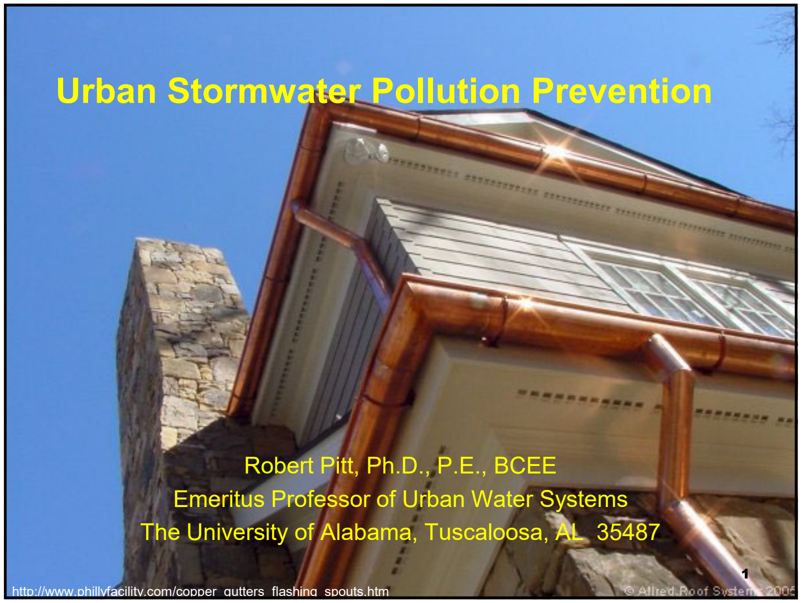


1

Presentation Topics

- Sources of heavy metals found in stormwater
- Initial laboratory and field tests for metal and selected organic releases from building roof materials
- Outdoor asphalt aging tests
- Laboratory material leaching tests
- Conclusions and recommendations
- Acknowledgements

2

Sources of Heavy Metals found in Stormwater

3

3

Galvanized (Galvalume) Roofing – Airport Facility

- 7 storms sampled of direct roof runoff
- Zinc
  - 0.42 to 14.7 mg/L (average 88% dissolved; COV = 7%).
- Copper
  - 0.01 to 1.4 mg/L (average 75% dissolved; COV = 24%).
- Lead
  - Not detected

From: Tobiason, S. (2004). Stormwater Metals Removal by Media Filtration: Field Assessment Case Study. *Proceedings of the Watershed 2004 Conference*. Water Environment Federation.

4

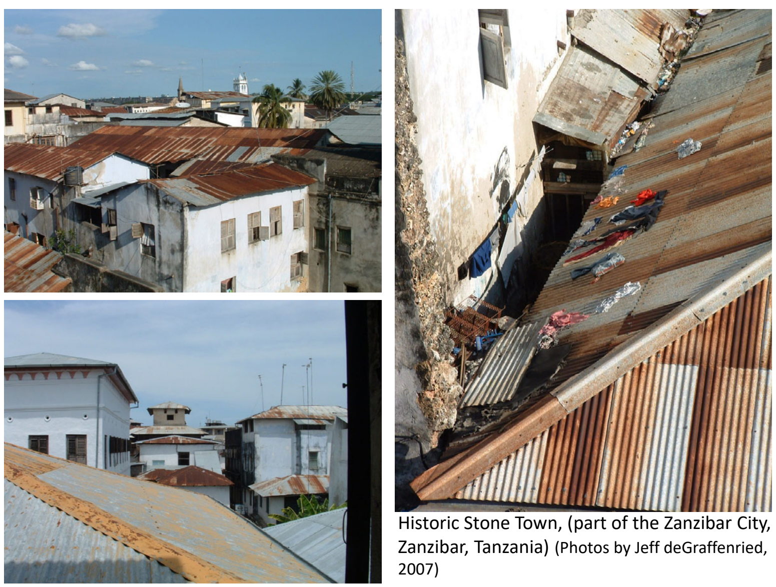
Scrapyard Stormwater (Filterable Concentrations)

Pollutant	Concentration (mg/L)
Phosphate	0.05 – 0.35
Copper	0.1 – 0.3
Lead	0.1 – 0.3
Zinc	0.1 – 6.7
Calcium	8 – 200
Magnesium	1.8 – 12

5

Galvalume roofing panels used on a building in Denali, Alaska

6



Historic Stone Town, (part of the Zanzibar City, Zanzibar, Tanzania) (Photos by Jeff deGraffenried, 2007)

7

Initial Laboratory and Field Tests for Metal and Selected Organic Releases from Building Roof Materials Conducted at Penn State - Harrisburg

8

8

Literature Review Major Findings

- The composition of roofing materials and the drainage system pipes can significantly affect the amounts of pollutants, such as heavy metals, released into the runoff, especially for roof runoff.
- Water chemistry and time of contact may also affect the release of the contaminants into the stormwater.
- Metal corrosion and paint have been identified as copper, lead, zinc, and chromium potential sources of stormwater contamination.
- Researchers have determined these heavy metals are common contaminants in roof runoff at potentially high concentrations.
- Factors that affect material deterioration include the chemical composition of water and the time of contact with it.

9

9

Methodology

- Summer 2002: Laboratory TCLP (acid rain simulation)
- Fall/Winter 2002 and Spring 2003: Laboratory investigation of selected materials using rainfall
- Spring 2003 – Fall 2004: Long-term, outdoor investigation from intact installations on test frames. Destroyed in Hurricane Ivan.
- Winter 2004 – Laboratory-testing of 60-year-old outdoor (painted) metal roofing panels.
- Spring 2005: Reconstruction of test frames at PSH and UAB. Slight design modifications resulting in larger surface area and decreased angle of roofing section to match typical construction guidelines.
- Summer 2005 – indefinite: Long-term, outdoor investigation from intact installations on test frames. Runoff samples analyzed regularly (every storm first two months; at least one storm per month after first two months).

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Categories of Roofing Materials Investigated

- galvanized metal
- aluminum gutters/siding
- vinyl siding
- asphalt roofing shingles
- roofing tar and felt
- membrane roofing
- faux slate shingles (made from recycled materials)
- untreated wood (with and without paint)
- treated wood (with and without paint

11

Roofing Compound Components

- Leak Stopper – Rubberized Roof Patch
  - Petroleum Distillate
  - Liquid Rubber
  - Penetrex™ (a penetrating oil)
- Silver Dollar Fibered Aluminum Roof Coating
  - Aluminum Flakes
  - Calcium Carbonate
  - Cellulose Fiber
  - Stoddard Solvent
  - Asphalt
- Gardner Wet-R-Dri™ All Weather Plastic Roof Cement
  - Petroleum Distillate
  - Asphalt
  - Cellulose Fiber
  - Silicate Mineral
  - Chrysotile Mineral Fiber

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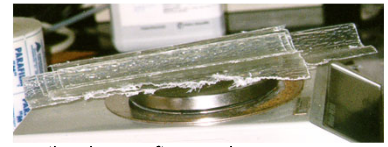
Laboratory Testing: Roofing Shingles (Asphalt)

Laboratory Testing: Roofing Panels

Ondura™ Vinyl Roofing Panels



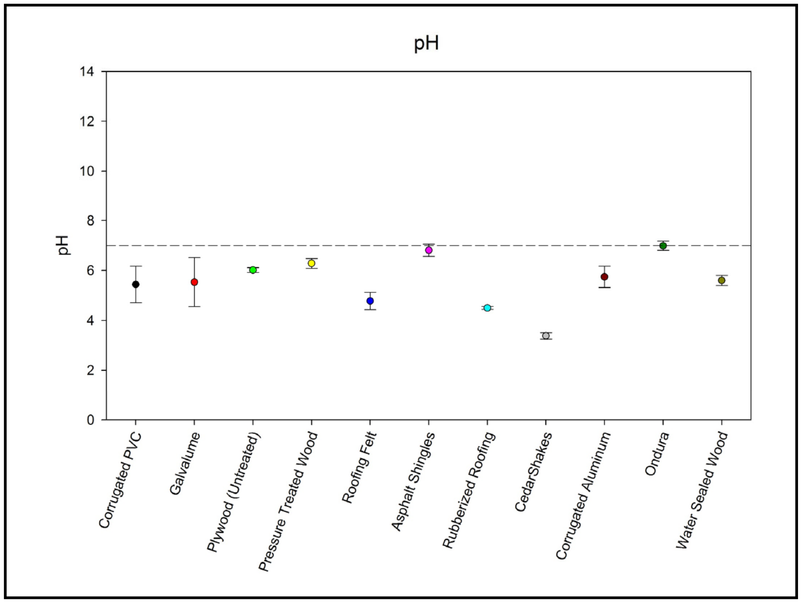
Fiberglass Roofing Panels

White Plastic Roofing Panels

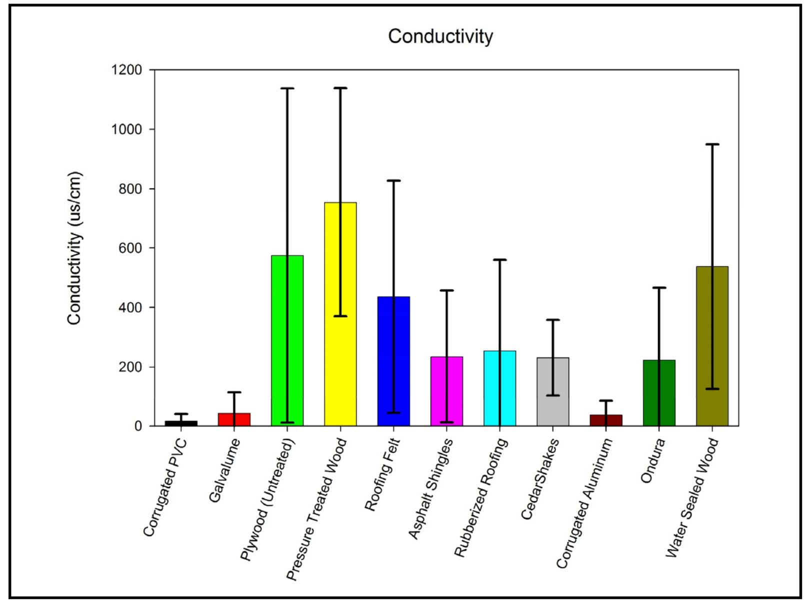
Laboratory Testing: Roof Coatings and Sealers

Analytes

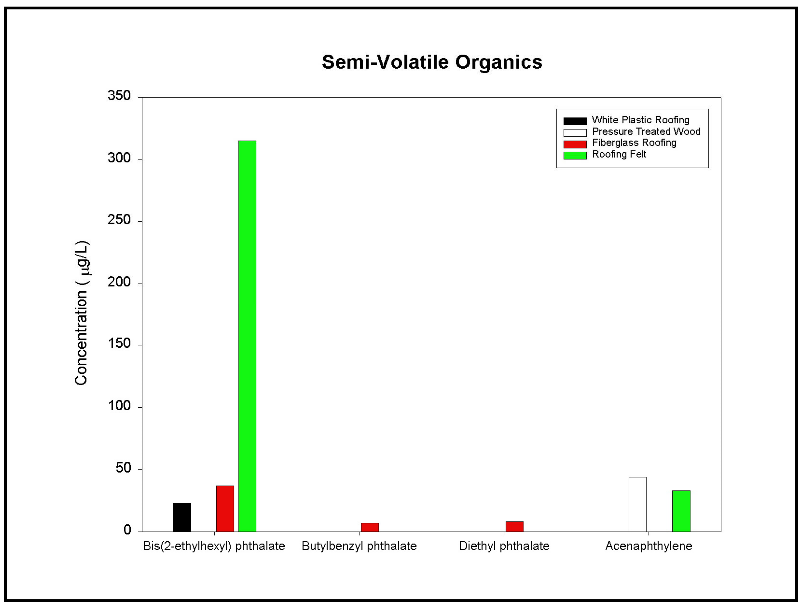
- pH
- Conductivity
- Chemical oxygen demand
- Semi-volatile organics (EPA Method 8270 and 608) – laboratory testing only
- Heavy metals and major cations (copper, chromium, cadmium, lead, zinc, arsenic, calcium, magnesium, sodium, potassium) [by ICP at UAB and by GF-AA at PSH]
- Nutrients (nitrate, ammonia, total nitrogen, phosphate, total phosphorus)
- Toxicity (Microtox™) on periodic PSH field samples


pH
pH
14
12
10
8
6
4
2
0
Corrugated PVC
Galvalume
Plywood (Untreated)
Pressure Treated Wood
Roofing Felt
Asphalt Shingles
Rubberized Roofing
CedarShakes
Corrugated Aluminum
Ondura
Water Sealed Wood

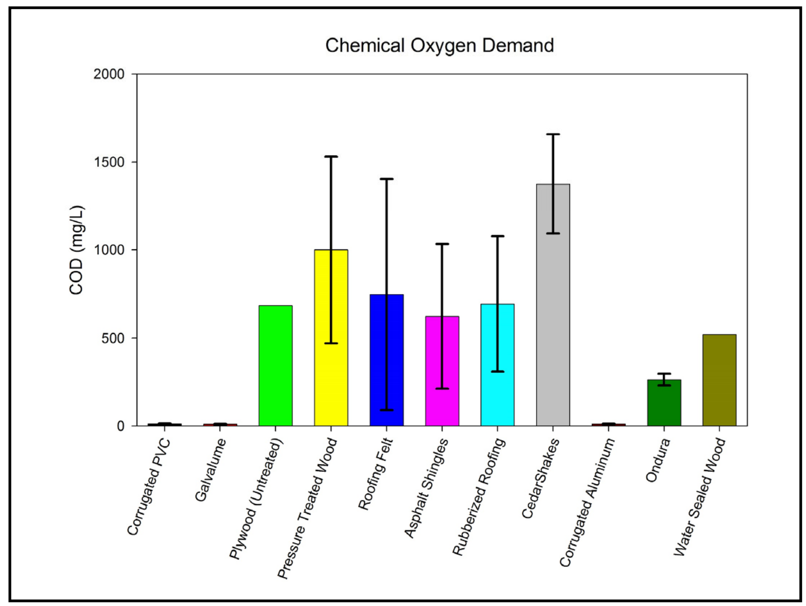
17


Conductivity
Conductivity (us/cm)
1200
1000
800
600
400
200
0
Corrugated PVC
Galvalume
Plywood (Untreated)
Pressure Treated Wood
Roofing Felt
Asphalt Shingles
Rubberized Roofing
CedarShakes
Corrugated Aluminum
Ondura
Water Sealed Wood

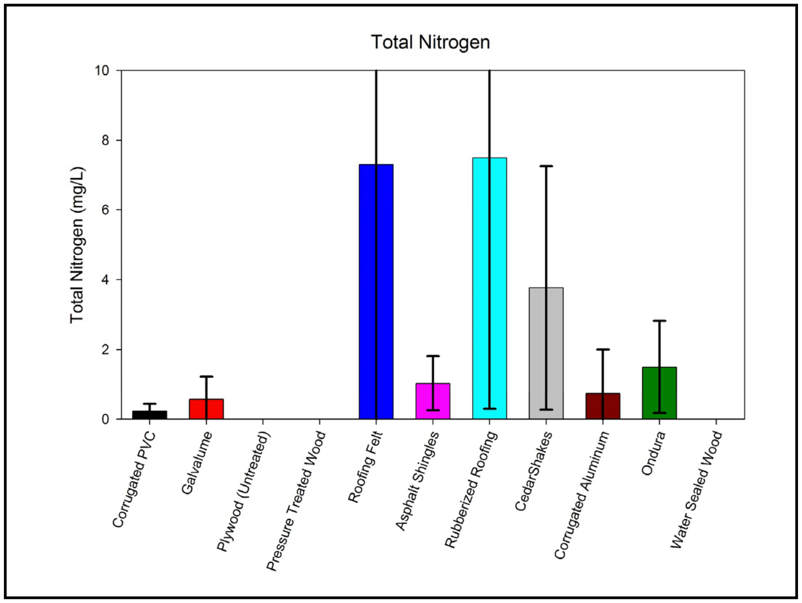
18


Semi-Volatile Organics
Concentration (µg/L)
350
300
250
200
150
100
50
0
White Plastic Roofing
Pressure Treated Wood
Fiberglass Roofing
Roofing Felt
Bis(2-ethylhexyl) phthalate
Butylbenzyl phthalate
Diethyl phthalate
Acenaphthylene

19


Chemical Oxygen Demand
COD (mg/L)
2000
1500
1000
500
0
Corrugated PVC
Galvalume
Plywood (Untreated)
Pressure Treated Wood
Roofing Felt
Asphalt Shingles
Rubberized Roofing
CedarShakes
Corrugated Aluminum
Ondura
Water Sealed Wood

20


Total Nitrogen
Total Nitrogen (mg/L)
0
2
4
6
8
10
Corrugated PVC
Galvalume
Plywood (Untreated)
Pressure Treated Wood
Roofing Felt
Asphalt Shingles
Rubberized Roofing
CedarShakes
Corrugated Aluminum
Ondura
Water Sealed Wood

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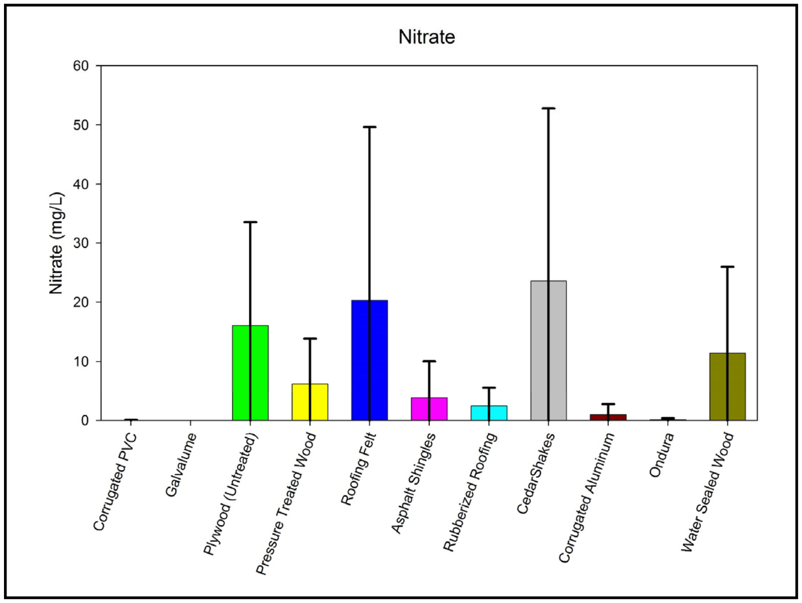
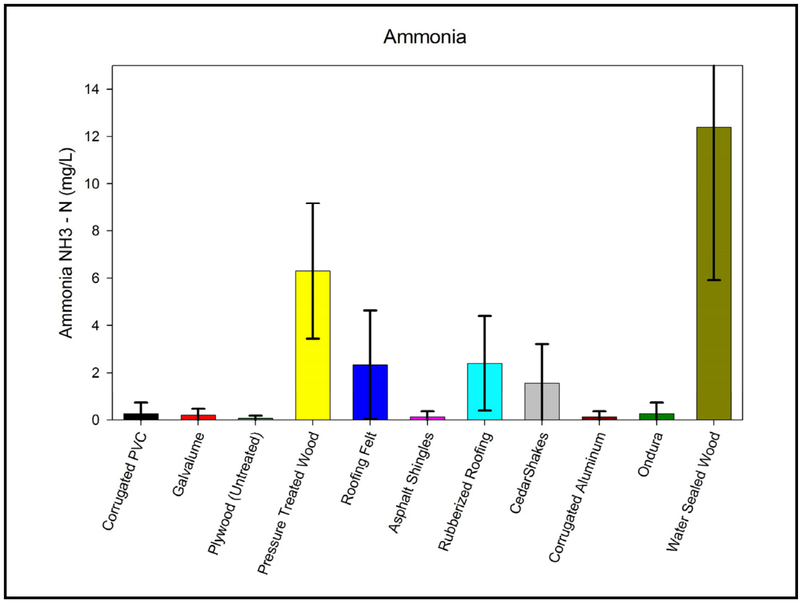
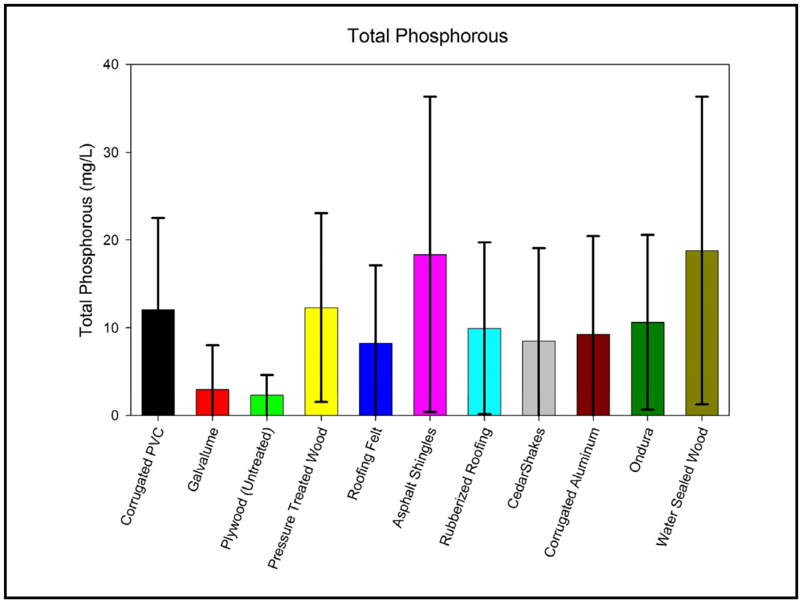

Nitrate
Nitrate (mg/L)
0
10
20
30
40
50
60
Corrugated PVC
Galvalume
Plywood (Untreated)
Pressure Treated Wood
Roofing Felt
Asphalt Shingles
Rubberized Roofing
CedarShakes
Corrugated Aluminum
Ondura
Water Sealed Wood

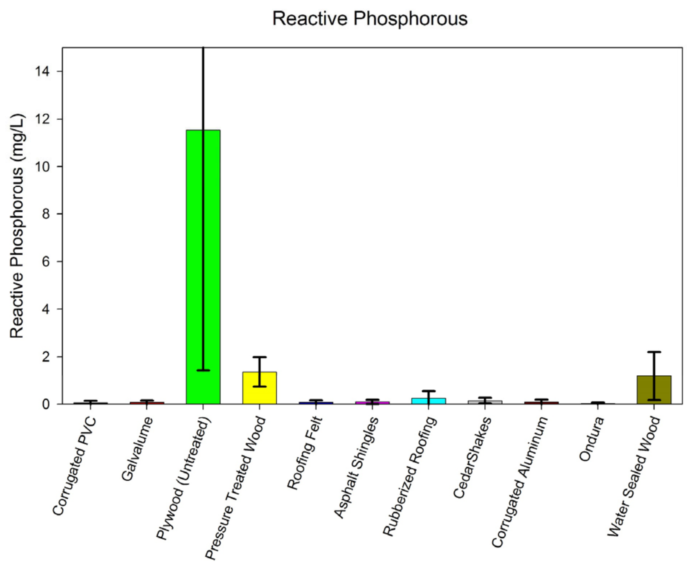
22


Ammonia
Ammonia NH3 - N (mg/L)
0
2
4
6
8
10
12
14
Corrugated PVC
Galvalume
Plywood (Untreated)
Pressure Treated Wood
Roofing Felt
Asphalt Shingles
Rubberized Roofing
CedarShakes
Corrugated Aluminum
Ondura
Water Sealed Wood

23


Total Phosphorous
Total Phosphorous (mg/L)
0
10
20
30
40
Corrugated PVC
Galvalume
Plywood (Untreated)
Pressure Treated Wood
Roofing Felt
Asphalt Shingles
Rubberized Roofing
CedarShakes
Corrugated Aluminum
Ondura
Water Sealed Wood

24



Summary of Initial Laboratory TCLP Tests

- Organics:
  - Most non-detects. Highest: roofing felt [bis(2-ethylhexyl) phthalate = 315 µg/L].
  - COD: Pressure-treated wood > Silver Dollar Aluminum Roofing Coating > Roofing felt.
- Nutrients:
  - Nitrate highest: roofing felt, the two woods, and Leak Stopper.
  - Ammonia high: galvanized metal and roofing felt.
  - Phosphate elevated: galvanized metal and Gardner Wet-R-Dri.
- Metals:
  - Copper highest in the two woods, followed by shingles and Silver Dollar Aluminum Coating (order of magnitude lower).
  - Lead highest: Leak Stopper.
    - Others high: Silver Dollar Coating and galvanized metal.
  - Zinc highest: galvanized metal (Zn is sacrificial cation).
  - Others elevated but four orders of magnitude less: waterproof wood, Leak Stopper, faux slate, and Kool-Seal White Acrylic.

- Aged roofing panels for both dissolution and TCLP:
  - 1 – 5 mg/kg of Cu
  - 1 – 10 mg/kg Cr
  - 30 – 70 mg/kg Pb.
  - Zinc 3 orders of magnitude higher than Pb (10 – 40 g/kg).
- Little difference noted between the rusted and non-rusted panels (testing on no-paint areas).
- Paint likely contributed Cr and Pb to leachate.
  - Overall Cr concentrations were higher when the painted panel was dissolved.
- Aged panels [simulated rainwater] had measurable releases of chromium, lead and zinc, although concentrations 2 – 4 orders of magnitude less than that released in TCLP test.
  - No Cu detected when panels exposed to simulated rainfall.
- Pollutant release in same TCLP tests (new and old material) showed similar results.

Results: Field Testing

- pH, conductivity, and COD values showed little variability between storms).
- Physical degradation of roofing panels, particularly the metal panels, is visible after two weeks of exposure.

Aged Roofing Panels

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Testing Set-Up at Penn State Harrisburg

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Testing Set-Up at UAB

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During Rain Storm, August 2005

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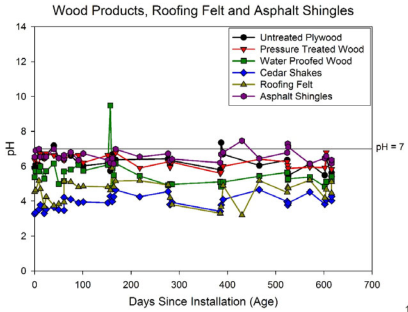
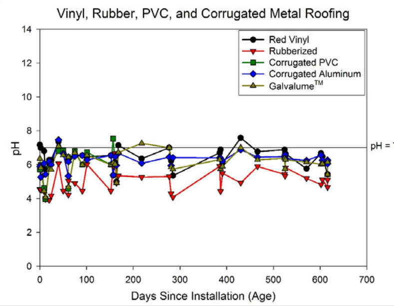
pH



Rainfall pH Range: 3.9 – 6.5

Cedar shakes, rubberized roofing, roofing felt runoff typically below pH 5.



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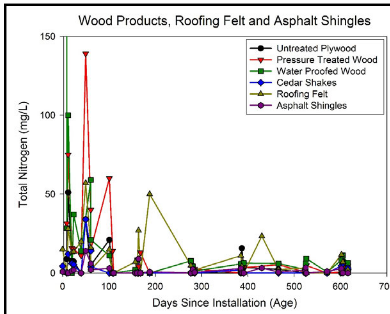
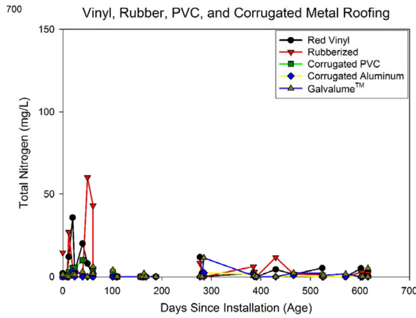
Total Nitrogen



Elevated early in water-proof wood (CCA+organic) and pressure-treated wood.

Concentration increases noted corresponding to visible degradation in some materials.



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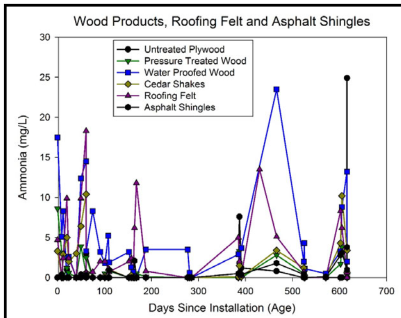
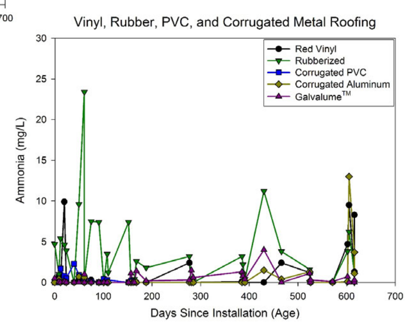
Ammonia



Concentration increases concurrent with visible degradation, especially in untreated plywood.



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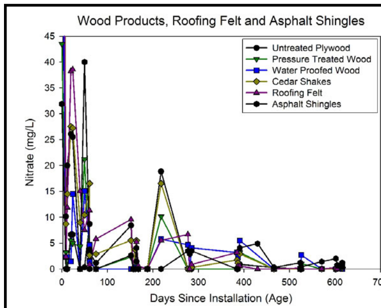
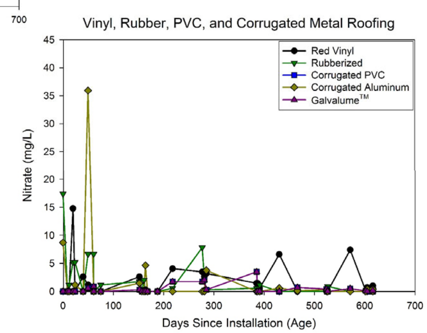
Nitrate



Elevated nitrate concentrations early.

Correlation with noted degradation at 40 – 50 days and at just over 200 days.

Currently at low background concentrations.



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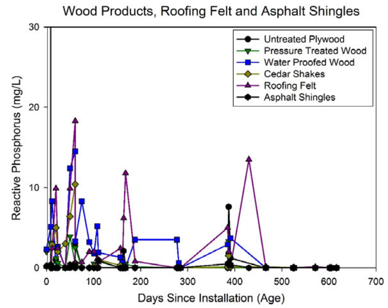
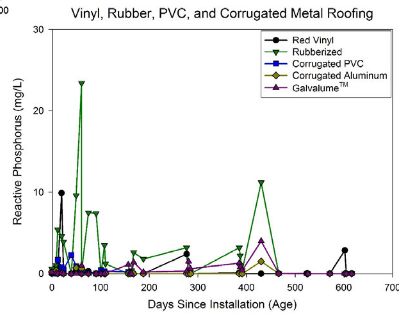


Reactive Phosphorus

Potential surface coating degradation for early spikes?

Leveling off to low background concentrations.



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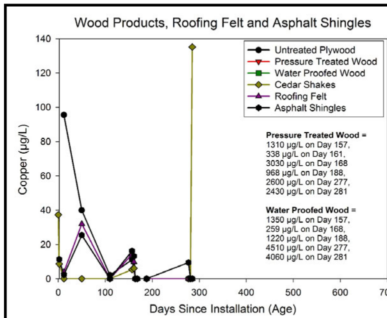
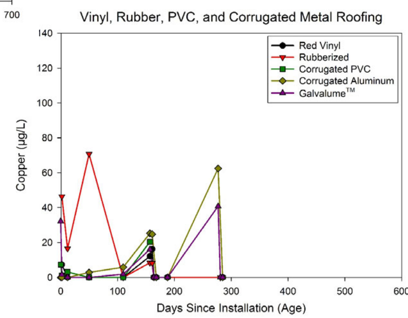


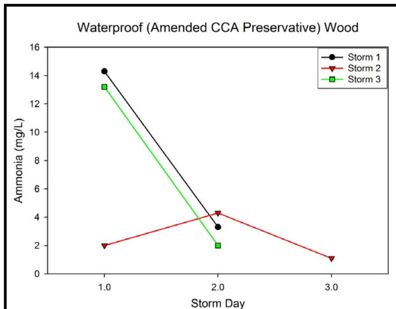
Copper

Elevated concentrations in pressure-treated woods. First 150 days, over-range (even with dilution) – potentially over 5 mg/L.

Low concentrations of As, Pb.

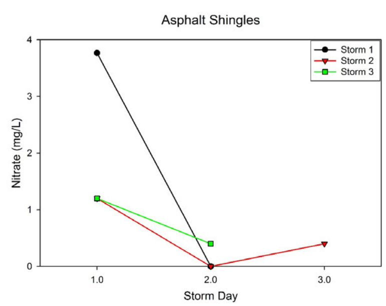


38



First Flush? If so, why?

First flush appears on some materials for some parameters. Initial concentration may not be related to age, but to other factors.



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Summary of Results of Outdoor Testing of Roofing Materials

- Minimal acid rain buffering in some materials.
- Nutrients – continuous release of nitrogen compounds; phosphorus release early but leveling off to background
- High early release of nitrogen – may be washoff or surface coating release
- Metals – lead and arsenic are very low, near background concentrations.
  - Arsenic was anticipated to be higher since copper is higher in the woods.
  - Copper elevated early in woods, possibly due to washoff of preservatives left on surface.
- First flush seen for some parameters and some materials.

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Outdoor Asphalt Aging Tests

Literature Review

In a study conducted by National Cooperative Highway Research Program on the impact of construction materials (asphalt and its additives) on surface and groundwater, individual components and the aggregates of the pavements were subjected to exposure and aging tests. Their conclusions were that:

- Although some construction materials caused high toxicity levels, this was reduced or eliminated when they were incorporated into the complete pavement assemblage.
- Leachate from short term aging and long term aging did not show any significant differences.
- Leaching reduces with time and that it is a function of wet weather hours, independent of dry weather. The toxicity of the leachate was found to reduce by photolysis, volatilization and degradation.

Azizian F. Mohammad et al., "Environmental impact of highway construction and repair materials on surface and groundwater", 2003.

- In 2005, parking lot sealants were identified as a major source of PAHs in Austin, TX runoff. Parking lots with coal tar based sealants were found to contribute 65 times more PAH mass in the runoff compared to unsealed parking lots.
- The sealing layer on these parking lots tends to wear off by vehicle use, with the crumbled seal coat losses producing up to 2,200 mg PAH/kg sediment of 12 PAHs, compared with 27 mg/kg from unsealed parking lots. *Parking Lot Sealant Identified as Major Contaminant* (USGS 2005) (http://www.usgs.gov/newsroom/article.asp?ID=718).
- This lead to various bans on coal tar based sealants in different areas of the US (Austin, TX, State of Washington).
- Most PAHs have a several year half-life for degradation in streams so immediate sediment quality improvement will not occur.

Asphalt Characteristics and Aging

- Asphalt is a viscoelastic material, a crude oil derivative and is obtained by controlled distillation of crude oil.
- It's a high molecular weight compound with complex structure and properties and its composition varies with the source of the crude oil. However, most asphalt contains about:
  - Carbon 82-88%
  - Hydrogen 8-11%
  - Sulfur 0-6%
  - Oxygen 0-1.5%
  - Nitrogen 0-1%

The Shell Bitumen Handbook, Fifth Edition, Thomas Telford Publishing ltd, London, 2003.

- Asphalt provides cohesion between the aggregate particles to maintain the integrity of the mixture in the road bed construction.
- Asphalt coats the aggregate particles and can also enter the pores and crevices of the aggregate.
- Aggregates have active sites for binding asphalt molecules at different levels. Their surface is frequently either fully charged or partially charged. Asphalt being a mixture of hydrocarbons that is organomettalic (contains nickel, vanadium and iron) and polar in nature gets attracted to the active sites on the aggregate surface.
- The bonds formed may include hydrostatic, electrostatic or Vander-Waal's forces.

Fundamental Properties of Asphalt-Aggregate Interactions Including Adhesion and Absorption, Strategic Highway Research Program, National Research Council, Washington DC, 1993

45

- Oxidation on the exposed surface of asphaltic pavements causes aging and the extent of aging is proportional to the surface area exposed (the surface and voids) to the atmosphere and the rate of diffusion of air into the pavement.
- The effect of aging is more rapid in the presence of light and air.
- The insoluble, condensation products formed as a result of the oxidation and the loss of volatile compounds from the pavements may effect the composition and the concentration of contaminants that leaches into the runoff with aging.

Fundamental Properties of Asphalt-Aggregate Interactions Including Adhesion and Absorption, Strategic Highway Research Program, National Research Council, Washington DC, 1993

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Method

- Three square pavement slabs were examined during this project.
- A Hot-mix asphalt pavement, freshly constructed and unsealed.
- A Warm-mix asphalt pavement, freshly constructed and unsealed.
- A Hot-mix asphalt pavement (two years old), freshly coated with asphalt sealant (coal tar sealant was to be tested also, but was not available for purchase in Alabama).
  - "Most consumer-grade sealers are water-based emulsions containing water, clay fillers, latex, polymers, additives and either coal tar (a byproduct of baking coal to make coke) or asphalt (a byproduct of petroleum refining). Some so-called "asphalt" emulsions also contain some coal tar" (http://www.naturalhandyman.com/iip/infdrivewaysealer/infdrivewaysealer.html).

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- The standard test slabs have a surface area of 0.25 m^2 and are 5 cm thick, prepared for this project by the National Center for Asphalt Technology (NCAT), at Auburn University, in Auburn, AL.
- The pavement slabs were set up outdoors and exposed to sun and rains, therefore being aged under natural conditions.
- An equivalent 0.5 in rain (using prior collected roof runoff) was used to obtain runoff on each of the pavement slabs periodically during the exposure perios.
- The resulting runoff was analyzed for contaminants and toxicity levels.

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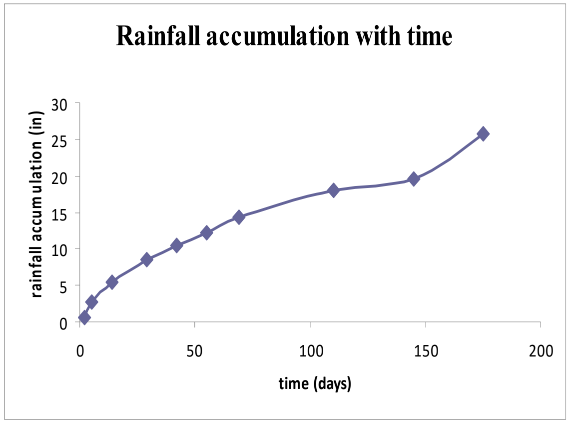
Natural rainfall accumulation during the project period



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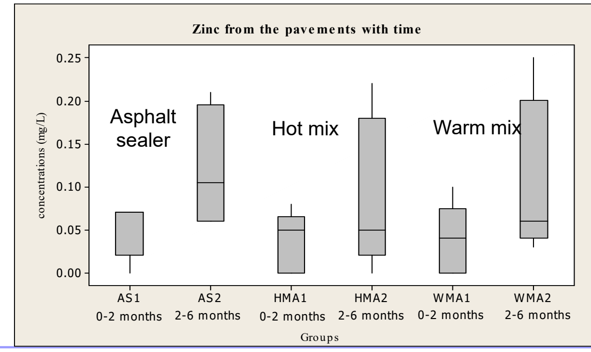
Zinc Concentrations in Pavement Runoff



- The runoff was analyzed for Pb, Cu, Cr, Zn and Cd.
- Cd and Cr always below the detection limits in all samples. Pb was detected for one sampling event.
- Zinc showed an increasing trend with the aging of the pavement from the samples, with the highest concentrations being 250 µg/L, 220 µg/L and 210 µg/L from HMA, WMA and AS respectively after the 6 month aging period.

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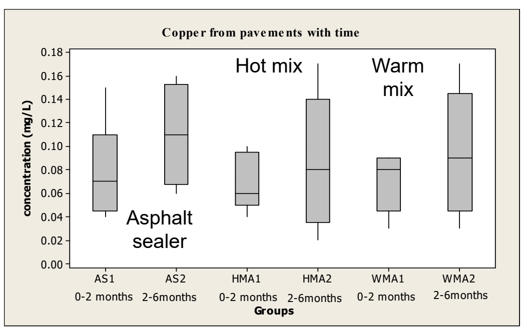
Copper Concentrations in Pavement Runoff



Cu release from the pavements showed a weak increasing trend with the highest concentrations being 170 µg/L, 170 µg/L and 160 µg/L for the final sample at the end of 6 months of aging of the pavements.

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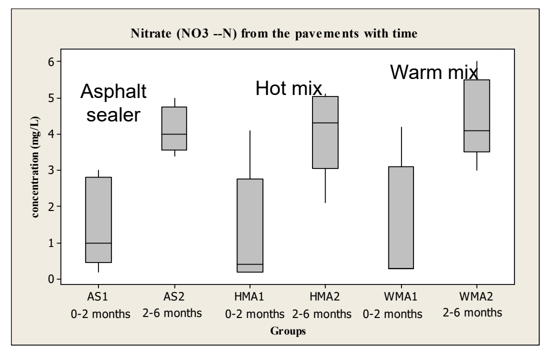
Nitrate Concentrations in Pavement Runoff



Mann-Whitney test results for loss of Nitrate	
Asphaltic Sealant (AS)	0.020
Hot Mix Asphalt (HMA)	0.037
Warm Mix Asphalt (WMA)	0.060

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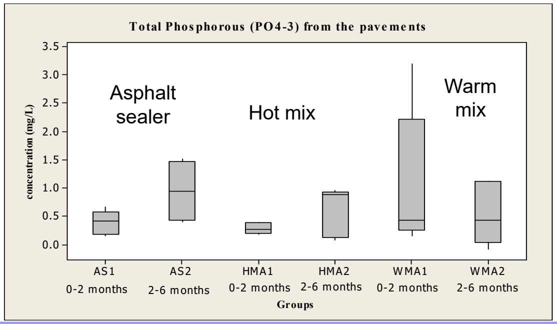
Phosphate Concentrations in Pavement Runoff



Mann-Whitney test results for loss of total phosphorous	
AS	0.178
HMA	0.465
WMA	0.676

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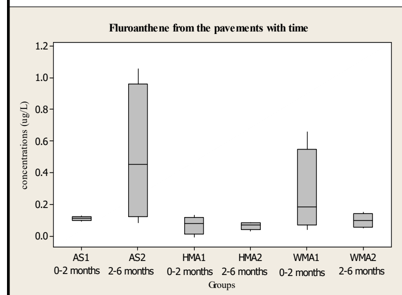
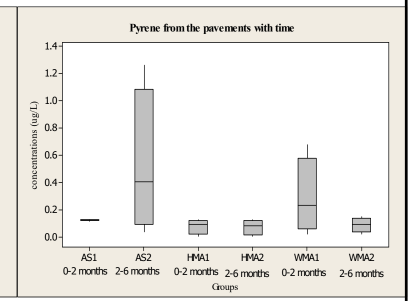
PAH Concentrations in Pavement Runoff

The Kruskal-Wallis test showed p values <0.1 for the following PAHs Acenapthene, fluoranthene, pyrene, benzo(k)fluoranthene, and benzo(ghi)perylene indicating an apparent difference in groups.





The PAH concentrations in the pavement runoff samples were very low (most less than 1 µg/L).

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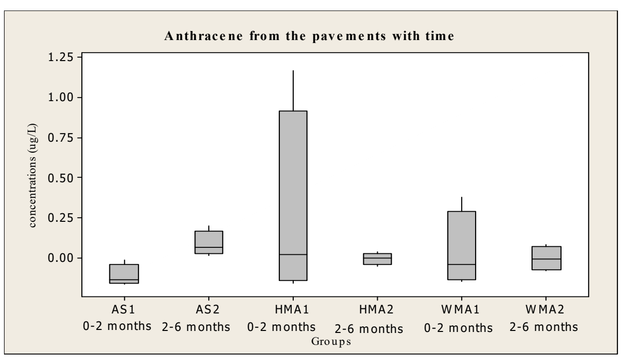
No significant differences were observed for the remainder of the PAHs analyzed based on the Kruskal-Wallis one-way ANOVA tests. However a Mann-Whitney test on the two exposure periods showed a significant difference for Anthracene.



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Laboratory Material Leaching Tests

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Objectives

- The purpose of this research was to investigate how the range of drainage system and tank materials, water characteristics, and exposure times affect heavy metal releases during controlled tests examining the expected range of these contaminants, and their toxicity.
- This research quantified the concentrations of these contaminants from different pipe and gutter materials for different conditions and predicted the forms of the leached metals.
- To determine which materials can be used during long exposures, such as for storage tanks, and which are suitable for drainage components (short exposures) and to identify conditions under which certain materials are to be avoided.

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Materials and Methods

- Two series of long-term leaching laboratory tests were conducted.
  - Eight gutter and pipe materials
- First series of experiments were conducted to investigate the heavy metal releases under two different controlled pH conditions.
  - Roof runoff and parking lot runoff were collected in the city of Tuscaloosa and adjusted to pH 5 and pH 8 values.
  - Disodium phosphate dehydrate and potassium phosphate monobasic ($Na_2HPO_4 * 2H_2O$ and KH_2PO_4) were used to create buffers.
  - Waters had high phosphate and high conductivity values from the buffers.

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- During the second testing stage, materials were immersed into un-buffered waters from Mobile Bay (saline) and the Black Warrior River (fresh water).
  - pH values approximately 8.
- 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.

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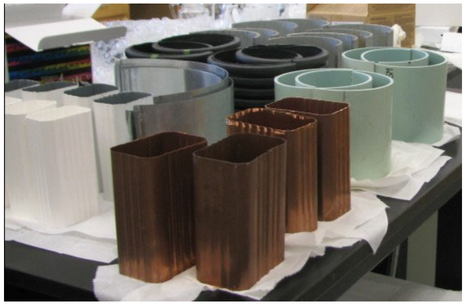
Gutter and Pipe Materials

- Gutter Materials: vinyl, aluminum, copper, and galvanized steel.
- Pipe Materials: concrete, HDPE, PVC, and galvanized steel.



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- New materials
- Concrete pipes - 15 cm long
- The rest of pipes - 30 cm long

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Materials and Methods

- Sampling times:
  - First testing stage: time zero (buffered water without pipes), 0.5 hr, 1 hr, 27 hr, 1 mo, 2 mo, 3 mo
  - Second testing stage: time zero (un-buffered water without pipes), 1 hr, 27 hr, 1 week, 1 mo, 2 mo, 3 mo
- Measured Constituents:
  - Metals (cadmium, chromium, lead, copper, zinc)
  - Toxicity (Microtox)
  - pH, conductivity, Eh
  - Selected samples were also analyzed for nitrogen compounds (ammonia nitrogen, total nitrogen, nitrate), aluminum, iron, phosphorus (only for non-buffered 2^{nd} test series), sulfates, chlorides, and COD.
- Number of Analyses:

16 test chambers * 2 test phases * 6 time periods = 192 samples

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Quality Control/Quality Assurance

- pH values with time in the containers were monitored.
- Metal analysis and associated laboratory quality control procedures were performed by Stillbrook Environmental Lab, in Fairfield, AL using inductively coupled plasma mass spectroscopy (ICP-MS).
- The labware preparation and sample storage and preservations requirements that were followed were from Eaton, *et al.* (2005) and Burton and Pitt (2002).
- The UA instruments were calibrated prior to each data collection (pH meter, conductivity meter).
- At UA, standards were run simultaneously with the samples for nutrient and toxicity analyses to confirm the instrument performance, and methods blanks were used.

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Statistical Analysis Components for Model Development

1
- Time Series plots
  - To illustrate metal release with exposure time.

2
- Spearman Correlation
  - To identify simple relationships between water quality parameters and contaminants

3
- Principal Component and Cluster Analysis
  - To evaluate complex associations between water quality parameters and contaminant releases and to identify groupings of samples with similar characteristics

4
- Full Factorial Analyses
  - To determine significant factors and their interactions on pollutant releases

5
- Empirical models were developed
  - to predict pollutant releases for different materials and uses, water types and exposure times.

6
- Chemical Modeling
  - To identify different chemical speciation and associations under different conditions and exposure periods

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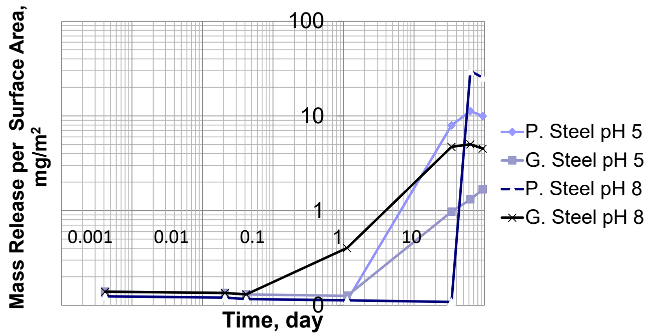
Lead Mass Release per Surface Area of Pipe/Gutter in Containers with pH 5 and pH 8



- ❑ Galvanized steel materials were the only source of lead released during both short and long exposure times.
- ❑ The loss of lead was higher for samples under pH 8 conditions compared to samples under pH 5 conditions.
- ❑ The highest lead concentrations were observed for galvanized steel pipe under pH 8 conditions and reached as high as 0.63-0.71 mg/L (corresponds to 25– 30 mg/m²).

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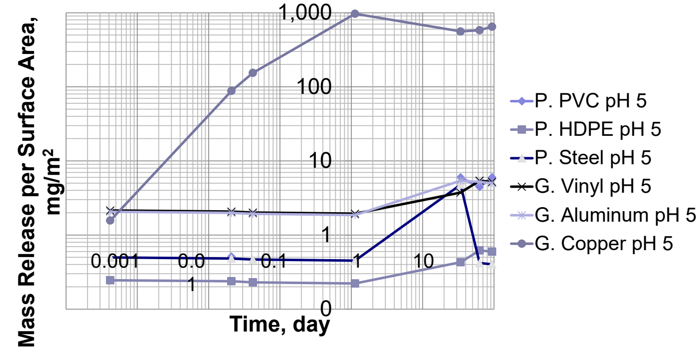
Copper Mass Release per Surface Area of Pipe/Gutter for Containers with pH 5



- ❑ The greatest copper concentrations were detected in containers with copper materials. 27 hr exposure resulted in copper releases exceeding 6 mg/L (up to 970 mg/m²).
- ❑ Copper releases were also found in containers with other materials, but at much lower concentrations.

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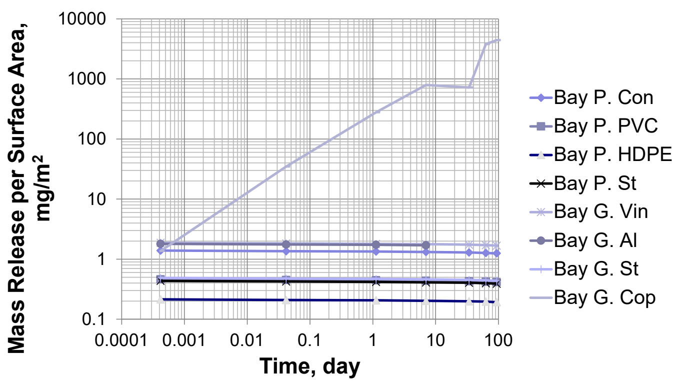
Copper Mass Release per Surface Area of Pipe/Gutter for Containers with Bay Water



- ❑ Copper materials resulted in very high copper concentrations.
- ❑ After 3 months of exposure copper concentrations reached 36 mg/L (corresponds to 4,400 mg/m²)
- ❑ The highest copper concentrations were detected in bay water samples compared to the other water conditions.

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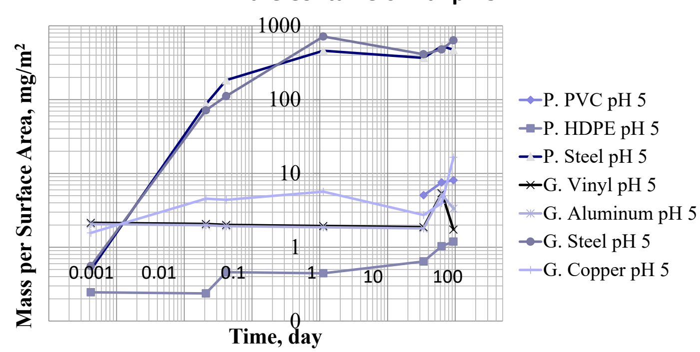
Zinc Mass Release per Surface Area of Pipe/Gutter in the Containers with pH 5



- ❑ The greatest zinc concentrations were detected for galvanized steel material exposures
- ❑ Copper materials were the second highest source of zinc loss
  - -Reached 0.13 mg/L (16 mg/m²) after long time exposure
  - -Higher losses at pH 5 compared to pH 8 conditions
- ❑ Concrete and Plastic materials were the lowest source of zinc

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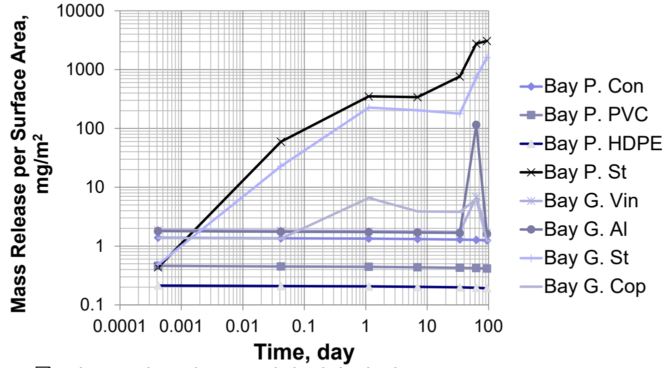
Zinc Mass Release per Surface Area of Pipe/Gutter for Containers with Bay Water



- ❑Galvanized steel materials had the highest zinc concentrations
  - ❑After 3 months of exposure, the zinc concentrations exceeded 78 mg/L (corresponds to 3,100 mg/m^2).
- ❑Zinc losses were greater under bay water conditions compared to controlled pH 5 conditions.

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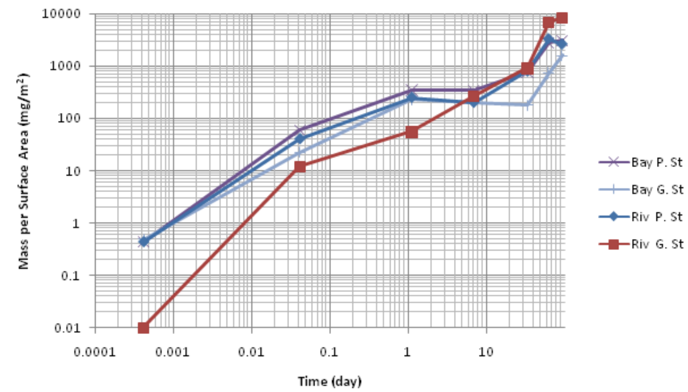
Zinc Mass Release per Surface Area of a Pipe/Gutter in the Containers with Bay and River Waters



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Spearman Correlation Tests

Examined correlations between:

- pH and metal releases
- pH and toxicity
- Metal releases and toxicity
- Conductivity and metal releases
- Conductivity and toxicity
- Exposure time and metal releases
- Exposure time and toxicity
- Were used to identify factors to include into factorial analyses.

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Spearman Correlation Matrices

- Determine the associations between the constituents for the samples collected during controlled and natural pH tests.
  - Pb, Cu, and Zn concentrations
  - pH
  - Conductivity
  - Toxicity of the samples at 5, 15, 25, and 45 min of bacteria exposure
  - Time of material exposure to the experimental water
  - For each pipe and gutter material.

Example: Galvanized steel pipe during the natural pH tests

	Pb	Zn	pH	Cond.	Tox. 5min	Tox. 15min	Tox. 25min	Tox. 45min	Time
Pb		-0.175	0.413	-0.406	-0.508	-0.462	-0.462	-0.427	-0.496
Zn			-0.0699	0.000	**0.853**	**0.846**	**0.846**	**0.860**	**0.905**
pH				**-0.902**	-0.399	-0.399	-0.399	-0.413	-0.0283
Cond.					0.392	0.399	0.399	0.399	0.000
Tox. 5min						**0.986**	**0.986**	**0.972**	**0.862**
Tox. 15min							**1.000**	**0.986**	**0.820**
Tox. 25min								**0.986**	**0.820**
Tox. 45min									**0.806**

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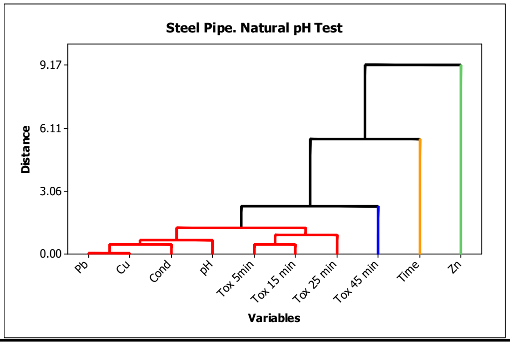
Cluster Analyses

- For each pipe and gutter material using the data for buffered and natural pH tests.
- For the same data that were used to compute the correlation matrices
- To identify more complex relationships between the parameters.

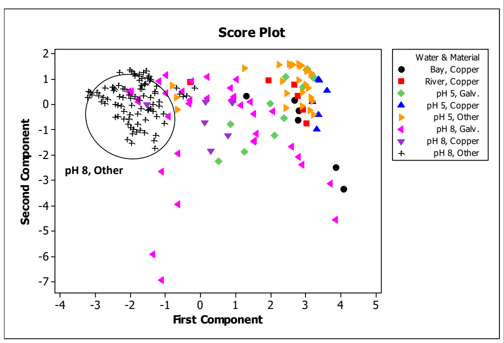


Cluster Analyses Conclusions

- pH and time of exposure affected the Pb, Cu, and Zn releases.
- Pb, Cu, and Zn concentrations were highly correlated with conductivity for all materials.
- Metal releases, conductivity, pH, and time of exposure all influence the toxicity.

Principal Components Analyses

- PCA was performed for all samples
- Score plot of the first two Principal Components shows groupings of samples having similar water quality characteristics.
- 1st PC (toxicity) accounts for 57% of the total variance in the data.
- 2nd PC (Pb, Zn, and time) accounts for the next 12% of the total variance.



Circled group:

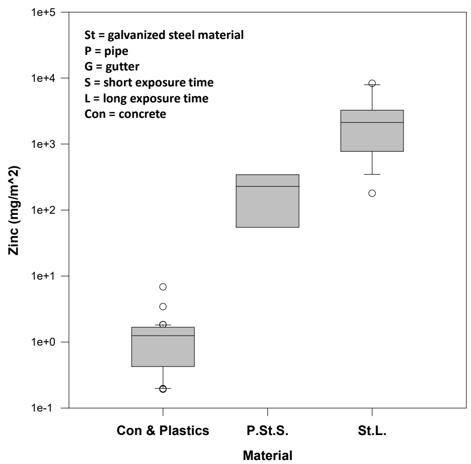
- Mostly concrete, PVC, HDPE, vinyl, and aluminum materials under controlled pH 8 conditions
- Low loadings of toxicity and metals

Factorial Analyses for Material Exposures

- Used during the first testing stage to estimate the effects of:
  - Exposure time (short and long)
  - pH value (5 and 8)
- Used during the second testing stage to evaluate the effects of:
  - Exposure time (short and long)
  - Salinity (high and low)
- The factorial analyses were used to identify the significant factors and their interactions.
- Conducted several series of 2^2 and 2^3 Factorial Analyses to isolate missing conditions that were impossible to obtain (such as low pH and low conductivity).

Group Box Plot for zinc releases (mg/m²) for various gutter and pipe materials immersed in bay and river waters.

- Zinc releases were the largest from galvanized steel materials.
- As the exposure time increased, the zinc releases also increased.
- During long exposure times, there was no difference between galvanized pipe and gutter samples.
- The box plot for other materials represents all the data combined (for bay and river waters and for short and long exposure times).



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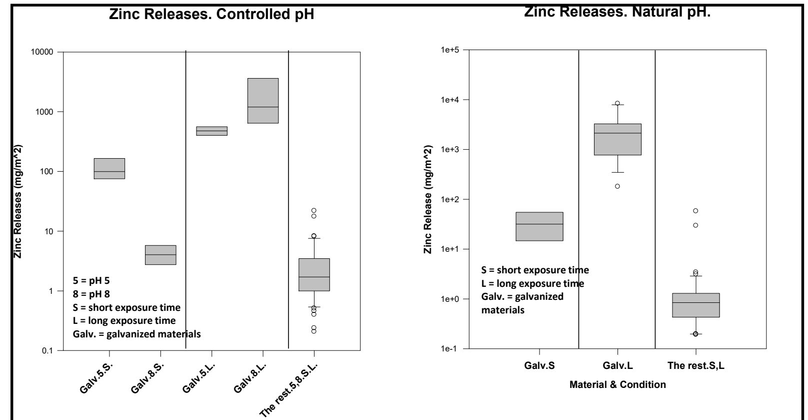

- Galvanized steel materials were the greatest source of zinc.
- Exposure time increased zinc releases in the samples with galvanized materials.
- Under controlled pH conditions, pH 5 conditions increased zinc releases from galvanized materials; zinc releases were also high for combination of pH 8 and long exposure times.
- Under natural pH conditions, the combination of galvanized materials and long exposure times significantly increased zinc releases.

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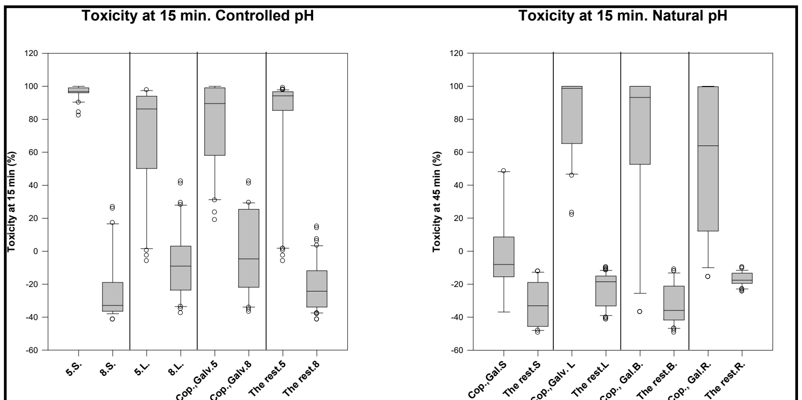

- Low pH conditions increased the toxicity effect.
- Under controlled pH conditions. pH had greater effect on toxicity. pH 5 conditions resulted in toxicity values approaching 100%. Concrete, plastic, and aluminum materials immersed in pH 8 water produced conditions that were the least toxic.
- Under natural pH conditions (pH ranged between 6.93 and 9.33), material had greater effect on toxicity. Copper and galvanized materials resulted in significant toxicity increases. Concrete, plastic, and aluminum materials resulted in the least toxic conditions.

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Model Fitting using Linear Regression

Objective:

- To predict metal releases from the exposure times for all test conditions.
- The regression requirements (normally distributed, zero mean, constant variance, independent) revealed that first order polynomials can be fitted to the log of metal releases vs. log of time.

Conducted on:

- For different pipe and gutter materials under controlled and natural pH conditions.
- Metals: Cu, Zn, Pb

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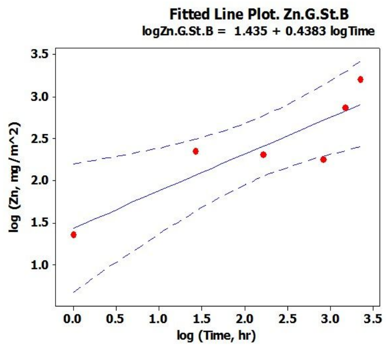
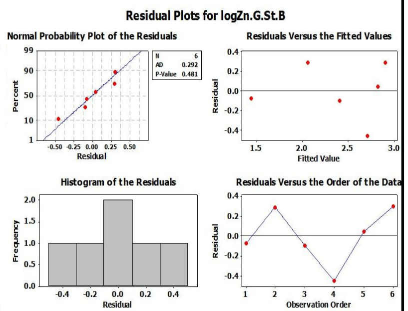
Zinc releases from galvanized steel gutter material immersed in bay water





- ANOVA analyses tested the significance of the slope and intercept terms and the overall model.

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Model for Galv. Steel Pipe under Natural pH Conditions

- Quantifying the expected contaminant releases

Constituent	Galvanized Steel Pipe. Natural pH Conditions				p-value
Pb, mg/m²	S.B.: Avg.= 0.4 (COV = 0.22)	S.R.: Avg.= 0.1 (COV = 0.02)	L.B.: Avg.= 0.1 (COV = 0.02)	L.R.: Avg.= 0.42 (COV = 0.79)	0.014 (for Cond.*Time)
Cu, mg/m²	ND in bay and river waters				
Zn, mg/m²	S.: Avg.= 208 (COV = 0.65)		L.: Avg.= 2230 (COV = 0.51)		0.002 (for Time)

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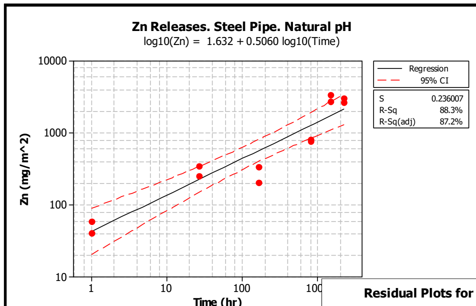

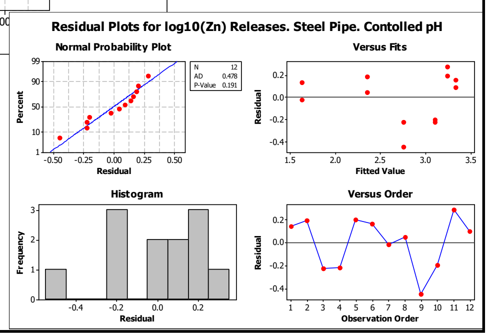

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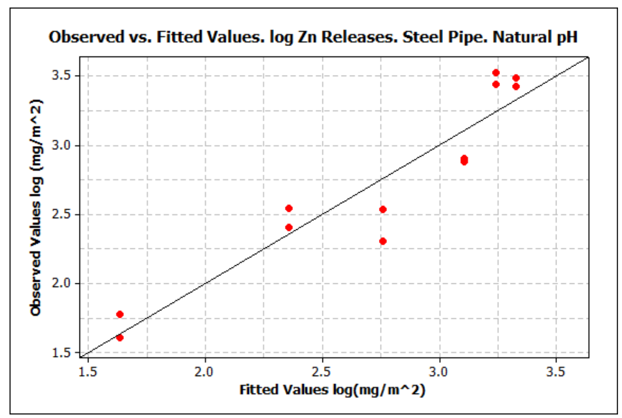
Zn Releases from Steel Pipe. Natural pH



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Water Chemistry Modeling using Medusa Software

- The Langelier Index
  - To determine whether the water was in equilibrium with $CaCO_{3(s)}$ and to detect the presence of protective calcium coatings.
- Log Concentration- pH, Fraction, and Eh-pH Diagrams and Medusa Modeling
  - To determine the forms of the metal species

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Chemical Speciation Modeling

Objective:

- To predict the forms of the measured metals and to predict the relative toxicities and treatabilities of the different metallic compounds and ionic species likely present.

Performed for:

- Time zero (without sample), 1 day of exposure (representing rain storm event and applicable to gutter and pipe materials), and 3 months of exposure (for tank materials).
- For different pipe and gutter materials under controlled and natural pH conditions.
- Diagrams and summary tables were made for the Zn, Cu, and Pb contaminants

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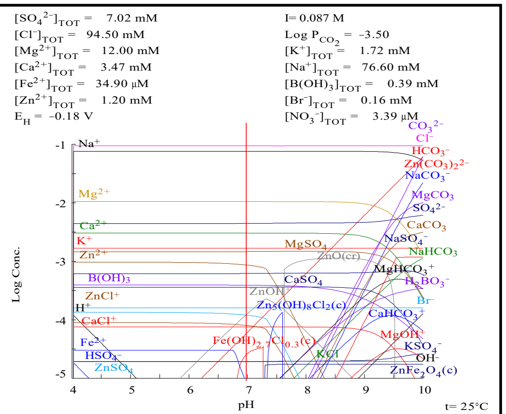
Phase diagram for steel pipe immersed in bay water after 3 mo. of exposure

- Shows the species of metals present and their concentrations.

The predominant species table

- Shows the predominant forms of Zn species that account for 99.9% of total metal concentration



Component	Log Concentration (mol/L)	Concentration (mol/L)	Zn Concentration (mg/L as Zn)	Cumulative Percentage of Zn
Zn^{2+}	-3.06	8.64E-04	56.48	71.96
$ZnOH^+$	-3.91	1.22E-04	7.96	82.09
$ZnSO_4$	-3.92	1.20E-04	7.86	92.11
$ZnCl^+$	-4.10	8.02E-05	5.24	98.79
$ZnCl_2$	-5.31	4.88E-06	3.19E-01	99.19
$Zn(SO4)_2^{2-}$	-5.36	4.32E-06	2.82E-01	99.55
$ZnHCO_3^+$	-5.63	2.32E-06	1.52E-01	99.75
$ZnCO_3$	-5.89	1.29E-06	8.45E-02	99.85
$Zn(OH)_2$	-5.94	1.15E-06	7.51E-02	99.95

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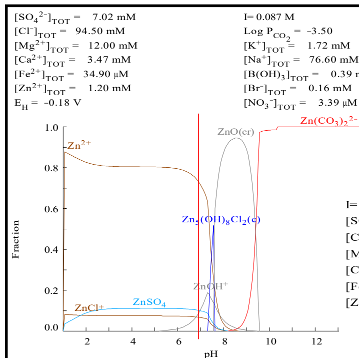
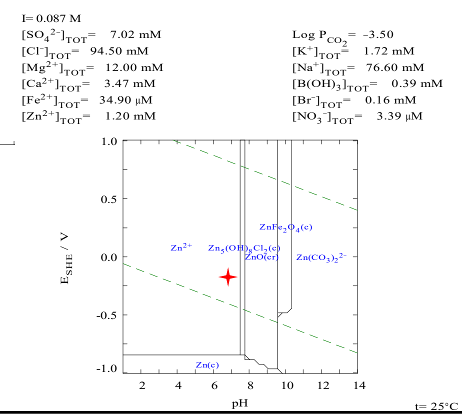


Fraction and Pourbaix diagrams of Zn for steel pipe immersed into bay water after 3 months of exposure



- Fraction and Pourbaix diagrams show the predominant species of metals and their concentrations.

Water Chemistry Modeling Conclusions.
Heavy Metal Treatability

- Medusa results showed that the valence states of the modeled metal species varied widely from being strongly charged (-2 to +2) to zero valence.
- As an example, for the predominant Zn^{+2} species, ion exchange may be an effective treatment method.
- Strong cation exchange materials include peat.

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The Langelier Index

Calculated to determine:

- Whether the leaching water for the concrete materials was in equilibrium, oversaturated, or undersaturated with respect to $CaCO_{3(s)}$. Langelier Index indicates whether concrete samples will deteriorate as a result of $CaCO_{3(s)}$ dissolution from the concrete.
- Whether $CaCO_{3(s)}$ that is present in the water will precipitate and form scale that may protect most type of material from corrosion.
- The waters in the containers with concrete pipes under pH 5 and pH 8 conditions were undersaturated with respect to $CaCO_{3(s)}$
  - the waters would have a tendency to dissolve $CaCO_{3(s)}$ from the concrete. Minor pitting of concrete pipes at pH 5 was observed.
- The waters in the containers with concrete pipes under natural pH conditions were oversaturated with respect to $CaCO_{3(s)}$
  - waters in these samples had a tendency to precipitate $CaCO_{3(s)}$ from the solution and there was no degradation of the concrete pipe after 3 months of exposure.
  - For bay and river waters, all the samples were oversaturated with respect to $CaCO_{3(s)}$ with the exception of steel pipe and gutter samples.

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Conclusions and Recommendations

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Roofing Material Test Conclusions

- Materials with metallic preservatives or metal skin coatings leached more of the measured metals. Treated woods contributed Cu significantly more than any other material.
- Nutrient concerns are primarily from organic products, unless it is known that there are concerns due to specific ingredients (such as a binder that contains nitrogen or phosphorus).
- Installation practices such as exposing cut edges and use of sealers may impact the temporal pattern of pollutant release from these materials.

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- pH: All samples had runoff pH between 5 – 6.5, except for roofing felt, rubberized roofing, and cedar shakes (all of which had runoff pH < 5).
- Wood panels, both treated and untreated, had high conductivity and COD levels.
- Roofing felt, cedar shakes, and water-proof wood highest nitrate concentrations. Water-proof wood also had high ammonia releases.
- Asphalt shingles yield total phosphorous levels four times greater than any other roofing panels, whereas untreated plywood generated elevated average phosphate levels.

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Asphalt Exposure Test Conclusions

- Zn and Cu were the only heavy metals that were detected in the runoff. They both had apparent concentration **increases** with exposure time for all samples. Pb was detected at only one sampling point. (Cr, Cd were not detected in any of the pavement runoff samples).
- Nitrates also had apparent concentration **increases** with exposure time for all samples. The phosphate changes were mixed and not very apparent.
- The PAH concentrations were very low (generally <1 µg/L). The asphaltic sealed pavement sample was the only sample showing apparent PAH concentration changes (**increases**) with time.

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- No obvious patterns were observed for the detergent concentrations (ranged between 0.25 to 1 mg/L).
- The apparent concentration changes observed were all increases with exposure time (most evident with the asphaltic sealer sample), while most literature indicated concentration decreases with aging. The six month test period was relatively short compared to pavement life and these results may indicate an initial increase in these contaminant releases before subsequent decreases in runoff concentrations.

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Asphalt Degradation References

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- *Colloid Chemistry of Asphalts* by Charles Mack.
- *Fundamental Properties of Asphalt-Aggregate Interactions Including Adhesion and Absorption*, Strategic Highway Research Program, National Research Council, Washington DC, 1993.
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- Pal Zakar, "Physical and Chemical Characteristics," in *Asphalt*, Chemical Publishing Company, Inc., New York, 1971.
- Usmani M. Arthur, "Oxidation of Asphalt Fractions," in *Asphalt Science and Technology*, Marcel Dekker Inc., 1997.

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Asphalt Degradation Test Recommendations

- Further research could be conducted with aged materials in order to investigate metal releases and toxicity under different water conditions for comparison with the results with the new drainage and piping materials.
- For the factorial analysis, midpoints could be used to determine the shape of the resulting response surface.
- Many other building materials also need similar testing to identify the role of material selection on stormwater quality (such as asphalt, along with building siding and fencing materials, for example). The benefits of coatings on the materials to reduce pollutant degradation and material damage should also be investigated.

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Drainage Material Exposure Test Conclusions

- 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 safely 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 and toxicities.

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Acknowledgements

- This research summarized here is from many different research projects and graduate student theses and dissertation. This work was partially supported from the NSF EPSCoR program and the U.S. EPA (Environmental Protection Agency), Urban Watershed Management Branch, Edison, NJ.
- Dr. Shirley Clark's research group at Penn State – Harrisburg conducted much of the early work on roofing material metal degradation.
- The Civil, Construction and Environmental Engineering Department, The University of Alabama, Tuscaloosa, also provided partial support to the many graduate students that participated on these projects.

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