L during first flush sample; 0.06 to6.7µg/L for later samples	Mendez, et al. (2011)

Laboratory Tests and Model Fitting to Predict Metal Releases from Material Exposures

Ogburn (2013) conducted exposure tests to determine the losses of heavy metals and other constituents as a function of exposure time under different pH and conductivity conditions. Roof runoff was used for roofing materials and parking lot runoff was used for the other piping materials; later tests used river water and saline bay water. She presented the data as time series plots indicating the accumulative total losses on an area basis. Linear regression analyses on the log-transformed metal releases per pipe surface area vs. log time for different pipe and gutter materials under controlled and natural pH conditions, after supporting statistical analyses were used to identify groupings of the data. The majority of the scatterplots revealed that first order polynomials can be fitted to the log of metal releases vs. log of time.

Modeling the Effects of Material Type, Exposure Time, pH, and Salinity on Metal Releases and Toxicity

Spearman correlation analyses were used to determine the associations 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 identified 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.

Full 2^3 Factorial Analyses

Full 2^3 factorial 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. The levels for the different factors defining how the data were organized are shown on the table below. Kruskal-Wallis tests were initially performed for each constituent to determine if the data for 1, 2, and 3 months of pipe and gutter exposure could be used together to represent 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.

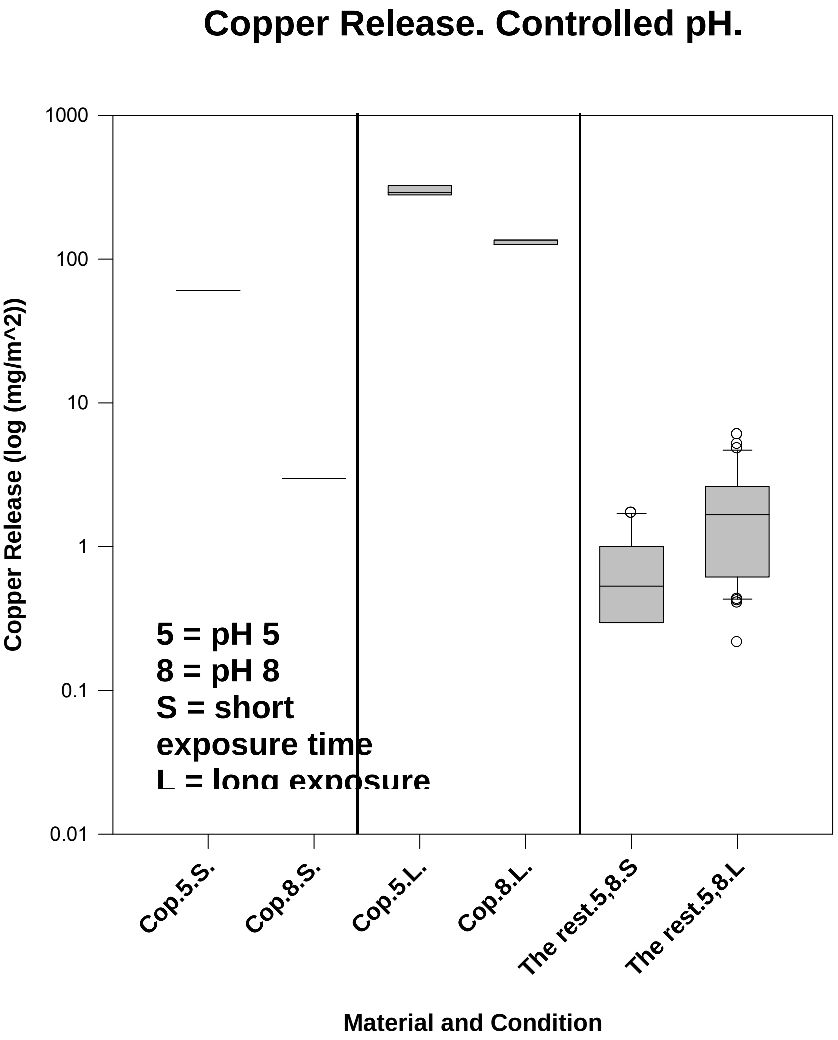
2^3 Factorial Experiment. Factors and levels (Ogburn 2013)

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 (+)

The factorial effect/pooled standard error ratio of the factorial analysis 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.

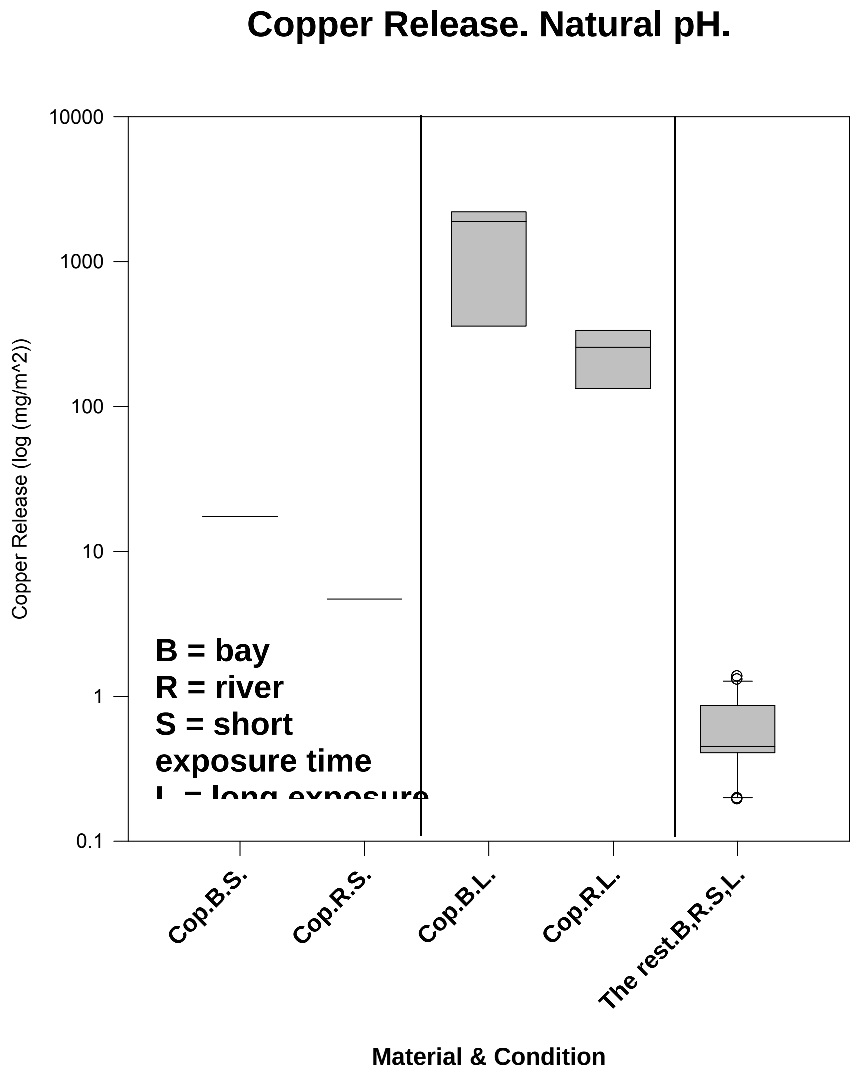
Combined Data Group Analyses

The following figures show metal releases for the combined data groups, based on the prior analyses. The significant factors and their interactions from 2^3 factorial 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. The group box plot of copper releases compares 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 2^3 factorial analyses showed that the three-way interaction of pH x material x time was significant, therefore the main effects should not be interpreted separately (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. The groups combining the rest of the materials for pH 5 and pH 8 conditions during short exposure time into one group is also shown, with the rest of the materials for pH 5 and pH 8 conditions during long exposure time combined into one group.



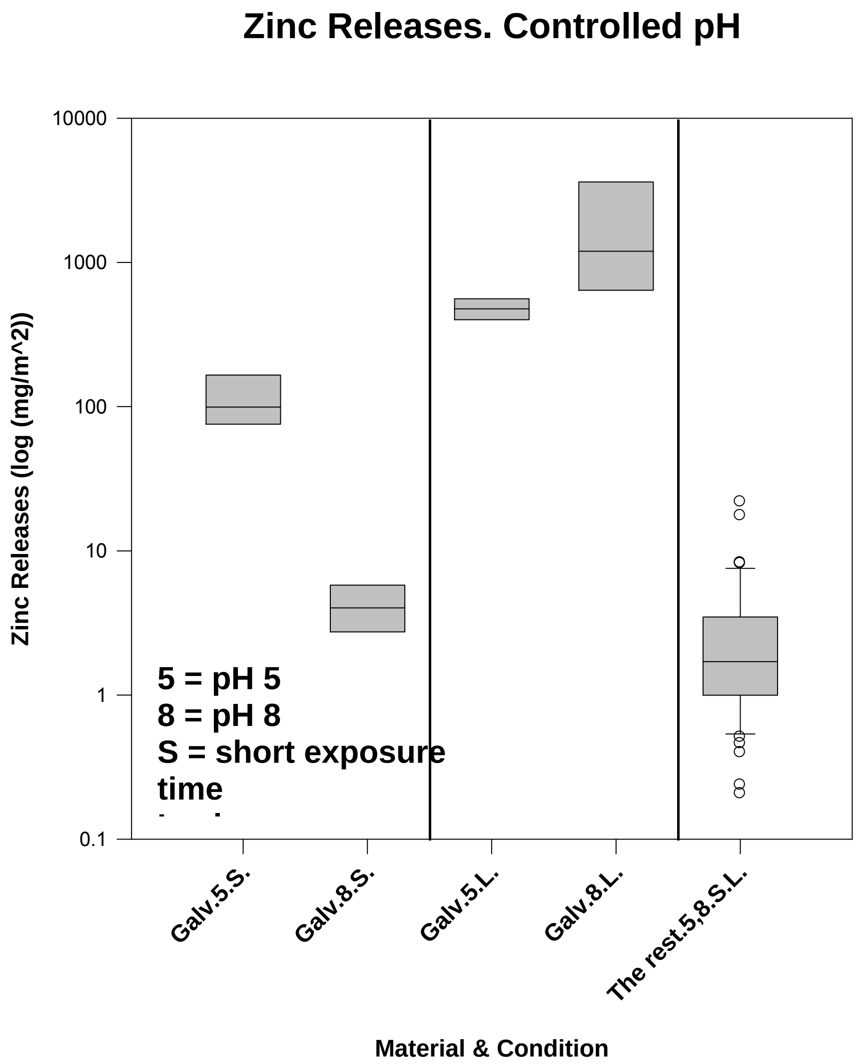
Group box plot for copper release in mg/m^2 for materials immersed in pH 5 and pH 8 waters (Ogburn 2013).

The following figure 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.



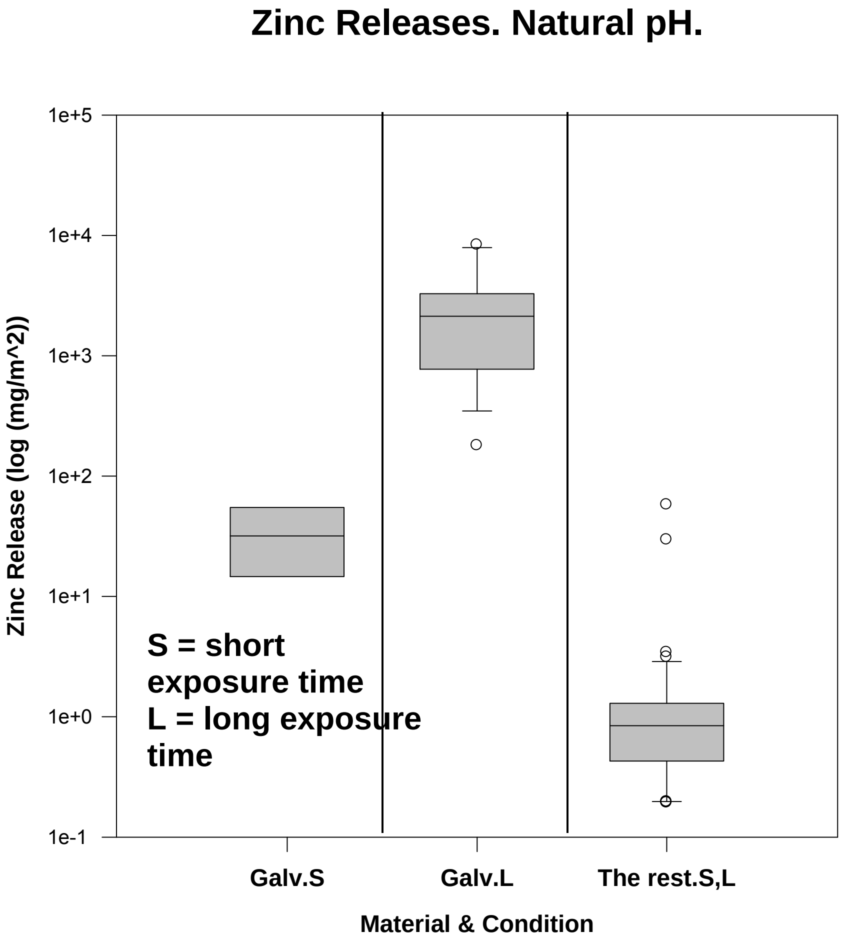
Group box plot for copper release in mg/m^2 for materials immersed in bay and river waters (Ogburn 2013).

The following figure is a group box plot of zinc releases for the galvanized steel samples compared to the rest of the material samples for pH 5 and8 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 resulted in significant increases in zinc releases during the short exposure periods. 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. The other figure shows “the rest” of the materials at pH 5 and pH 8 conditions during short and long exposure periods combined into one group.



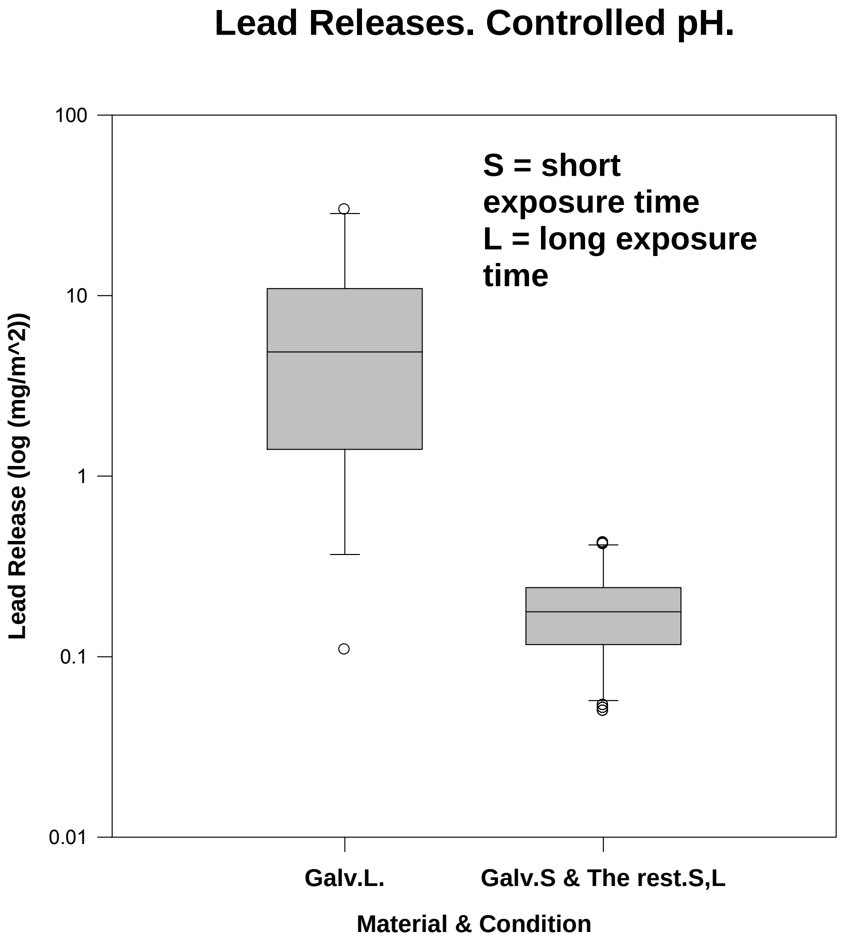
Group box plot for zinc release in mg/m^2 for materials immersed in pH 5 and pH 8 waters (Ogburn 2013).

Zinc releases also increased with exposure time for galvanized steel pipes and gutters immersed in bay and river waters. In this example, the interaction of material and exposure time was significant. Galvanized materials exposed to natural pH waters resulted in elevated zinc releases even during short periods. The combination of galvanized materials exposed to natural pH waters for long periods further increased zinc releases.



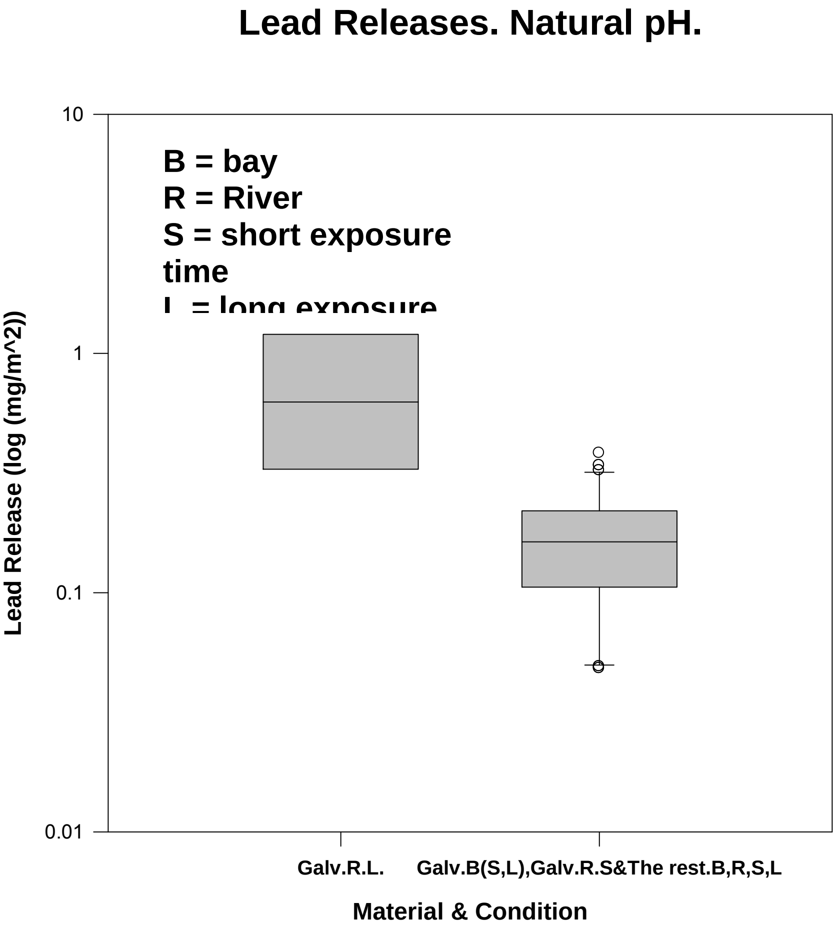
Group box plot for zinc release in mg/m^2 for materials immersed in bay and river waters (Ogburn 2013).

Galvanized steel materials were the only source of lead releases detected. For lead releases under controlled pH conditions, 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.



Group box plot for lead release in mg/m^2 for materials immersed in pH 5 and pH 8 waters (Ogburn 2013).

Long exposure periods increased lead releases in the samples with galvanized materials immersed into river water. 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. Lead releases were combined in two groups.



Group box plot for lead release in mg/m^2 for materials immersed in bay and river waters (Ogburn 2013).

Predictive Models of Metal Releases from Different Pipe and Gutter Materials

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.

The following tables 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.

Model based on 2^2 Factorial analyses. Steel pipe. Controlled pH tests (Ogburn 2013)

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

Model based on 2^2 Factorial analyses. Steel materials. Controlled pH tests (Ogburn 2013)

Constituent	Galvanized Steel Materials (Pipe and Gutter). Controlled pH Conditions	
Zn, mg/m^2	Log Zn (mg/m^2) @pH5 = 2.138 +0.1904*logTime (hr); R^2 = 68.2%; p-value for regression = 0.001	Log Zn (mg/m^2) @pH8 = 0.7236 +0.7643*logTime (hr); R^2 = 94.0%; p-value for regression = 0.000

Model groups based on 2^2 Factorial analyses. Steel pipe. Natural pH tests (Ogburn 2013)

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.

Model based on 2^2 Factorial analyses. Copper gutter. Controlled pH tests (Ogburn 2013)

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.

Model based on 2^2 Factorial analyses. Copper gutter. Natural pH tests (Ogburn 2013)

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.

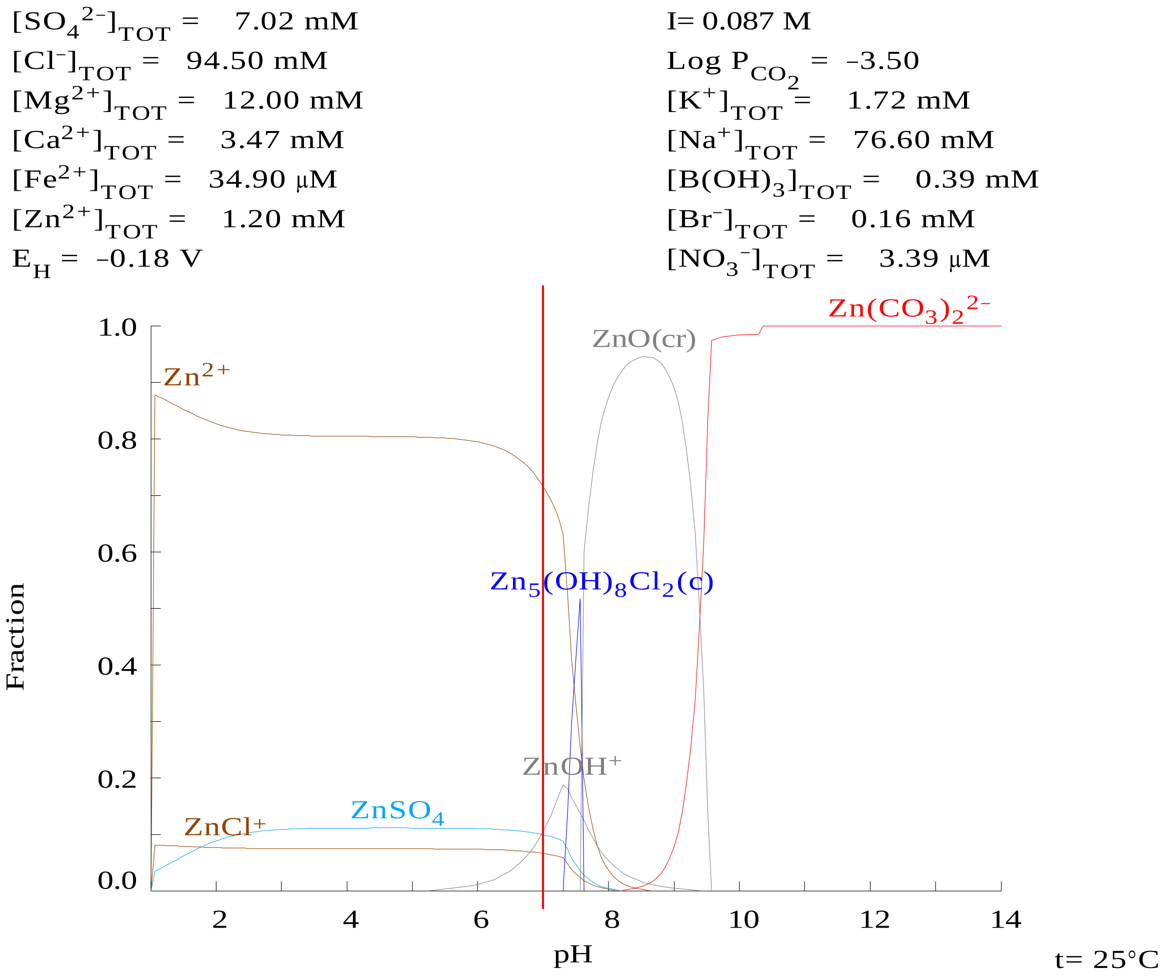
The models showed that copper materials had elevated copper releases in pH 5 waters (250 mg/m^2) and in bay and river waters during short exposure times (180 and 840 mg/m^2 respectively). Long term exposure periods of copper materials under both high and low salinity conditions also resulted in high 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 480 and 1860 mg/m^2 for galvanized steel materials at pH 5 and pH8 conditions respectively during long exposure time). 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.

Chemical Speciation Modeling of Heavy Metals (Medusa Water Chemistry Modeling Environment)

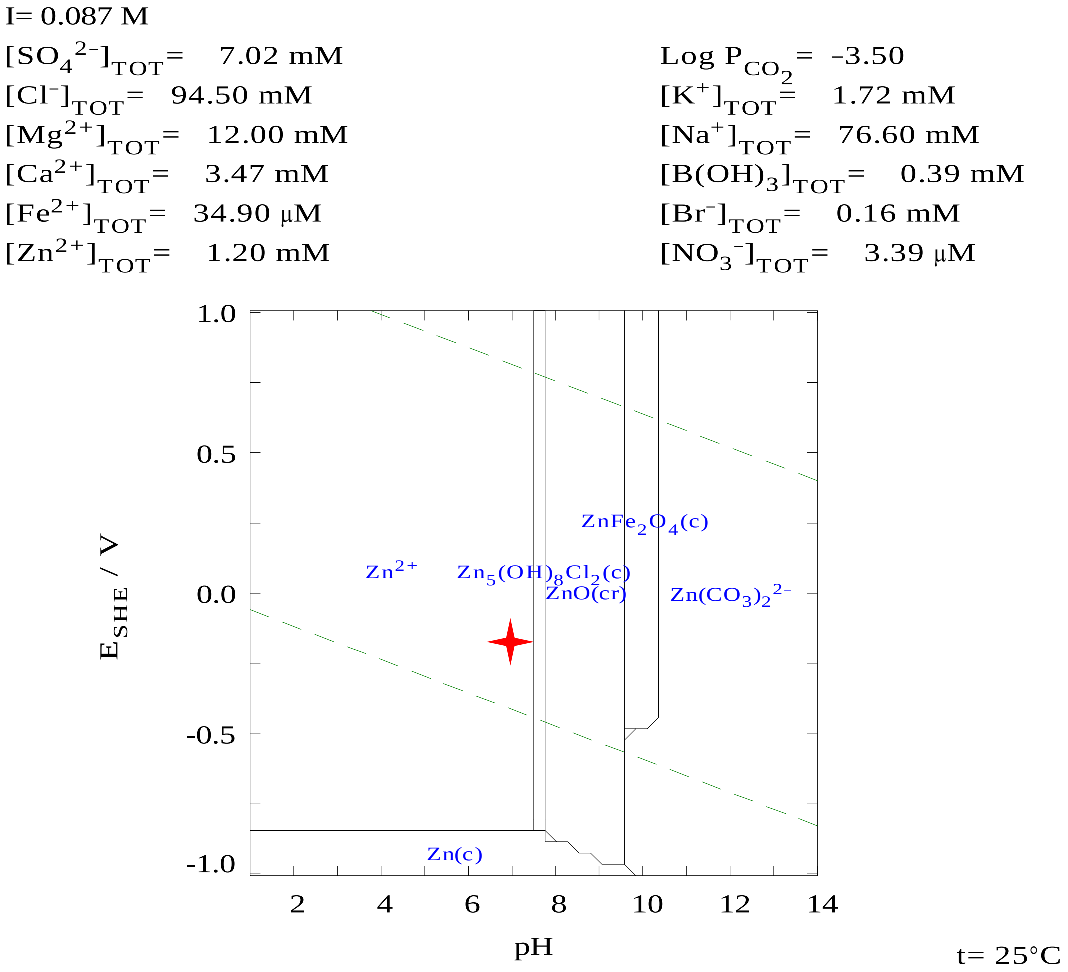
In stormwater, many heavy metals can sorb to inorganic and organic particulate matter that accumulate as bed sediments. Water chemistry, the suspended sediment and substrate sediment composition influence the behavior of heavy metals in natural waters. The sorption of heavy metals to particulates is 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 zinc, copper, and lead.

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 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, the following figure 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. Also shown 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 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.



Fraction diagram of zinc for steel pipe section immersed into bay water after three months of exposure (Ogburn 2013).



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 (Ogburn 2013).

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

The solubility of several compounds:

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

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

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

The solubility of compounds with the KtAn formula (Kreshkov 1971):
Solubility $KtAn^-$ = (Solubility $Product_{KtAn}/(\gamma_{Kt}\ \gamma_{An}))^{1/2}$

Where,
Kt = cation
An = anion
γ = activity coefficient of cation or anion.

The solubility of compounds with the $KtAn_2$ formula (Kreshkov 1971):
Solubility $KtAn_2$ = (Solubility $Product_{KtAn2}/(4\ \gamma_{Kt}\ (\gamma_{An})^2))^{1/3}$

The solubility of compounds with the Kt_2An formula (Kreshkov 1971):
Solubility Kt_2An = (Solubility $Product_{Kt2An}/(4\ (\gamma_{Kt})^2\ \gamma_{An}))^{1/3}$

The solubility of compounds with the Kt_3An_2formula (Kreshkov 1971):
Solubility Kt_3An_2 = (Solubility $Product_{Kt3An2}/(108\ (\gamma_{Kt})^3\ (\gamma_{An})^2))^{1/5}$

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

The following table 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/.

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) likely precipitated in the containers with galvanized steel pipe immersed in pH 5 and pH 8 waters after three months of exposure. 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.

The following tables show total measured metal concentrations and modeled metal species at time zero (base water alone), 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. The following tables summarize these observations.

Total measured zinc concentrations and modeled species after one day (Ogburn 2013)

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+} $Zn(SO_4)_2^{2-}$	2.6E-05 $ZnOH^+$ $ZnHCO_3^+$	1.0E-05 $ZnSO_4$ $ZnCO_3$ $Zn(OH)_2$	100	0.13	0.05
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

Total measured zinc concentrations and modeled species after one day (Ogburn 2013), continued

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

Total measured copper concentrations and modeled species after one day (Ogburn 2013)

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

Total measured lead concentrations and modeled species after one day (Ogburn 2013)

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

Washdown Tests of Exposed Materials at Naval Facilities

SPAWARSYSCEN-PACIFIC Navy personnel conducted a series of material washoff tests as part of this research project. The following pictures show the how these tests were conducted for several different types of materials. Generally, 2 to 4 L of DI water was gently sprayed over a known area (about 2 ft^2) with the wash water collected in a plastic tray. Each test lasted about 15 to 30 minutes. The wash water was then chemically analyzed for a suite of heavy metals. This section includes photographs of many of the materials tested, and the data grouped by material type. The 79 materials were sorted into the following 16 categories for these data summaries: aluminum ramp, artificial turf, brick wall, concrete, galvanized metal (bare), galvanized metal (painted), galvanized metal (coated), barge hull, metal (bare), metal (painted), plaster, roof, rubber, wood (bare), wood (painted), and wood (treated). Some of these categories have only a single sample, while others have many.

The data are presented by metal. The first table shows the available data for each category, along with simple summary statistics. These data were then evaluated in SigmaPlot (version 15) using the non-parametric Kruskal-Wallis one way analysis of variance on ranks to determine if at least one group is significantly different from any of the others (this test only examines single groups). Simultaneously, grouped box and whisker plots were prepared in SigmaPlot for these groups. These results were then used to group the groups into a fewer number of combined groups indicating materials that had low washoff concentrations, high concentrations, and the other categories. Box and whisker plots and Kruskal-Wallis analyses were also used to evaluate these categories. These data summaries, plots, and analyses were made for both the concentration and the unit area loading washoff data.

Washdown setups showing sprayer, plastic sheet below target area and plastic tray to capture washdown water (barge hull).

Washdown sampling for untreated wood.

Washdown sampling for engine block.

 Washdown sampling for tires.	 Washdown sampling of galvanized stair steps.

1) Aluminum ramp

Walkway, aluminum; Everett

2) Artificial turf

Turf, artificial; NBSD

3) Brick wall

Wall, brick; NB Kitsap

4) Concrete

 Concrete wall; SSC-PAC	 Concrete barrier, uncoated; Saint Julian

5) Galvanized, bare

 Galvanized shed, sides; NBK Bangor	 Galvanized rail; SUBASE

 Galvanized fence; SUBASE	 Galvanized scaffold stack, laydown area; SUBASE
 Causeway, portion with zinc anode; Little Creek	 Pallet, galvanized (folded); Saint Julian
 Utility pole, galvanized; NB Kitsap	 Sheath, over concrete barrier edge; Everett

 Stairs, galvanized; Everett	 Scaffold parts, galvanized; Pt. Loma Subase
 Grate 1, stormwater drain; NBSD	 Grate 2, stormwater drain; NBSD

6) Galvanized, painted


Galvanize siding, painted, chipped; NBK Bangor


Metal panel, painted galvanized, building side; Saint Julian


Fence, painted galvanized; NB Kitsap

7) Galvanized, coated

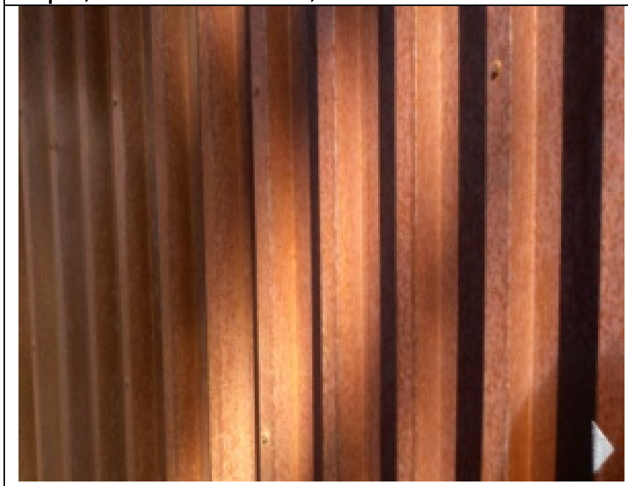
Coated galvanized fence; SSC=PAC

8) Barge hull

Barge hull; Little Creek

Barge hull; Little Creek

9) Metal, bare

 Pipe, uncoated steel; Little Creek	 Engine block; Saint Julian
 Metal panel, uncoated iron, "weathered"; Bangor	

10) Metal, painted

 Dumpster, green; SSC-PAC	 Building side, yellow, panels; NAS Whidbey
 Building side, yellow, panels; NAS Whidbey	 Building side, yellow, panels; NAS Whidbey
 Building side, green coated metal;	 AC unit, gray; SSC-PAC

NAVSTA Everett	
 Electrical vault, green; SSC-PAC	 Keel blocks, metal painted; Little Creek
 Causeway, gray painted side; Little Creek	 Metal panel, light yellow (temp. buildings); NB Kitsap
 Metal panel, painted light yellow; Bangor	 Metal, painted, brick red; Bangor

Fire hydrant, red; Everett

Guard rail, painted yellow; Pt. Loma Subase

Water riser, potable, blue (w/brass part); Pt. Loma Subase

Water riser, potable, blue; Pt. Loma Subase

Pipe supports, metal, painted brown; Pt. Loma Subase

Dumpster (blue), cardboard recycle; SSC-PAC

 Dumpster (blue), cardboard recycle w/guano, heron; SSC-PAC	

11) Plaster siding

 Plaster wall, painted white; SSC-PAC

12) Roof

 Shed roof, green coated metal; NAVSTA Everett	 Shingles, asphalt; Bangor
 Roof, (via gutter); Bangor	

13) Rubber


Cable, black, 4” diameter; SUBASE


Cable, black, 4” diameter; SUBASE


Tires, rubber; Saint Julian

Bumpers, large, black; Everett


Cables, electrical 3 in. diameter; Pt. Loma Subase

14) Wood, bare


Crate, wooden; Saint Julian

15) Wood, painted

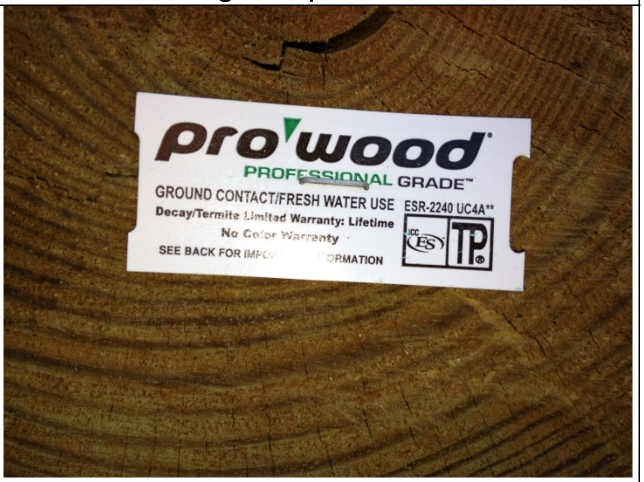

Wood wall, painted; SSC-PAC

16) Wood, treated


Wood, treated, green; NBK Bangor


Treated wood, green painted; SUBASE


Wood, treated (copper azole); Little Creek



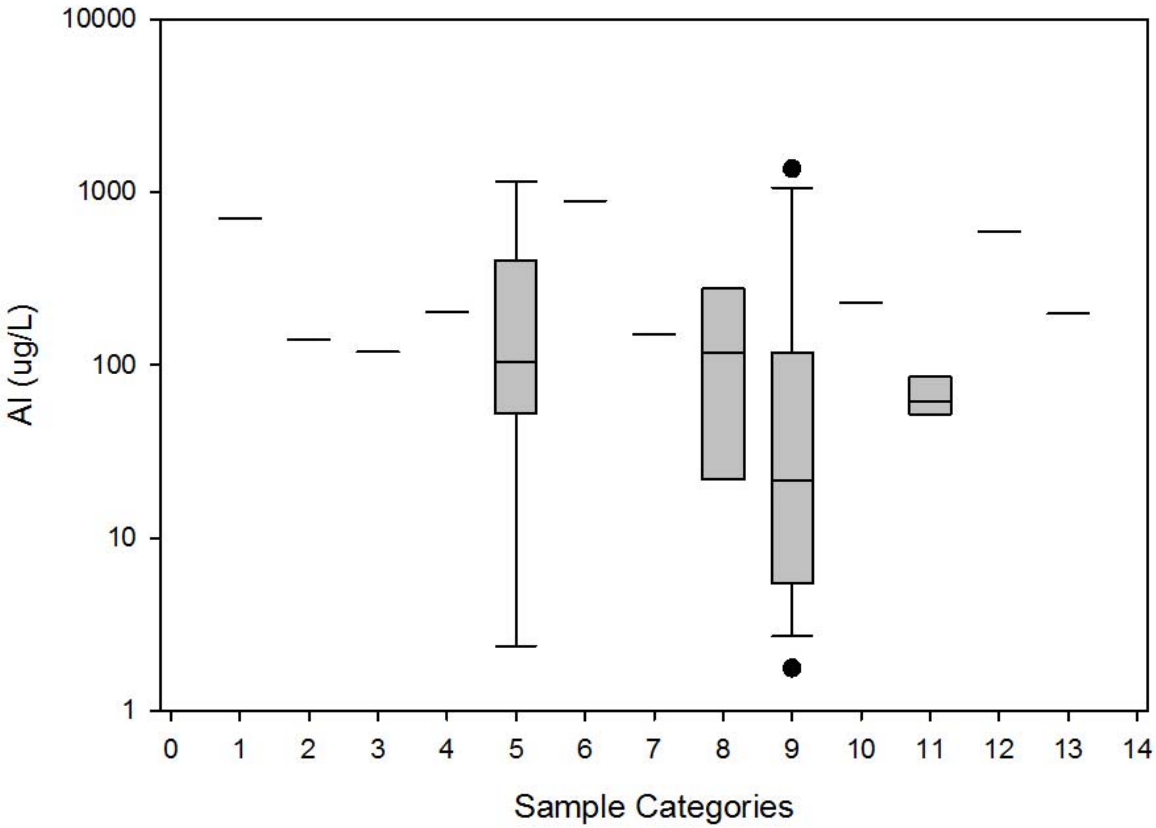
Treated wood label; Little Creek

Aluminum

Aluminum Washdown Concentrations (µg/L)

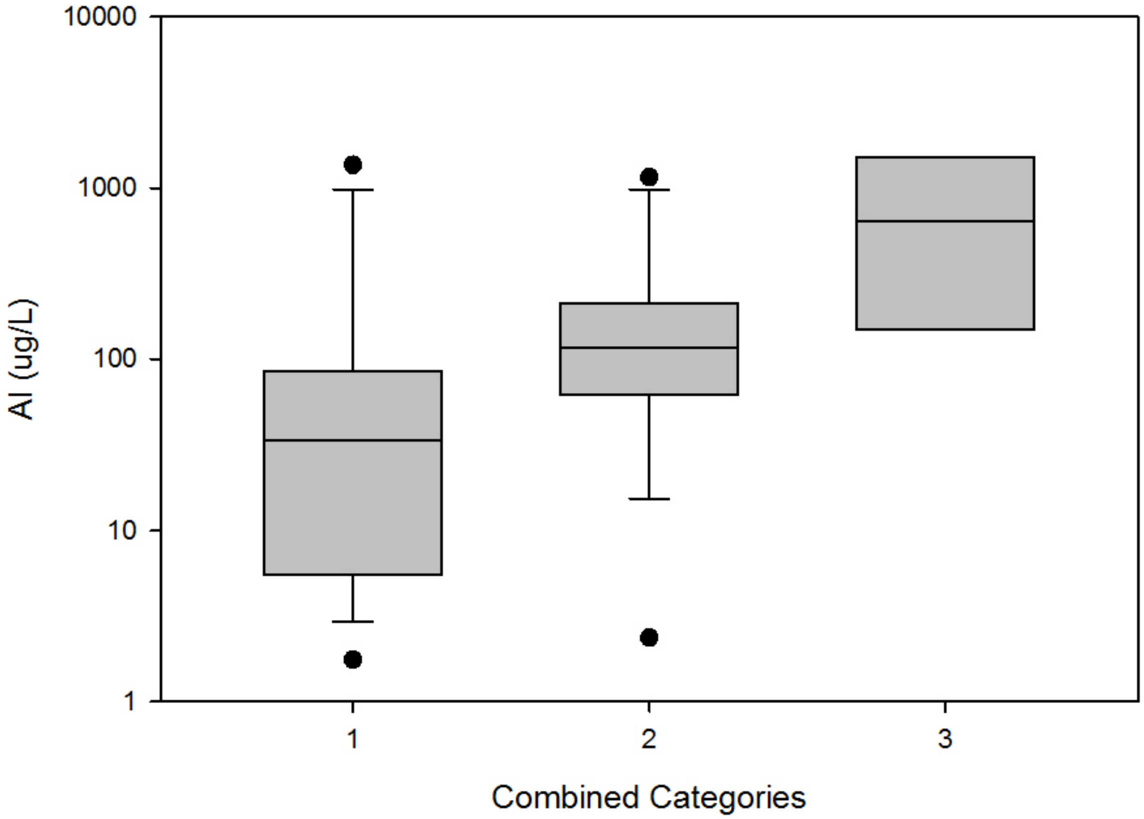
Grouped Category:	high	other	other	other	other	high	other	other	low	other	low	high	other
Sample Category:	Al ramp	artificial turf	brick wall	concrete	galv bare	galv painted	barge hull	metal bare	metal painted	roof	rubber	wood bare	wood treated
	702	141	119	204	103	1,777	150	20	185	446	52	586	197
					584	4		211	22	11	85		
					115			26	8		62		
					46			298	48				
					2				1,364				
					214				46				
					60				51				
					69				6				
					1,153				597				
									14				
									5				
									2				
									4				
Grouped Category:	high	other	other	other	other	high	other	other	low	other	low	high	other
Sample Category:	Al ramp	artificial turf	brick wall	concrete	galv bare	galv painted	barge hull	metal bare	metal painted	roof	rubber	wood bare	wood treated
number	1	1	1	1	9	2	1	4	13	2	3	1	1
min					2	4		20	2	11	52		
max					1,153	1,777		298	1,364	446	85		
average					261	890		139	181	229	66		
median	702	141	119	204	103	890	150	118	22	229	62	586	197
st dev					377	1,253		138	391	308	17		
COV					1.4	1.4		1.0	2.2	1.3	0.3		

Aluminum Washdown Tests



Kruskal-Wallis One Way Analysis of Variance on Ranks (Al concentrations)

Normality Test (Shapiro-Wilk)	Failed	(P < 0.050)			
Group	N	Missing	Median	25%	75%
low	14	0	34	5.5	85
others	12	0	117	62	211
high	4	0	644	150	1510
H = 4.947 with 2 degrees of freedom. (P = 0.08)					



10000
1000
100
10
1
Al (ug/L)
1
2
3
Combined Categories

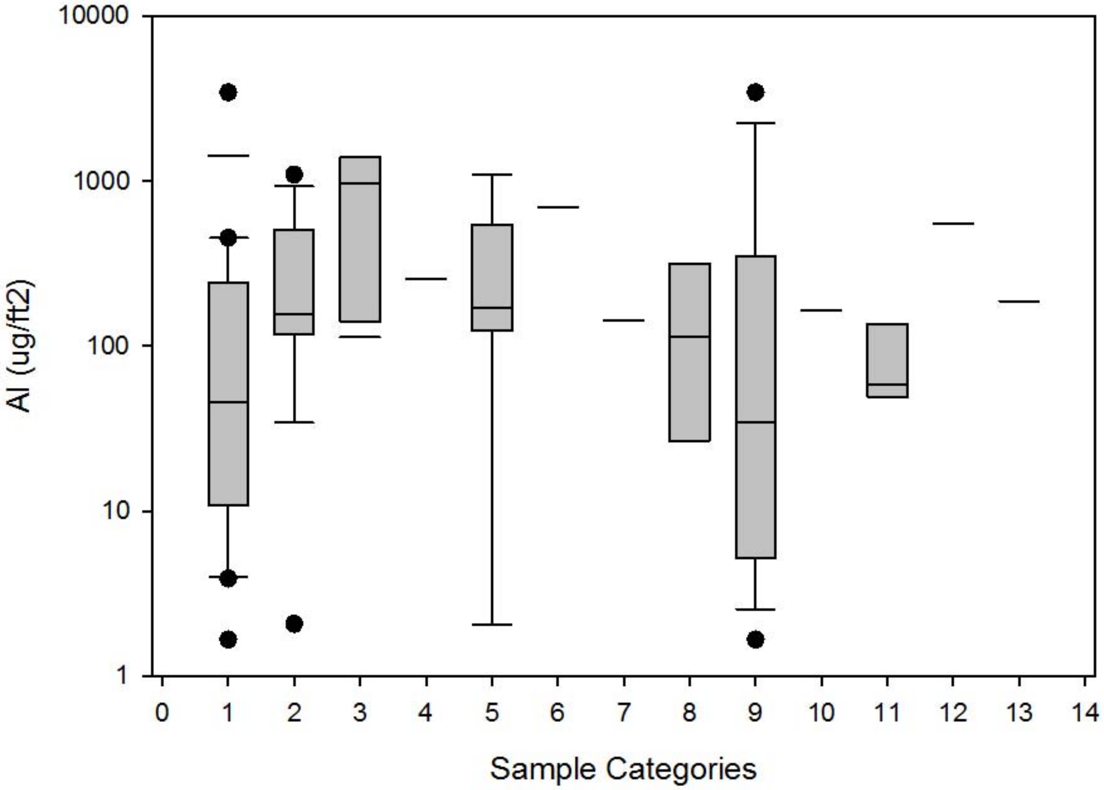
Summary Statistics for Aluminum Concentration Grouped Categories

Grouped category:	low	all others	high
Sample Category in Groups:	metal painted rubber	artificial turf brick wall concrete galv bare barge hull metal bare roof wood treated	Al ramp galv painted
number	14	12	4
min	1.8	2.4	4.0
max	1,360	1,150	1,780
average	172	234	770
median	34	117	644
st dev	380	326	739
COV	2.2	1.4	1.0

Aluminum Washdown Mass (µg/ft^2)

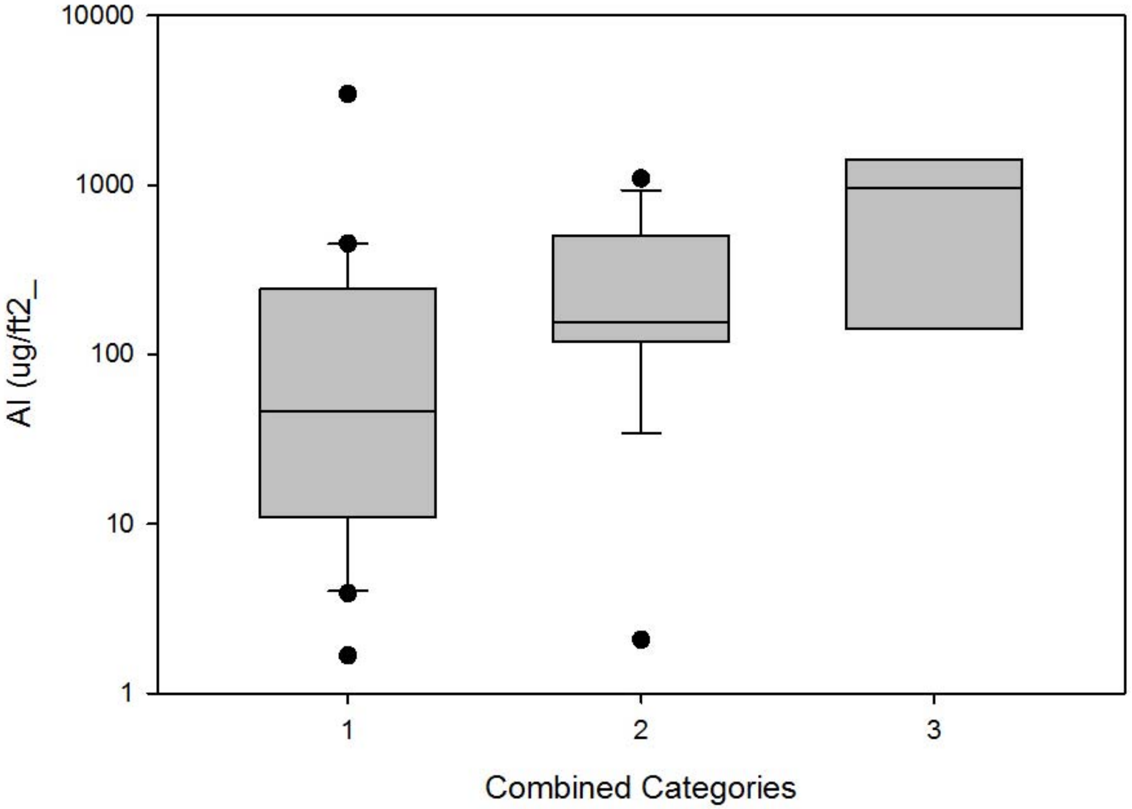
Grouped Category:	high	other	other	other	other	high	other	low	low	other	low	high	other
Sample Category:	Al ramp	artificial turf	brick wall	concrete	galv bare	galv painted	barge hull	metal bare	metal painted	roof	rubber	wood bare	wood treated
	1,418	133	113	257	391	1,378	142	26	4	317	49	555	187
					552	4		200	447	10	137		
					109			29	20		58		
					138			357	8				
					2				116				
					540				3,442				
					169				43				
					140				259				
					1,091				5				
									452				
									35				
									5				
									2				
Grouped Category:	high	other	other	other	other	high	other	low	low	other	low	high	other
Sample Category:	Al ramp	artificial turf	brick wall	concrete	galv bare	galv painted	barge hull	metal bare	metal painted	roof	rubber	wood bare	wood treated
number	1	1	1	1	9	2	1	4	13	2	3	1	1
min					2	4		26	2	10	49		
max					1,091	1,378		357	3,442	317	137		
average					348	691		153	372	164	81		
median	1,418	133	113	257	169	691	142	114	35	164	58	555	187
st dev					341	972		158	937	217	48		
COV					1.0	1.4		1.0	2.5	1.3	0.6		

Aluminum Washdown Tests (by mass)



Kruskal-Wallis One Way Analysis of Variance on Ranks (Al mass)

Normality Test (Shapiro-Wilk)	Failed	(P < 0.050)			
Group	N	Missing	Median	25%	75%
low	20	0	46	11	240
others	12	0	155	120	500
high	4	0	970	140	1410
H = 5.077 with 2 degrees of freedom. (P = 0.079)					


10000
1000
100
10
1
Al (ug/ft2_
1
2
3
Combined Categories

Summary Statistics for Aluminum Mass Grouped Categories

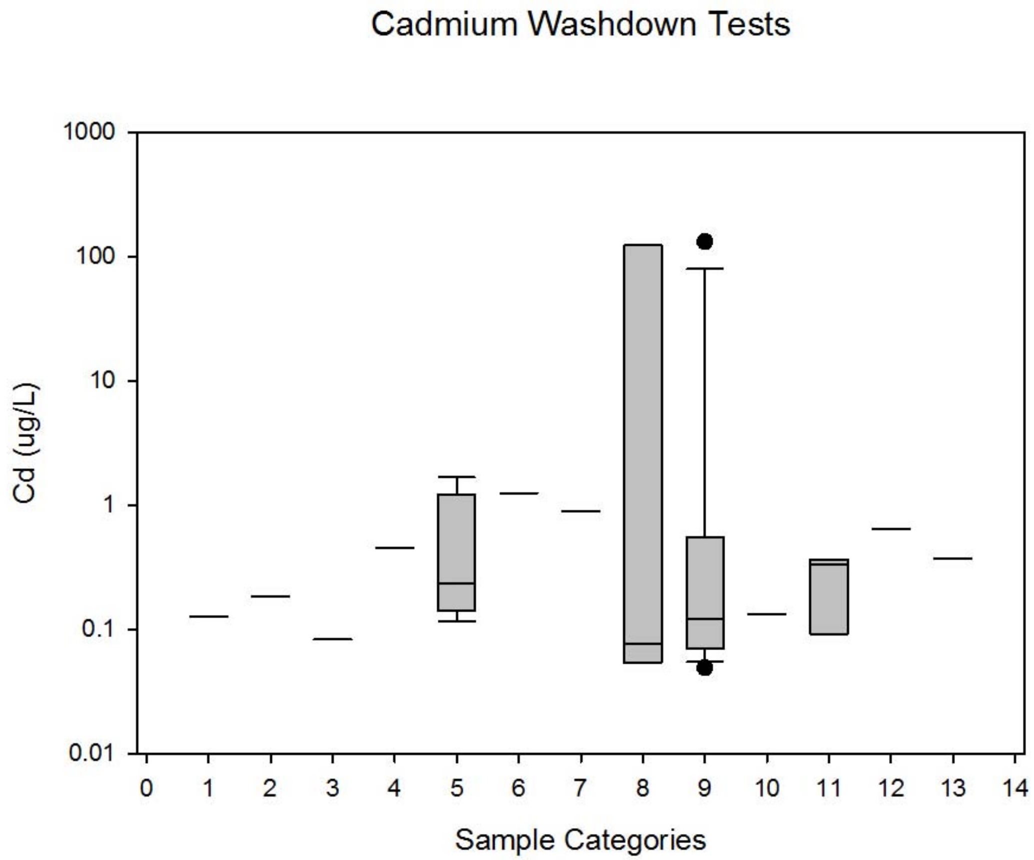
Grouped Category:	low	others	high
Sample Categories in Groups:	metal bare metal painted rubber	artificial turf brick wall concrete galv bare barge hull roof wood treated	Al ramp galv painted wood bare
number	20	12	4
min	1.7	2.1	3.8
max	3,440	1,090	1,420
average	285	303	839
median	46	155	966
st dev	758	304	684
COV	2.7	1.0	0.8

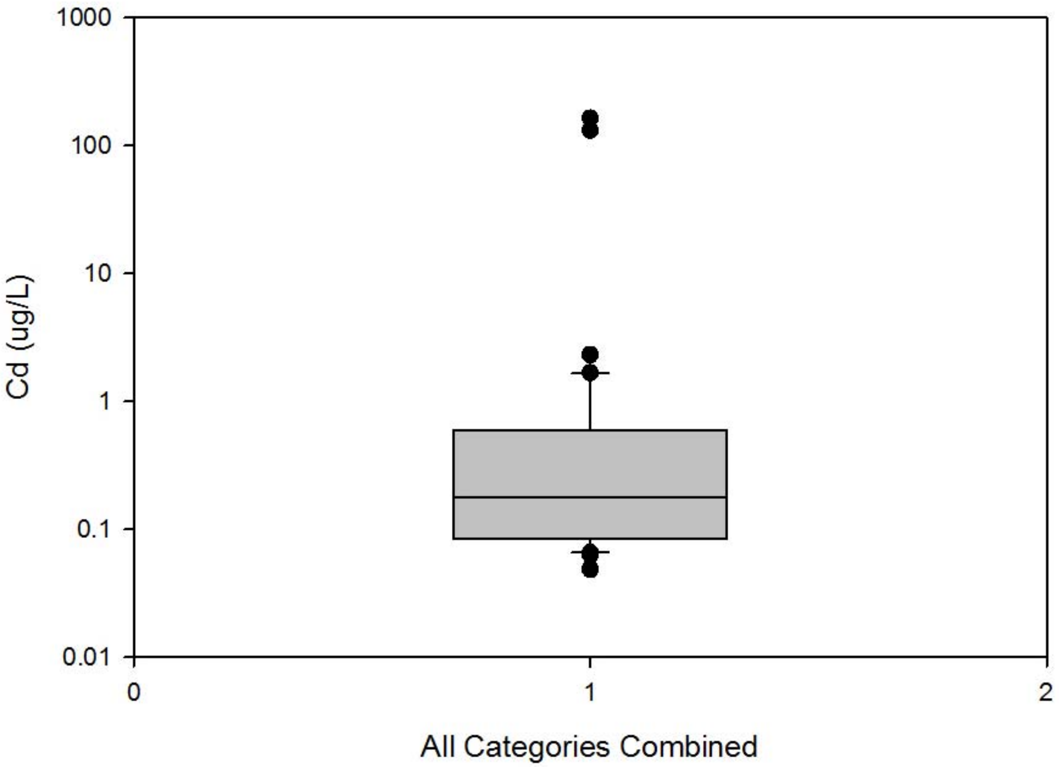
Cadmium

Cadmium Washdown Concentrations (µg/L)

Grouped Category:	other	other	other	other	other	other	other	other	other	other	other	other	other
Sample Category:	Al ramp	artificial turf	brick wall	concrete	galv bare	galv painted	barge hull	metal bare	metal painted	roof	rubber	wood bare	wood treated
	0.1	0.2	0.1	0.5	0.1	2.3	0.9	0.1	0.0	0.2	0.1	0.6	0.4
					1.1	0.2		163	131	0.1	0.4		
					0.1			0.1	0.2		0.3		
					1.7			0.0	0.1				
					0.3				0.2				
					1.4				0.9				
					0.2				0.1				
					0.2				0.1				
					0.1				0.1				
									0.9				
									0.2				
									0.1				
									0.1				
Sample Category:	Al ramp	artifical turf	brick wall	concrete	galv bare	galv painted	barge hull	metal bare	metal painted	roof	rubber	wood bare	wood treated
number	1	1	1	1	9	2	1	4	13	2	3	1	1
min					0.1	0.2		0.0	0.0	0.1	0.1		
max					1.7	2.3		163.0	131.3	0.2	0.4		
average					0.6	1.2		40.8	10.3	0.1	0.3		
median	0.1	0.2	0.1	0.5	0.2	1.2	0.9	0.1	0.1	0.1	0.3	0.6	0.4
st dev					0.6	1.5		81.5	36.4	0.1	0.1		
COV					1.1	1.2		2.0	3.5	0.6	0.6		

One bare metal and one painted metal sample had very high (>100 ug/L) Cd concentrations; all others were very low (<1 µg/L). No significant groupings of data.





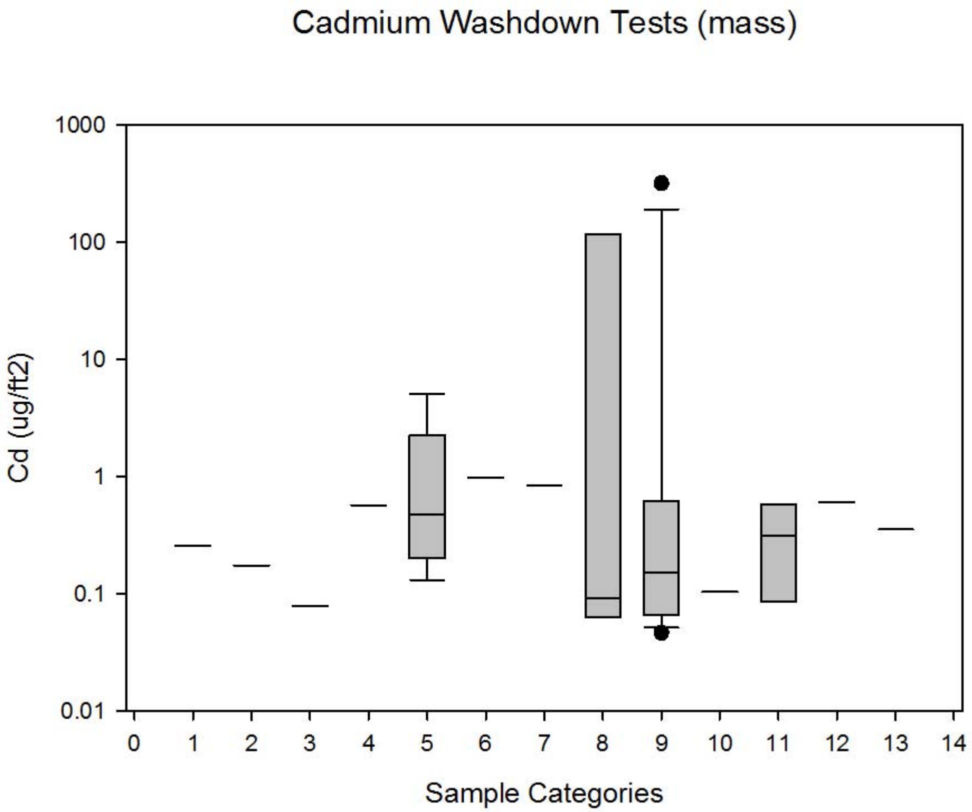
Summary Statistics for Cadmium Concentration Grouped Categories

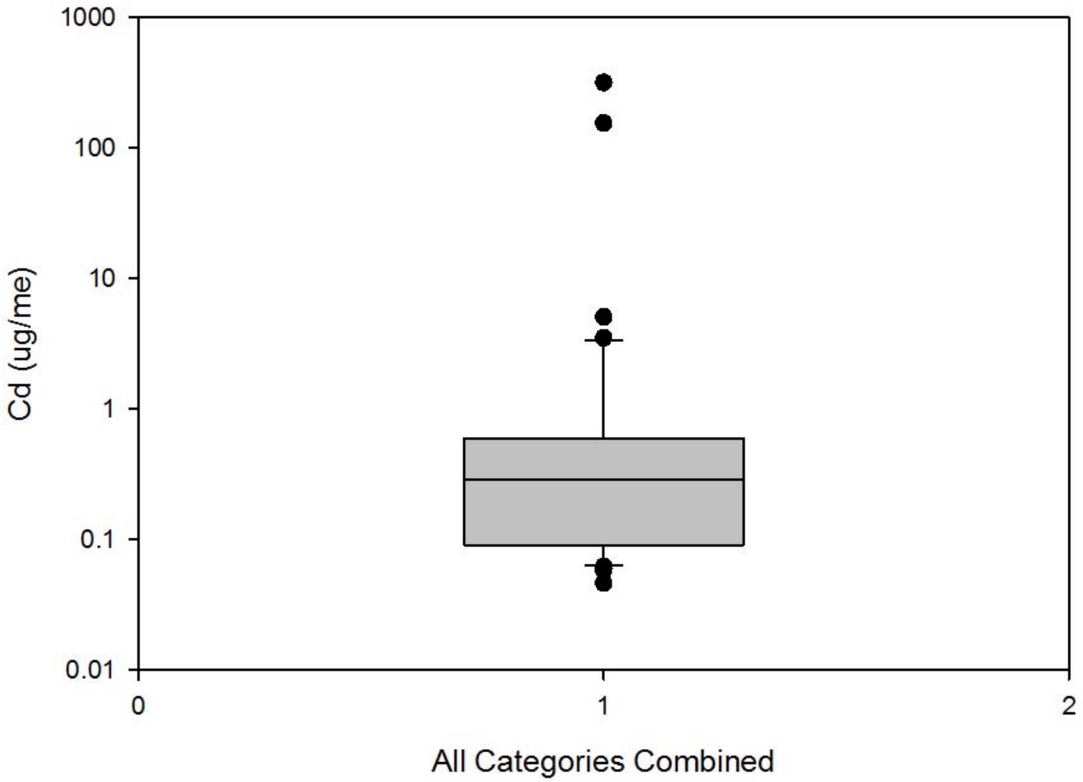
	All combined
number	40
min	0.05
max	160
average	7.7
median	0.18
st dev	33
COV	4.2

Cadmium Washdown Mass (µg/ft^2)

Grouped Category:	other	other	other	other	other	other	other	other	other	other	other	other	other
Sample Category:	Al ramp	artificial turf	brick wall	concrete	galv bare	galv painted	barge hull	metal bare	metal painted	roof	rubber	wood bare	wood treated
	0.3	0.2	0.1	0.6	0.4	1.8	0.8	0.1	0.0	0.1	0.1	0.6	0.4
					1.0	0.2		154.4	316.6	0.1	0.6		
					0.1			0.1	0.2		0.3		
					5.1			0.1	0.1				
					0.3				0.5				
					3.5				2.3				
					0.5				0.1				
					0.5				0.6				
					0.1				0.1				
									0.7				
									0.4				
									0.1				
									0.1				
Sample Category:	Al ramp	artifical turf	brick wall	concrete	galv bare	galv painted	barge hull	metal bare	metal painted	roof	rubber	wood bare	wood treated
number	1.0	1.0	1.0	1.0	9.0	2.0	1.0	4.0	13.0	2.0	3.0	1.0	1.0
min					0.1	0.2		0.1	0.0	0.1	0.1		
max					5.1	1.8		154	317	0.1	0.6		
average					1.3	1.0		38.7	24.7	0.1	0.3		
median	0.3	0.2	0.1	0.6	0.5	1.0	0.8	0.1	0.2	0.1	0.3	0.6	0.4
st dev					1.8	1.1		77.2	87.7	0.0	0.2		
COV					1.4	1.2		2.0	3.5	0.4	0.8		

One bare metal and one painted metal had very high Cd washdown masses (>150 µg/ft^2); two bare galv, one painted galv, and one painted metal had a moderate washdown Cd mass (1.7 to 5.1 µg/ft^2); all the others were <1 µg/ft^2. Combined together as no significant groupings identified.





Summary Statistics for Cadmium Mass Grouped Categories

	All Combined
number	40
min	0.05
max	316
average	12.3
median	0.29
st dev	55
COV	4.5

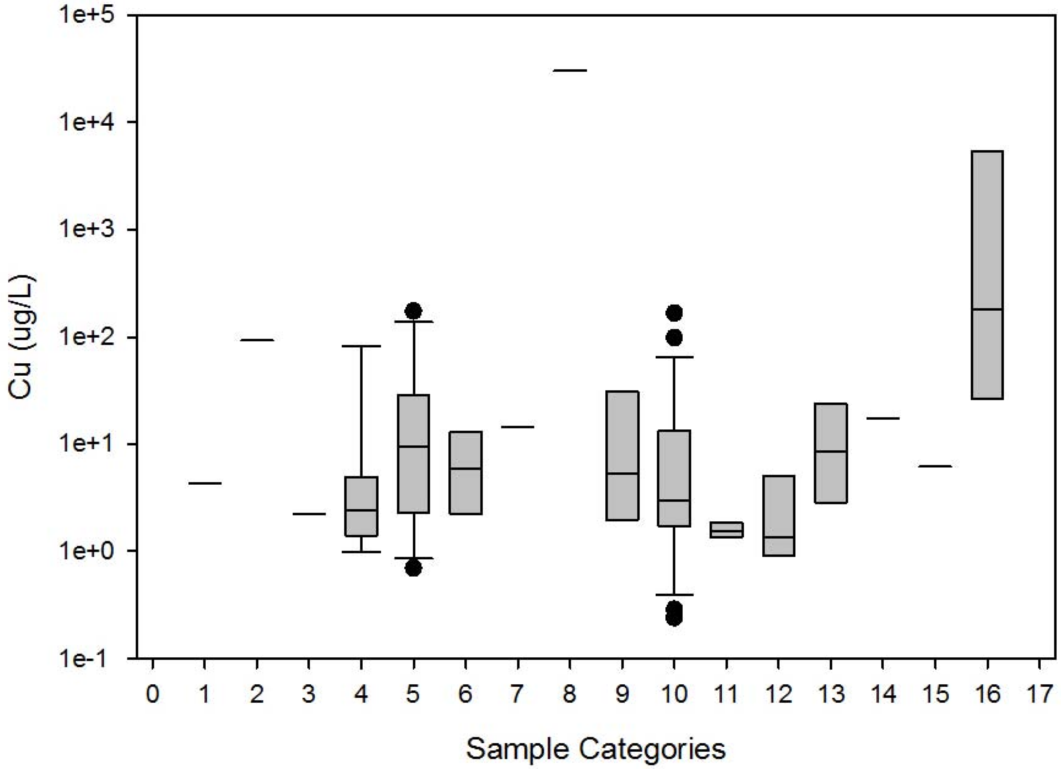
Copper

Copper Washdown Concentrations (µg/L)

Grouped Category:	low	other	low	low	other	other	other	high	other	other	low	low	other	other	other	high
Sample Category:	Al ramp	artificial turf	brick wall	concrete	galv bare	galv painted	galv coated	barge hull	metal bare	metal painted	plaster	roof	rubber	wood bare	wood painted	wood treated
	4	93	2	81	1	6	15	30,334	57	42	2	5	1	17	6	5,417
				1	2	13			5	12	2	5	20			179
				2	29	2			1	4	1	1	6			27
				2	7				3	51		1	34			
				1	2				5	10		1	11			
				1	1					4			3			
				3	3					98						
				6	52					167						
				4	12					3						
					27					3						
					174					3						
					22					2						
										1						
										2						
										24						
										3						
										1						
										19						
										0						
										11						
										2						
										0						
										0						
										3						
										3						
										3						
Grouped Category:	low	other	low	low	other	other	other	high	other	other	low	low	other	other	other	high
Sample	Al	artificial	brick	concrete	galv	galv	galv	barge	metal	metal	plaster	roof	rubber	wood	wood	wood

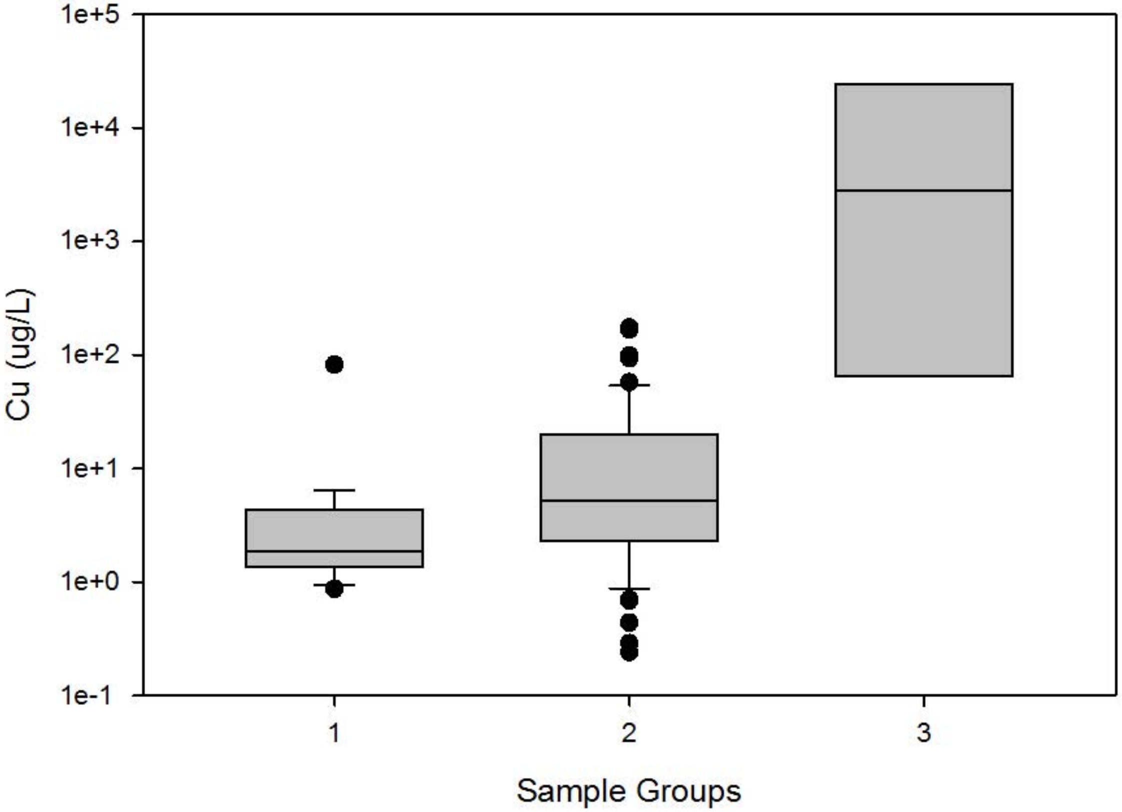
Category:	ramp	turf	wall		bare	painted	coated	hull	bare	painted				bare	painted	treated
number	1	1	1	9	12	3	1	1	5	26	3	5	6	1	1	3
min				1	1	2			1	0	1	1	1			27
max				81	174	13			57	167	2	5	34			5,417
average				11	28	7			14	18	2	3	13			1,874
median	4	93	2	2	9	6	15	30,334	5	3	2	1	9	17	6	179
st dev				26	49	5			24	37	0	2	13			3,069
COV				2.3	1.8	0.8			1.7	2.1	0.2	0.8	1.0			1.6

Copper Washdown Tests



Kruskal-Wallis One Way Analysis of Variance on Ranks (Cu concentrations)

Kruskal-Wallis One Way Analysis of Variance on Ranks	Sunday, August 04, 2013, 4:39:28 PM				
Normality Test (Shapiro-Wilk)	Failed	(P < 0.050)			
Group	N	Missing	Median	25%	75%
low	19	0	1.866	1.346	4.301
all others	56	0	5.25	2.293	19.969
high	4	0	2797.907	64.806	24104.41
H = 15.654 with 2 degrees of freedom. (P = <0.001)					
The differences in the median values among the treatment groups are greater than would be expected by chance; there is a statistically significant difference (P = <0.001)					
To isolate the group or groups that differ from the others use a multiple comparison procedure.					
All Pairwise Multiple Comparison Procedures (Dunn's Method) :					
Comparison	Diff of Ranks	Q	P<0.05		
high vs low	47.605	3.771	Yes		
high vs all others	32.518	2.738	Yes		
all others vs low	15.087	2.476	Yes		


1e+5
1e+4
1e+3
1e+2
1e+1
1e+0
1e-1
Cu (ug/L)
1
2
3
Sample Groups

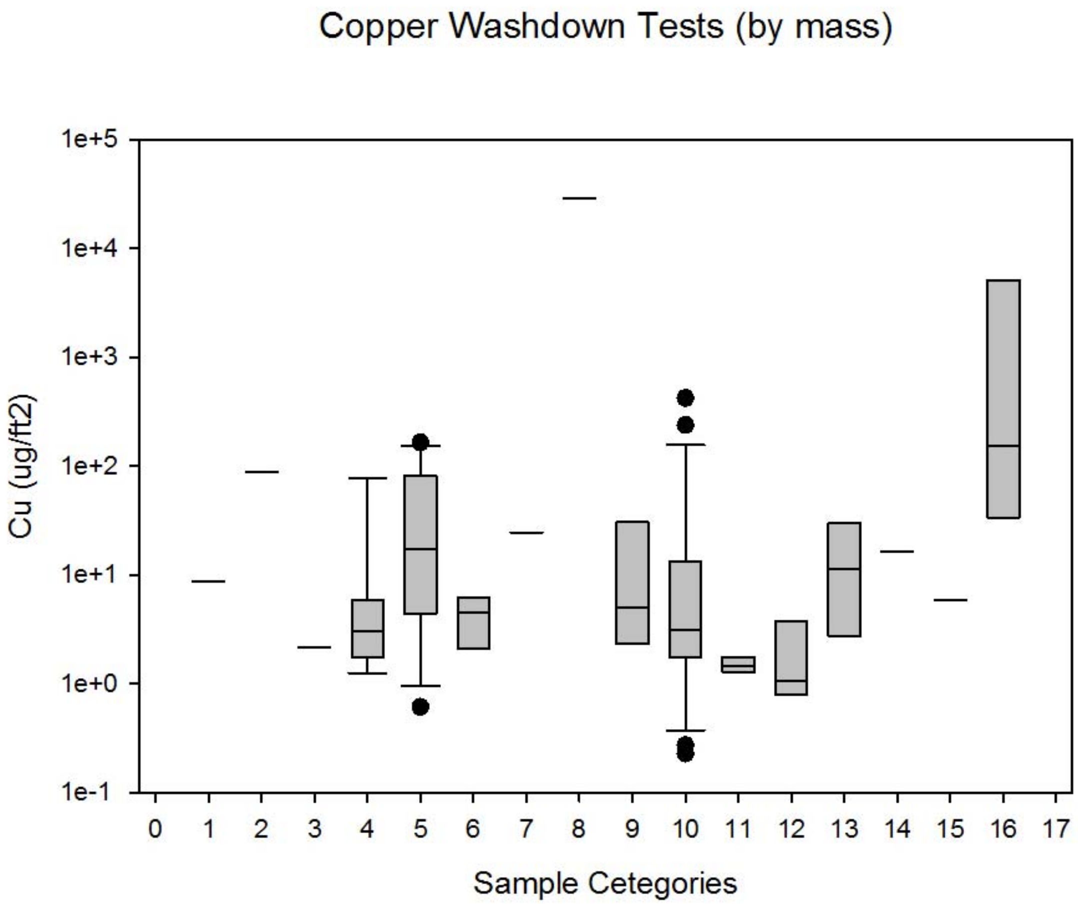
Summary Statistics for Copper Concentration Grouped Categories

Grouped category:	low	all others	high
Sample Category in Groups:	Al ramp brick wall concrete plaster roof	artificial turf galv bare galv painted galv coated metal bare metal painted rubber wood bare wood painted	barge hull wood treated
number	19	47	4
min	1	0	27
max	81	174	30334
average	7	21	8989
median	2	4	2798
st dev	18	39	14449
COV	2.7	1.8	1.6

Copper Washdown Mass (µg/ft2)

Grouped Category:	others	others	low	low	others	low	others	high	others	others	low	low	others	others	others	high
Sample Category:	Al ramp	artificial turf	brick wall	concrete	galv bare	galv painted	galv coated	barge hull	metal bare	metal painted	plaster	roof	rubber	wood bare	wood painted	wood treated
	9	88	2	77	5	5	24	28,703	7	40	2	3	1	16	6	5,125
				2	2	6			54	12	1	4	33			153
				2	28	2			1	4	1	1	7			34
				3	7				4	122		1	29			
				1	7				5	9		1	16			
				2	1					4			3			
				4	4					237						
				8	131					420						
				3	34					3						
					93					2						
					164					2						
					44					2						
										1						
										2						
										16						
										2						
										1						
										95						
										0						
										9						
										4						
										0						
										0						
										3						
										3						
										3						
Grouped Category:	others	others	low	low	others	low	others	high	others	others	low	low	others	others	others	high
Sample Category:	Al ramp	artificial turf	brick wall	concrete	galv bare	galv painted	galv coated	barge hull	metal bare	metal painted	plaster	roof	rubber	wood bare	wood painted	wood treated
number	1	1	1	9	12	3	1	1	5	26	3	5	6	1	1	3

min				1	1	2			1	0	1	1	1			34
max				77	164	6			54	420	2	4	33			5,125
average				11	43	4			14	38	2	2	15			1,771
median	9	88	2	3	17	5	24	28,703	5	3	1	1	11	16	6	153
st dev				25	56	2			22	94	0	2	13			2,906
COV				2.2	1.3	0.5			1.6	2.5	0.2	0.8	0.9			1.6


Copper Washdown Tests (by mass)
Cu (ug/ft2)
1e+5
1e+4
1e+3
1e+2
1e+1
1e+0
1e-1
0
1
2
3
4
5
6
7
8
9
10
11
12
13
14
15
16
17
Sample Cetegories

Kruskal-Wallis One Way Analysis of Variance on Ranks (Cu mass)

Normality Test (Shapiro-Wilk)	Failed	(P < 0.050)			
Group	N	Missing	Median	25%	75%
low	21	0	2.133	1.37	3.848
others	54	0	6.198	2.395	30.124
high	4	0	2639.045	63.388	22808.8
H = 16.060 with 2 degrees of freedom. (P = <0.001)					

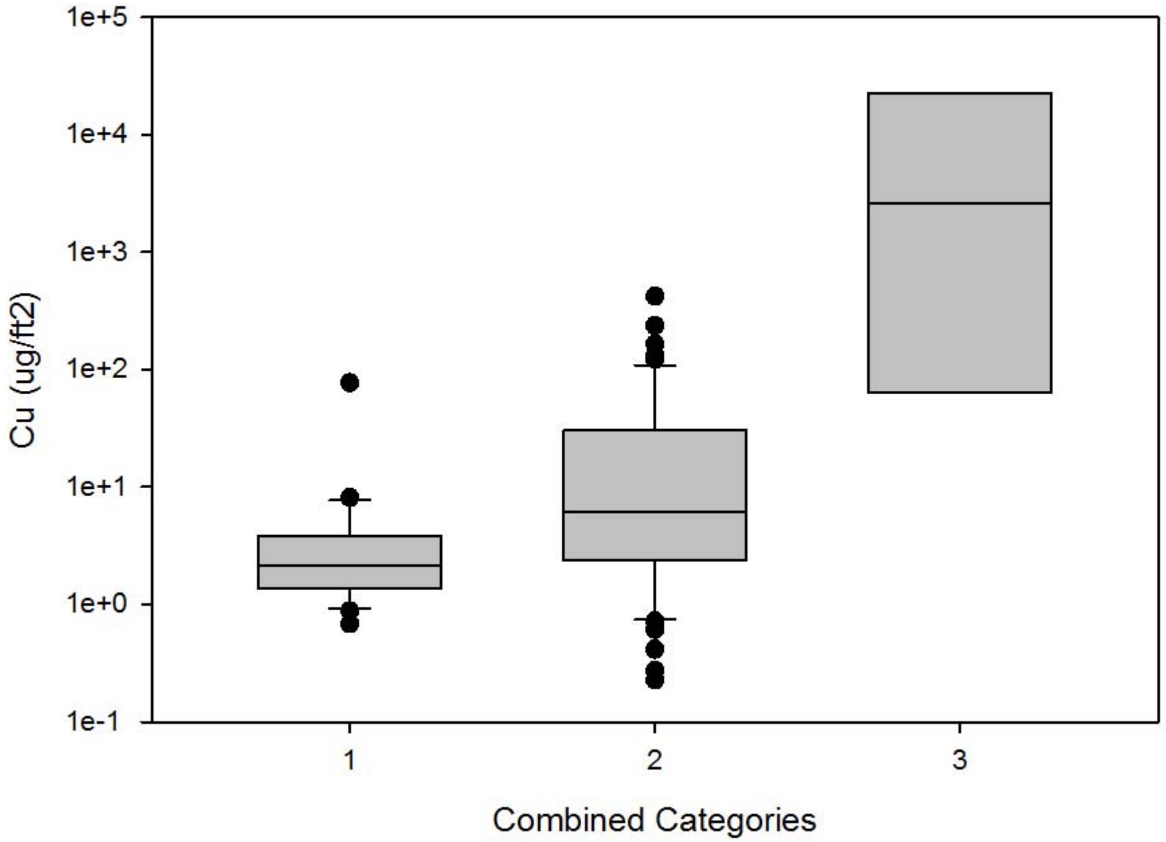
The differences in the median values among the treatment groups are greater than would be expected by chance; there is a statistically significant difference (P = <0.001)

To isolate the group or groups that differ from the others use a multiple comparison procedure.

All Pairwise Multiple Comparison Procedures (Dunn's Method) :

Comparison	Diff of Ranks	Q	P<0.05
high vs low	46.595	3.722	Yes
high vs others	30.889	2.597	Yes
others vs low	15.706	2.661	Yes

Note: The multiple comparisons on ranks do not include an adjustment for ties.


1e+5
1e+4
1e+3
1e+2
1e+1
1e+0
1e-1
Cu (ug/ft2)
1
2
3
Combined Categories

Summary Statistics for Copper Mass Grouped Categories

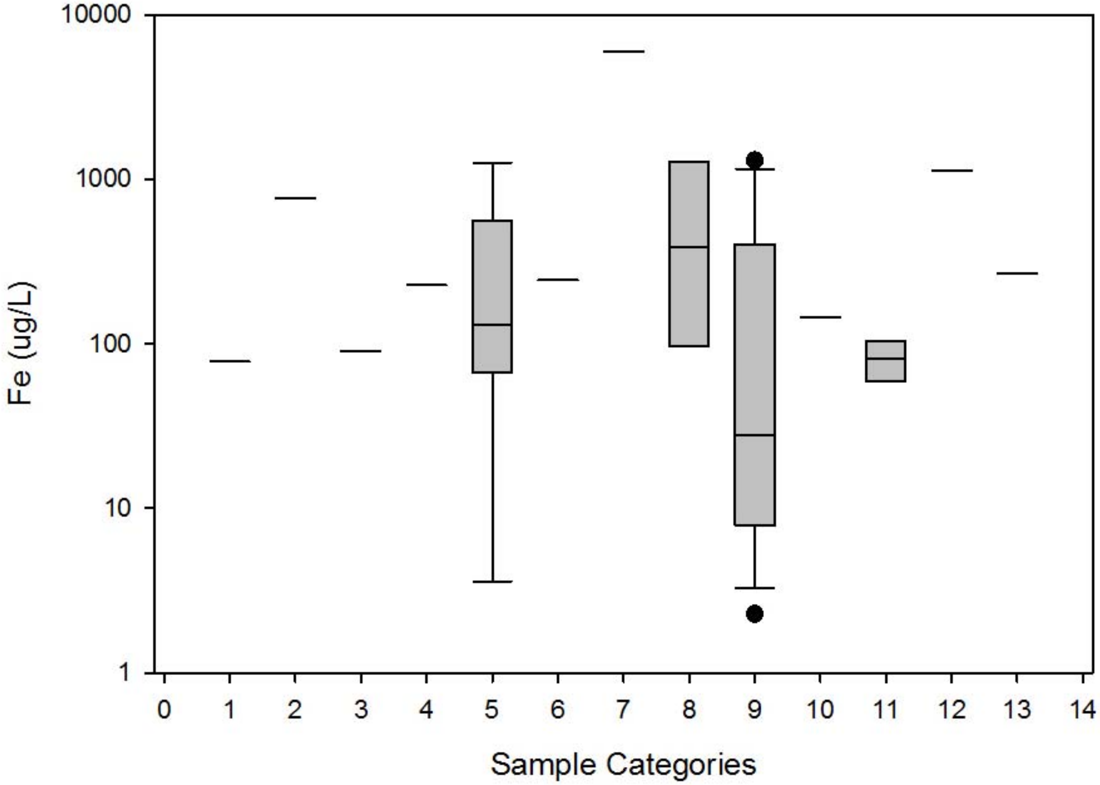
Grouped Category:	low	others	high
Sample Categories in Groups:	brick wall concrete galv painted plaster roof	Al ramp artificial turf galv bare galv coated metal bare metal painted rubber wood bare wood painted	barge hull wood treated
number	21	54	4
min	1	0	34
max	77	420	28,703
average	6	34	8,504
median	2	6	2,639
st dev	16	71	13,674
COV	2.6	2.1	1.6

Iron

Iron Washdown Concentrations (µg/L)

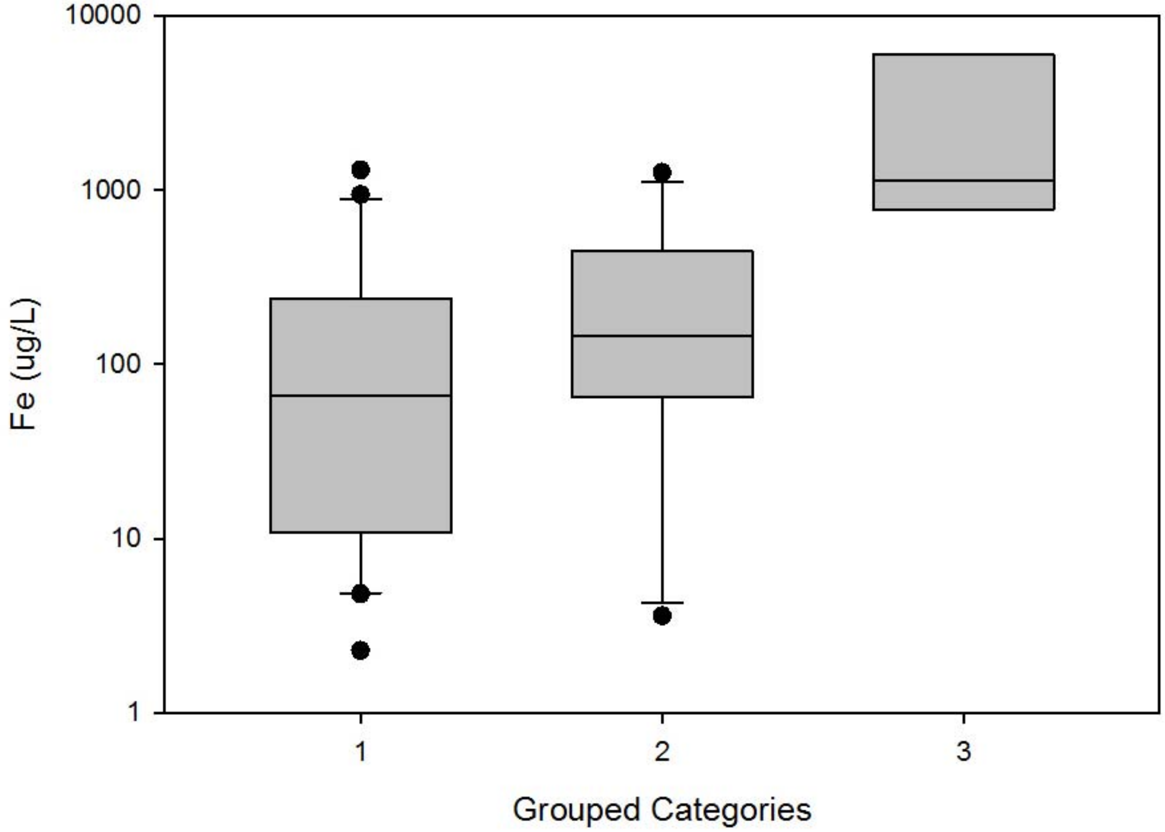
Fe (µg/L)	low	high	low	other	other	other	high	other	low	low	low	high	other
	Al ramp	artificial turf	brick wall	concrete	galv bare	galv painted	barge hull	metal bare	metal painted	roof	rubber	wood bare	wood treated
	78	769	90	227	71	480	5,995	373	16	281	59	1,135	269
					783	6		399	393	6	103		
					158			4	28		81		
					63			1,571	10				
					4				46				
					332				1,301				
					74				74				
					131				412				
					1,258				6				
									938				
									13				
									5				
									2				
Grouped Category:	low	high	low	other	other	other	high	other	low	low	low	high	other
Fe (µg/L)	Al ramp	artificial turf	brick wall	concrete	galv bare	galv painted	barge hull	metal bare	metal painted	roof	rubber	wood bare	wood treated
number	1	1	1	1	9	2	1	4	13	2	3	1	1
min					4	6		4	2	6	59		
max					1,258	480		1,571	1,301	281	103		
average					319	243		587	249	143	81		
median	78	769	90	227	131	243	5,995	386	28	143	81	1,135	269
st dev					425	335		680	418	194	22		
COV					1.3	1.4		1.2	1.7	1.4	0.3		

Iron Washdown Tests



Kruskal-Wallis One Way Analysis of Variance on Ranks (Fe concentrations)

Normality Test (Shapiro-Wilk)	Failed	(P < 0.050)			
Group	N	Missing	Median	25%	75%
low	20	0	66.461	10.813	236.464
others	12	0	144.818	64.608	443.176
high	3	0	1134.599	768.534	5995.28
H = 7.405 with 2 degrees of freedom. (P = 0.025)					
The differences in the median values among the treatment groups are greater than would be expected by chance; there is a statistically significant difference (P = 0.025)					
To isolate the group or groups that differ from the others use a multiple comparison procedure.					
All Pairwise Multiple Comparison Procedures (Dunn's Method) :					
Comparison	Diff of Ranks	Q	P<0.05		
high vs low	16.9	2.664	Yes		
high vs others	12.667	1.915	No		
others vs low	4.233	1.131	No		
Note: The multiple comparisons on ranks do not include an adjustment for ties.					


10000
1000
100
10
1
Fe (ug/L)
1
2
3
Grouped Categories

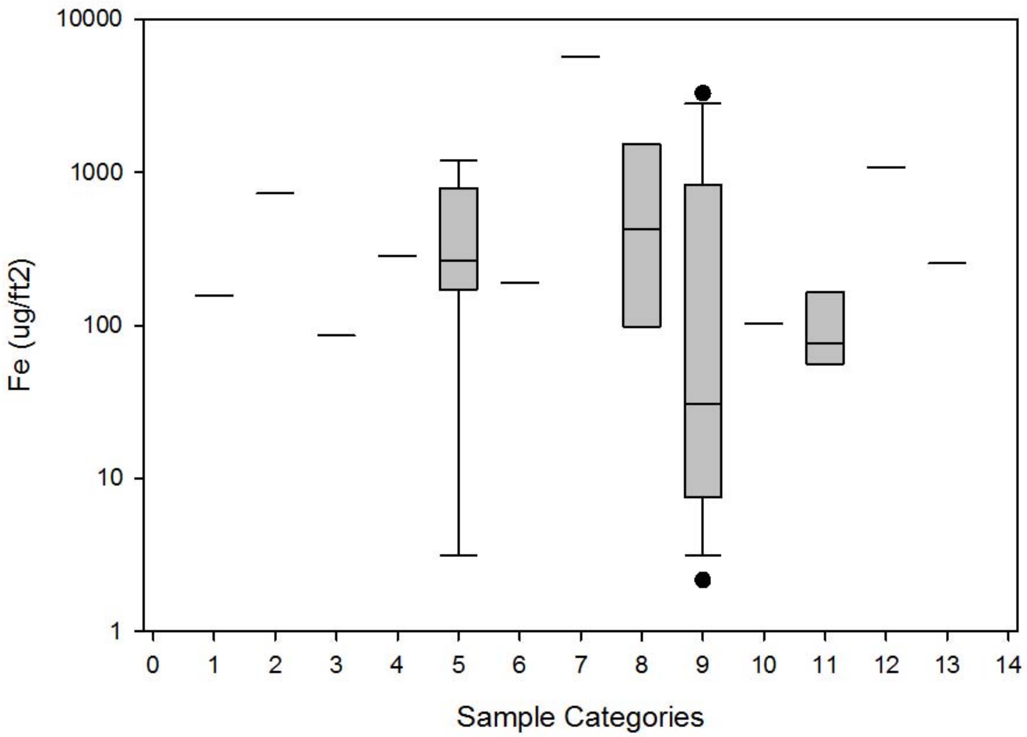
Summary Statistics for Iron Concentration Grouped Categories

Grouped category:	low	others	high
Sample Category in Groups:	Al ramp brick wall metal painted roof rubber	concrete galv bare galv painted metal bare wood treated	artificial turf barge hull wood bare
number	20	12	3
min	2	4	769
max	1,301	1,258	5,995
average	197	299	2,633
median	66	145	1,135
st dev	344	378	2,918
COV	1.7	1.3	1.1

Iron Washdown Mass (µg/ft2)

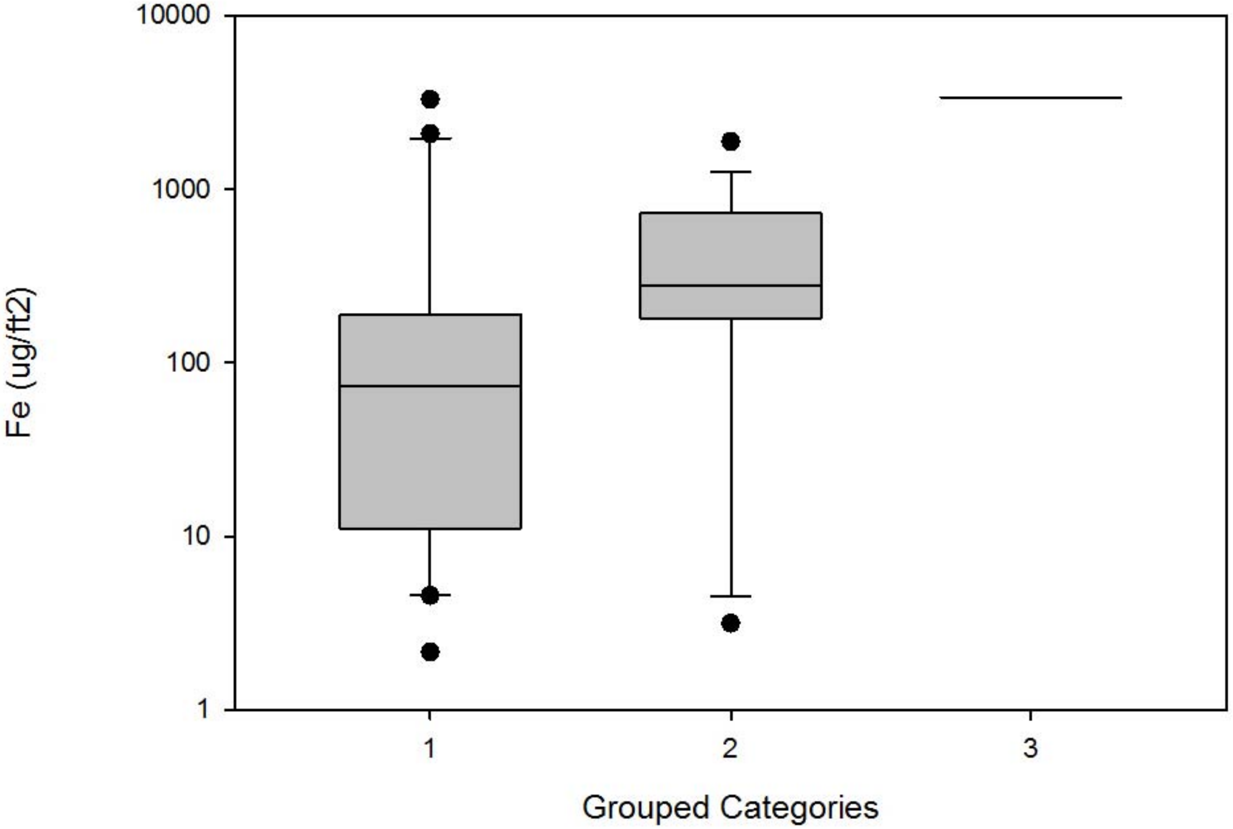
	low	other	low	other	other	other	high	other	low	low	low	high	other
	Al ramp	artificial turf	brick wall	concrete	galv bare	galv painted	barge hull	metal bare	metal painted	roof	rubber	wood bare	wood treated
	157	727	85	286	267	372	5,673	471	15	199	56	1,074	254
					741	6		378	949	6	165		
					150			5	26		76		
					190			1,882	10				
					3				110				
					839				3,282				
					212				70				
					265				2,078				
					1,191				5				
									710				
									30				
									5				
									2				
	low	other	low	other	other	other	high	other	low	low	low	high	other
	Al ramp	artificial turf	brick wall	concrete	galv bare	galv painted	barge hull	metal bare	metal painted	roof	rubber	wood bare	wood treated
number	1	1	1	1	9	2	1	4	13	2	3	1	1
min					3	6		5	2	6	56		
max					1,191	372		1,882	3,282	199	165		
average					429	189		684	561	103	99		
median	157	727	85	286	265	189	5,673	424	30	103	76	1,074	254
st dev					397	259		824	1,018	137	58		
COV					0.9	1.4		1.2	1.8	1.3	0.6		

Iron Washdown Tests (mass)



Kruskal-Wallis One Way Analysis of Variance on Ranks (Fe mass)

Normality Test (Shapiro-Wilk)	Failed	(P < 0.050)			
Group	N	Missing	Median	25%	75%
low	20	0	73.065	11.011	190.947
others	18	0	276.548	179.659	730.653
high	2	0	3373.324	1073.614	5673.034
H = 8.140 with 2 degrees of freedom. (P = 0.017)					
The differences in the median values among the treatment groups are greater than would be expected by chance; there is a statistically significant difference (P = 0.017)					
To isolate the group or groups that differ from the others use a multiple comparison procedure.					
All Pairwise Multiple Comparison Procedures (Dunn's Method) :					
Comparison	Diff of Ranks	Q	P<0.05		
high vs low	21.35	2.463	Yes		
high vs others	14.056	1.613	No		
others vs low	7.294	1.921	No		
Note: The multiple comparisons on ranks do not include an adjustment for ties.					


10000
1000
100
10
1
Fe (ug/ft2)
1
2
3
Grouped Categories

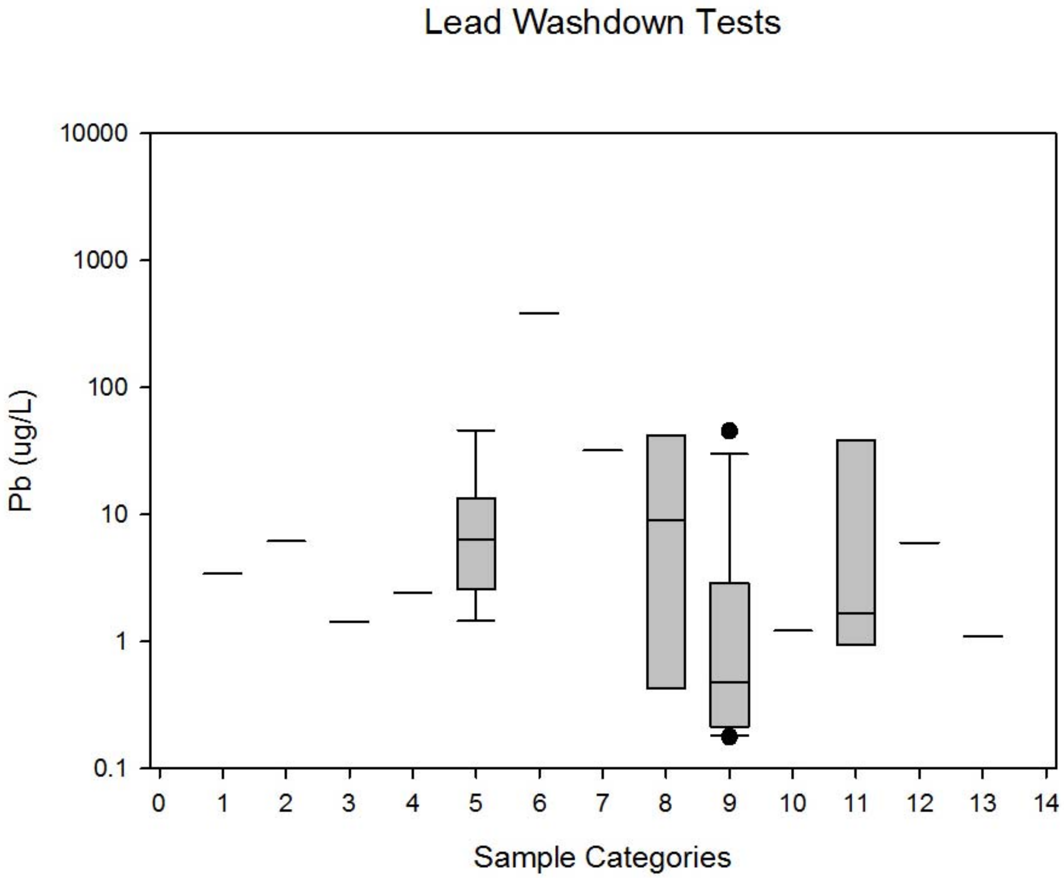
Summary Statistics for Iron Mass Grouped Categories

Grouped Category:	low	others	high
Sample Categories in Groups:	Al ramp brick wall metal painted roof rubber	artificial turf concrete galv bare galv painted metal bare wood treated	barge hull wood bare
number	20	18	2
min	2	3	1,074
max	3,282	1,882	5,673
average	402	458	3,373
median	73	277	3,373
st dev	840	477	3,252
COV	2.1	1.0	1.0

Lead

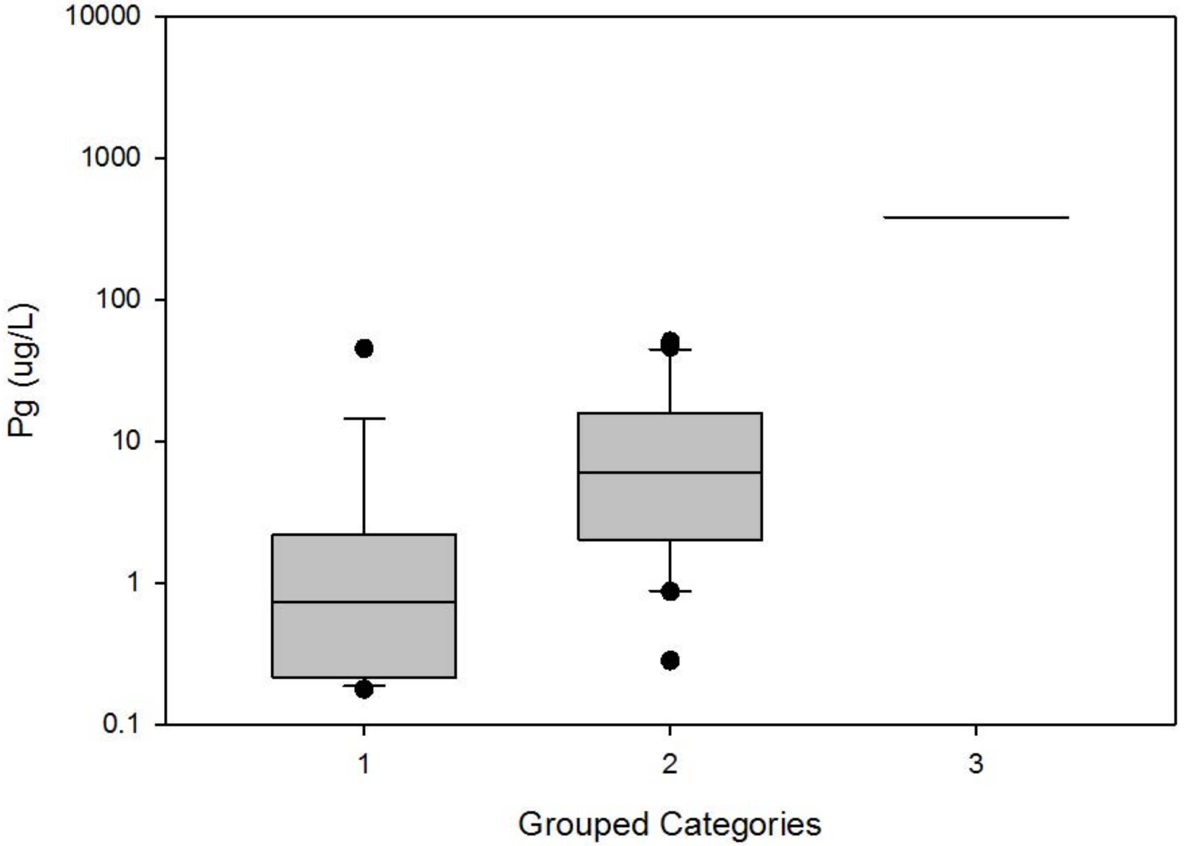
Lead Washdown Concentrations (µg/L)

Grouped Category:	other	other	low	other	other	high	other	other	low	low	other	other	low
Sample Category:	Al ramp	artificial turf	brick wall	concrete	galv bare	galv painted	barge hull	metal bare	metal painted	roof	rubber	wood bare	wood treated
	3.4	6.2	1.4	2.4	1.4	764.0	31.9	0.3	0.2	2.2	0.9	6.0	1.1
					46.2	1.5		50.7	3.6	0.2	38.5		
					2.7			17.1	0.7		1.7		
					12.1			0.9	0.5				
					4.2				2.1				
					14.6				45.3				
					6.4				0.2				
					10.5				1.8				
					2.4				0.2				
									6.7				
									0.3				
									0.2				
									0.2				
Grouped Category:	other	other	low	other	other	high	other	other	low	low	other	other	low
Pb (µg/L)	Al ramp	artificial turf	brick wall	concrete	galv bare	galv painted	barge hull	metal bare	metal painted	roof	rubber	wood bare	wood treated
number	1	1	1	1	9	2	1	4	13	2	3	1	1
min					1.4	1.5		0.3	0.2	0.2	0.9		
max					46.2	764.0		50.7	45.3	2.2	38.5		
average					11.2	382.8		17.3	4.8	1.2	13.7		
median	3.4	6.2	1.4	2.4	6.4	382.8	31.9	9.0	0.5	1.2	1.7	6.0	1.1
st dev					13.9	539.2		23.6	12.3	1.4	21.5		
COV					1.2	1.4		1.4	2.6	1.2	1.6		


Lead Washdown Tests
10000
1000
100
10
1
0.1
Pb (ug/L)
0
1
2
3
4
5
6
7
8
9
10
11
12
13
14
Sample Categories

Kruskal-Wallis One Way Analysis of Variance on Ranks (Pb concentrations

Normality Test (Shapiro-Wilk)	Failed	(P < 0.050)			
Group	N	Missing	Median	25%	75%
low	17	0	0.735	0.216	2.186
other	21	0	6.002	2.03	15.841
high	2	0	382.757	1.514	764
H = 11.673 with 2 degrees of freedom. (P = 0.003)					
The differences in the median values among the treatment groups are greater than would be expected by chance; there is a statistically significant difference (P = 0.003)					

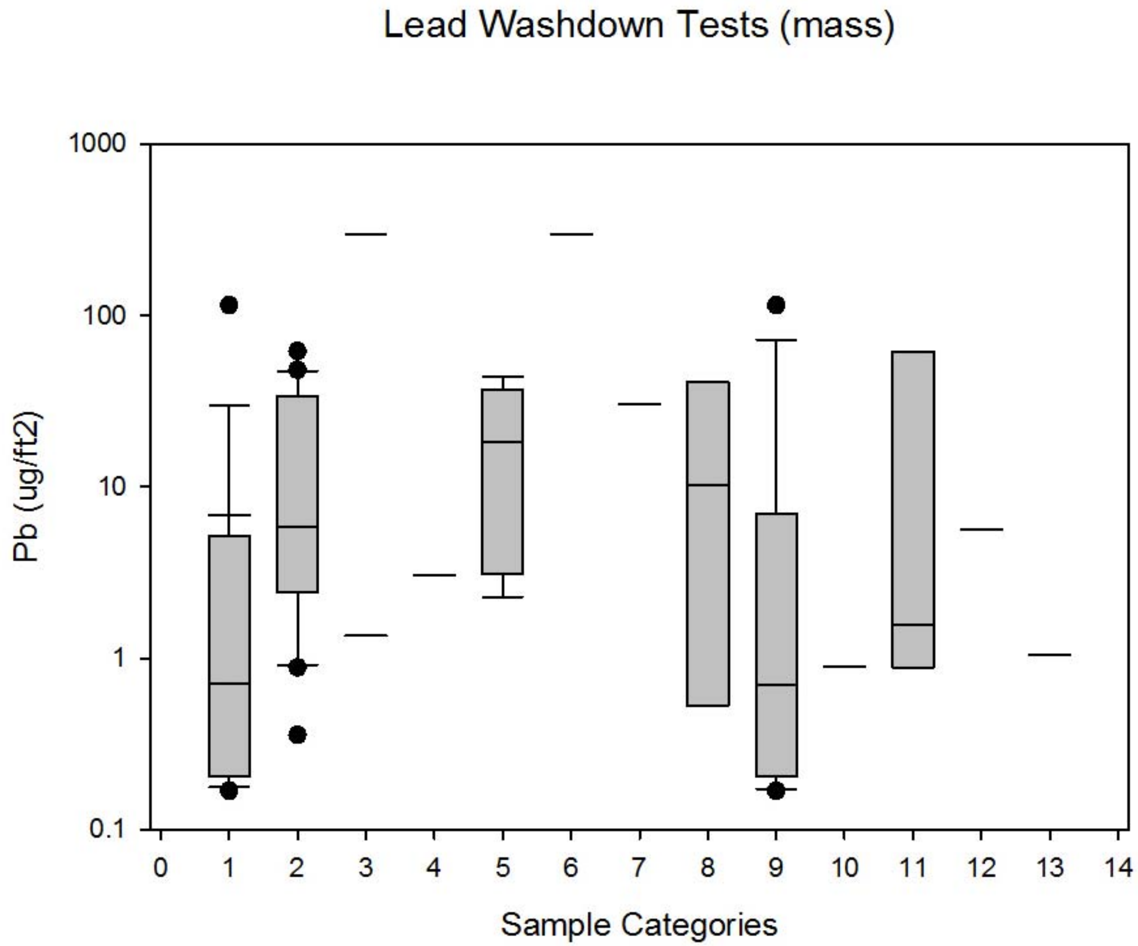

10000
1000
100
10
1
0.1
Pg (ug/L)
1
2
3
Grouped Categories

Summary Statistics for Lead Concentration Grouped Categories

Grouped category:	low	others	high
Sample Category in Groups:	brick wall metal painted roof wood treated	Al ramp artificial turf concrete galv bare barge hull metal bare rubber wood bare	galv painted
number	17	21	2
min	0.2	0.3	1.5
max	45.3	50.7	764.0
average	3.9	12.4	382.8
median	0.7	6.0	382.8
st dev	10.8	15.7	539.2
COV	2.7	1.3	1.4

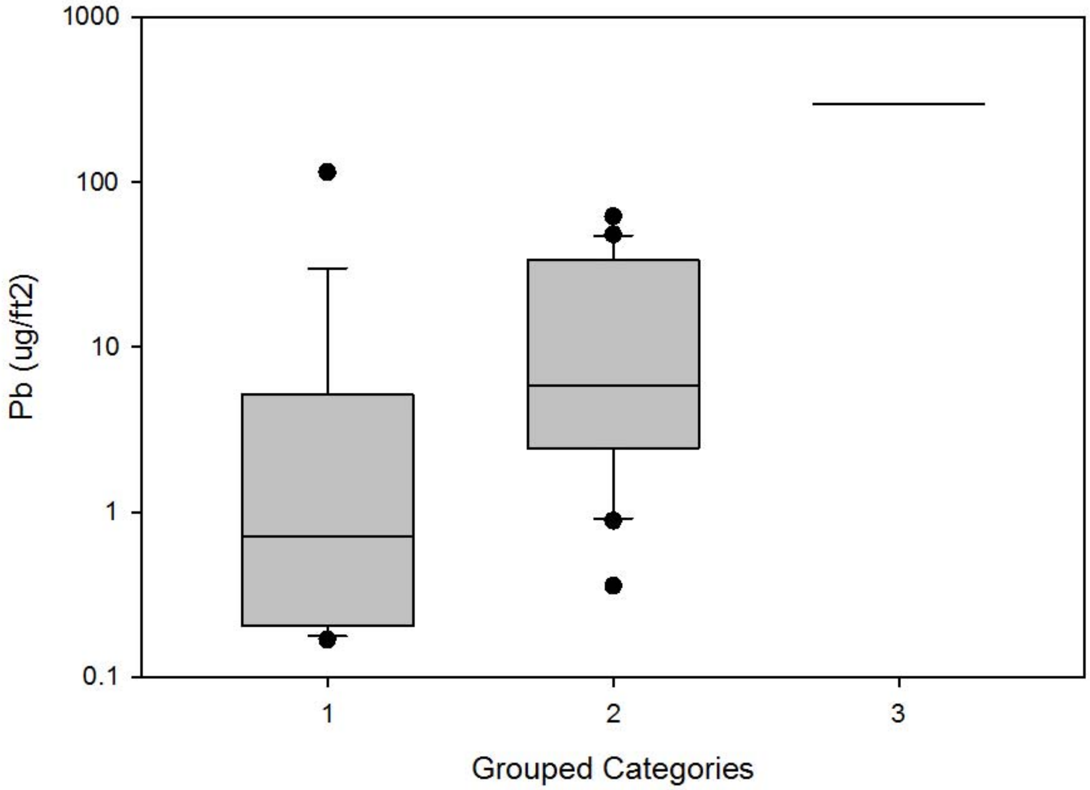
Lead Washdown Mass (µg/ft2)

Grouped Category:	other	other	low	other	other	high	other	other	low	low	other	other	low
Sample Category:	Al ramp	artificial turf	brick wall	concrete	galv bare	galv painted	barge hull	metal bare	metal painted	roof	rubber	wood bare	wood treated
	6.9	5.8	1.4	3.1	5.5	592.6	30.2	0.4	0.2	1.6	0.9	5.7	1.0
					43.7	1.4		48.0	8.7	0.2	61.8		
					2.6			19.5	0.7		1.6		
					36.7			1.0	0.4				
					3.6				5.2				
					36.7				114.4				
					18.1				0.2				
					21.1				8.8				
					2.3				0.2				
									5.1				
									0.7				
									0.2				
									0.2				
Grouped Category:	other	other	low	other	other	high	other	other	low	low	other	other	low
Sample Category:	Al ramp	artificial turf	brick wall	concrete	galv bare	galv painted	barge hull	metal bare	metal painted	roof	rubber	wood bare	wood treated
number	1	1	1	1	9	2	1	4	13	2	3	1	1
min					2.3	1.4		0.4	0.2	0.2	0.9		
max					43.7	592.6		48.0	114.4	1.6	61.8		
average					18.9	297.0		17.2	11.2	0.9	21.4		
median	6.9	5.8	1.4	3.1	18.1	297.0	30.2	10.2	0.7	0.9	1.6	5.7	1.0
st dev					16.6	418.0		22.4	31.2	1.0	35.0		
COV					0.9	1.4		1.3	2.8	1.1	1.6		


Lead Washdown Tests (mass)
1000
100
10
1
0.1
Pb (ug/ft2)
0
1
2
3
4
5
6
7
8
9
10
11
12
13
14
Sample Categories

Kruskal-Wallis One Way Analysis of Variance on Ranks (Pb mass

Normality Test (Shapiro-Wilk)	Failed	(P < 0.050)			
Group	N	Missing	Median	25%	75%
low	17	0	0.705	0.204	5.129
others	21	0	5.82	2.438	33.43
high	2	0	297.001	1.433	592.57
H = 10.049 with 2 degrees of freedom. (P = 0.007)					
The differences in the median values among the treatment groups are greater than would be expected by chance; there is a statistically significant difference (P = 0.007)					


1000
100
10
1
0.1
Pb (ug/ft2)
1
2
3
Grouped Categories

Summary Statistics for Lead Mass Grouped Categories

Grouped Category:	low	others	high
Sample Categories in Groups:	brick wall metal painted roof wood treated	Al ramp artificial turf concrete galv bare barge hull metal bare rubber wood bare	galv painted
number	17	21	2
min	0.2	0.4	1.4
max	114.4	61.8	592.6
average	8.8	16.9	297.0
median	0.7	5.8	297.0
st dev	27.4	18.7	418.0
COV	3.1	1.1	1.4

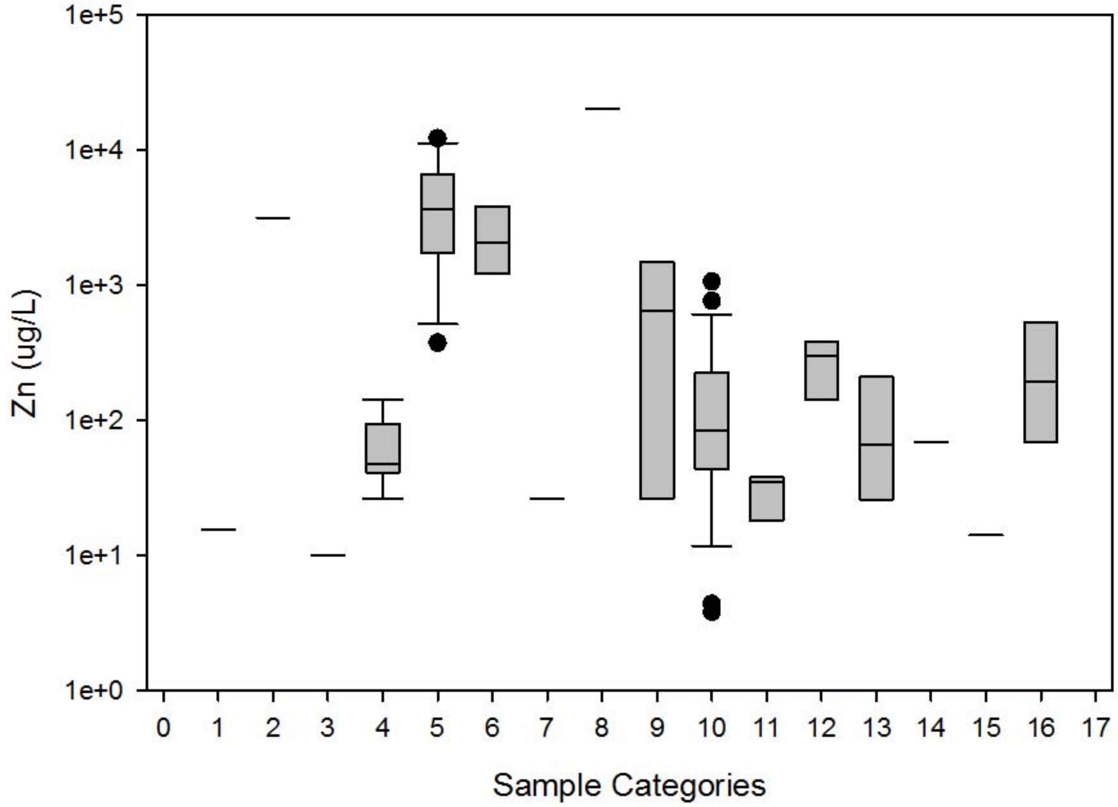
Zinc

Zinc Washdown Concentrations (µg/L)

Grouped Category:	low	high	low	other	high	high	low	high	other	other	low	other	other	other	low	other
Sample Category:	Al ramp	artificial turf	brick wall	concrete	galv bare	galv painted	galv coated	barge hull	metal bare	metal painted	plaster	roof	rubber	wood bare	wood painted	wood treated
	16	3,155	10	127	377	1,216	27	20,269	7	1,070	38	284	6	70	14	69
				63	6,942	3,855			650	86	35	447	148			534
				55	9,214	2,062			45	85	18	320	45			193
				48	3,287				1,705	547		304	401			
				47	4,112				1,290	118		4	89			
				41	850					15			33			
				41	4,097					85						
				27	12,281					548						
				142	3,261					293						
					5,907					73						
					1,491					48						
					2,417					46						
										36						
										66						
										33						
										96						
										78						
										4						
										151						
										79						
										15						
										4						
										440						
										205						
										121						
										768						

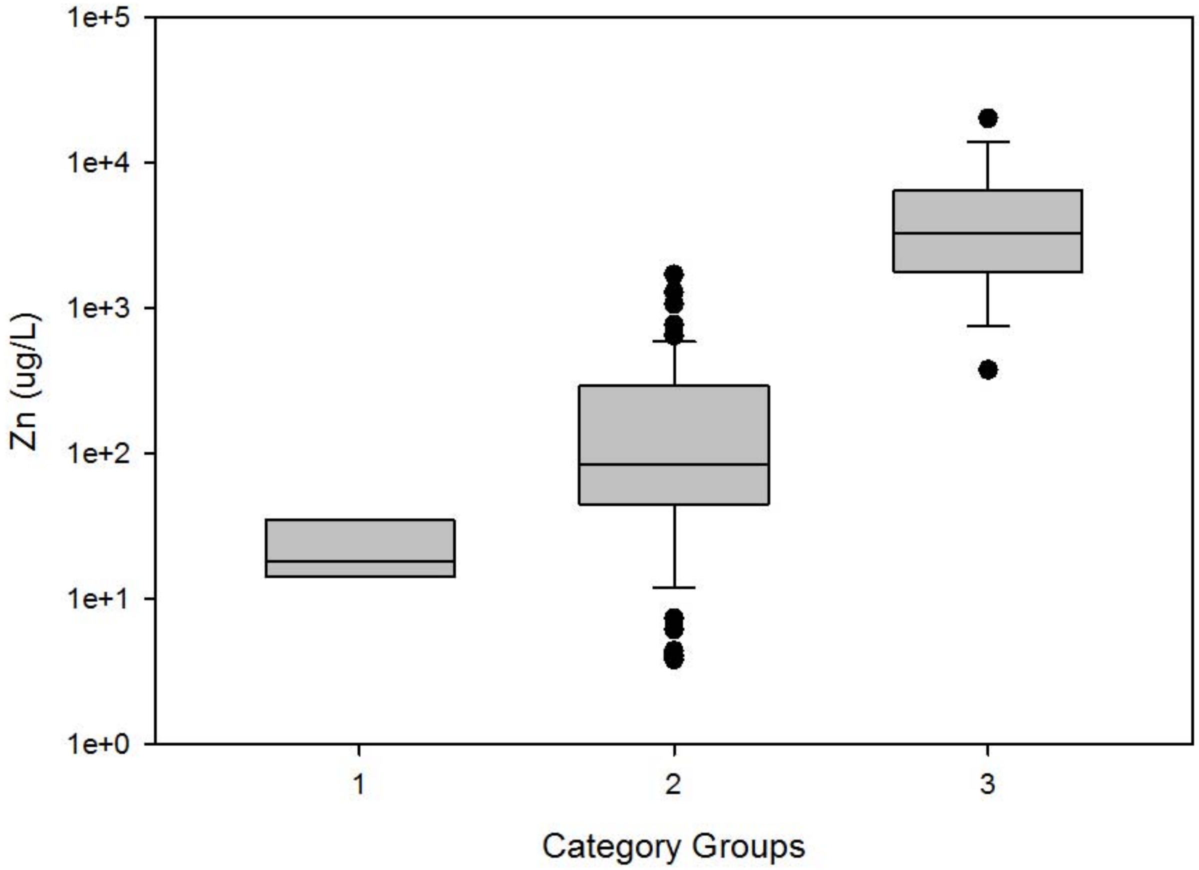
Grouped Category:	low	high	low	other	high	high	low	high	other	other	low	other	other	other	low	other
Sample Category:	Al ramp	artificial turf	brick wall	concrete	galv bare	galv painted	galv coated	barge hull	metal bare	metal painted	plaster	roof	rubber	wood bare	wood painted	wood treated
number	1	1	1	9	12	3	1	1	5	26	3	5	6	1	1	3
min				27	377	1,216			7	4	18	4	6			69
max				142	12,281	3,855			1,705	1,070	38	447	401			534
average				66	4,520	2,378			740	197	30	272	120			265
median	16	3,155	10	48	3,692	2,062	27	20,269	650	85	35	304	67	70	14	193
st dev				40	3,539	1,347			752	266	11	163	146			241
COV				0.6	0.8	0.6			1.0	1.4	0.4	0.6	1.2			0.9

Zinc Washdown Tests



Kruskal-Wallis One Way Analysis of Variance on Ranks (Zn concentrations)

Normality Test (Shapiro-Wilk)	Failed	(P < 0.050)			
Group	N	Missing	Median	25%	75%
low	7	0	18.094	14.203	35.11
others	55	0	84.609	44.581	292.835
high	17	0	3286.721	1776.302	6424.577
H = 43.131 with 2 degrees of freedom. (P = <0.001)					
The differences in the median values among the treatment groups are greater than would be expected by chance; there is a statistically significant difference (P = <0.001)					
To isolate the group or groups that differ from the others use a multiple comparison procedure.					
All Pairwise Multiple Comparison Procedures (Dunn's Method) :					
Comparison	Diff of Ranks	Q	P<0.05		
high vs low	58.429	5.669	Yes		
high vs others	35.655	5.599	Yes		
others vs low	22.774	2.473	Yes		
Note: The multiple comparisons on ranks do not include an adjustment for ties.					


1e+5
1e+4
1e+3
1e+2
1e+1
1e+0
Zn (ug/L)
1
2
3
Category Groups

Summary Statistics for Zinc Concentration Grouped Categories

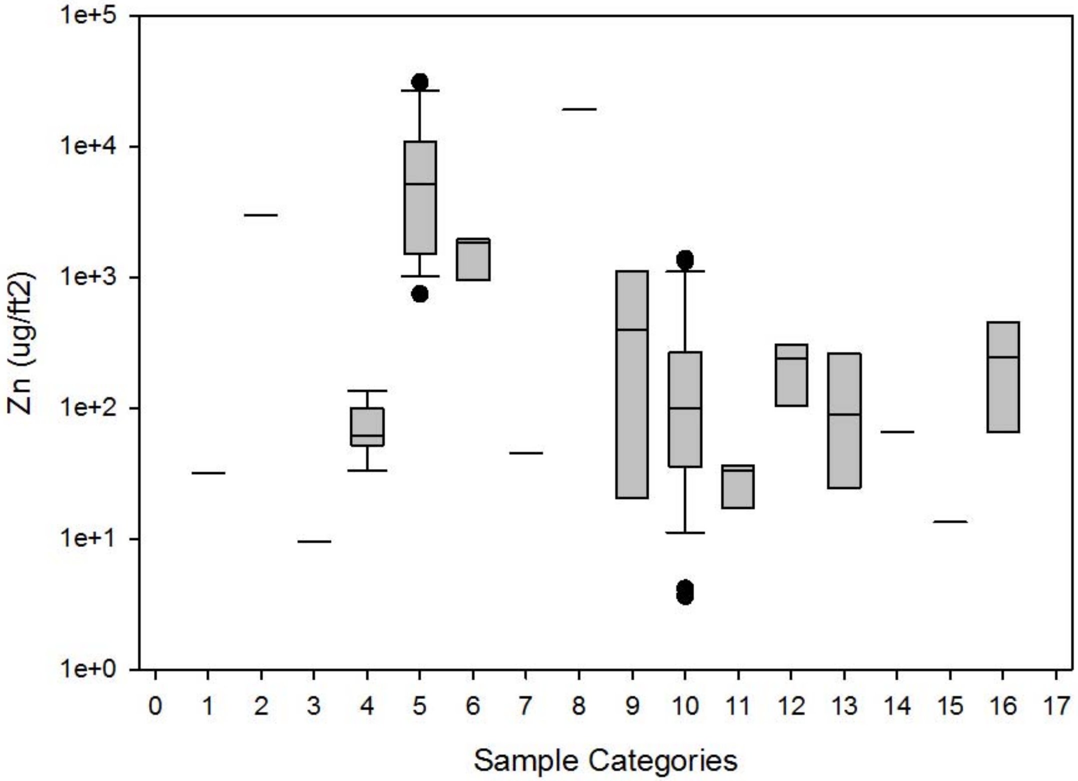
Grouped category:	low	all others	high
Sample Category in Groups:	Al ramp brick wall galv coated plaster wood painted	concrete metal bare metal painted roof rubber wood bare wood treated	artificial turf galv bare galv painted barge hull
number	7	51	17
min	10	4	377
max	38	1,705	20,269
average	23	225	4,988
median	18	85	3,287
st dev	11	343	5,008
COV	0.5	1.5	1.0

Zinc Washdown Mass (µg/ft2)

Grouped Category:	low	high	low	low	high	high	low	high	other	other	low	other	other	other	low	other
Sample Category:	Al ramp	artificial turf	brick wall	concrete	galv bare	galv painted	galv coated	barge hull	metal bare	metal painted	plaster	roof	rubber	wood bare	wood painted	wood treated
	32	2,986	9	120	1,427	944	45	19,180	9	1,012	36	202	6	66	13	66
				79	5,375	1,824			1,221	89	33	353	237			455
				70	8,719	1,951			739	80	17	253	54			243
				61	3,110				54	1,319		240	343			
				59	12,451					111		4	124			
				52	743					14			31			
				52	5,169					206						
				34	30,990					1,382						
				135	9,279					727						
					20,123					222						
					1,411					55						
					4,879					36						
					1,613					35						
										41						
										44						
										31						
										78						
										395						
										4						
										115						
										191						
										14						
										4						
										416						
										194						
										114						

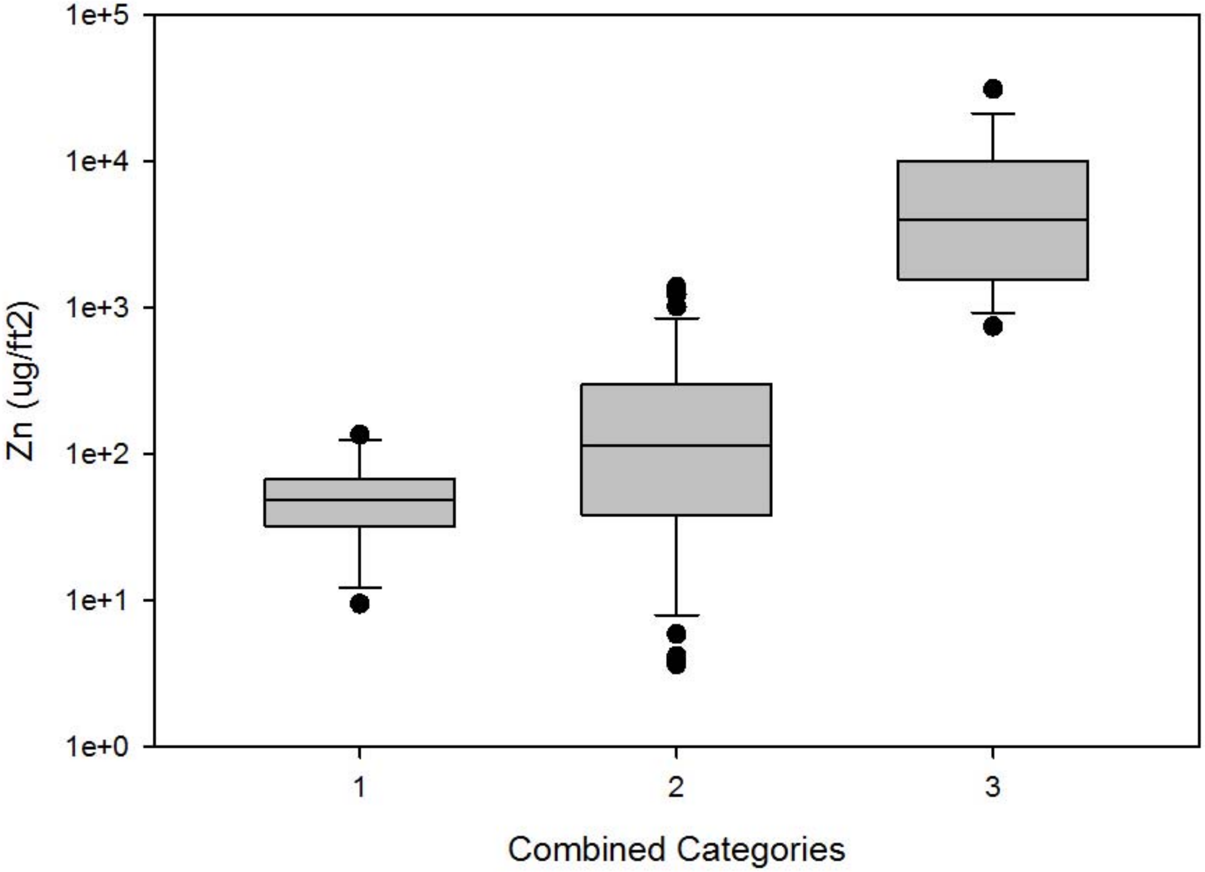
Grouped Category:	low	high	low	low	high	high	low	high	other	other	low	other	other	other	low	other
Sample Category:	Al ramp	artificial turf	brick wall	concrete	galv bare	galv painted	galv coated	barge hull	metal bare	metal painted	plaster	roof	rubber	wood bare	wood painted	wood treated
number	1	1	1	9	13	3	1	1	4	26	3	5	6	1	1	3
min				34	743	944			9	4	17	4	6			66
max				135	30,990	1,951			1,221	1,382	36	353	343			455
average				73	8,099	1,573			506	267	29	210	132			254
median	32	2,986	9	61	5,169	1,824	45	19,180	397	100	33	240	89	66	13	243
st dev				33	8,784	549			582	396	10	128	132			195
COV				0.5	1.1	0.3			1.2	1.5	0.4	0.6	1.0			0.8

Zinc Washdown Tests (by mass)



Kruskal-Wallis One Way Analysis of Variance on Ranks (Zn mass)

Normality Test (Shapiro-Wilk)	Failed	(P < 0.050)			
Group	N	Missing	Median	25%	75%
low	16	0	48.381	32.152	67.343
others	45	0	114.072	38.359	297.853
high	18	0	3994.475	1566.44	10072.18
H = 43.608 with 2 degrees of freedom. (P = <0.001)					
The differences in the median values among the treatment groups are greater than would be expected by chance; there is a statistically significant difference (P = <0.001)					
To isolate the group or groups that differ from the others use a multiple comparison procedure.					
All Pairwise Multiple Comparison Procedures (Dunn's Method) :					
Comparison	Diff of Ranks	Q	P<0.05		
high vs low	48.306	6.126	Yes		
high vs others	35.589	5.561	Yes		
others vs low	12.717	1.904	No		
Note: The multiple comparisons on ranks do not include an adjustment for ties.					


1e+5
1e+4
1e+3
1e+2
1e+1
1e+0
Zn (ug/ft2)
1
2
3
Combined Categories

Summary Statistics for Zinc Mass Grouped Categories

Grouped Category:	low	others	high
Sample Categories in Groups:	Al ramp brick wall concrete galv coated plaster wood painted	metal bare metal painted roof rubber wood bare wood treated	artificial turf galv bare galv painted barge hull
number	16	45	18
min	9	4	743
max	135	1,382	30,990
average	53	258	7,343
median	48	114	3,994
st dev	35	355	8,377
COV	0.7	1.4	1.1

Summary of Washoff Tests

Due to the varying number of observations for the different material categories, some of the test statistics are incomplete, but they do enable the identification of the types of materials of greatest interest. The following table summarizes the “low,” “other,” and “high” categories for each sample type and metal. In almost all cases, the concentration and mass washoff categories are the same; for the few that differ, the differences are not large (low/other or other/high). Most of these groupings are obvious and as expected, such as the bare galvanized metal being the highest category for zinc, and the aluminum ramp being the highest for aluminum. Other findings are interesting and potentially important, such as:

- Aluminum ramp high for aluminum (as expected)
- Artificial turf high for zinc and possibly high for iron, possibly due to recycled rubber tire crumbles used to support artificial grass leaves
- Bare galvanized metal high for zinc (as expected)
- Painted galvanized metal high for zinc, and high for aluminum and lead (the aluminum and lead are higher than for bare galvanized materials, likely due to the metal primers or paints; coated galvanized metals were much lower for all metals)
- Barge hull high for zinc, copper, and iron, possibly associated with anti-fouling paints
- Bare wood high for aluminum and iron
- Treated wood high for copper (as expected)

The high metals associated the artificial turf and the high metals associated with the barge hull are important findings, but are only represented by single samples. Additional sample collections representing these two categories are therefore highly recommended to determine if these findings are consistent.

Summary of Washdown Tests for Various Materials

	Al ramp	artificial turf	brick wall	concrete	galv bare	galv painted	galv coated	barge hull	metal bare	metal painted	plaster	roof	rubber	wood bare	wood painted	wood treated
Zn conc	low	high	low	other	high	high	low	high	other	other	low	other	other	other	low	other
Zn mass	low	high	low	low	high	high	low	high	other	other	low	other	other	other	low	other
Cu conc	low	other	low	low	other	other	other	high	other	other	low	low	other	other	other	high
Cu mass	others	others	low	low	others	low	others	high	others	others	low	low	others	others	others	high
Al conc	high	other	other	other	other	high	n/a	other	other	low	n/a	other	low	high	n/a	other
Al mass	high	other	other	other	other	high	n/a	other	low	low	n/a	other	low	high	n/a	other
Fe conc	low	high	low	other	other	other	n/a	high	other	low	n/a	low	low	high	n/a	other
Fe mass	low	other	low	other	other	other	n/a	high	other	low	n/a	low	low	high	n/a	other
Cd conc	other	other	other	other	other	other	n/a	other	other	other	n/a	other	other	other	n/a	other
Cd mass	other	other	other	other	other	other	n/a	other	other	other	n/a	other	other	other	n/a	other
Pb conc	other	other	low	other	other	high	n/a	other	other	low	n/a	low	other	other	n/a	low
Pb mass	other	other	low	other	other	high	n/a	other	other	low	n/a	low	other	other	n/a	low

Contaminated Soils Analyses at Navy Facilities

In addition to the washoff tests described above, SPARWARS-PACIFIC personnel also collected several soil and sediment samples, especially from likely contaminated areas. The following photographs are examples of some of these sampling activities.

Contaminated dry soil sampling.

Clean dry soil sampling.

Sampling of accumulated sediment near inlet.

Sampling of sediment in ponded water.

Comparison of Recent Navy Facility Source Area Water Quality Observations with Other Data (WinSLAMM Calibration File Preparation)

The following tables summarize the literature information, along with recent short-term leachate results, and recent washoff test results for different materials likely exposed to rainwater and stormwater. These results are shown as concentrations and as mass losses. The results are not directly comparable due to the different testing conditions used (water chemistries, water volumes, and contact times), but do illustrate typical concentrations that have been observed and identify the most consistently problematic materials.

The most common material associated with elevated heavy metal concentrations are galvanized metals: painted or bare galvanized steel and galvanized aluminum resulting in very high zinc concentrations. The single test for artificial turf also resulted in very high zinc concentrations. Factory coated galvanized materials are shown to usually have much lower resulting zinc concentrations in the leachate or washoff water, if the coatings are in good condition.

Any exposed copper (especially aged patinated copper) also results in very high copper concentrations, but these materials are most likely limited to older roof flashings. Treated wood and special paints used on ship hulls (based on a single barge hull analysis) also result in elevated copper concentrations.

High lead concentrations were reported in the literature and observed during the washoff tests associated with uncoated galvanized materials and some water distribution systems. Some high cadmium concentrations were observed associated with uncoated galvanized steel and drinking water systems. Very high iron concentrations were associated with uncoated galvanized materials, bare wood and painted barge hull (single samples). The highest aluminum concentrations were associated with the exposed aluminum materials and painted galvanized metals.

During the controlled leachate tests, almost all metal concentrations increased dramatically with increased exposure times. The data presented in this section focused on one hour exposure periods, but if materials were exposed for extended periods (such as for water storage tanks or if materials were in ponds or small puddles), then the concentrations could be more than 100 times higher than indicated here. In addition, in most cases, reduced pH (about 5) resulted in much greater concentrations compared to higher pH (about 8) conditions. Lower pH would be associated with roof exposures, while higher pH occurs after runoff flows across most surfaces or is discharged into receiving waters.

These data are used in developing the special WinSLAMM categories for material exposures (mainly exposed galvanized metals and scrapyard/storage yard contaminated soils) and associated expected concentrations from those areas.

Literature, Leaching Tests, and Washoff Data Comparisons for Zinc

	uncoated galvanized steel		coated galvanized steel		painted galvanized steel		uncoated galvanized aluminum		coated galvanized aluminum		water systems with some galv pipe	
	concentration (µg/L)	mass loss (g/m^2/yr)	concentration (µg/L)	mass loss (g/m^2/yr)	concentration (µg/L)	mass loss (g/m^2/yr)	concentration (µg/L)	mass loss (g/m^2/yr)	concentration (µg/L)	mass loss (g/m^2/yr)	concentration (µg/L)	mass loss (g/m^2/yr)
literature	90 to 30,000	2.4 to 8.5	160 to 30,000	0.07 to 15	n/a	n/a	200 to 1,600	n/a	60 to 180	n/a	6 to 2,000	n/a
	galvanized steel		copper		other materials (aluminum, concrete, plastics)							
UA (1 hr exposure)	concentration (µg/L)	mass loss (g/m^2)	concentration (µg/L)	mass loss (g/m^2)	concentration (µg/L)	mass loss (g/m^2)						
avg	1,600	0.055	15	0.001	11	0.001						
range	150 to 2,500	0.005 to 0.15	<10 to 30	0 to 0.002	<10 to 15	0.0005 to 0.002						
Navy Washoff Tests	low (Al ramp, brick wall, galv coated, plaster, and wood painted)		others (concrete, metal bare, metal painted, roof, rubber, wood bare, and wood treated)		high (artificial turf, galv bare, galv painted, and barge hull)							
	concentration (µg/L)	mass loss (g/m^2)	concentration (µg/L)	mass loss (g/m^2)	concentration (µg/L)	mass loss (g/m^2)						
avg	23	0.57	53	2.80	5,000	79						
range	10 to 38	0.10 to 1.5	4 to 1,700	0.04 to 15	380 to 20,200	8 to 335						

Literature, Leaching Tests, and Washoff Data Comparisons for Copper

	Uncoated copper roofing		Other roofing materials (galv, Al, vinyl, shakes)		Aged (Patinated) copper		Copper pipes	
	concentration (µg/L)	mass loss (g/m^2/yr)	concentration (µg/L)	mass loss (g/m^2/yr)	concentration (µg/L)	mass loss (g/m^2/yr)	concentration (µg/L)	mass loss (g/m^2/yr)
literature	2 to 175	1 to 33	<1 to 250	n/a	900 to 9,000	0.75 to 9	200 to 10,000	3.5 to 8
	galvanized steel		copper		other materials (aluminum, concrete, plastics)			
UA (1 hr exposure)	concentration (µg/L)	mass loss (g/m^2)	concentration (µg/L)	mass loss (g/m^2)	concentration (µg/L)	mass loss (g/m^2)		
avg	<1	0.001	360	0.03	15	<0.001		
range	<1	<0.001 to 0.004	50 to 1,000	<0.01 to 0.08	<10 to 30	<0.001		
Navy Washoff Tests	low (Al ramp, brick wall, concrete, plaster, and roof)		others (artificial turf, galv bare, galv painted, galv coated, metal bare, metal painted, rubber, wood bare, and wood painted)		high (barge hull and wood treated)			
	concentration (µg/L)	mass loss (g/m^2)	concentration (µg/L)	mass loss (g/m^2)	concentration (µg/L)	mass loss (g/m^2)		
avg	7	0.06	21	0.37	9,000	91		
range	1 to 81	0.01 to 0.8	0 to 174	0 to 4.5	27 to 30,000	0.4 to 310		

Literature, Leaching Tests, and Washoff Data Comparisons for Lead

	uncoated galvanized steel		uncoated galvanized aluminum		coated galvanized aluminum		painted wood		water distribution systems	
	concentration (µg/L)	mass loss (g/m^2/yr)	concentration (µg/L)	mass loss (g/m^2/yr)	concentration (µg/L)	mass loss (g/m^2/yr)	concentration (µg/L)	mass loss (g/m^2/yr)	concentration (µg/L)	mass loss (g/m^2/yr)
literature	1 to 2,700	n/a	<0.1 to 6	n/a	<10 to 200	n/a	<2 to 400	n/a	<5 to 1,000	n/a
	galvanized steel		copper		other materials (aluminum, concrete, plastics)					
UA (1 hr exposure)	concentration (µg/L)	mass loss (g/m^2)	concentration (µg/L)	mass loss (g/m^2)	concentration (µg/L)	mass loss (g/m^2)				
avg	<5	<0.001	<5	<0.001	<5	<0.001				
range	<5	<0.001	<5	<0.001	<5	<0.001				
Navy Washoff Tests	low (brick wall, metal painted, roof, and wood treated)		others (Al ramp, artificial turf, concrete, galv bare, barge hull, metal bare, rubber, and wood bare)		high (galv painted)					
	concentration (µg/L)	mass loss (g/m^2)	concentration (µg/L)	mass loss (g/m^2)	concentration (µg/L)	mass loss (g/m^2)				
avg	3.9	0.09	12	0.18	380	3.2				
range	0.2 to 45	0.002 to 1.2	0.3 to 51	0.004 to 0.7	1.5 to 770	0.015 to 6.4				

Literature, Leaching Tests, and Washoff Data Comparisons for Cadmium

	uncoated galvanized steel		Drinking water systems	
	concentration (μg/L)	mass loss (g/m^2/yr)	concentration (μg/L)	mass loss (g/m^2/yr)
literature	<0.02 to 32	15 to 25	<0.02 to 88	n/a
Navy Washoff Tests	all sources			
	concentration (μg/L)	mass loss (g/m^2)		
avg	7.7	0.13		
range	0.05 to 160	0.0005 to 3.4		

Literature, Leaching Tests, and Washoff Data Comparisons for Iron

	uncoated galvanized aluminum		coated galvanized aluminum		drinking water systems	
	concentration (μg/L)	mass loss (g/m^2/yr)	concentration (μg/L)	mass loss (g/m^2/yr)	concentration (μg/L)	mass loss (g/m^2/yr)
literature	18 to 1,700	n/a	6 to 24	n/a	0.06 to 1.4	n/a
Navy Washoff Tests	low (Al ramp, brick wall, metal painted, roof, and rubber)		others (artificial turf, concrete, galv bare, galv painted, metal bare, and wood treated)		high (barge hull and wood bare)	
	concentration (μg/L)	mass loss (g/m^2)	concentration (μg/L)	mass loss (g/m^2)	concentration (μg/L)	mass loss (g/m^2)
avg	200	4.3	300	4.9	2600	36.6
range	2 to 1,300	0.02 to 36	4 to 1,260	0.03 to 21	770 to 6,000	12 to 62

Literature, Leaching Tests, and Washoff Data Comparisons for Aluminum

Navy Washoff Tests	low (metal painted and rubber)		others (artificial turf, brick wall, concrete, galv bare, barge hull, metal bare, roof, and wood treated)		high (Al ramp and galv painted)	
	concentration (µg/L)	mass loss (g/m^2)	concentration (µg/L)	mass loss (g/m^2)	concentration (µg/L)	mass loss (g/m^2)
avg	172	3.1	230	3.2	770	9.0
range	1.8 to 1,400	0.02 to 37	2.4 to 1,200	0.023 to 12	4 to 1,800	0.04 to 15

Trace 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 groundwater 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), in addition to increasing the sodium adsorption ratio (SAR) that can greatly hinder infiltration rates in soils or media having even small amounts of clay. 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).

The 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 and 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 microanaerobic 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 by Ogburn (2013). Analytical methods having smaller detection limits are necessary to account for non-detected values. The following tables 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.

Filterable and particulate fractions of lead and zinc in buffered waters after three months of exposure (Ogburn 2013)

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	< 2.0	> 98	24	76
	Vinyl Gutter	n/a	n/a	n/a	n/a
	Aluminum Gutter	n/a	n/a	100	0
	Steel Gutter	< 13.5	> 86	51	49
	Copper Gutter	n/a	n/a	< 15	> 85
pH 8	Concrete Pipe	n/a	n/a	< 67	> 33
	PVC Pipe	n/a	n/a	18	82
	HDPE Pipe	n/a	n/a	100	0
	Steel Pipe	76	24	0.34	100
	Vinyl Gutter	n/a	n/a	100	0
	Aluminum Gutter	n/a	n/a	24	76
	Steel Gutter	96	4	1.7	98
	Copper Gutter	n/a	n/a	100	0

Filterable and particulate fractions of copper and aluminum in buffered waters after three months of exposure (Ogburn 2013)

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

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%).

The following table 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.

Filterable and particulate fractions of iron in natural pH waters after three months of exposure (Ogburn 2013)

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 sheetflow 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; Wilkin 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 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. Current work on the removal of nitrogen compounds is focusing on denitrification in anaerobic systems and on bacterial processes in subsurface gravel wetlands and biofilters.

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.

Summary of Heavy Metal Treatability

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, and particulate organic matter. The treatability of stormwater solids and associated heavy metals is dependent on their size. The removal of dissolved contaminants may be needed to meet stringent numeric discharge permit requirements and reduce surface and groundwater contamination potentials.

The valence charge of a metal and its complexation, among other contaminant properties, influence the choice of stormwater treatment technology. Strongly charged, small molecules can be removed effectively by zeolites. Zeolites are not effective in the removal of compounds of zero valence and compounds with large size. Peat can be used as a filtration media for treatment of heavy metals and likely their complexes. 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. An advantage of peat media is that it can treat many heavy metals during relatively short (as short as 10 minutes) contact times.

Tests were conducted over a three month exposure period of pipe, gutter, and storage tank materials. 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 after three months of exposure. 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. For plastic PVC and HDPE pipes immersed in pH 5 buffered stormwater, 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.

Prior research found that ionic fractions for zinc, copper, and cadmium in stormwater can range from 25 to 75%. 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 fractions 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 valences 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.

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