11

The Effects of Water Quality Characteristics on Pollutant Releases from Drainage Materials

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During the last twenty years, the leaching of heavy metals (mainly zinc) from roofing materials has become recognized as a significant source of heavy metals in stormwater (He et al., 2001a). A number of field studies have been conducted to quantify the metal release rates from various roofing materials, including new and naturally aged copper and zinc sheeting under different atmospheric conditions (He et al., 2001a, b., He, W., 2002, Clark et al., 2008 a, b, Wallinder et.al., 2002a, Wallinder et.al. 2009, Veleva et al., 2010). Roof runoff heavy metal discharges has been found to be an important factor in the degradation of water quality in urban receiving waters (Burton and Pitt 2002, Pitt et al. 1995, NRC, 2008). The drainage system components of roofs are frequently constructed of metals, including aluminum, zinc, lead, and copper. These heavy metals can be found in potentially high concentrations in roof runoff (Clark et al. 2008 a, b; Clark et al. 2007, Wallinder 2001, Pitt et al. 1995, Forster 1996, Morquecho 2005, Tobiason 2004).

Studies conducted by previous researchers indicated that the contamination of roof runoff is dependent on the type of roofing materials used and the quality of the rainfall (NRC, 2008, Clark et al., 2008 a, b, Wallinder et al., 2000, Wallinder et al., 2001, Corvo et al., 2005, Veleva et al., 2010, Faller and Reiss, 2005). A smaller number of studies have also investigated pipe materials and how

they affect storm-water quality (Lasheen et al., 2008; Al-Malack et. al, 2001).

The purpose of this study was to investigate heavy metal releases from different pipe, gutter, and storage tank materials under a wide range of environmental conditions. The influence of pH, salinity, and time of contact were examined. The awareness of the quantity of the pollutants released by the gutter and piping materials will facilitate the selection of drainage system components (and building materials) that have minimal environmental effects.

This research was conducted to investigate how various drainage system and tank materials, exposure time, and water quality affect pollutants released into stormwater runoff. Two series of static long-term leaching laboratory tests were conducted over a three month period using eight new gutter and pipe materials. The first series of experiments was conducted to investigate heavy metal releases under controlled pH conditions. The materials were immersed in locally collected roof runoff and parking lot runoff that were adjusted to pH 5 and pH 8 using buffer chemicals added to the runoff water (disodium phosphate dehydrate and potassium phosphate monobasic). These buffered runoff waters had high phosphate and high conductivity values. Therefore, a second testing series was also conducted using the same eight gutter and pipe materials that were immersed in un-buffered waters collected from Mobile Bay, Alabama, (saline) and the Black Warrior River at Tuscaloosa, Alabama. These experiments were performed to investigate the metal releases under natural pH conditions with varying salinity values associated with natural brackish bay water and river water. Water samples from leaching containers were periodically analyzed for a wide range of metallic constituents, nutrient contaminants, and toxicity.

Some of these materials were found to release high concentrations of zinc, copper, and lead during the controlled and natural pH tests, with galvanized steel materials being the most significant source of lead and zinc, and copper materials being the greatest source of copper (as expected). Zinc, copper, and lead releases were detected during both short and long exposure times under controlled and natural pH conditions.

Statistical analyses were performed to determine the effect of time, pH, salinity, and type of material on the release of the metals. Model fitting was performed on the time series plots to predict the release rate of metals as a function of exposure time.

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11.1 Introduction

The dissolution of roof and pipe material is influenced by rainwater pH (Lasheen et al., 2008; Al-Malack et. al, 2001). Calcareous materials from cement roofs and concrete pipes and metal ions from metal and plastic materials can be dissolved by acidic rainwater (Degremont 1979, Horvath, 2011). These processes result in weathering and deterioration of the roofing and piping materials. Material deterioration is dependent on such parameters as the time of contact with water and its chemical composition. Metal ions leaching from roofing materials are often in the most bioavailable form, and consequently, roof stormwater runoff can be a substantial source of toxicity.

Zinc, copper, aluminum, and other heavy metals are commonly utilized in the construction of outdoor structures. For example, in southeastern Mexico, 63% of roofs and walls are constructed using galvanized metals, which are subjected to corrosion. When zinc corrosion products are dissolved by rain and dew, zinc ions are leached from the corroded surfaces (Veleva et al., 2010). The annual stormwater runoff from zinc roofs in Paris, France, released approximately 34 to 64 metric tons of zinc which amounts to about half the total produced by stormwater runoff from the entire city (Gromaire, et al. 2002).

The reaction products are created under ambient conditions by a gaseous oxidizing atmosphere which ends in the physical adsorption of oxygen, resulting in the formation of one or more oxide monolayers. A potential is created by the occurrence of electron tunneling through the stable oxide film to the adsorbed oxygen. Consequently, a film rearrangement takes place which leads to the creation of oxide grain boundaries. Initially, the oxide films that are created at ambient temperatures are continuous and amorphous but then may be subject to local crystallization with the incorporation of the oxide "islands". The crystallization is promoted by water, heat, electric fields, and mechanical stress. In dry air, films consisting primarily of an anhydrous oxide may attain thicknesses of 3 nm. However, in the presence of water, ranging from condensed films accumulated from humid atmospheres to bulk aqueous phases, increases in electron tunneling conductivity will produce further thickening with an increase in partial hydration. Other constituents, such as H_2S, SO_2, CO_2, and Cl^- which may be present in contaminated atmospheres, could also become incorporated in the condensed films (Shreir, 1976). Even though the metal itself retains a negative charge when immersed in an electrolyte

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solution, positively charged ions have a tendency to dissolve (Garrels and Christ, 1990, Degremont 1979).

11.2 Materials and Methods

Two series of long term-leaching laboratory tests were conducted using eight new gutter and pipe materials including those that are also used in tank construction. The first series of experiments were conducted to investigate the heavy metal releases under controlled pH conditions. Pipe and gutter materials were immersed for a three month period into locally collected roof runoff and parking lot runoff that were adjusted to pH 5 and pH 8 values using buffer chemicals added to the runoff water (disodium phosphate dehydrate and potassium phosphate monobasic). These buffered runoff waters had high phosphate and high conductivity values. During this test, the effects of pH, time, and material type on contaminants leaching out of the drainage system materials were investigated. During the second testing series, the same eight pipe and gutter materials were immersed into un-buffered waters from Mobile Bay (saline) and the Black Warrior River in Alabama. These experiments were performed to examine the effects of salinity on the metal releases under natural pH conditions.

The gutter materials used in the experiments included copper, aluminum, vinyl, and galvanized steel, while the pipe materials were concrete, PVC, HDPE, and galvanized corrugated steel. All of the pipe and gutter materials were acquired from local building material stores. Galvanized steel, aluminum, PVC, HDPE, and concrete materials are also often used in water tank construction. The pipe and gutter sections examined for the two pH tests were nearly identical. The test sections used in the natural water tests with varying salinity were also identical. All the pipe and gutter test segments were 30.5 cm long, with the exception of the concrete pipes, which were 15.3 cm long in the first series of the tests, and in the second series of the experiments, a section of the 15.3 cm long pipe was used. The diameters for concrete, PVC, HDPE, and galvanized steel pipe sections were 41.2, 15.7, 17.5, 16.4 cm respectively. The diameters of galvanized steel gutter specimens were 15.2 cm. The cross-sectional dimensions of vinyl, aluminum, and copper gutter segments were 5 by 8, 8.4 by 5.6, and 10.6 by 7.2 cm, respectively. The PVC, HDPE, and galvanized steel pipes weighed approximately 1,096, 409, and 8,000 g, respectively. The approximate weights of the vinyl, aluminum, galvanized steel, and copper pipes were 100, 79, 704, and 503 g, respectively. The

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weight of the concrete segments used in the first testing series was approximately 22,400 g each; in the second testing series, the concrete pipe sections used weighed approximately 4,400 g.

In the course of the first testing series with buffered pH waters, each section of pipe and gutter material was submerged into sixteen liter plastic buckets, or 80 liter containers for the concrete specimens, which contained the buffered roof runoff and parking lot runoff water that was adjusted to pH values of 5 and 8. Roof runoff collected from roof downspouts was used in the gutter material experiments and stormwater from parking areas before drain inlet was utilized in pipe material tests. During the first series of experiments the water from the containers was sampled and analyzed at time zero (water with adjusted pH but without specimens), 0.5 hr, 1 hr, 27 hrs, 1 month, 2 months, and 3 months for total concentrations of cadmium, chromium, lead, copper, and zinc. Total aluminum and iron and filterable concentrations of lead, copper, zinc, and aluminum were also analyzed after 3 months of exposure. Samples were also screened using Microtox toxicity and analyzed for nutrient constituents (ammonia nitrogen, total nitrogen, and nitrate) and COD.

During the second series of tests, fourteen liter leaching containers with un-modified bay and river waters were sampled at time zero (natural bay and river waters without pipes), 1 hr, 27 hrs, 1 week, 1 month, 2 months, and 3 months for total concentrations of lead, copper and zinc, and also screened for toxicity. Concentrations in mg/L were converted to mg of constituent per surface area of a pipe/gutter in order to account for different area surfaces of the pipes and water volumes.

Total iron and aluminum and filterable concentrations of iron were determined in the containers after 3 months of exposure. Throughout the first and second testing series, pH, conductivity, and Eh were measured and alkalinity, total and calcium hardness, chloride, and sulfate analysis were also performed.

Metal concentrations were determined using Inductively Coupled Plasma Mass Spectroscopy (ICP-MS). Detection limits for zinc, copper, and lead concentrations were 20, 20, and 5 µg/L, respectively. The detection limits for cadmium and chromium were 5 and 20 µg/L respectively, for aluminum and iron 100 and 20 µg/L respectively.

For the first series of tests, the data for 0.5 hr, 1 hr, and 27 hrs were defined as short exposure periods, and for 1, 2, and 3 months

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as long term exposure periods. For the second series of the experiments, the data for 1 hr, 27 hrs, and 1 week were defined as short exposure periods, and for 1, 2, and 3 months as long term exposure periods.

Half of the detection limit values were substituted for metal releases that were below the detection limit values. In the graph legends P stands for pipe, G stands for gutter.

11.3 Results and Discussions

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

11.3.1 Copper releases under controlled pH conditions.

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

After the first day of exposure, copper concentrations in copper samples were approximately 7 mg/L under pH 5 conditions and less than 1 mg/L under pH 8 conditions. Greater and faster releases occurred at lower pH conditions. Copper concentrations greater than 5 mg/L (650 mg/m^2) were detected in the copper gutter samples under pH 5 conditions after long-term exposure, compared to 2 mg/L (270 mg/m^2) values under the pH 8 conditions. The greatest copper releases (greater than 6 mg/L equivalent to 970 mg/m^2) were detected from copper materials after 27 hours of exposure before they started to level off. Some of the plastic, aluminum, and galvanized steel materials also released copper, but the concentrations were much lower. After the copper materials, PVC pipes samples had the highest copper releases of approximately 5 mg/m^2 after long exposure periods. Copper releases were detected in galvanized steel gutter and pipe samples under pH 8 conditions, however under pH 5 conditions, the copper release was detected

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only at 1 month of exposure for steel pipes. HDPE and galvanized steel materials had the lowest copper releases of up to 60 µg/L and 30 µg/L, respectively. Copper releases were not detected in the concrete pipes samples at both pH 5 and pH 8 values.

Copper concentrations resulting from different materials during the buffered tests are shown in Figure 11.1 and Figure 11.2.
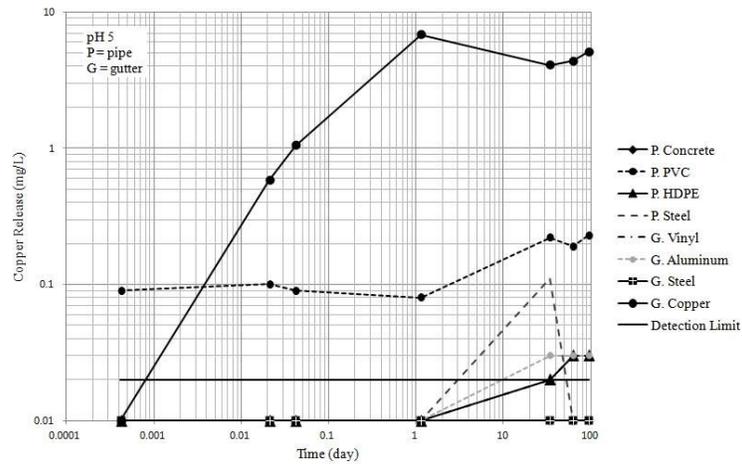
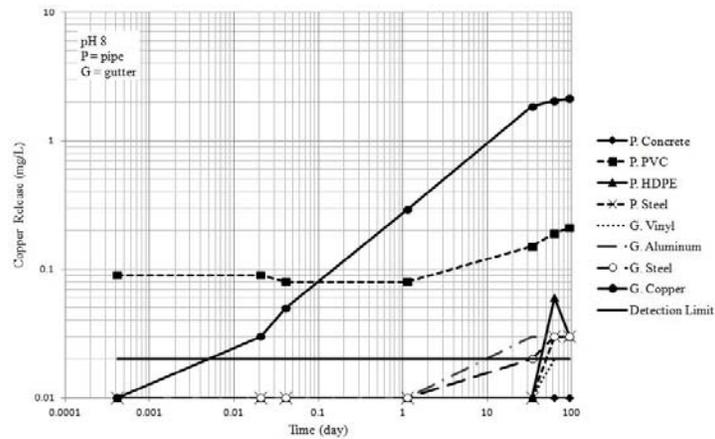Figure 11.1 Total copper concentrations in containers with pH 5 water. (Ogburn and Pitt 2001a)

Figure 11.2 Total copper concentrations in containers with pH 8 water. (Ogburn and Pitt 2001a)

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11.3.2 Copper releases under natural pH conditions.

Under natural pH conditions in the river and saline bay samples , copper releases were detected only from copper materials during both short and long exposure times.

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

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

Copper concentrations released from various materials during the un-buffered tests are shown in Figure 11.3 and Figure 11.4.
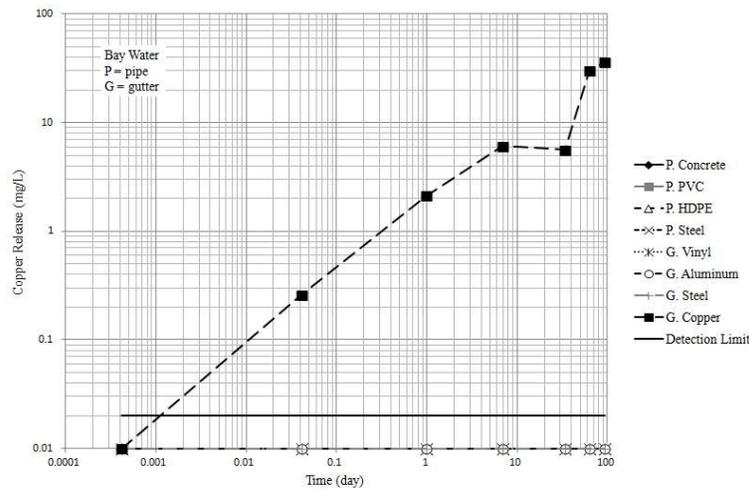

Figure 11.3 Total copper concentrations in containers with bay water.
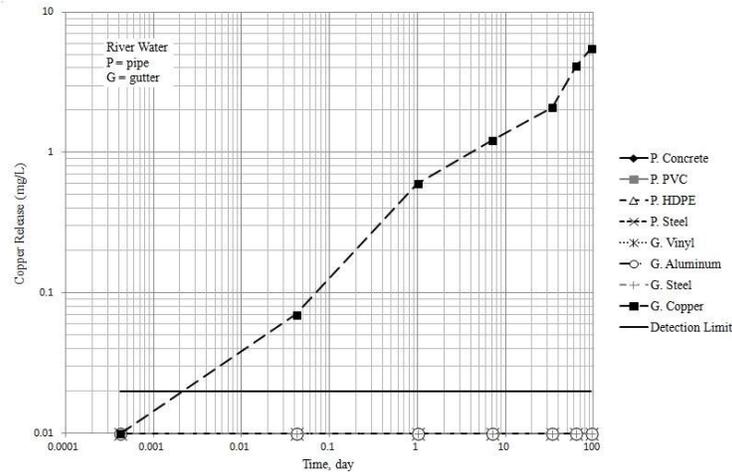(Ogburn et al., 2012)

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Figure 11.4 Total copper concentrations in containers with river water.
(Ogburn et al., 2012)

11.3.3 Zinc releases under controlled pH conditions.

During short-term exposures, zinc was released from the galvanized steel pipe and gutter at both low and high pHs, as well as from the copper and HDPE gutter samples at pH 5, and from vinyl and aluminum gutters at pH 8. For other materials, zinc releases were noted after 1 or 2 months of exposure. After the first day of exposure, the galvanized steel pipes and gutters had very high levels of zinc concentrations (from 1 to more than 14 mg/L), with greater and faster releases observed under lower pH conditions. Zinc releases were the highest from galvanized steel materials. During long-term exposures (after 1 month), zinc concentrations in the samples with galvanized metals under pH 8 conditions were greater than 90 mg/L, compared with 14 mg/L values under the pH 5 conditions. The second highest sources of zinc were the copper gutters; greater releases occurred under pH 5 conditions (exceeding 0.13 mg/L; 17 mg/m^2). Zinc was also released from plastic materials, but the resultant concentrations were much lower. The least sources of zinc were concrete (up to 30 µg/L) and plastic materials (for PVC pipes up to 680 µg/L, for HDPE pipes up to 50 µg/L, and for vinyl gutters up to 40 µg/L).

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Figure 11.5 and Figure 11.6 show zinc concentrations released from different gutter and pipe materials during the buffered experiments.
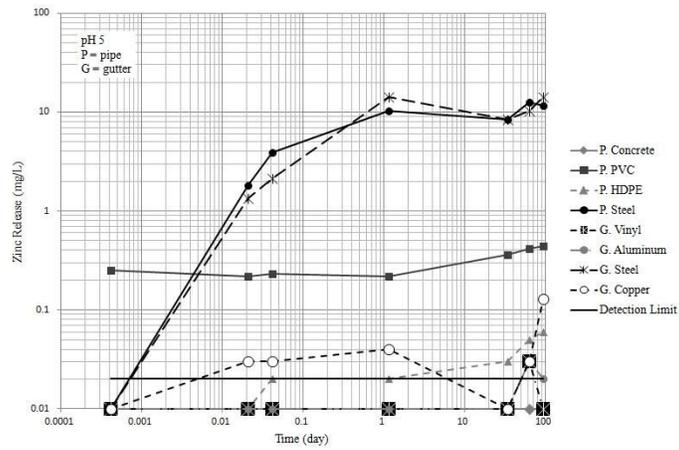

Figure 11.5 Total zinc concentrations in containers with pH 5 water.
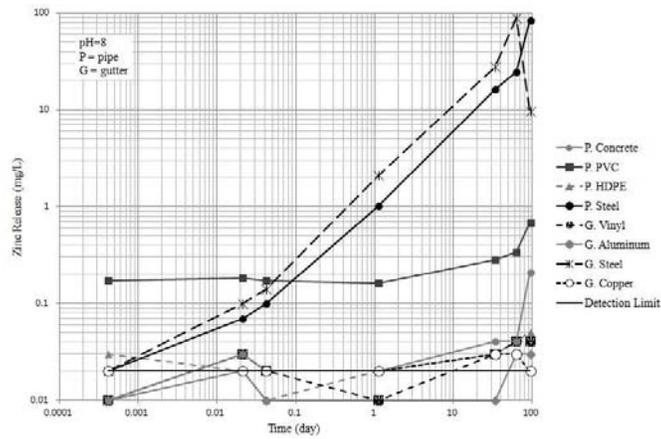(Ogburn and Pitt 2001a)

Figure 11.6 Total zinc concentrations in containers with pH 8 water.
(Ogburn and Pitt 2001a)

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11.3.4 Zinc releases under natural pH conditions.

Short-term exposures (up to 1 week) resulted in zinc releases from the galvanized steel pipe and gutter materials immersed in both bay and river water and from copper gutter materials immersed in bay water. Zinc losses from the other materials were noted after 1 or 2 months of exposure. As for controlled pH conditions, galvanized steel materials in the containers under natural pH conditions were the greatest sources of zinc releases. The samples with galvanized steel gutters and pipes had very high levels of zinc concentrations (5 to more than 8 mg/L) after the first day of exposure with greater releases observed for samples immersed into bay water. However, after one day of exposure, those concentrations were lower compared to zinc concentrations in containers at controlled pH 5 conditions (exceeding 14 mg/L) and greater than zinc releases in containers at controlled pH 8 tests (exceeding 2 mg/L).

After 1 month of exposure, zinc releases from galvanized materials immersed in containers with river water exceeded those in bay tests. After long-term exposures of up to three months, samples with galvanized steel materials immersed into bay waters had zinc concentrations that exceeded 70 mg/L, while those in river water exceeded 180 mg/L, compared to zinc losses from galvanized steel materials under controlled pH 5 conditions that reached 14 mg/L and for controlled pH 8 conditions that reached 90 mg/L.

The second highest sources of zinc releases were the copper materials, with higher concentrations observed in containers with river water samples (0.48 mg/L) compared to bay samples. Plastic and aluminum materials had much lower zinc releases. Zinc was not detected in concrete pipe samples with either bay or river waters.

Typically, under natural pH conditions, zinc concentrations were higher in galvanized steel pipe samples compared to galvanized gutter samples, however under controlled pH conditions, zinc releases were greater in galvanized steel gutter samples compared to samples with galvanized pipes.

Due to the high chloride content of the bay water, the zinc releases from galvanized steel pipe tended to be greater in bay water samples compared to river water samples. Figure 11.7 and Figure 11.8 show zinc concentrations resulted from various gutter and pipe materials during the un-buffered experiments.

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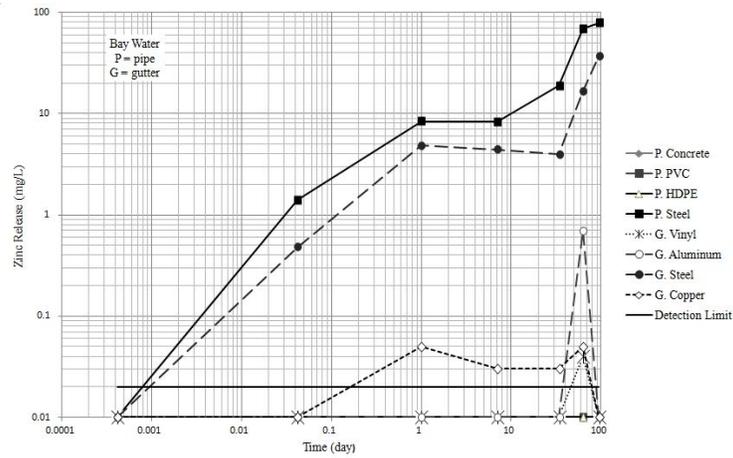so vertical dimension
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Figure 11.7 Total zinc concentrations in containers with bay water.
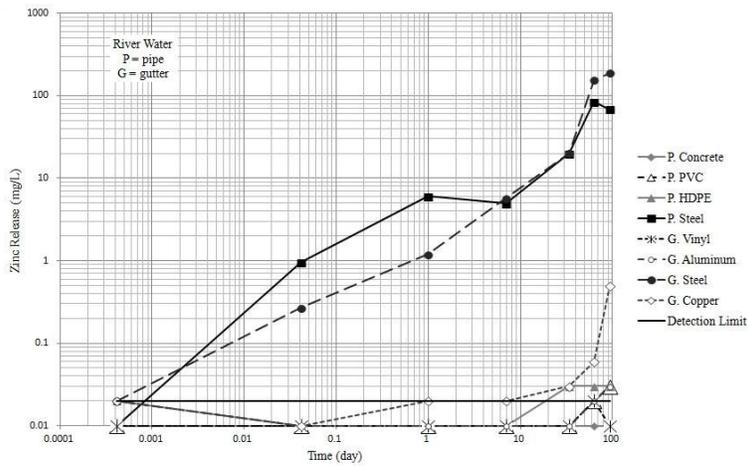(Ogburn et al., 2012)

Figure 11.8 Total zinc concentrations in containers with river water.
(Ogburn et al., 2012)

11.3.5 Lead releases under controlled pH conditions.

Only galvanized materials were a source of lead releases during both short (0.5 hr-27 hrs) and long (1-3 months) exposure periods.

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During short exposure times, lead was not detected in any of the containers having galvanized steel with the exception of the galvanized steel gutter sample under the pH 8 conditions. This sample had a lead concentration of 8 µg/L (0.4 mg/m^2) at 27 hrs of exposure. For the steel pipe and gutter specimens exposed at pH 5, lead was detected after 1 month of exposure, while the steel pipe sample exposed to pH 8 conditions released lead after 2 months. Under both pH 5 and pH 8 conditions, the release of lead was greater for steel pipe samples than for steel gutter samples. For a given material, the releases of lead were greater at high pH conditions compared to low pH conditions.

The greatest lead releases were observed for the galvanized steel pipe sample at pH 8 which reached lead concentrations of 600 to 700 µg/L (25-30 mg/m^2), followed by the galvanized steel pipe sample at pH 5 with concentrations of 250 µg/L after 3 months of exposure. Samples with aluminum, copper, and plastic materials did not contain any detectable lead concentrations.

Lead concentrations resulting from different materials during the buffered tests are shown in Figure 11.9 and Figure 11.10.
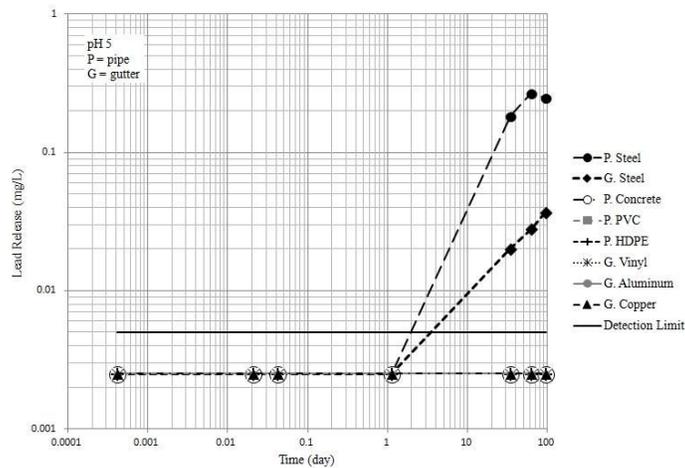

Figure 11.9 Total lead concentrations in containers with pH 5 water.
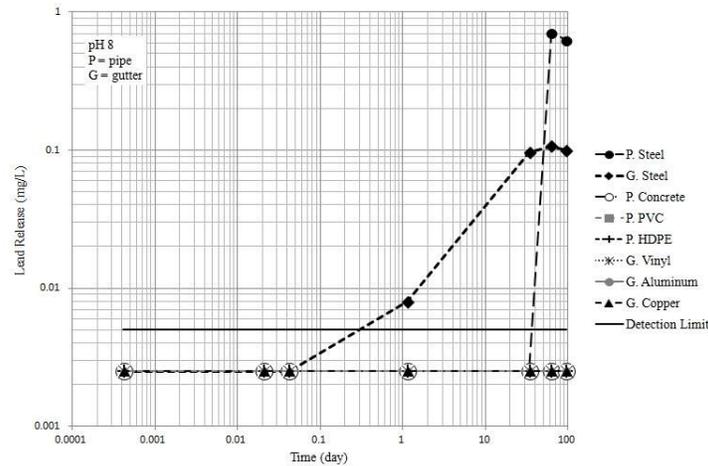
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Figure 11.10 Total lead concentrations in containers with pH 8 water.

11.3.6 Lead releases under natural pH conditions.

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

During long exposure periods (1 month to 3 months), periodic lead concentrations were detected only for galvanized steel materials immersed in containers having either bay or river waters. The greatest lead release of 0.058 mg/L was observed after 3 months of exposure of the steel gutter sample with river water. For galvanized steel materials, lead releases were greater in samples under controlled pH conditions compared to samples under natural pH conditions.

Figure 11.11 and Figure 11.12 show lead releases resulting from various pipe and gutter materials during the un-buffered experiments.

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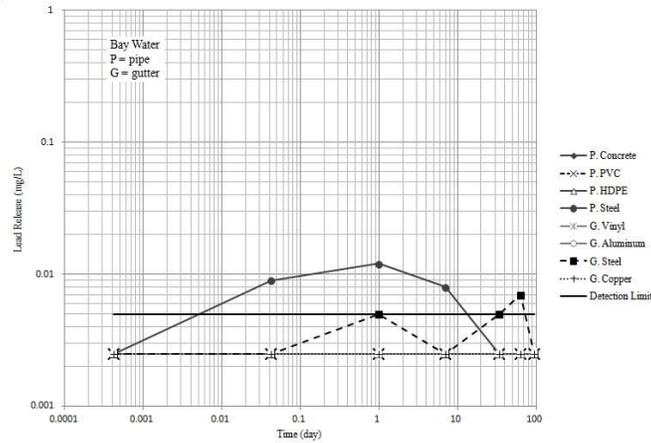so vertical dimension
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Figure 11.11 Total lead concentrations in containers with bay water.
(Ogburn et al., 2012)
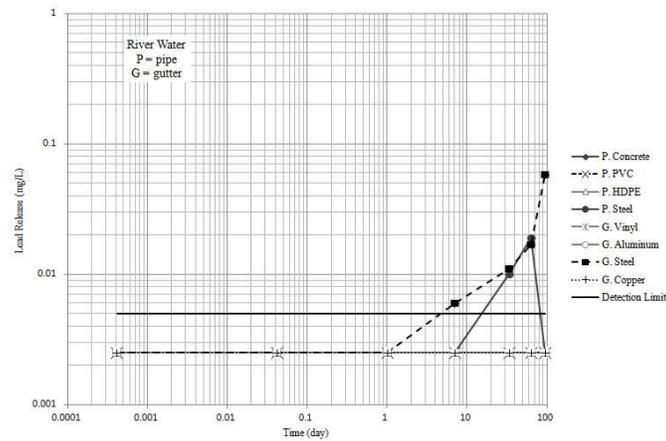
Figure 11.12 Total lead concentrations in containers with river water.
(Ogburn et al., 2012)

11.3.7 Iron and Aluminum releases under controlled and natural pH conditions.

Iron releases from galvanized steel materials exceeded those from other materials and were greater under pH 5 conditions than under pH 8 conditions. At pH 5 the releases ranged between 6 and 22 mg/L and around 1 mg/L at

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pH 8. Iron releases from the galvanized steel specimens submerged into bay and river water were between 1 to 2 mg/L and were similar to iron releases at pH 8 values. Iron concentrations leached from concrete pipes in bay water (more than 2 mg/L) were greater than those in river water (less than 1 mg/L). The highest concentrations of aluminum were detected in the containers with aluminum materials and were 1 mg/L or less for all conditions.

11.3.8 Statistical Analysis.

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

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

Next, 2^2 Factorial Analyses were performed to evaluate the effects of exposure times (short vs. long) and pH (low vs. high) and the interactions of those factors on the metal releases in mg per surface area for each pipe and gutter material during the first series of tests. During the second test series, 2^2 Factorial Analyses were conducted to estimate the effect of exposure time and salinity (high vs. low), and the interaction of those factors.

By using P-value and the Factorial Effect/Pooled Standard Error Ratio of the Factorial Analysis, a determination was made as to whether or not the data could be combined into groups for each pipe and gutter material based on the effect (or absence of effect) of the factors and their interactions.

Next, to determine whether there was a statistically significant difference between the groups, Mann-Whitney tests were performed. The Mann-Whitney test was used because some of the data didn't meet the assumptions of normality and/or equal vari-

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ance. Group box plots were plotted on a log scale for each metal constituent.

Figure 11.13 is a group box plot of copper releases from copper materials under pH 5 vs. pH 8 conditions. Low pH conditions and exposure time increased released copper. The 75th percentile of the box plot for copper releases under pH 5 conditions during short time exposure is higher than that of for copper releases under the same conditions during long exposure time and was an unusually high value.

Figure 11.3 Group Box Plot for copper release in mg/m^2 for copper materials immersed in pH 5 and pH 8 waters.

Figure 11.14 shows copper releases from copper materials in bay and river waters. The copper release increased with the exposure time; greater concentrations were observed for the samples in the bay water likely due to the higher content of the chloride ion.

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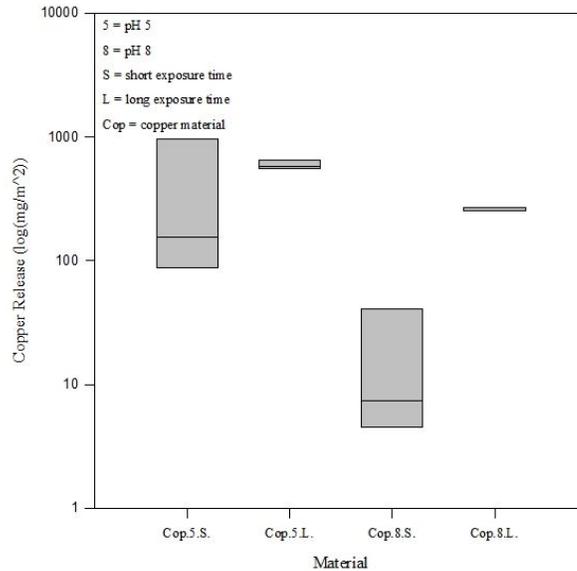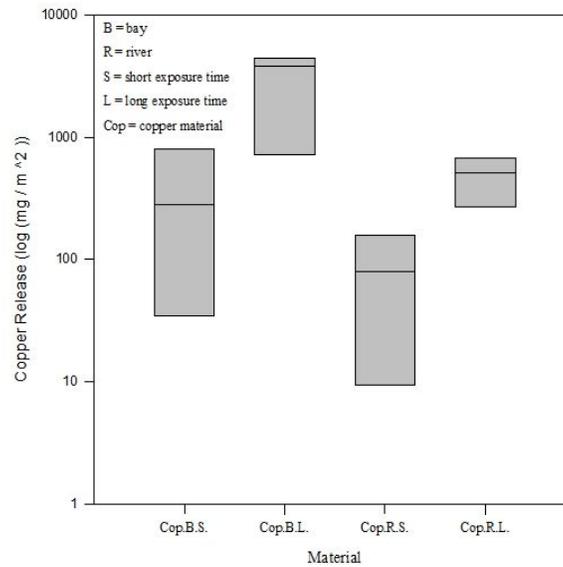so vertical dimension
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Figure 11.14 Group Box Plot for copper release in mg/m^2 for copper materials immersed in bay and river waters.

Figure 11.15 shows zinc releases from various gutter and pipe materials under controlled pH conditions. Concrete, galvanized steel, and aluminum box plots represent all the data combined (short and long exposure times for both pH 5 and pH 8 conditions). Box plots for PVC and HDPE materials show the data during long term exposure, both pH 5 and pH 8 combined. Box plots for vinyl and copper materials represent the data with short and long exposure times combined. Box plots that had negative or zero values were not plotted on the logarithmic scale. Galvanized steel materials have significantly higher zinc releases compared to the rest of materials.

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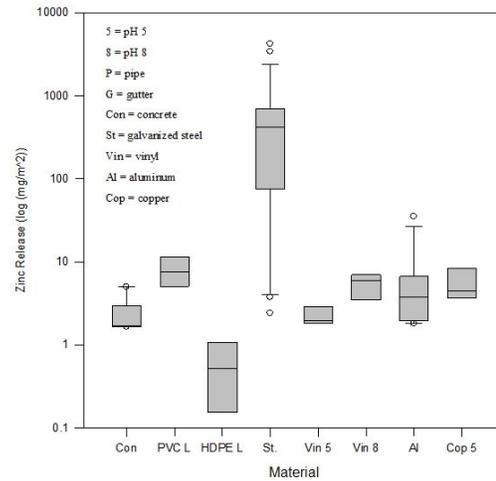
Figure 11.15 Group Box Plot for zinc release in mg/m^2 for different gutter and pipe materials immersed in pH 5 and pH 8 waters.

Figure 11.16 shows zinc releases for the materials exposed to bay and river waters. The box plots for plastics represents all the data combined (for bay and river waters and for short and long exposure times). As the exposure time increased, the zinc releases also increased.

Figure 11.16 Group Box Plot for zinc release in mg/m^2 for various gutter and pipe materials immersed in bay and river waters.

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Figure 11.17shows lead releases from galvanized steel materials under controlled pH conditions. Box plots for lead releases from galvanized steel pipes during short exposure times at pH 5 and 8, as well as from galvanized steel gutters during short exposure times at pH 5, were below detection limits and therefore were not plotted. As can be seen from the figure, exposure time increased lead releases.
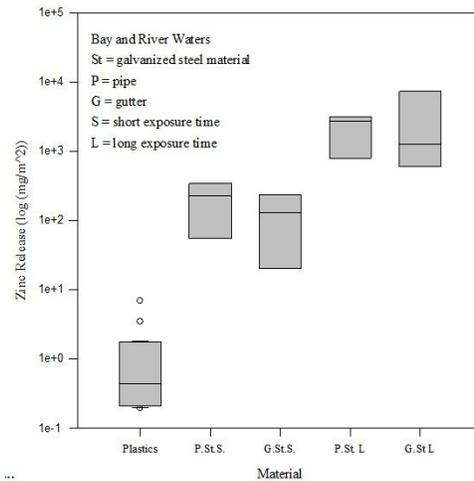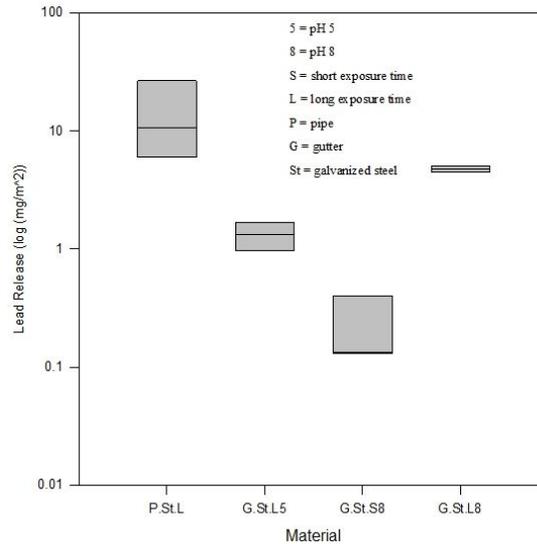

Figure 11.17 Group Box Plot for lead release in mg/m^2 for galvanized steel materials immersed in pH 5 and pH 8 waters.
(Ogburn and Pitt 2011 b)

Figure 11.18 represents lead releases from galvanized steel materials under natural pH conditions. Lead releases during both short and long exposure times and under both bay and river conditions do not differ significantly between the groups, with the group of lead releases from galvanized steel gutters immersed into river water during long exposure times being slightly higher than the rest of the groups.
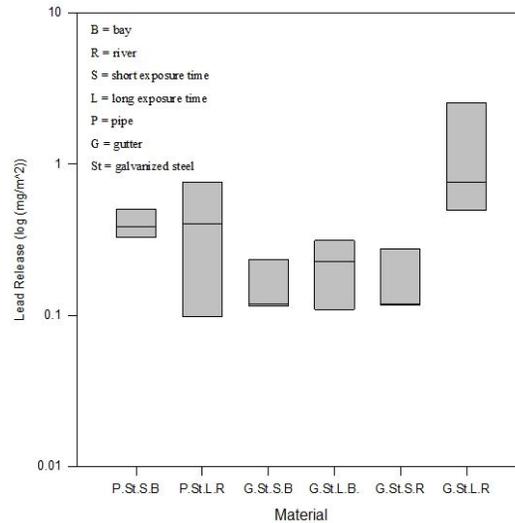
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Figure 11.18 Group Box Plot for lead release in mg/m^2 for galvanized steel materials immersed in bay and river waters.

11.3.9 Toxicity under controlled and natural pH conditions.

During the controlled pH tests, the highest toxicities were found for copper and aluminum material exposures; the samples from concrete containers were the least toxic. In containers with bay and river waters, copper materials had the highest toxicity values, followed by galvanized steel materials.

11.3.10 Model fitting.

Linear regression was conducted on time series plots of log metal releases per pipe surface area vs. log time for different pipe and gutter materials under controlled and natural pHs in order to acquire regression equations to predict the metal release from the exposure time of the material. There were six data points for each time series. The majority of the scatterplots revealed that first order polynomials can be fitted to the log of metal concentration vs. log of time.

The time series of lead releases from steel gutters at pH 5 and of steel pipes at pH 8 were not fitted with linear equations due to the nature of the data. In the container with steel gutters at pH 5, no lead was detected until after 1 month of exposure: after one month

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of exposure, the lead release reached 0.97 mg/m^2 (0.02 mg/L) and after 2 months of exposure, the lead release exceeded 1 mg/m^2 (0.028 – 0.037 mg/L). There were only three detected lead concentrations in the data series. In the containers with steel pipe at pH 8, lead releases were detected after two months of exposure and exceeded 29 mg/m^2 (0.71 mg/L). Two concentration values above the detection limits were available.

Time series for copper releases from copper gutters under pH 5 conditions showed an increase in the copper concentrations after half an hour of exposure, and after 27 hours, reached 970 mg/m^2 (corresponding to 6.8 mg/L). However, after 27 hours, copper concentrations leveled off. All the data was fitted using first order polynomial and 2 segment liner equations. The numbers of data points in these time series were limited and the high concentration observed after 27 hours of exposure could have been an unusually (non-repeatable) high value. On the other hand, cupric ions could have been combined with the orthophosphate from the solution and thereby reducing copper solubility. Edwards (2001) observed that higher doses of orthophosphate tend to decrease solubility of copper.

Pearson Product Moment Correlation or Spearman Rank Order Correlations were computed to determine if the data were statistically significantly correlated. To investigate the goodness of model fit, residual plots were inspected to determine if the least squares assumptions for errors were met. To check the constant variance assumption, the plots of residuals vs. the fitted values were inspected and the Levene Median test was conducted to detect the differences in the variance values. To evaluate the normality of the residuals, Normal Probability Plots and Histograms of the residuals were also constructed. The Anderson-Darling test statistic was also calculated to check for normality. The zero mean of the residuals assumption was checked by examining the descriptive statistics and graphs of the residuals vs. fitted values and vs. the order of the observations. To determine if the residuals were independent from each other, graphs of the residual vs. observation number were examined. Also the Durbin-Watson statistic was calculated.

ANOVA tables were used to determine if the regression coefficients were not equal to zero and were statistically significant and to evaluate if the overall regression equation was significant. The coefficient of determination (R^2) was also calculated.

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The residuals for most of the regression equations met the assumptions of normality, constant variance, zero mean, and independence. P-values for some regression analysis were higher than desired which could have been explained by the fact that there were few data points overall. The examination of the residual plots vs. fitted values for some of the samples showed that there was more spread in the residuals for the higher fitted values, but the assumption of the constant variance of the residuals was not rejected because of the few data points available. The Spearman rank correlation between the absolute values of the residuals and the observed value of the dependent variable was calculated to test the assumption of constant variance, which may be violated if the Spearman rank correlation was statistically significant. Levenes test was also used to determine if the residuals have constant variance. The results of Levenes test showed that the assumption of equal variance was met for most of the data, for the rest of the time series, the hypothesis of equal variances was not rejected due to the limited data.

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

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

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

For all of the regression equations, the constant term was significant with the exception for zinc releases from galvanized steel gutters in river water (P-value > 0.05) and therefore, the intercept term was not used in the regression equations (0 releases at 0 time, a reasonable assumption). Additionally, ANOVA tables indicated that the slope terms were significant for all regression equations.

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11.3 Conclusions

Gutter and pipe materials can release high concentrations of zinc, copper, and lead under controlled and natural pH conditions during both short and long exposure periods. Galvanized steel materials were the most significant source of lead and zinc, while copper materials were the greatest source of copper.

The greatest copper concentrations were detected in copper gutter samples. During short-term exposures, only copper materials were a source of copper under both high and low pH during the controlled pH experiments. Under natural pH conditions, copper concentrations were detected only for copper materials during both short and long exposure times and exceeded 35 mg/L in bay samples after three months of exposure. Concrete pipes were not a source of copper under either controlled or natural pH conditions. Other than for the concrete tests, the smallest copper concentrations were found in the samples with HDPE, vinyl, galvanized, and aluminum materials under controlled pH conditions.

The greatest sources of zinc were galvanized steel materials. Zinc releases from galvanized steel materials were detected during both short (0.5 hr to 27 hrs) and long exposure (after one to three months).

Under controlled pH conditions, zinc releases in the samples with galvanized steel materials were greater and more rapidly released at higher pH values during long exposure time materials. The least sources of zinc were concrete and plastic materials.

Lead concentrations were released only from galvanized steel materials, but were released during both short and long exposure times and for both controlled and uncontrolled pH tests. The highest aluminum concentrations were noted from aluminum materials. For controlled pH conditions, the largest concentrations of iron (more than 20 mg/L at pH 5) were found to be leaching from galvanized steel materials. During natural pH conditions, concrete and galvanized steel materials were the greatest sources of iron. Tables 11.1 and 11.2 show zinc, lead, and copper releases from the most significant sources after 3 months of exposure.

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Table 11.1 Final zinc and lead releases.

Metal	Material	pH 5	pH 8	Bay	River
Zn, mg/m^2	P. Galv. Steel	470	3400	3100	2600
Zn, mg/m^2	G. Galv. Steel	640	4200 *	1600	8300
Pb, mg/m^2	P. Galv. Steel	10	25	ND	ND
Pb, mg/m^2	G. Galv. Steel	1.7	4.5	ND	2.5

* After 2 months of exposure

Table 11.2 Final copper releases.

Metal	Material	pH 5	pH 8	Bay	River
Cu, mg/m^2	G. Copper	650	270	4400	670

Table 11.3 shows significant groupings for each sample type for the different exposure conditions for zinc, lead, and copper releases according to the separate 2^2 factorial analyses.

Table 11.3 Significant groups for lead, copper, and zinc releases.

Metal	Constituent	Varying pH Conditions	Varying Conductivity Conditions
Concrete (pipe sample)	Pb	ND	ND
	Cu	ND	ND
	Zn	all combined into one group	ND
PVC (pipe sample)	Pb	ND	ND
	Cu	short* vs. long** exp periods	ND
	Zn	short vs. long exp periods	all combined into one group
HDPE (pipe sample)	Pb	ND	ND
	Cu	short vs. long exp periods	ND
	Zn	pH5 vs. pH8; and short vs. long exp periods	Short bay vs. short river vs. long bay vs. long river
Galvanized steel (pipe sample)	Pb	short vs. long exp periods	Short bay vs. short river vs. long bay vs. long river
	Cu	all combined into one group	ND
	Zn	all combined into one group	short vs. long exp periods

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Vinyl (gutter sample)	Pb	ND	ND
	Cu	Short at pH5 vs. short at pH 8 vs. long at pH5 vs. long at pH 8	ND
	Zn	pH5 vs. pH8	all combined into one group
Aluminum (gutter sample)	Pb	ND	ND
	Cu	short vs. long exp periods	ND
	Zn	all combined into one group	all combined into one group
Galvanized steel (gutter sample)	Pb	short at pH5 vs. short at pH8 vs. long at pH5 vs. long pH8	all combined into one group
	Cu	Short at pH5 vs. short at pH 8 vs. long at pH5 vs. long at pH 8	ND
	Zn	all combined into one group	short vs. long exp periods
Copper (gutter sample)	Pb	ND	ND
	Cu	pH5 vs. pH8	short vs. long exp periods
	Zn	pH5 vs. pH8	all combined into one group

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

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

Acknowledgements

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