Environmental Performance of Treated Wood Cooperative

Eighth Annual Report

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Personnel

Matthew J. Konkler, Acting Director, Faculty Research Assistant

About Acting Director

Many of you do not know me as I have been in the background designing and performing many of the tests. I am originally from Ohio and hold a B.S. in Environmental Science and an M.S. in the same area. Prior to coming to OSU, I worked for a consulting firm managing the collection of environmental samples. I have an extensive background in analytical chemistry, environmental monitoring, modeling, wood science, and durability.

Since joining OSU over five years ago, I have worked hard to improve the analytical capabilities of my group in the areas of organics analysis and have been involved in virtually every area related to preservative treatments and their potential environmental effects.

I look forward to working with each of you in the coming years and appreciate your willingness to support my work through the coop.

TABLE OF CONTENTS

Executive Summary

The Environmental Performance of Treated Wood Research Cooperative (EPTW) was established to improve knowledge related to the use and disposal of treated wood. The Coop has been active in a number of areas; progress on each will be reviewed below.

We have completed all of the waterborne BMP tests with the exception of one micronized copper azole formulation with southern pine. Micronized copper was not in the AWPA standards at the time we initiated these tests. Hem-fir lumber will also be treated with both formulations of micronized copper so we can begin BMP testing shortly. The remaining trials show that BMP processes do differ in their ability to limit metal migration. Similar trials with pentachlorophenol treated material show that steaming reduces subsequent penta losses. Finally, tests on steaming of creosote treated wood show that longer steaming periods produce a more beneficial effect. All of these data were used to modify the current BMP processing guidelines to make sure that the most appropriate processes are coupled with each preservative system.
Field trials in our test pond continue to show that metal and polycyclic aromatic hydrocarbon levels are elevated immediately adjacent to the treated wood but decline within 0.3 to 0.9 m away. These results are consistent with previous trials and we have submitted a paper to the Journal of Environmental Science and Pollution for publication.

Field trials on a bridge containing both penta and copper naphthenate treated wood are complete. Both preservatives were detected in runoff, however, modeling these data with available stream flow measurements indicated that concentrations never approached the minimum effects levels. The results also illustrate how the Environmental Assessment Modeling Tool can be used to predict the risk of exceeding minimum effects levels under varying stream conditions. We have submitted a paper describing these data to the journal of Hölzforschung. We will continue to periodically monitor this site to determine if migration rates change as the wood weathers. We are seeking additional projects to monitor and have plans to sample a number of bridges in the Minneapolis, MN area this spring.

Trials of polyurea coatings continue to show that the barrier is highly effective at limiting metal migration into surrounding seawater. We have also removed portions of the coating to evaluate how much damage can occur before metal levels become a concern and necessitate repair. We will continue to apply increasing amounts of damage to identify a threshold and initiate a more controlled test using freshly-coated pilings.

We have established tests to monitor the levels of wood particles or fibres that are eroded from decks in service. The loss of fibres due to normal foot traffic has been raised as a possible source of elevated preservative migration in decks over aquatic environments. The samples are in a public foot bridge and mass loss will be used as an indirect measure of fibre loss.

The EPTW website now hosts the Environmental Assessment Modeling Tool, following its update by Western Wood Preservers Institute (WWPI). We have had a number of inquiries about how to use the model. While further workshops are planned, efforts are also underway to create videos so that the materials can be more widely distributed without the need for extensive travel. In general, users find the new model much easier to use.

INTRODUCTION

Treated wood is widely used in a variety of environments and has a well-known ability to markedly extend the service life of products, thereby reducing the need to harvest additional trees. At the same time, however, the chemicals used to protect wood from degradation are toxic at some levels and all are known to migrate, to some extent, from the products treated with these chemicals into the surrounding environment. The concerns about this migration are highest in aquatic environments where the potential toxic effects are greatest. Previous studies have shown that the levels of migration are generally low and predictable, and the Environmental Assessment Modeling Tool has been developed to predict the rates of migration from various treated wood commodities under a range of conditions. The treating industry also uses modified production procedures, Best Management Practices (BMPs), for some site-specific applications to improve the quality of these products, to reduce the presence of surface deposits, limit over-treatment, and, as far as practical, produce products with a reduced environmental footprint. While these actions have proven useful, there are few data demonstrating the benefits of these procedures and a continuing need to better understand the environmental behavior of treated wood products. The Environmental Performance of Treated Wood Cooperative (EPTW) was established to help develop data on the performance of treated wood, beginning with aquatic applications. The program is an extension of studies begun by Dr. Kenneth Brooks of Aquatic Environmental Sciences (Port Townsend, WA).

OBJECTIVES

The overall goal of the EPTW is to develop knowledge that improves the ability to use and dispose of treated wood in a safe and environmentally sensitive manner. This goal is being addressed through the following objectives:

1. Develop fundamental data on preservative migration from wood
2. Develop standardized accelerated methodologies for assessing treated wood risks
3. Work cooperatively to develop and improve models to predict the risk of using treated wood in various applications
4. Identify improved methods for reducing the potential for migration
5. Evaluate the environmental impacts and identify methods for reuse, recycling and/ or disposal of preserved wood that is removed from service
6. Deliver educational outreach programs on the proper use of treated wood in relation to BMPs

ACCOMPLISHMENTS

Over the past year, we have continued a number of efforts under some of these objectives, with involvement of the advisory committee. The results will be summarized by Objective.

OBJECTIVE 1

DEVELOP FUNDAMENTAL DATA ON PRESERVATIVE MIGRATION FROM WOOD

A. Evaluate the Effects of Best Management Practices on Preservative Migration Patterns:

In previous reports, we have described efforts to develop data for BMPs on preservative migration. The results have been mixed. In some cases, the results suggest a benefit for using these practices, but many tests suggest that BMPs have little effect. We believe these results occurred because most of the material was already air-dried prior to exposure; in essence, receiving one of the BMPs (air-seasoning). Best management practices were originally developed in response to situations where freshly treated wood was taken out of the cylinder, transported to a site and then installed in projects where it was subjected to nearly immediate rainfall or soaking (WWPI, 2011). To work around this problem and examine the real effect of BMPs on migration, we moved to a smaller scale test where we could control all aspects of the process to produce more reproducible results under worst case conditions.

In last year's report, we described results from spruce-pine-fir (SPF), southern pine (SYP), and Douglas-fir (DF) treated with copper azole (CA), alkaline copper quaternary (ACQ), chromated copper arsenate (CCA), and/or ammoniacal copper zinc arsenate (ACZA; depending on the wood species). We also described results from pentachlorophenol and creosote treated materials. These results will not be presented here, but can be found in the 7th Annual Report. Peer reviewed papers are being prepared for all of these results.

This past year, we continued BMP tests on micronized copper azole (MCA) treated SP as well as copper naphthenate (CuNaph) treated SP and SPF. We are currently treating SP with a different MCA preservative and we will treat hem-fir (HF) lumber with both MCA preservatives as well. Once these tests are performed, we will have completed the initial BMP testing. However, it is important to note that these tests have only used existing BMPs and were intended to demonstrate that BMPs made a difference. The next step will be to use these data to improve the BMP processes.

- **Post-Treatment with BMPs:** Frozen samples were defrosted before being subjected to one of nine treatments listed in the Western Wood Preservers Institute (WWPI) Best Management Practices requirements. The methods were applied to sub-samples of each board treated with a water-based chemical even though we recognize that not all of these processes are currently listed as BMPs for all chemicals.

    - **Air-Drying:** Samples were placed on stickers at ambient temperature (20-25 ℃), to encourage air-flow, and conditioned to a target moisture content below 19% over a four-week conditioning period. No supplemental airflow was supplied.

    - **Kiln Drying:** The samples were placed in a steam-fired kiln on stickers to enhance air flow. Samples were dried over a one-week kiln schedule at a dry-bulb temperature of 48.9 ℃ and wet-bulb depression of 5.6 ℃. This cycle limited drying, but the heat encouraged ammonia or amine loss. Wood moisture contents in these samples were below 19% when subjected to overhead leaching.

    - **Steaming:** Samples were subjected to 1, 3, or 6 hours of steaming at 100 ℃ with stickers between samples. Steaming was performed in an autoclave where steam entered the vessel and was allowed to exit so that pressure remained near atmospheric.

    - **Hot Water Bath:** Samples were soaked in water at 100 ℃ for 1 or 3 hours.

    - **Ammonia Bath:** Samples were soaked in aqueous 2% ammonia at 100 ℃ for 1 or 3 hours.

  Samples were frozen (-10 °C) after being subjected to a given BMP until needed. Each treatment was replicated on one section cut from each board treated with a given preservative to help reduce the potential for variability between boards.

This resulted in each portion of a single parent board being subjected to a given BMP.

- **Leaching Tests:** Samples were thawed overnight before testing. The potential for preservative migration was evaluated in a specially constructed overhead leaching apparatus that applied a controlled amount of simulated rainfall at a desired temperature (Figure 1). Previous studies (Simonsen et al, 2008) have shown that migration is independent of both temperature and rainfall rate so the device operated at room temperature (20~28 ℃) and a rainfall rate ranging from 0.1 cm/h to 0.3 cm/h.

Figure 1. Overhead leaching apparatus used to evaluate the effects of BMPs on metal migration from preservative treated wood.

The apparatus (1.5 m wide x 0.6 m long x 0.9 m) was constructed with stainless steel and a plastic panel and had eight 152 mm wide x 457 mm long x 51 mm high sample holders. Holders were placed on a shelf with a 4.5° incline from the horizontal to allow water to flow down the wood. Simulated rainfall was produced by four spray nozzles connected to a deionized water supply. The rate of water spray was controlled by a small pump and an electronic controller. A pressure gauge near the spray nozzles also helped control flow.

BMP-treated samples were placed into each holder and subjected to simulated overhead rainfall for 2 hours. Previous tests had shown that metal levels in runoff drop off sharply to a steady state by this time. Runoff was collected in tared 250 mL Erlenmeyer flasks that were weighed after rainfall exposure to determine the total volume of water applied per board for each time period. The weight of water was recorded and 4.85 mL of each water sample was placed into a vial. Water was collected at 15-minute intervals for the first hour then at 30-minute intervals for the last hour. Preservative retention in the samples was determined using either net solution uptake for SP samples treated with waterbornes or by x-ray fluorescence for both SP and SPF samples.

- **Chemical Analysis:** Runoff from samples treated with waterborne preservatives was acidified by adding 0.15 mL of 1 N nitric acid into 4.85 mL of leachate. The samples were stored at 4 ^{0}C until they could be analyzed for residual metal using a Perkin Elmer Optima 3000DV inductively-coupled plasma optical emission spectrometer with a diode array detector (ICP) at the Oregon State University Central Analytical Laboratory. Water samples collected over the first two hours of simulated rainfall were tested for copper, zinc, chromium, or arsenic (depending on the treatment). The exposed wood samples were frozen and retained in the event we needed to perform additional rainfall exposures. Copper concentrations were used as a measure of BMP effectiveness, although chromium, zinc, and arsenic were also measured when those metals were present in a preservative.

  Retentions were high for CuNaph and CCA treated SP, slightly above target for MCA, and slightly below the targets for ACQ and CA (Table 1). SPF retentions were just above target for ACZA, just below target for CuNaph, and well below that level for CCA, ACQ, and CA (Table 1).

Table 1. Target and actual retentions of CCA, ACZA, ACQ, CA, Penta, Creosote, CuNaph, and MCA in SP or SPF lumber used to evaluate the BMP processes.

Treatment	Target Retention (kg/m^3)	Retention (kg/m^3)[a]		
		Southern Pine		SPF
		Net Uptake	XRF	XRF
CCA	6.4	5.92 (1.07)	9.46 (0.33)	2.43 (0.18)
ACQ	6.4	6.18 (0.25)	5.86 (0.07)	0.52 (0.04)
CuA	2.4	2.50 (0.92)	2.37 (0.04)	0.73 (0.03)
ACZA	6.4	Not tested	Not tested	7.26 (0.29)
Penta	8.0	-	7.87 (0.23)	-
Creosote	160.0	-	-	-
CuNaph	0.96	-	3.66 (0.08)	0.89 (0.05)
MCA (MP200)	5.0	4.20	5.50	Not tested

[a] Values represent means of 8 samples for net uptake and 3 replicates for XRF (x-ray fluorescence) retentions. Figures in parentheses represent one standard deviation.

- **Copper Levels in Rainfall from MCA Treated Lumber:** Copper levels in runoff were highest in the first 15 minutes of rainfall on boards receiving no BMPs and then declined by approximately 50% with an additional 15 minutes of rain (Figure 2, Table 2 & 3, MCA and CA data are separated into a second table for simplicity). Copper levels were consistently lower in runoff from boards subjected to some form of BMP, although there was considerable variation within a given BMP treatment. Air drying was associated with the lowest copper concentrations in runoff followed by one hour in a hot water bath or 1 or 3 hours of ammonia streaming. Interestingly, exposing samples to a 3 hour hot water bath was associated with higher copper levels. It is unclear why additional exposure increased copper losses. This effect was not noted in runoff from boards subjected to steaming. Copper levels continued to decline after an additional 15 minutes of rainfall and were lower than runoff from the comparable non-BMP treated samples at the same rainfall point. Interestingly, one hour of steaming produced more variable results.

Results from MCA treated pine (Figure 2) were compared with those from the traditional CA treated lumber of the same species (Table 2 & 3). When MCA was first developed, there was concern that the copper might not be as available as it would be in traditional solubilized preservatives. Conversely, this lack of availability might also translate to reductions in copper migration. Subsequent performance testing has shown that MCA performs well when the wood is properly treated.

Simulated rainfall tests showed that copper levels in MCA treated SP not subjected to a BMP were actually higher than those found with comparable CA treatments. This result was surprising given the differences in formulation chemistry; however, MCA retention levels were nearly twice those of the CA treated materials and this may explain the elevated copper levels. Copper levels remained elevated in non-BMP treated MCA runoff for the entire 2 hour exposure period.

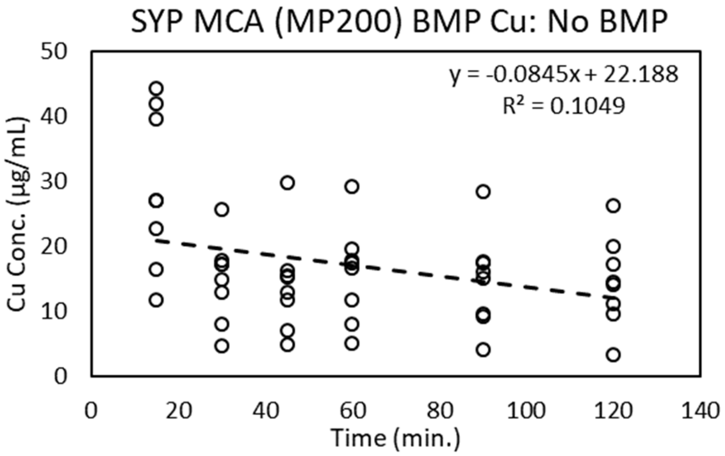
As noted above, BMPs were associated with decreased copper levels in the first 15 minutes of simulated rainwater runoff, but these levels were still much higher in runoff from MCA treated samples than in CA samples subjected to comparable BMP treatments. Copper levels declined sharply with an additional 15 minutes of rainfall and were similar for both MCA and CA treated materials after 30 and 120 minutes.

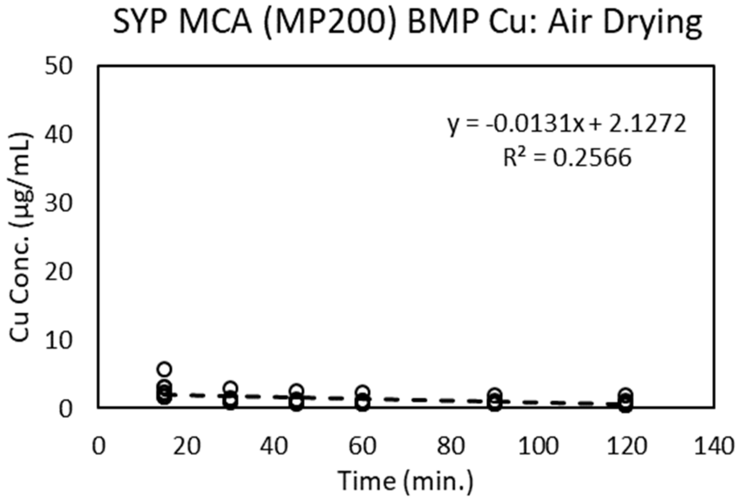
The results clearly show that BMPs help reduce copper losses from MCA treated pine. Additional tests are planned for SP treated with another MCA formulation and HF lumber treated with both MCA formulations.

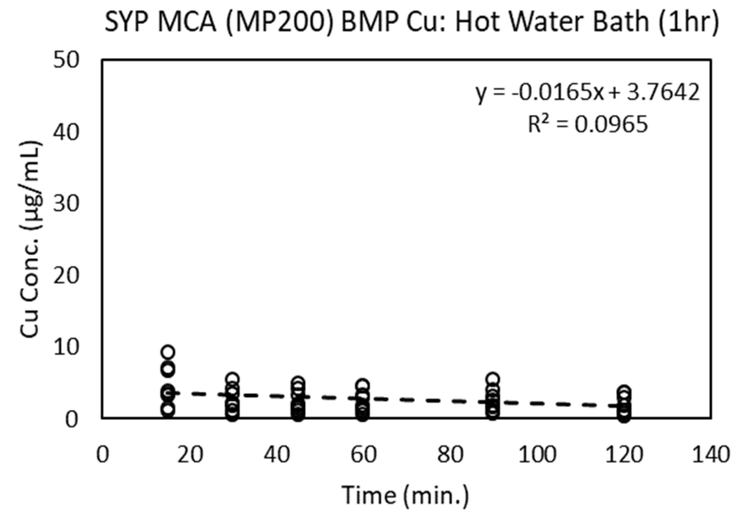
- **Copper Levels in Rainfall from CuNaph Treated Lumber:** Non-BMP treated SPF samples were associated with the lowest copper concentrations in runoff over the first 15 minute collection period, but levels appeared to increase slightly over the remaining rainfall exposure (Tables 2 & 4, Figures 3 & 4). A similar trend occurred with copper levels from SP samples. Application of a 6 hour post-treatment vacuum period had little effect on copper levels in runoff compared to the steaming treatments, especially for SPF. The application of a post-treatment steaming period had more variable effects on subsequent copper levels. One hour of steaming was associated with lower copper levels in runoff for both species over the entire 2 hour test. There appeared to be little benefit to prolonged steaming as levels were similar for 1, 3, or 6 hour steaming treatments. Copper levels in runoff from SP samples subjected to steaming were far more variable than those from SPF lumber subjected to the same treatment.

Levels appeared slightly higher with prolonged steaming (3 or 6 hours), but the variability within treatments makes it difficult to delineate differences between BMP processes. Although non-BMP treated samples were associated with some of the lowest average copper levels in the runoff, they also showed the highest standard deviations which indicates a high degree of variability between treated boards. BMPs help to reduce that variation. The results also show that care must be taken when using averaged data.

Figure 2. Effect of various BMP processes on copper losses from MP200 MCA treated SP lumber exposed to simulated rainfall.



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R² = 0.0965
Cu Conc. (µg/mL)
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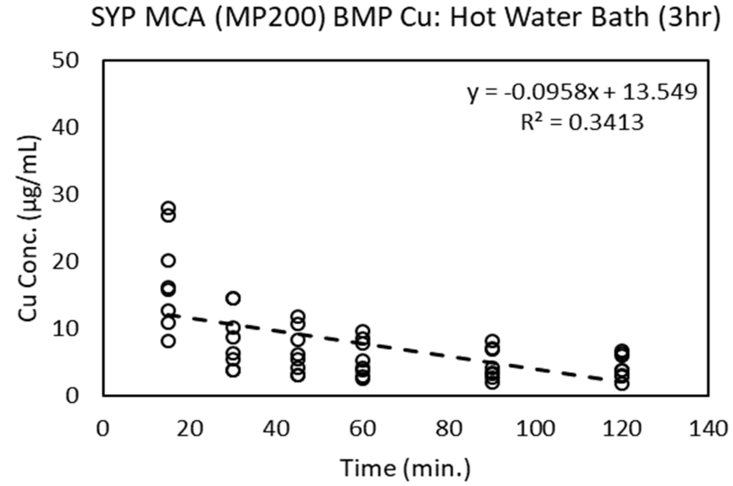
10
20
30
40
50
0
20
40
60
80
100
120
140
Time (min.)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R² = 0.3413
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40
50
0
20
40
60
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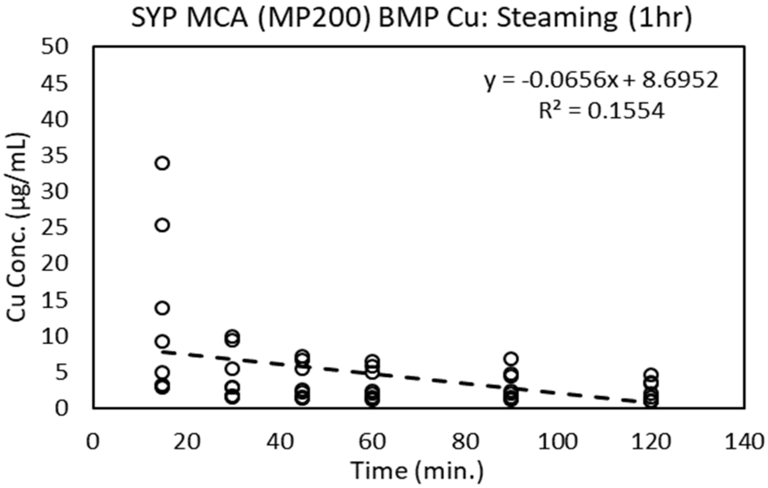
100
120
140
Time (min.)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R² = 0.1554
Cu Conc. (µg/mL)
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25
30
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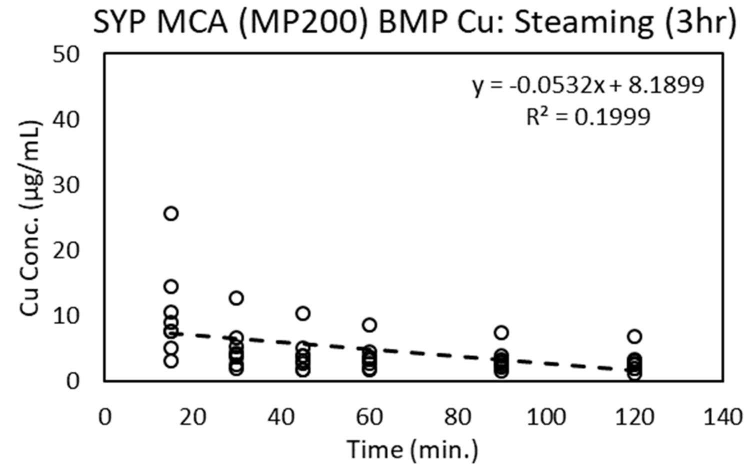
100
120
140
Time (min.)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R² = 0.1999
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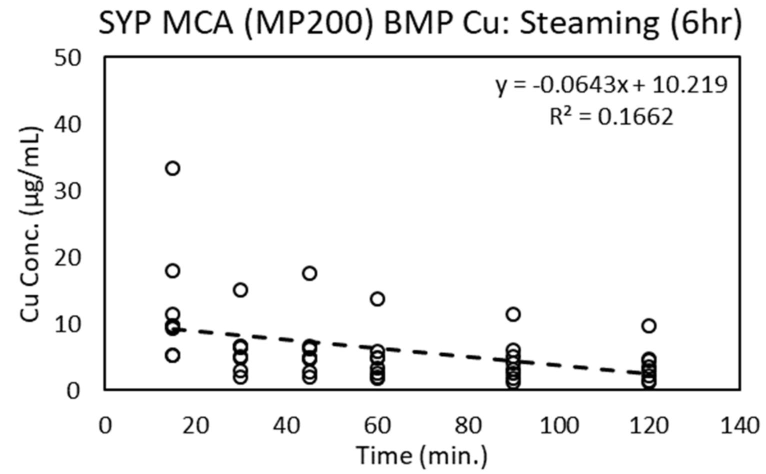
100
120
140
Time (min.)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R² = 0.1662
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40
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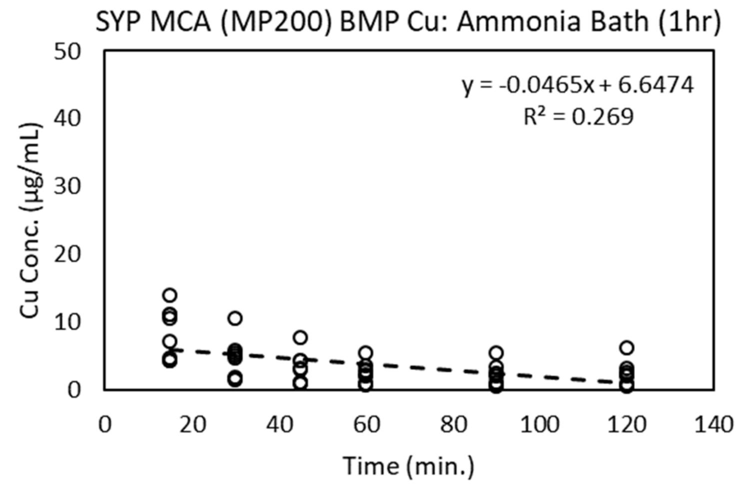
100
120
140
Time (min.)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50
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60
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100
120
140
Time (min.)

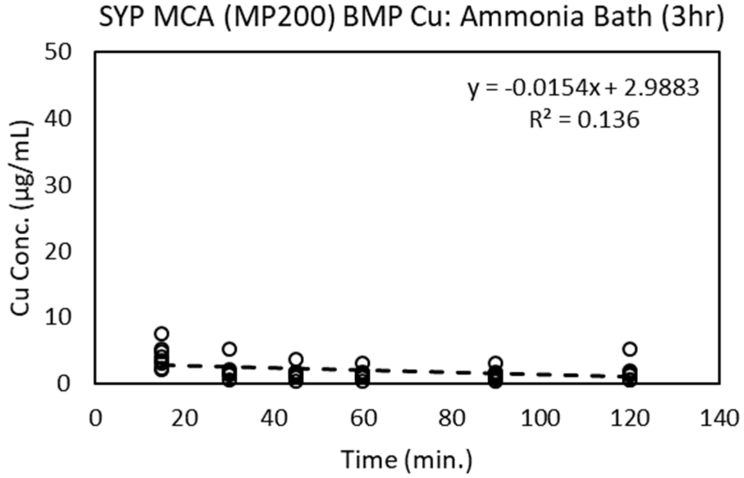
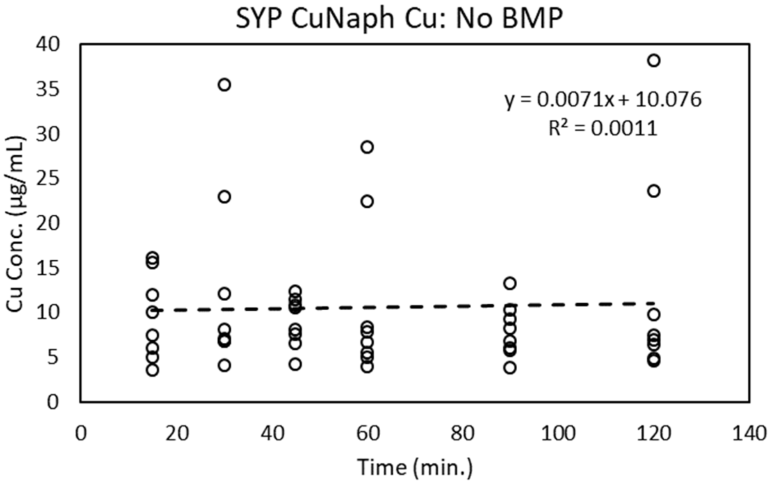
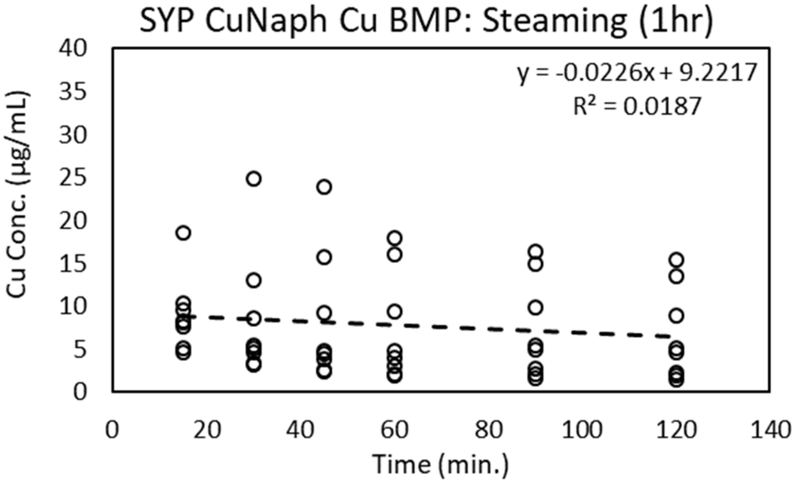
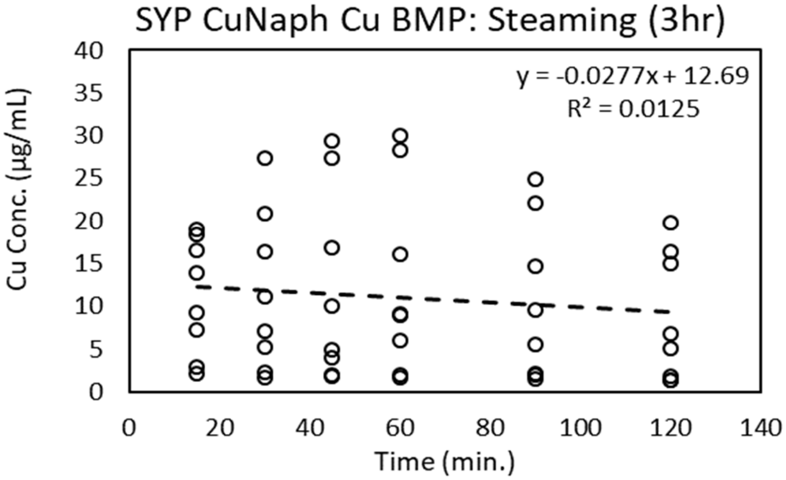
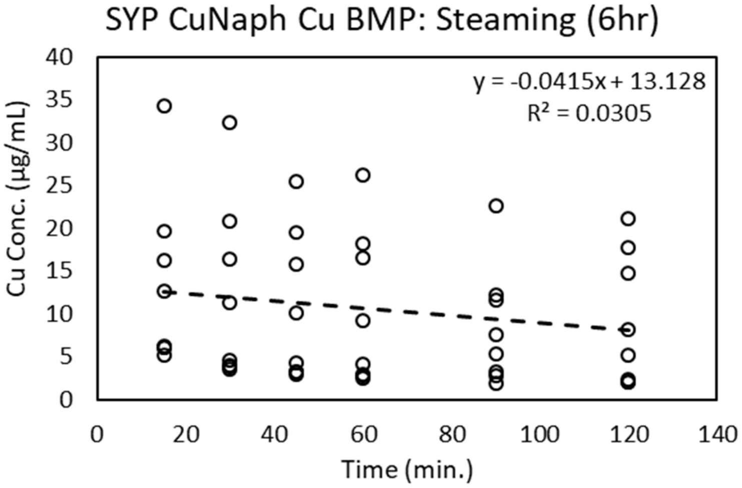


Figure 3. Effect of various BMP processes on copper losses from CuNaph treated SP lumber exposed to simulated rainfall.






SYP CuNaph Cu BMP: Steaming (3hr)


SYP CuNaph Cu BMP: Steaming (6hr)

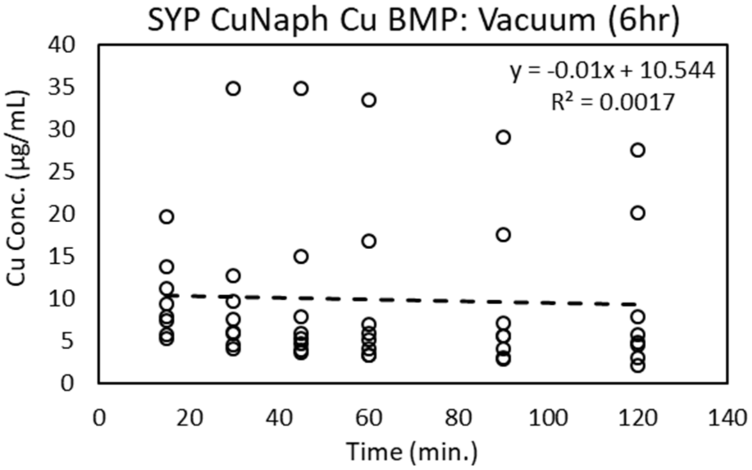
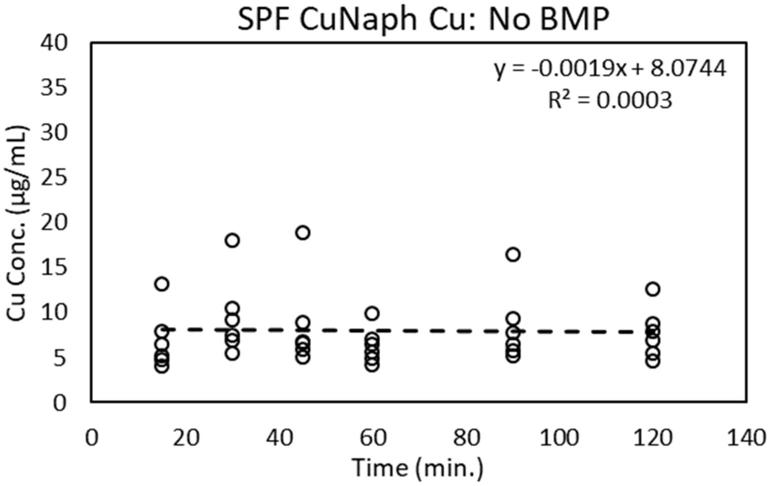
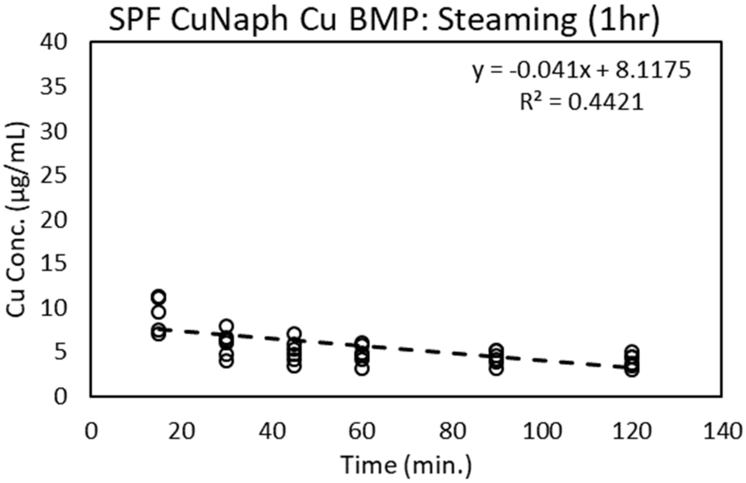
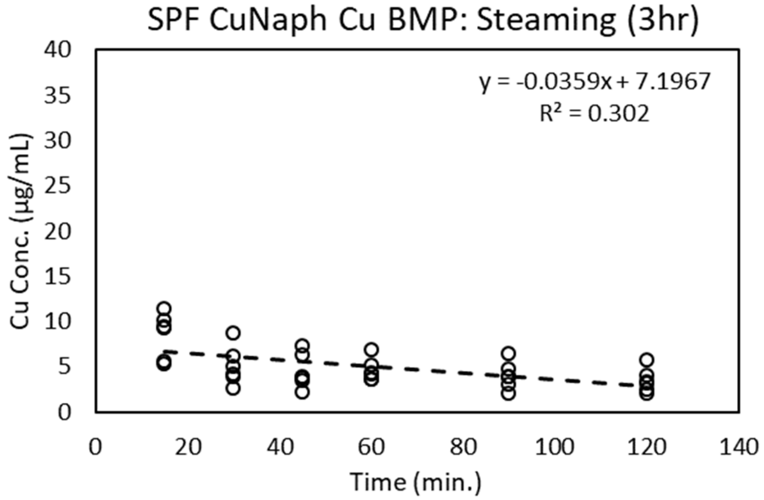
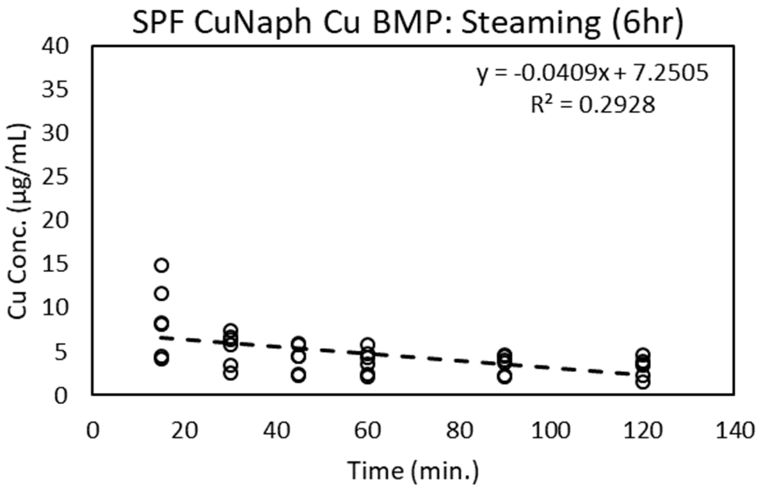

SYP CuNaph Cu BMP: Vacuum (6hr)

Figure 4. Effect of various BMP processes on copper losses from CuNaph treated SPF exposed to simulated rainfall.








SPF CuNaph Cu BMP: Steaming (6hr)
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R² = 0.2928
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20
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30
35
40
Time (min.)
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120
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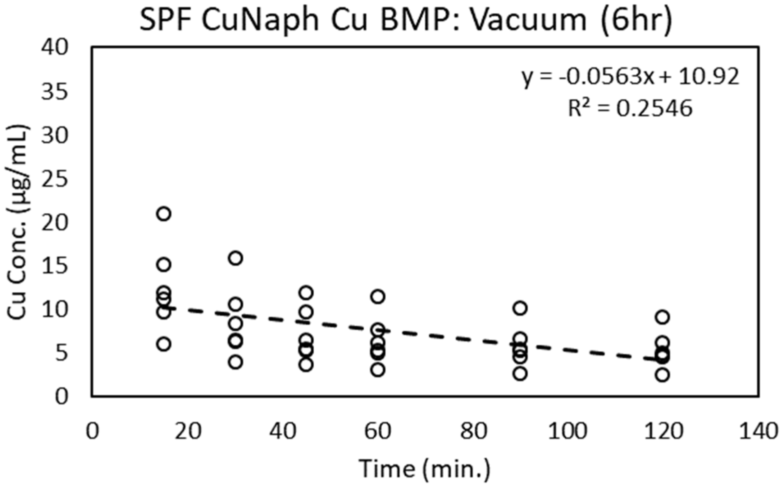
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R² = 0.2546
Cu Conc. (µg/mL)
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30
35
40
Time (min.)
0
20
40
60
80
100
120
140

Table 2. Copper levels in runoff from SP and SPF decking materials treated with selected copper based preservatives and subjected to 15, 30, and 120 minutes of simulated rainfall.

System	Wood Species	Rainfall Time (Min)	Copper Levels in Runoff (µg/mL)[a]										
			None	Air Dry	Kiln dry	Hot water		Steam			Ammonia Bath		Vacuum
						1 hr	3 hr	1 hr	3 hr	6 hr	1 hr	3 hr	6hr
CA	SPF	15	9.26 (3.47)	4.08 (1.48)	5.38 (1.47)	3.36 (1.16)	7.57 (3.21)	10.56 (6.64)	6.70 (2.84)	3.78 (1.98)	1.77 (1.01)	3.04 (3.29)	-
		30	5.21 (1.89)	2.70 (1.09)	2.97 (1.04)	1.56 (0.51)	3.92 (1.98)	6.09 (3.30)	3.65 (1.47)	2.35 (1.00)	2.97 (1.04)	1.34 (0.98)	-
		120	2.01 (0.95)	1.42 (0.56)	1.60 (0.53)	0.75 (0.37)	1.48 (0.58)	2.74 (1.34)	1.69 (0.66)	1.57 (0.73)	0.45 (0.24)	0.62 (0.23)	-
	SYP	15	18.15 (9.00)	18.11 (9.05)	17.23 (8.13)	6.10 (2.89)	4.53 (2.03)	7.83 (2.15)	6.89 (2.05)	5.65 (1.96)	3.44 (1.27)	6.09 (3.12)	-
		30	9.54 (6.44)	11.98 (6.67)	14.64 (9.95)	3.10 (1.70)	2.22 (1.13)	3.62 (0.98)	2.91 (0.84)	2.51 (1.16)	1.45 (0.52)	3.07 (1.36)	-
		120	4.48 (3.55)	8.02 (3.98)	10.93 (4.23)	1.71 (1.34)	1.28 (0.62)	1.79 (0.48)	1.41 (0.40)	1.59 (1.06)	0.95 (0.21)	1.97 (1.49)	-
	DF	15	-	24.42 (8.47)	45.17 (17.59)	22.88 (20.37)	14.62 (11.39)	39.93 (25.56)	34.38 (18.49)	44.05 (44.16)	20.62 (16.48)	22.96 (29.62)	-
		30	-	32.07 (16.35)	42.41 (13.08)	22.47 (20.66)	11.52 (7.77)	38.38 (27.68)	34.24 (21.66)	47.62 (51.25)	21.98 (18.76)	24.15 (31.29)	-
		120	-	26.99 (17.78)	40.08 (15.20)	14.18 (11.27)	7.01 (3.68)	24.22 (15.76)	22.16 (13.08)	27.53 (23.40)	18.41 (16.16)	14.27 (14.62)	-
ACQ	SPF	15	2.79 (2.38)	5.17 (5.17)	5.71 (2.22)	1.38 (1.16)	3.66 (3.26)	7.03 (3.60)	7.61 (5.24)	12.56 (16.37)	1.37 (1.13)	1.76 (1.20)	-
		30	1.60 (1.36)	3.28 (3.22)	2.99 (1.28)	0.75 (0.66)	2.03 (1.72)	3.92 (2.27)	3.87 (2.58)	5.95 (7.67)	0.76 (0.77)	0.63 (0.45)	-
		120	0.65 (0.46)	1.39 (1.44)	1.39 (0.88)	0.37 (0.34)	0.96 (0.87)	1.38 (0.73)	2.11 (1.57)	3.02 (2.93)	0.39 (0.36)	0.23 (0.13)	-
	SYP	15	47.84 (24.72)	18.09 (3.33)	15.83 (5.00)	15.34 (4.53)	8.48 (1.65)	15.57 (5.02)	13.92 (4.49)	13.68 (8.95)	8.11 (5.32)	7.28 (1.40)	-
		30	23.72 (10.12)	14.00 (3.68)	12.27 (4.06)	5.26 (2.92)	3.48 (1.25)	6.82 (2.55)	6.89 (3.23)	4.70 (3.12)	3.34 (2.00)	3.64 (1.26)	-
		120	12.04 (3.66)	8.00 (1.76)	8.16 (2.35)	3.04 (1.03)	1.89 (0.69)	3.56 (0.99)	3.33 (1.41)	2.46 (1.06)	1.97 (1.34)	1.66 (0.63)	-
	DF	15	-	15.70(6.32)	17.28 (7.57)	24.93 (11.95)	13.85 (11.55)	16.33 (4.48)	18.37 (5.71)	16.30 (7.52)	17.15 (15.76)	12.15 (7.18)	-
		30	-	15.55 (6.93)	20.17 (9.70)	19.09 (6.28)	12.46 (10.67)	17.27 (6.77)	17.22 (6.42)	16.10 (10.32)	16.38 (12.59)	12.85 (6.84)	-
		120	-	12.03 (3.45)	16.17 (8.65)	18.44 (7.75)	9.42 (5.64)	14.42 (3.49)	15.43 (0.55)	15.34 (8.79)	16.95 (8.52)	14.82 (7.87)	-
CCA	SPF	15	1.31 (0.49)	0.23 (0.11)	0.14 (0.05)	0.67 (0.23)	1.69 (0.28)	1.60 (087)	3.47 (0.46)	3.71 (2.06)	0.22 (0.12)	0.31 (0.16)	-
		30	0.73 (0.26)	0.12 (0.04)	0.10 (0.00)	0.36 (0.10)	0.92 (0.21)	0.84 (0.57)	2.09 (0.36)	1.95 (0.98)	0.10 (0.00)	0.16 (0.06)	-
		120	0.44 (0.12)	0.10 (0.01)	0.10 (0.00)	0.17 (0.05)	0.44 (0.09)	0.37 (0.14)	0.93 (0.33)	1.16 (0.79)	0.10 (0.00)	0.11 (0.02)	-
	SYP	15	1.18 (0.48)	0.48 (0.45)	0.45 (0.31)	3.18 (2.04)	1.30 (0.42)	2.37 (0.85)	3.08 (1.96)	6.30 (2.27)	0.28 (0.13)	0.78 (0.86)	-
		30	0.98 (0.33)	0.28 (0.33)	0.20 (0.09)	1.33 (0.56)	0.83 (0.31)	1.20 (0.58)	1.58 (0.95)	3.05 (0.96)	0.10 (0.06)	0.33 (0.38)	-
		120	0.80 (0.25)	0.15 (0.18)	0.12 (0.08)	0.97 (0.47)	0.65 (0.20)	0.67 (0.30)	0.87 (0.48)	1.63 (0.87)	0.03 (0.05)	0.15 (0.20)	-
ACZA	SPF	15	60.95 (47.44)	2.33 (1.03)	3.70 (5.35)	37.80 (26.23)	27.69 (25.72)	38.94 (35.50)	36.70 (26.01)	13.73 (13.72)	58.99 (30.92)	37.67 (26.76)	-
		30	36.43 (25.23)	4.46 (8.51)	1.69 (2.43)	22.28 (15.31)	9.54 (10.45)	20.03 (17.54)	18.00 (14.29)	5.33 (5.14)	37.66 (24.82)	23.03 (15.65)	-
		120	14.16 (8.12)	0.77 (0.26)	0.61 (0.93)	9.61 (6.43)	4.90 (2.69)	8.14 (5.84)	6.58 (4.93)	2.19 (1.78)	12.99 (7.12)	9.83 (5.74)	-
	DF	15	-	10.97 (2.85)	12.47 (4.07)	57.07 (60.08)	58.20 (51.25)	26.57 (14.53)	35.65 (23.50)	44.83 (29.79)	66.18 (71.42)	36.85 (32.37)	-
		30	-	8.29 (2.11)	10.82 (3.42)	63.22 (76.54)	43.87 (38.94)	26.82(11.97)	33.97 (23.97)	36.94 (25.34)	56.90 (64.38)	31.58 (32.10)	-
		120	-	4.04 (1.57)	6.00 (1.80)	36.65 (38.09)	19.97 (17.36)	16.87 (6.45)	15.97 (9.05)	18.77 (11.83)	34.18 (35.74)	16.09 (16.90)	-
CuNaph	SPF	15	6.95 (3.35)	-	-	-	-	9.63 (1.92)	8.54 (2.50)	8.62 (4.19)	-	-	12.39 (5.11)
		30	9.59 (4.50)	-	-	-	-	5.96 (1.38)	5.11 (2.09)	5.35 (1.90)	-	-	8.53 (4.19)
		120	7.70 (2.84)	-	-	-	-	4.05 (0.73)	3.50 (1.30)	3.22 (1.13)	-	-	5.28 (2.20)
	SYP	15	9.45 (4.77)	-	-	-	-	9.02 (4.32)	11.15 (6.74)	13.31 (10.04)	-	-	10.08 (4.80)
		30	12.93 (10.83	-	-	-	-	8.54 (7.37)	11.49 (9.28)	12.09 (10.50)	-	-	10.69 (10.21)
		120	12.73 (12.00)	-	-	-	-	6.63 (5.39)	8.44 (7.50)	9.16 (7.68)	-	-	9.49 (9.24)
MCA (MP200)	SYP	15	28.90 (12.07)	2.70 (1.32)	-	4.56 (2.86)	17.32 (7.19)	12.08 (11.70)	10.45 (7.06)	12.73 (9.20)	8.41 (3.77)	4.06 (1.77)	-
		30	14.77 (6.43)	1.38 (0.64)	-	2.62 (1.63)	8.42 (4.36)	4.42 (3.43	5.20 (3.39)	6.16 (3.97)	4.58 (3.07)	2.01 (1.39)	-
		120	14.51 (6.95)	0.86 (0.44)	-	1.95 (1.33)	4.28 (1.82)	2.28 (1.44)	2.99 (1.71)	3.75 (2.69)	2.33 (1.83)	1.78 (1.47)	-

[a] Values represent means of 8 replicates per treatment while figures in parentheses represent one standard deviation.

Table 3. Effect of post-treatment practices on copper levels in simulated rainwater runoff from SP lumber treated with CA or MCA.

Treatment	Leaching Time (min)	Copper concentration in runoff (µg/mL)[a]								
		No BMP	Air Dry	Hot Water Bath		Steaming			Ammonia bath	
				1 hr	3 hr	1 hr	3 hr	6 hr	1 hr	3 hr
CA	15	18.15 (9.00)	18.11 (9.05)	6.10 (2.89)	4.53 (2.03)	7.83 (2.15)	6.89 (2.05)	5.65 (1.96)	3.44 (1.27)	6.09 (3.12)
	30	9.54 (6.44)	11.98 (6.67)	3.10 (1.70)	2.22 (1.13)	3.62 (0.98)	2.91 (0.84)	2.51 (1.16)	1.45 (0.52)	3.07 (1.36)
	120	4.48 (3.55)	8.02 (3.98)	1.71 (1.34)	1.28 (0.62)	1.79 (0.48)	1.41 (0.40)	1.59 (1.06)	0.95 (0.21)	1.97 (1.49)
MCA	15	28.90 (12.07)	2.70 (1.32)	4.56 (2.86)	17.32 (7.19)	12.08 (11.70)	10.45 (7.06)	12.73 (9.20)	8.41 (3.77)	4.06 (1.77)
	30	14.77 (6.43)	1.38 (0.64)	2.62 (1.63)	8.42 (4.36)	4.42 (3.43	5.20 (3.39)	6.16 (3.97)	4.58 (3.07)	2.01 (1.39)
	120	14.51 (6.95)	0.86 (0.44)	1.95 (1.33)	4.28 (1.82)	2.28 (1.44)	2.99 (1.71)	3.75 (2.69)	2.33 (1.83)	1.78 (1.47)

[a]Values represent the average of 8 replicates per treatment while figures in parentheses represent one standard deviation.

Table 4. Effect of post-treatment steaming or vacuum on copper levels in simulated rainwater runoff from SPF or SP lumber treated with CuNaph.

Species	Leaching Time (min)	Copper Levels in runoff (µg/mL)[a]				
		No BMP	Steaming			Vacuum
			I Hour	3 Hours	6 Hours	6 Hours
SPF	15	6.95 (3.35)	9.63 (1.92)	8.54 (2.50)	8.62 (4.19)	12.39 (5.11)
	30	9.59 (4.50)	5.96 (1.38)	5.11 (2.09)	5.35 (1.90)	8.53 (4.19)
	120	7.70 (2.84)	4.05 (0.73)	3.50 (1.30)	3.22 (1.13)	5.28 (2.20)
SYP	15	9.45 (4.77)	9.02 (4.32)	11.15 (6.74)	13.31 (10.04)	10.08 (4.80)
	30	12.93 (10.83	8.54 (7.37)	11.49 (9.28)	12.09 (10.50)	10.69 (10.21)
	120	12.73 (12.00)	6.63 (5.39)	8.44 (7.50)	9.16 (7.68)	9.49 (9.24)

[a]Values represent the average of 8 replicates per treatment while figures in parentheses represent one standard deviation.

B. Assessment of Preservative Migration from Submerged Wood Using a Soil Sachet Method:

Preservatives markedly extend the service life of timber exposed under adverse conditions conducive to biological deterioration thereby reducing the need to harvest additional timber (Hunt and Garratt, 1967; Zabel and Morrell, 1992). One attribute of nearly all preservatives used for wood protection is that they have some degree of water solubility. Water solubility ensures that some level of biocide is present in water within the wood, where it can interact and inhibit growth of attacking organisms. At the same time, water solubility ensures that some preservative can migrate out of the wood and into the surrounding environment. For decades, preservative migration was viewed as a positive attribute, provided it was not excessive, because it created a protective zone around the treated product. However, preservative migration has received increasing scrutiny because of its potential to affect non-target organisms, particularly in aquatic applications (Brooks, 2011). A number of studies have examined preservative migration from wood treated with creosote, penta, and the inorganic arsenicals exposed in terrestrial environments (Lebow, 1996; Morrell and Chen, 2008; Morell et al., 2003, 2010; Rhatigan and Morrell, 2000; Stilwell and Graetz, 2001; Stilwell and Korny, 1997; Wendt et al., 1996). These studies are relatively simple because they require analysis of soil at increasing distances from the treated product. Assessing migration from preservative treated wood into surrounding sediment is inherently more complicated. Obtaining water samples is relatively simple, although care must be taken to ensure accurate sampling of the entire water column. Sediment cores become increasingly difficult to collect with increasing water depth and difficult substrate composition (e.g. extensive organic matter that collapses as the corer is driven into the sediment). This can result in collections not being representative of the sample site. Differences in sediment organic matter may affect decomposition rates of organic preservatives or limit the ability to reliably recover specific preservative components. As a result, many studies of preservative movement in aquatic environments use mesocosms with large quantities of treated wood in small amounts of water or they depend on case studies of structures already in service (Brooks, 2011). While useful, these studies are either artificial, (e.g. mesocosms) or variable (e.g. field case studies). These data are becoming increasingly important as regulators seek to minimize the potential environmental effects of development using sound, science-based data.

Developing a reliable, reproducible method for assessing preservative migration from docks, bridges, or submerged pilings into surrounding sediment would facilitate studies examining the effects of preservatives on the environment and help regulators make more informed decisions concerning treated wood use. In this report, we describe a sachet method for capturing compounds migrating from preservative treated pilings exposed in a freshwater pond.

- **Materials and Methods:** Douglas-fir poles (125-150 mm in diameter by 1.8 m long) were treated to the American Wood Protection Association (AWPA) Use Category 5a with either creosote or ACZA to target retentions of 384 kg/m^3 or 24 kg/m^3 for creosote or ACZA, respectively. These levels correspond to retentions required for use in salt water exposures north of San Francisco Bay (AWPA, 2017). The materials were subjected to an initial vacuum (91 kPa), preservative was introduced to the treatment vessel and the pressure was raised (1.03 MPa) and held until the gauges indicated that a sufficient amount of preservative had been delivered into the wood. The pressure was released and the solution was withdrawn. The posts were then subjected to one of the Western Wood Preservers Institute BMPs (WWPI, 2012). In the case of creosote, this consisted of post treatment steaming with an extended vacuum, while ACZA had a long vacuum coupled with drawing air over the wood to hasten ammonia evaporation and metal deposition. These procedures were used to reduce the presence of surface deposits and, in the case of ACZA, immobilize the metals. The posts were then removed and stored under cover for 6 months prior to use to ensure that any reactions between the preservatives and wood had been completed.

    - **Sediment Collection Apparatus:** A soil mixture was obtained from a local garden center. Background copper, zinc and arsenic levels in the soil prior to exposure were 2.95, 6.58 and 0.05 ppm, respectively. The soil contained 42, 49, and 9% sand, silt and clay, had a pH of 7.56 and contained 1.5% organic matter. Soil analysis revealed that no polycyclic aromatic hydrocarbons (PAHs) typically used to assess creosote were present at detectable levels.

      Soil was placed into 200 mm long sachets, approximately 25 mm in diameter, made from heat sealable polyester mesh (25 µm; ANKOM Technology, Macedon, NY; Figure 5) which allowed liquids to pass through but was of a sufficient pore size to limit soil loss. In preliminary trials, three creosote treated posts were placed into individual 18.5 L buckets half-filled with soil while the remainder were filled with distilled water. Sachets were placed into sediment immediately adjacent to the posts and removed after 1, 2, or 3 weeks of exposure. Once removed, sachets were frozen and cut into three equal lengths. Each section was again cut lengthwise so that half of the sachet was directly exposed to the post and the other half was unexposed. Soil was removed from the sachets and extracted as described below. The sachet material itself was similarly extracted. The extracts were analyzed for PAHs as described below and the results were used to calculate total PAHs on the basis of the proportion of soil and sachet material in each sachet packet.

Preliminary tests indicated creosote and metals could migrate from adjacent preservative treated materials into the sachets (Table 5). While the mesh selectively retained some PAHs and metals these results were viewed as positive because this would increase the potential for capturing compounds migrating from wood.

- **Test Establishment:** Creosote and ACZA treated poles were sunk to a depth of 0.6 m in a freshwater pond located approximately 20 km west of Corvallis, Oregon. Water and sediment samples were collected prior to introduction of treated wood and retained for analysis of metals or PAHs as described later. Six sachets were wired directly around a treated post or affixed to one of two 1.8 m long coated metal t-posts. Small wires were attached to the top of each sachet and connected to the pole or t-post above the water line so that it would be easy to remove individual sachets as needed with minimal disturbance to the other sachets. T-posts were driven into the sediment on the downstream side of a given post so that the top of the sachet was even with the top of the surrounding sediment. T-posts were driven 0.3 m and 0.9 m away from a post. A preliminary trial evaluated two posts treated with creosote or ACZA, while a second trial examined four or five posts treated with creosote or ACZA, respectively.

Sachets removed at selected time intervals after installation were immediately frozen (-10 ºC) until they could be analyzed. The sachets were thawed, the sediment was separated from the sachet and each component was oven dried at 100 ºC. The sediment in a sachet was thoroughly mixed and then three 10 g subsamples were taken from the homogenized sediment. Samples surrounding ACZA treated posts were microwave-digested. Briefly, oven dry soil was ground to ensure homogeneity, using stainless steel or Nylon to minimize contamination. Five hundred mg of sediment was weighed into a Teflon microwave digestion tube. Ten mL of nitric acid was added to each tube and agitated to ensure samples were thoroughly wetted. Samples were microwave digested using the EPA 3051A method and the resulting solution was analyzed for total copper, zinc, and arsenic by ICP. A weighed section of the sachet material was similarly digested and analyzed by ICP. The resulting metal levels in soil and sachet material were expressed on a µg/g of dry soil basis.

Sachets surrounding creosoted posts were similarly disassembled and the soil was thoroughly mixed and extracted using a modified QuEChERS method (Forsberg et al, 2011). Soil was left wet and extracted to limit volatilization of any compounds. Three 10 g sub-samples of soil were placed into 50 mL centrifuge tubes. Sachet material was split into two sections and analyzed separately from the sediment in the same manner. Twenty mL of a 2:2:1 acetone:ethyl acetate:iso-octane mixture was added to the centrifuge tubes. The tubes were vigorously agitated for 5 minutes to ensure that sediment was in intimate contact with solvent. The samples were then treated with a salt mixture containing 6 g of magnesium sulfate and 1.5 g of sodium acetate. The mixture was again agitated for 5 minutes and then centrifuged for 5 minutes. A 1.5 mL aliquot of supernatant was removed and added to a 2 mL dispersive solid-phase micro-extraction tube (SPME) and agitated further for 5 minutes. These dual procedures were used to precipitate polar compounds, lipids, fatty acids, sterols and other compounds that could interfere with analyses. Tubes were then centrifuged again for 5 minutes and a 1 mL aliquot of the supernatant was removed for analysis by gas chromatography-mass spectrometry (GC-MS; Forsberg et al, 2011; Martinez et al, 2004; Anastassiades and Lehotay, 2003).

Samples were analyzed using a Shimadzu QP2010S GC-MS operated in scan mode, mz range 50-300, with a splitless injection. One µL of sample was injected and analyses were performed with the following conditions: Oven temperature: 70 °C held for 2 minutes then increased to 265 at 10 °C a min. and held at 265 °C for 15.5 min until Benzo(ghi)perylene eluted (total run time 37 minutes), ion source temperature: 225 °C, interface temperature: 275 °C, injection temperature 275 °C. The samples were analyzed on an RXI-5ms column (0.25 mm inner diameter by 30 mm long) at a flow rate of 2.5 mL/min. Results were compared with seven prepared standards that contained 16 EPA priority PAH pollutants. Information for each PAH examined using this method are listed in Table 6.

Figure 5. Example of a sachet used to evaluate preservative migration from submerged DF posts.

- **Results and Discussion:**
    - **Preliminary Sachet Exposure:** Our preliminary exposure study showed that PAH levels were higher on the side of the sachet immediately adjacent to the posts as well as nearer to the sediment surface. The presence of higher PAH's adjacent to the posts and nearer to the sediment surface suggests creosote movement occurred both outward and downward (Table 5). The results indicated that sachets were capable of capturing PAHs as they migrated from posts into the surrounding sediment.

    - **PAH Recovery from Spiked Samples:** One mL of a 500 µg/mL PAH standard solution, containing all 16 EPA priority pollutants, was spiked into an unexposed sachet and extracted and analyzed as previously described. Fifty mL of solvent was used for the extraction so recoveries could be compared to our 10 µg/mL standard. Ten spike-analyses were preformed to obtain adequate replication to determine extraction efficacy and efficiency (Table 6).

    - **PAHs in Sachets from Submerged Pilings:** Ten PAHs were detected in at least one of the samples evaluated. Benzo(a)anthracene, benzo(b)fluoranthene, benzo(k)flouranthene, dibenzo(a,h)anthracene, benzo(g,h,i)perylene, and ideno(1,2,3, cd)pyrene were below the detection limits in all samples examined.

As expected, PAH levels were elevated immediately adjacent to the posts (Table 7). Naphthalene was detected in every sample analyzed over the 49 month immersion test. Naphthalene is a common component of creosote and has higher water solubility than most other components (Table 6). This would make it among the most likely materials to migrate from wood and be detected, especially immediately after immersion. The occurrence was more variable for the other 9 PAHs. In general, PAHs were present at elevated levels immediately adjacent to the posts, but then declined with distance. Acenaphthene, fluorene, phenanthrene, and fluoranthrene were all detected at levels above 10 µg/g of sediment over the entire test, while acenaphthylene, pyrene, benzo(α)pyrene, and chrysene were present at much lower levels.

While PAH levels were highly variable, there were no consistent increases or decreases over time (Table 7-9). These findings could reflect a limited loss of PAHs at the start of the test followed by declining levels after the initial losses, or they could reflect continued degradation of PAHs as they entered the sachet soil. The latter would create a steady state sachet PAH level. The method utilized cannot distinguish between the two possibilities.

PAH levels 0.3 and 0.9 m away from posts were generally lower, although there were some exceptions, reflecting both the dilution effects of an increasing sediment pool with distance from a post and the potential for catabolism of migrating creosote components in the sediment. Previous assessments of creosote treated pilings in salt water environments showed similar declines in PAH levels with distance from the piling (Brooks, 2011). Data from the Brooks studies have been used to construct a predictive model that helps determine leaching rates of compounds from preservative treated structures (WWPI, 2012).

The results indicate that PAH migration was very limited around creosote treated posts and most PAHs did not migrate for substantial distances into the surrounding sediment. The sachets provided a uniform material with which to capture and analyze PAHs. Sachets were also easy to install, retrieve, and analyze. Several elements in this study were not explored: the effects of soil type on creosote capture and degradation, migration from similarly treated materials exposed at different sites, and the effects of various post-treatment practices on preservative migration. However, the sachet approach permits the use of uniformly mixed soil/sediment at multiple sites thereby allowing more direct comparisons of PAH migration.

- **Metal Losses from ACZA Treated Posts:** Metal levels in the first trial that only exposed two ACZA treated posts were generally high immediately adjacent to the posts and declined sharply with increasing distance from the post (Table 10). Metal levels in sediment were not proportional to those found in the original treatment. Copper, zinc, and arsenic represent 20, 21, and 59% of the total treatment solution, respectively, on a weight basis. Conversely, arsenic was always present at the lowest levels in the sediment, while copper was most abundant. Previous studies suggest that copper interacts with both zinc and arsenic in the wood as ammonia evaporates from the treatment solution (Lebow and Morrell, 1995; Ruddick, 1996; 2003). Some copper is also reacted with the wood; however, this represents a relatively small fraction of the total copper delivered (Cooper, 1991; Dahlgren and Hartford, 1972a, b, Pizzi 1981a, b). Other leaching studies have also shown that copper migrates from treated wood at far higher rates than either zinc or arsenic (Morrell et al., 2003; Ye and Morrell, 2015). Arsenic is often difficult to accurately quantify in soils and the sachet data reflects that difficulty with arsenic concentrations below the detection limit in 7 of 15 samplings, but present at 57.9 ppm in one sample immediately adjacent to a post after 41 months of exposure. Copper levels were extremely high immediately adjacent to the posts, then declined with distance. Copper and zinc levels 0.3 and 0.9 m away from the posts were near background levels for the first two sample points, then rose steadily with increasing time, suggesting that sachets were capturing the migrating metals.

  The second trial was only sampled for 9 months, but contained higher replication. Metal levels immediately adjacent to the posts were much higher than those found in the first trial (Table 11). Copper, zinc, and arsenic levels averaged 427, 522, and 88 mg/kg respectively after 3 months of exposure. These levels declined slightly after 9 months, but were much higher than those found in the first test. Metal levels 0.3 and 0.9 m away were also higher than those found in the first trial and remained well above the levels originally present in the sediment.

  Both field trials clearly showed that metals were migrating from posts into surrounding sediment, demonstrating the ability of sachets to intercept metals as they moved away from the wood. One aspect that could not be assessed was the differences in metals or PAHs found in native sediment at the site versus those captured by the sachets. The sediment at the site was extremely soft, loose, and contained large quantities of leaf litter. We experienced tremendous difficulty in obtaining uniform core samples for analysis. This was the original reason for developing sachets.

- **Conclusions:** The use of soil in permeable sachets to capture preservatives migrating from submerged, treated wood provided a simple, reproducible method for detecting and quantifying preservative components at selected distances from the treated product with minimal disturbance and increased comparability across sampling times. Further studies are planned to examine the effects of soil type in sachets and how this parameter affects migration under similar environmental conditions.

Table 5. Ability to recover PAHs from sachets placed immediately adjacent to creosote treated DF piling for 3 weeks with no water circulation.

Sampling Time (weeks)	Total Conc. (ppm) of PAHs in Sachet Zones							Sum of PAHs in Entire Sachet
	Top Front (TF)	Top Back (TB)	Middle Front (MF)	Middle Back (MB)	Bottom Front (BF)	Bottom Back (BB)	Bottom Tip (BT)	
1	1.38	3.01	2.87	2.55	3.04	6.37	6.41	25.63
	6.03	26.86	13.67	3.72	0.00	4.63	0.52	55.43
	0.00	0.00	0.00	0.00	0.00	0.00	3.07	3.07
2	1.03	7.95	8.29	5.32	6.30	6.15	23.72	58.77
	21.99	24.57	25.47	3.07	29.40	4.06	3.93	112.49
	0.00	2.12	13.13	4.66	10.13	2.52	5.45	38.01
3	33.89	16.10	13.70	4.54	8.97	4.38	19.65	101.24
	79.74	93.66	25.72	71.83	31.91	4.22	7.52	314.60
	87.28	57.88	106.10	32.63	NA	6.11	22.96	312.95

Table 6. Properties of polycyclic aromatic hydrocarbons analyzed in soil surrounding creosote treated DF posts.

PAH	Elution time	Molecular weight	Water Solubility @ 25 ºC (mg/L)	Quantitation Ion	Reference Ion	r^2	Recovery %[a]	IDL (µg/kg)[b]
Naphthalene	6.914	128.17	31.00	128	127, 129	0.998	107 (4)	1
Acenaphthylene	10.754	152.20	3.93	152	151, 150	0.995	100 (4)	1
Acenaphthene	11.230	154.21	3.90	153	154, 152	0.996	113 (5)	1
Fluorene	12.491	166.22	1.69	166	165, 167	0.998	106 (5)	1
Phenanthrene	14.853	178.23	1.10	178	176, 179	0.998	97 (5)	5
Anthracene	14.961	178.23	$4.32\text{x}10^{-2}$	178	176, 179	0.999	97 (5)	5
Fluoranthrene	17.847	202.26	0.20	202	203, 200	0.999	94 (5)	1
Pyrene	18.380	202.26	0.14	202	200, 203	0.999	95 (5)	1
Benz(α)pyrene	21.444	252.32	$1.62\text{x}10^{-3}$	228	226, 229	0.999	58 (12)	5
Chyrsene	21.544	228.29	$2.00\text{x}10^{-3}$	228	226, 229	0.999	57 (12)	5

[a] Values represent means of 10 spiked soil samples taken through the entire extraction process. Values in parentheses represent one standard deviation.
[b] Instrument detection limit (IDL) when method is operated in SIM mode.

Table 7. PAHs in soil sachets placed immediately adjacent to creosote treated DF poles in a freshwater pond.[a]

PAH	PAH Level (µg/g soil)					
	5 months	19 months	29 months	34 months	39 months	49 months
Naphthalene	33.65 (18.58)	33.70 (23.83)	30.27 (27.09)	15.83 (14.72)	26.94 (24.18)	61.25 (20.20)
Acenaphthylene	1.11 (1.53)	0.25 (0.17)	0.34 (0.70)	0.12 (0.30)	0.08 (0.15)	1.61 (3.12)
Acenaphthene	46.77 (16.91)	26.51 (7.71)	24.33 (19.65)	14.87 (9.30)	20.06 (10.93)	66.05 (50.69)
Fluorene	26.63 (10.77)	16.91 (4.11)	16.72 (11.66)	9.99 (5.19)	16.35 (5.96)	46.82 (35.78)
Phenanthrene	49.95 (23.24)	43.21 (1.94)	33.96 (24.36)	28.89 (14.38)	62.11 (12.83)	65.62 (28.66)
Anthracene	3.79 (2.22)	3.55 (0.18)	3.22 (2.14)	1.86 (1.19)	4.06 (1.40)	6.62 (2.09)
Fluoranthrene	20.68 (12.67)	18.13 (5.61)	21.29 (9.39)	7.11 (4.94)	34.51 (10.71)	49.63 (24.88)
Pyrene	4.77 (7.32)	12.04 (4.21)	13.26 (6.46)	4.03 (3.04)	23.00 (7.85)	39.69 (16.29)
Benzo(α)pyrene	2.09 (0.98)	1.89 (1.28)	1.38 (0.49)	0.39 (0.39)	3.69 (1.90)	5.25 (3.36)
Chrysene	1.50 (0.98)	1.52 (1.03)	1.17 (0.52)	0.04 (0.11)	3.51 (2.49)	2.86 (3.03)

[a]Values represent means of 4 to 6 analyses per time point per PAH. Values in parentheses represent one standard deviation. BDL=Below detection limit.

Table 8. PAHs in soil sachets placed 0.3 m from creosote treated DF poles in a freshwater pond.

PAH	PAH Level (µg/g soil)[a]					
	5 months	19 months	29 months	34 months	39 months	49 months
Naphthalene	1.94 (1.87)	0.32 (0.10)	1.76 (2.02)	0.57 (0.28)	1.61 (0.17)	0.83 (0.75)
Acenaphthylene	0.26 (0.36)	BDL	0.08 (0.04)	BDL	0.14 (0.01)	BDL
Acenaphthene	0.43 (0.60)	0.38 (0.55)	0.52 (1.14)	0.10 (0.03)	0.49 (0.50)	1.07 (2.14)
Fluorene	0.64 (0.59)	0.25 (0.07)	0.30 (0.40)	0.10 (0.09)	0.78 (0.25)	0.89 (1.79)
Phenanthrene	0.26 (0.36)	0.22 (0.31)	0.03 (0.04)	0.19 (0.43)	1.79 (3.45)	0.82 (0.99)
Anthracene	0.41 (0.43)	0.10 (0.14)	0.13 (0.10)	0.07 (0.04)	0.35 (0.02)	0.09 (0.17)
Fluoranthrene	0.23 (0.32)	0.05 (0.07)	0.30 (0.54)	BDL	0.86 (1.60)	2.41 (2.50)
Pyrene	0.33 (0.35)	0.07 (0.02)	0.24 (0.26)	0.03 (0.04)	067 (0.95)	1.34 (1.53)
Benzo(α)pyrene	0.90 (0.26)	0.74 (0.13)	0.81 (0.04)	0.63 (0.01)	1.59 (0.06)	0.18 (0.37)
Chrysene	0.19 (0.26)	0.06 (0.06)	0.09 (0.04)	BDL	0.16 (0.02)	BDL

[a]Values represent means of 4 to 6 analyses per time point per PAH. Values in parentheses represent one standard deviation. BDL=Below detection limit.

Table 9. PAHs in soil sachets placed 0.9 m from creosote treated DF poles in a freshwater pond.[a]

PAH	PAH Level (µg/g soil)					
	5 months	19 months	29 months	34 months	39 months	49 months
Naphthalene	0.70 (0.11)	0.70 (0.17)	0.84 (0.19)	8.99 (13.60)	1.63 (0.05)	2.11 (3.22)
Acenaphthylene	0.11 (0.16)	BDL	0.07 (0.06)	0.10 (0.25)	0.15 (0.03)	BDL
Acenaphthene	0.16 (0.22)	0.08 (0.11)	0.43 (0.97)	5.86 (8.78)	0.21 (0.10)	0.69 (1.31)
Fluorene	0.37 (0.20)	0.20 (0.01)	0.41 (0.48)	4.61 (6.87)	0.63 (0.11)	0.37 (0.74)
Phenanthrene	0.07 (0.10)	BDL	0.19 (0.40)	6.28 (10.22)	0.23 (0.23)	2.29 (3.81)
Anthracene	0.21 (0.15)	0.19 (0.02)	0.29 (0.53)	0.52 (0.73)	0.31 (0.12)	BDL
Fluoranthrene	0.11 (0.16)	BDL	0.26 (0.50)	11.40 (16.02)	0.19 (0.17)	0.63 (1.25)
Pyrene	0.20 (0.17)	0.04 (0.06)	0.25 (0.24)	7.83 (11.14)	0.33 (0.07)	0.37 (0.75)
Benzo(α)pyrene	0.84 (0.16)	0.80 (0.12)	0.83 (0.06)	1.75 (2.12)	1.57 (0.10)	0.06 (0.22)
Chrysene	0.11 (0.15)	0.09 (0.01)	0.11 (0.02)	1.17 (1.98)	0.14 (0.07)	BDL

[a] Values represent means of 4 to 6 analyses per time point per PAH. Values in parentheses represent one standard deviation. BDL=Below detection limit.

Table 10. Copper, zinc and arsenic levels in sediments exposed immediately, 0.3 and 0.9 m away from an ACZA treated DF piling 1 to 47 months after installation.

Time (months)	Distance from pile (m)	Metal level in soil (ppm)[a]		
		Cu	Zn	As
1	0.3	3.05	4.00	BDL
	0.9	3.35	4.55	BDL
3	0	117.95	57.60	0.35
	0.3	4.65	5.55	BDL
	0.9	3.85	5.00	BDL
31	0	496.25	564.31	34.10
	0.3	30.85	67.58	BDL
	0.9	6.50	3.98	BDL
41	0	244.5	618.00	57.85
	0.3	39.09	84.28	2.05
	0.9	34.22	81.73	1.96
47	0	182.50	363.50	12.05
	0.3	11.27	11.51	0.05
	0.9	7.47	10.43	0.05

[a] Values represent means of two samples per time per location. BDL= below the detection limit (<0.1 ppm) for that analysis. Assay sensitivity improved in subsequent years.

Table 11. Metal levels in soil samples removed from various distances around ACZA treated DF posts 3 or 9 months after immersion.

Distance from Post (m)	Time in Test (Months)	Metal Levels in Sediment (mg/kg)[a]		
		Cu	Zn	As
0	3	427.23 (114.06)	521.68 (154.32)	88.21 (32.99)
	9	256.28 (115.23)	306.67 (71.26)	11.29 (2.70)
0.3	3	39.10 (2.49)	78.50 (6.48)	2.20 (0.21)
	9	39.25 (73.41)	38.35 (64.95)	1.45 (3.15)
0.9	3	33.07 (2.61)	77.60 (4.15)	1.99 (0.06)
	9	15.51 (16.46)	19.92 (19.1)	0.40 (0.53)

[a] Values represent the means of analyses of samples around 5 posts. Figures in parentheses represent one standard deviation. Control samples were exposed up-current from the test piling.

C. Effect of Damage to Polyurea Coatings on Metal Losses from Ammoniacal Copper Zinc Arsenate Treated Douglas-Fir Pile Sections:

Preservative treatments markedly extend the useful life of wood products. Virtually all preservatives have some degree of water solubility (Graham, 1973). While solubilities are extremely low in many cases, the ability to remain in solution within the wood plays an important role in the ability of these systems to inhibit invading organisms before wood damage occurs (Arsenault, 1973; Hartford, 1973). For decades, the ability of preservatives to migrate from wood was viewed as a positive attribute as long as the levels did not result in chemical depletion and loss of protection. In soil environments, migrating chemical created a zone of protection around the treated wood (EPRI, 1997; Morrell et al., 2003). In water applications, the lost chemical was assumed to be rapidly diluted and pose little risk. Increasing knowledge about the risks of uncontrolled chemical losses from all materials has created a general concern about the potential for preservative migration.

Environmental concerns have been especially strong in the U.S. Pacific Northwest, where various state and federal environmental regulatory agencies have worked to save several endangered salmon species. Among their efforts has been a move to reduce heavy metal inputs into regional coastal waters. These efforts have led to substantial restrictions on the use of preservative treated wood over and in aquatic environments. The development of BMPs has allowed the use of treated wood in some applications (WWPI, 2012), but many regulators have moved to further restrict the use of treated wood and mandate the use of alternative materials such as concrete, steel, or even recycled plastic. Each of these materials has its own environmental footprint, but are viewed as more environmentally friendly.

One option that has arisen for using preservative treated wood in aquatic applications is to encapsulate the wood with an impermeable coating such as fiberglass, polyethylene or polyurea. Fiberglass has long been used for repairing and reinforcing damaged pilings in marine applications, while polyethylene has been used for limiting further access of marine borers to damaged pilings (Morrell et al., 1984). Studies at the Port of Los Angeles found that polyurethane coatings limited marine borer attack of untreated pilings and an IRG international collaborative study found that the coatings were effective under a range of exposure conditions (Horeczko, 1984; 1987; Steiger and Horeczko. 1981, Eaton, 1986). Barriers have also been assessed to improve performance in terrestrial environments (Behr et al., 1996; Morrell, 2016). While these trials have shown the ability of coatings to improve resistance to attack by wood degrading organisms, none have examined the ability of these coatings to limit preservative migration.

In preliminary tests, we evaluated the ability of a 250 mil thick polyurea coating to restrict metal migration from DF pilings treated with ACZA immersed in seawater (Konkler, 2017). Results showed that the polyurea barrier completely stopped metal migration into either the surrounding sea water or the sediment. While these results supported the use of coated pilings in sensitive applications, materials in marine environments are subjected to considerable wear and tear that might damage the coating, thereby allowing metal migration to occur. As regulators examined the use of coatings to limit preservative migration, a question arose concerning the amount of damage that a piling could sustain before repair would be required. The objective of this most recent test was to determine the effects of increasing degrees of coating damage on metal migration for the same piling used in the initial studies.

- **Materials:** Douglas-fir pilings, 153 mm diameter by 1.4 m long, were treated to the AWPA Use Category 5B (40 kg/m^3) with ACZA and subjected to one of the WWPI BMP processes (AWPA, 2017; WWPI, 2012). Three pilings were left without a coating, while four others were commercially coated with a ~250 mil thick polyurea layer from the butt to the tip by Thunderbolt Wood Treating (Riverbank, CA; Figure 6). The coating was only on the vertical surfaces, not the cross sections.

    - **Piling Exposure:** Pilings were buried to a depth of 400 mm in soil in 208 L Nalgene tanks and the tanks were filled with artificial seawater (1.5% salt) to a depth of 600 mm so that the base of each piling was in sediment, but the remaining 400 mm of the section was not immersed. Tanks were covered to limit evaporation and stored at room temperature. Sediment and water were periodically sampled for copper, zinc, and arsenic. Coated pilings were installed November 20, 2015, while the non-coated pilings were installed January 27, 2016. Both sets of materials were exposed to the same conditions after installation.

- **Chemical Analysis:** Sediment samples were microwave-digested. Briefly, oven dry soil was ground to ensure homogeneity, using stainless steel or Nylon to minimize contamination. Five hundred mg of sediment was weighed into a Teflon microwave digestion tube. Ten mL of nitric acid was added to each tube and agitated to ensure samples were thoroughly wetted. Samples were microwave digested using the EPA 3051A method and the resulting solution was analyzed for total copper, zinc, and arsenic by ICP. The resulting soil metal levels were expressed on a µg/g of dry soil basis. Water samples were collected by gently agitating the water to evenly distribute any metals and minimize sediment disturbance. A 20 mL sample of water was removed, acidified with 1 N nitric acid, and analyzed for metal content by ICP. Initial sampling was frequent (daily, then weekly), but decreased as trends became evident. Detection limits for copper, zinc, and arsenic were <0.05 mg/kg for all three metals.

- **Coating Damage Procedures:** Pilings were exposed for 384 days before initial experiment termination. Non-coated pilings were removed and retained for possible later use. A 50 mm wide strip of the polyurea coating on each of the four coated pilings was removed. This represented approximately 8% of the surface area exposed in the immersion test. The pilings were then replaced into the tanks as previously described and water samples were collected over a 100-day immersion period. At the end of 100 days, an additional 8% of the coating (16% total) was removed before the samples were again immersed and sampled over a 96 day exposure. Finally, another 8% of the coating area was removed and the pilings were submerged for 43 days under the same conditions (24% of total coating area).

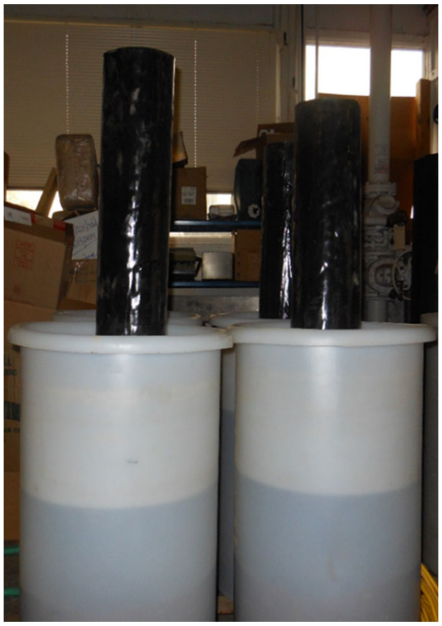

Figure 6. Example of polyurea coated pilings in exposure tanks.

- **Initial Exposure:** Metal levels in the water column in tanks containing coated ACZA were below detection limits (0.05 mg/kg for each element) over the entire 384 day exposure period. Results illustrate the ability of these coatings to contain metallic elements in salt water. Metal levels in water containing non-coated piling exposed in the same manner steadily increased over the exposure period (Figure 7), although there was some variation in levels with prolonged exposure as a result of less frequent sampling. The overall concentration trend, however, was steadily upwards with the possible exception of the 2 final collections that suggested a plateau had been reached. Interestingly, there did not appear to be a large surge in metal concentrations in the water immediately after installation; copper, zinc, and arsenic levels steadily increased over the exposure period. Previous reports have shown that metal levels in water surrounding a sample of treated wood sharply increased following immersion, as residual metals on the wood surface are solubilized (Brooks, 2011). These pilings were subjected to post-treatment BMPs according to procedures described in WWPI guidelines (WWPI, 2012). While these processes reduce the presence of surface deposits and help ensure metal immobilization, the lack of any noticeable surge is interesting, although not pertinent to the current test (Ye and Morrell, 2015). Metal levels in sediment after 309 and 340 days of exposure remained exceedingly low in the sediment around coated samples (Table 12). These results agree with the water column analysis and indicate coatings are restricting metal movement.

Table 12. Residual copper, zinc, and arsenic in sediment surrounding non-coated and polyurea coated ACZA treated DF.[a]

Treatment	Exposure Time (Days)	Metal Concentration (µg/kg of sediment)		
		Copper	Zinc	Arsenic
Coated	309	2.38 (1.90)	3.48 (0.90)	1.18 (1.33)
	340	3.40 (0.54)	4.00 (1.70)	0.75 (0.85)
Non-Coated	241	81.37 (106.97)	46.57 (39.49)	15.07 (10.43)
	272	188.50 (200.34)	70.33 (38.47)	11.73 (8.03)

[a] Values represent means of 3 or 4 samples per time point. Figures in parentheses represent one standard deviation.

Metal levels in sediment surrounding non-coated samples were more than 10 times those found around uncoated samples. Although sediment was only sampled two times, results suggest sediment metal levels surrounding the non-coated samples was increasing. The results clearly illustrate the benefits of using barriers to limit metal migration from ACZA treated wood.

The polyurea coating completely inhibited copper, zinc, and arsenic migration from ACZA treated piling in synthetic salt water in a non-circulating environment where metal build-up would be especially critical. The results illustrate the benefits of these types of coatings.

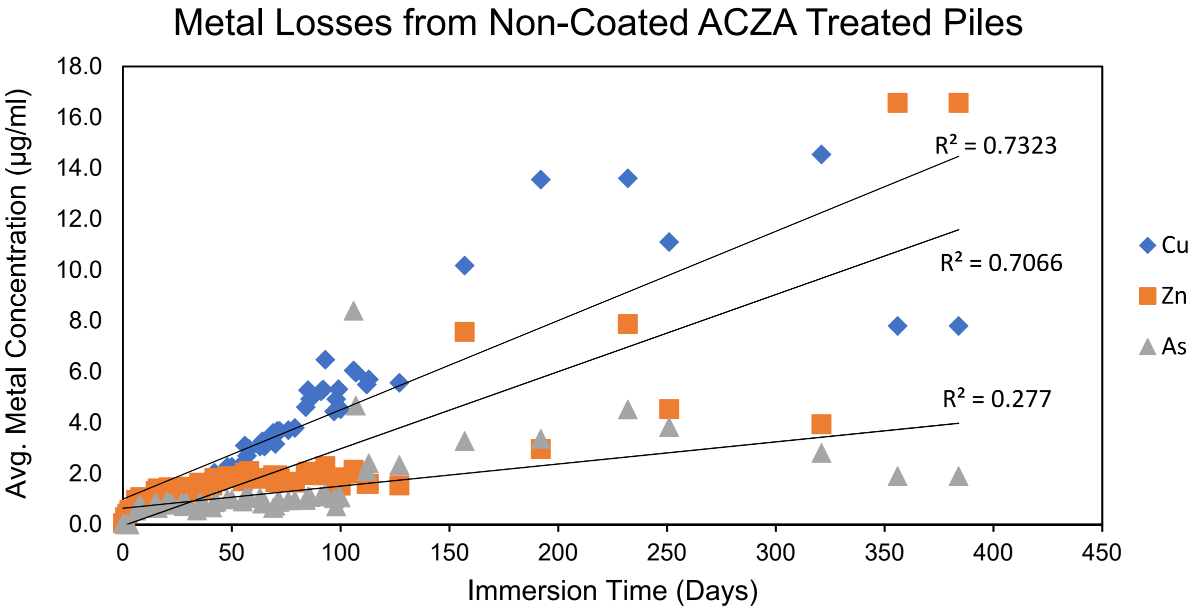

Figure 7. Copper, zinc, and arsenic levels in salt water samples removed over a 384 day period from tanks containing ACZA treated DF piling with no polyurea coating. Values represent means of 4 samples per time point per element.

- **Effect of Coating Damage on Migration:** Background seawater metal levels were 0.034, 0.113, and 0.063 µg/mL of seawater for Cu, Zn, and As, respectively, at the start of the test. As expected, metal levels rose in all tanks with damaged pilings. Removing 8% of the coating surface area resulted in metal levels that were approximately 0.09, 0.40, and 0.85 µg/mL for arsenic, zinc, and copper, respectively, after 100 days of immersion (Figure 8). It is difficult to directly assess the effects of barrier damage; however, we used the metal levels detected in the water columns around non-coated pilings from the initial trial at the same time points. Arsenic, zinc, and copper levels in water collected around pilings with 8% damage were 8.7, 21.6 and 14% of those found with non-coated pilings after a similar immersion period. Concentrations differed from those found in the original preservative system, likely reflecting immobilization as the ammonia evaporated after treatment (Lebow and Morrell, 1995). The slightly higher zinc levels were interesting because this metal is presumed to co-precipitate during the immobilization process following treatment.

  Metal levels in water surrounding pilings with 16% coating damage were similar for arsenic and zinc, but much higher for copper after 100 days of immersion (Figure 9). Arsenic levels were only 9.7% of those found in water from non-coated pilings, while zinc levels were 26.5% of the non-coated levels. The disproportionately lower arsenic levels were interesting, while zinc appeared to be moving out of the wood at a rate proportional to the exposed surface area. Conversely, copper levels were 58% of those found with non-coated pilings. It is unclear why copper levels were so much higher than those found with the 8% coating damage.

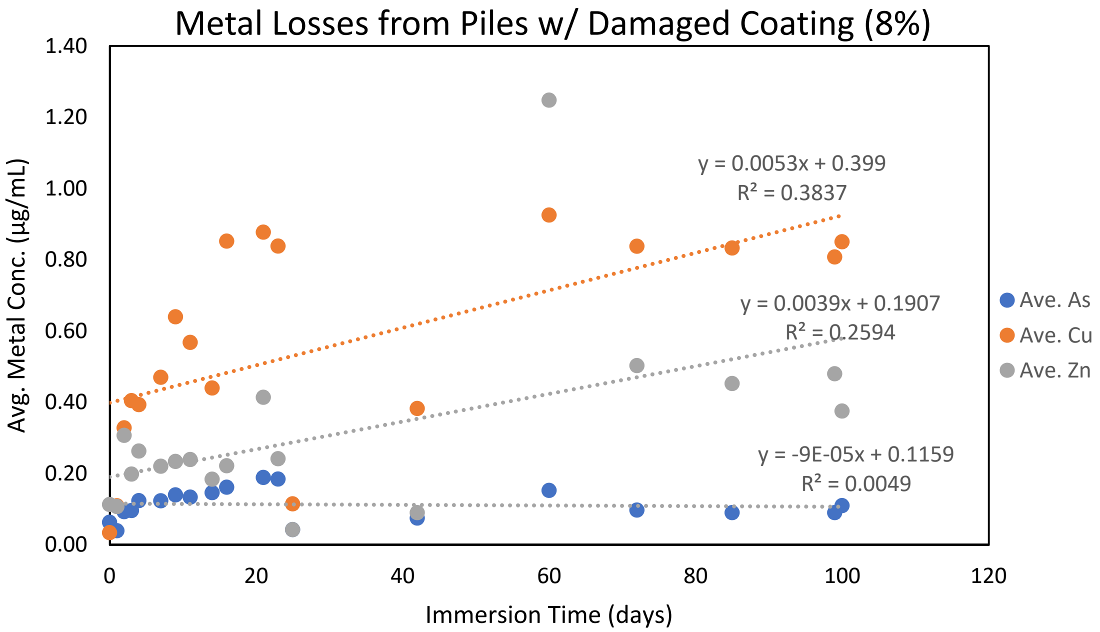

Figure 8. Copper, zinc, and arsenic levels in seawater surrounding polyurea coated ACZA treated piling with 8% of the coating area removed. Values represent means of 4 samples per time point per element.

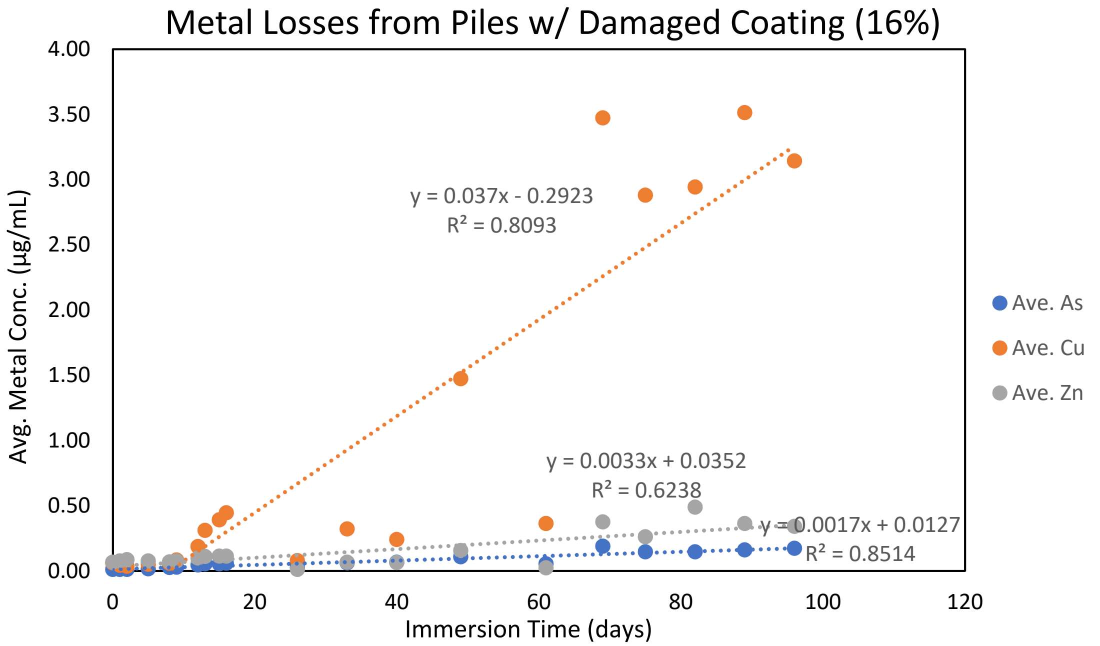

Figure 9. Copper, zinc, and arsenic levels in seawater surrounding polyurea coated ACZA treated piling with 16% of the coating area removed. Values represent means of 4 samples per time point per element.

The piling with 24% of the coating area removed were only exposed for 43 days after being damaged. Removing this amount of coating was associated with arsenic, zinc, and copper levels that were 70.8, 48.6 and 22.9% of those found after 43 days of immersion of non-coated piling (Figure 10). The large increase in arsenic levels was especially perplexing given the low levels detected when 8 or 16% of the coating area was removed. Arsenic levels in water around pilings with 24% of the coating removed increased rapidly and were more than twice the 100 day concentrations found in water from pilings with less damage after only 4 days. Arsenic has typically been found at low levels in water runoff from ACZA treated wood (Ye et al., 2015) and these piling had been subjected to WWPI BMPs that are designed to reduce post-treatment preservative migration. However, it is important to note that these samples were treated to the higher retentions required for marine exposures (40 kg/m^3 vs 16 kg/m^3 for terrestrial applications such as utility poles). It is possible that the high levels of treatment left pockets of elevated metals on some portions of the piling surface prior to coating. Further tests are underway to better define the effects of damage on metal losses.

It is important to note that these results represent limited sample size and more tests are being performed. However, the current recommendations for the use of polyurea coated materials requires periodic coating inspection to ensure that they are not severely damaged and mandates some form of active repair should more than 25% of the coating be removed. Preliminary results suggest that this figure is appropriate for minimizing the risk of excessive metal migration.

- **Conclusions:** Polyurea coatings were highly effective at containing metals from ACZA treated DF pilings. As expected, damaging the protective coating resulted in increased metal migration. While there were some variations in concentrations of the different levels after damage, the results generally support using a threshold of 25% damage before a coating repair is initiated.

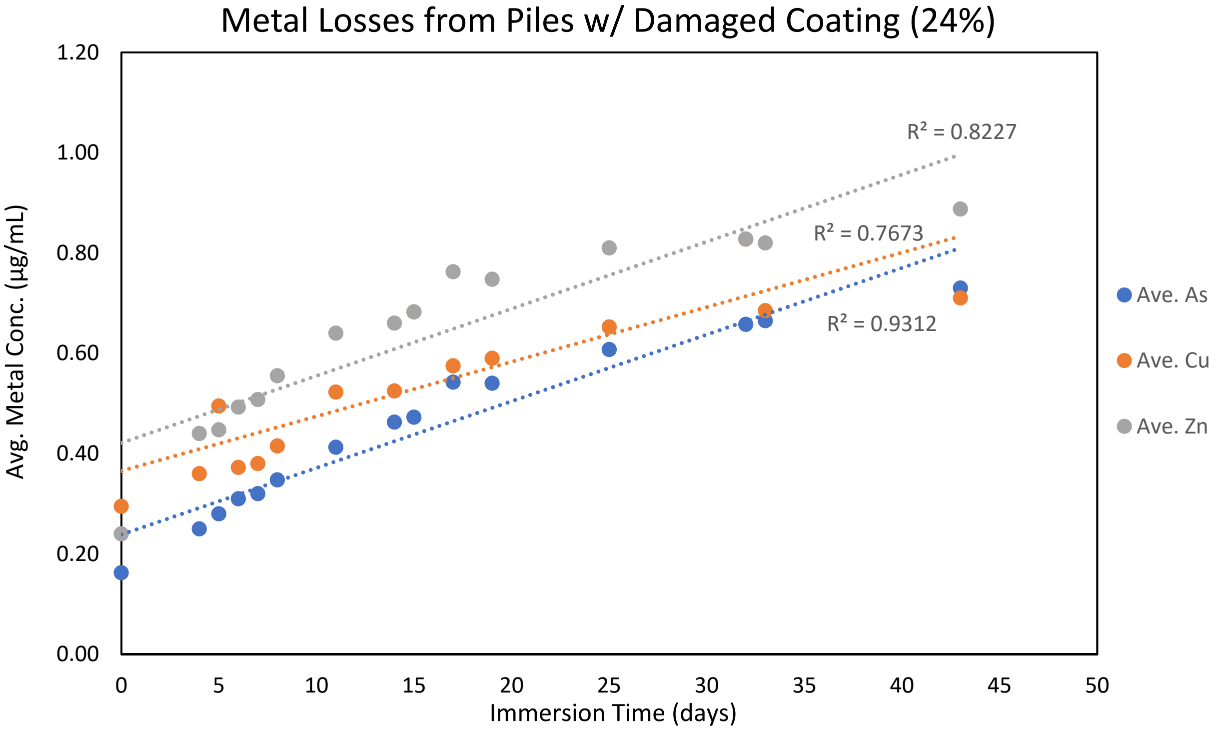

Figure 10. Copper, zinc, and arsenic levels in seawater surrounding polyurea coated ACZA treated pilings with 24% of the coating area removed. Values represent means of 4 samples per time point per element.

D. Establish Additional Field Monitoring Sites:

While controlled BMP tests are useful, they need to be accompanied by field monitoring of sites with different preservative treatments and environmental conditions. We have been fortunate enough to get the opportunity to monitor Jackson Frazier Wetland decking and the Santiam Bridge, but these sites are all located in Oregon. There is a critical need to identify other treated structures so we can begin to build a series of case studies.

While there have been a few false starts in regard to identifying suitable structures, we now have a plan to sample a series of bridges on the outskirts of Minneapolis, MN. The structures are located in the town of Chaska which has installed a number of bridges over the years, treated with either penta or CuNaph. In previous tests, we periodically set up a water collection system to capture rainwater runoff from a structure. That will not be possible in Chaska. Instead, we will collect sediment samples upstream, underneath, and downstream of a given structure. These samples will be analyzed for either penta or copper as described earlier. The first samples will be taken in May of

2019, depending on the weather, with a goal of sampling 10 or more bridges. We will return 1, 2, and 3 years thereafter for additional collections.

There is also the possibility of a second site in Rhode Island at a former amusement park that is being redeveloped.

While these developments are promising, we are still seeking additional monitoring sites. High on the list would be structures treated with waterborne preservatives, especially southern pine structures.

E. Effect of Abrasion on Metal Levels in Aquatic Applications of Treated Wood:

Over the past five years we have worked to evaluate the effects of various BMPs on subsequent migration of preservatives from treated wood. One subject that keeps arising is the contribution of surface abrasion. While wood is a reasonably abrasion-resistant material, repeated pedestrian or vehicle traffic can result in the loss of wood particles. These particles have very high surface to volume ratios that could potentially result in disproportionate preservative releases over time, especially in high traffic areas. However, it is important to note that the chemicals in these particles are largely immobilized and should therefore be less susceptible to migration. There are no realistic data that exclusively examine the contribution of particle abrasion on total preservative losses from a given structure, although Brooks considered losses of particles during sawing or drilling at the time of installation as a major source of contamination and included recommendations to contain these materials as part of BMPs.

We have been working to develop realistic tests examining the potential contribution treated wood particles have on preservative losses. Previously, sawdust from preservative treated lumber was immersed in several treatments: deionized and tap water, pH 6, 7, and 8 water, and hard and soft water. The results were as expected; the particles lost substantial quantities of copper. However, our sawdust was fragmented and that often exposes interior lumens to possible leaching, while naturally abraded fibres will retain more of their original cell geometry. These differences could markedly alter the resistance of a preservative to migrate.

Due to the difficulty of creating representative particles, we also established a field trial to assess the rate of wear on treated wood decking. Collecting fibres from bridges is problematic because they sluff off slowly and mix with the ground below, making them difficult to recover. Setting up fibre collection systems beneath a structure might be functional but we chose, instead, to use changes in conditioned mass of full scale test samples installed on a bridge as the measure of wear.

A trail bridge located in the McDonald-Dunn Research Forest of Oregon State University was selected for study. The bridge is located immediately adjacent to the Peavy Arboretum Starker Post Farm. It is heavily used by various school groups and visitors. The bridge is constructed using nominal 2 by 6 inch by 6 foot long ACQ treated decking and has been in place for at least a decade. The bridge crosses a seasonal wetland.

Copper azole treated DF lumber was purchased locally and cut to length. Samples were retained for later analysis, if needed. The lumber was conditioned to constant weight at 23 °C and 65% relative humidity before being weighed. The samples were then installed as replacement boards on the bridge (Figure 11). They will be removed at 6 month intervals and reconditioned prior to weighing to determine mass loss, if any. We do not expect this to be a short-term project, but over time, it should begin to provide data on material loss rates. One other aspect of this project will be a need to determine the number of pedestrians crossing the structure. We examined various counter systems, but none were suitable for this application. Instead, students will be periodically stationed adjacent to the bridge at various times of day to count the number of people passing over the structure. In addition, we will continue to seek out other structures that might be monitored for surface wear rates.

Figure 11. Deck boards used to assess abrasion rates in the bridge at Peavy Arboretum.

OBJECTIVE II

DEVELOP STANDARDIZED ACCELERATED METHODOLOGIES FOR ASSESSING TREATED WOOD RISKS

We are working to develop a number of standardized methodologies that can be used to assess preservative mobility under varying regimes. These include small-scale BMP verification procedures, sachets used to detect preservative migration in aquatic environments, and our efforts to quantify PAH levels in the water column. Our intent is to publish the results of these tests in peer-reviewed journals and, once accepted, move to standardize these methods under the appropriate organizations.

OBJECTIVE III

WORK COOPERATIVELY TO DEVELOP AND IMPROVE MODELS TO PREDCT THE RISK OF USING TREATED WOOD IN VARIOUS APPLICATIONS

The BMP verification studies, coupled with field trials provide us with a wealth of data that can be used to assess the accuracy of the Environmental Assessment Modeling Tool. We are still sorting through these data, but the intent will be to use these results to examine the efficacy of various BMPs and to make recommendations to the BMP Coalition concerning the most appropriate BMPs for a given preservative.

OBJECTIVE IV

IDENTIFY IMPROVED METHODS FOR REDUCING THE POTENTIAL FOR MIGRATION

We have only undertaken a limited amount of research on this topic. Studies undertaken to evaluate the effects of various BMPs on metal migration from treated DF, SPF, and SP lumber have provided valuable information on the effects of BMPs on metal migration from wood treated with various preservatives. We intend to use these data to explore improved methods to reduce metal loss. We explored the potential for using lignosulfonate, a compound commonly used to control road dust, as a surface treatment to limit copper migration from ACZA treated wood. These trials were unsuccessful.

OBJECTIVE V

EVALUATE THE ENVIRONMETNAL IMPACTS AND IDENTIFY METHODS FOR REUSE, RECYCLING, AND/OR DISPOSAL OF PRESERVED WOOD THAT IS REMOVED FROM SERVICE

We continue to examine treated wood entering the recycling stream. The Pacific Regional Compost Center where we have performed these studies has changed their operation, making it difficult to regularly access the site. We are working with the facility to identify a sampling procedure that meets their safety concerns, while allowing access to the materials in a timely fashion.

OBJECTIVE VI

DELIVER EDUCATIONAL OUTREACH PROGRAMS ON THE PROPER USE OF TREATED WOOD IN RELATION TO THE BEST MANAGEMENT PRACTICES (BMPs)

Meetings were held with the National Marine Fisheries Service in July and August where a presentation was made on the Coop and use of treated wood. We will continue to seek out opportunities to use my extensive background in environmental chemistry and wood protection to explain the function of the EPTW and how to use treated wood as opportunities arise.

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