

Environmental Performance of Treated Wood Cooperative

Sixth Annual Report

Matthew Konkler

Department of Wood Science & Engineering

Oregon State University

Corvallis, Oregon



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Executive Summary

The Environmental Performance of Treated Wood Research Cooperative 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.

- A. The Best Management Practices (BMP) verification studies are progressing. We have completed analysis of the BMP processes on southern pine lumber treated with waterborne preservatives. The results were consistent with those found with Douglas-fir and showed that most heat treating processes produced better immobilization, but there were some variations with treatment type. Chromated copper arsenate (CCA) treatments resulted in the lowest metal losses when exposed to rainfall, followed by copper azole and finally alkaline copper quat. We expect to begin assessment of BMP steaming treatments on pentachlorophenol treated lumber shortly. All the materials have been steamed, frozen, and are awaiting exposure. We also have Spruce-Pine Fir lumber treated and exposed and are awaiting analytical results.

Once rainfall exposure has been completed on all three species, we expect to prepare an update with recommendations on the most appropriate BMP processes for each chemical and possibly species combination.

- B. Evaluations of metal and polycyclic aromatic hydrocarbons (PAH) migration from post (small piling) treated with ammoniacal copper zinc arsenate or creosote have also been underway. Fifteen of the 16 PAH's we examined were detected in sediment immediately adjacent to and within 300 mm of the piling, but the levels declined sharply with distance from the wood. These results are consistent with previous tests. Similar results were found with metals in sediment around ammoniacal copper zinc arsenate (ACZA) treated wood. These results verify the finding that there is relatively little migration away from treated wood into the surrounding sediment. As noted last year, we have not been able to detect any PAH's or elevated metals levels in pond water immediately adjacent to the posts, even with selective filtering and concentration.
- C. We have performed one additional sampling of the House Rock bridge. This structure contains pentachlorophenol treated decking and copper naphthenate treated stringers. The copper analysis from the most recent sample is still in process, but the penta levels had declined sharply from the previous two samples. An analysis of potential penta levels in the water column showed that the levels possible in the receiving stream were well below the minimum effects level. We will continue to monitor this bridge and plan to provide a short report to the Forest Service.
- D. We have also exposed polyurea coated and non-coated ACZA in small scale tanks to assess the effects of the barrier on preservative migration. Water and sediment samples taken over a 340 day period show that there was no detectable increase in copper, zinc, or arsenic levels in soil or water surrounding the coated piling. Metal levels have steadily increased in sediment and the water column around non-oated piling. The results illustrate the benefits of coatings for allowing use in sensitive environments.

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 models have 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 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 little 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 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 EPTWC 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 the Best Management Practices*

ACCOMPLISHMENTS

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

1. Develop fundamental data on preservative migration from wood

A. Evaluate the BMPS to determine if they alter preservative migration patterns

In previous reports, we have described efforts to develop data on the effects of the BMP's on preservative migration. The results have been mixed, in some cases suggesting a benefit for using these practices, but mostly suggesting that BMP's had little effect. We believe these results occurred because most of the material that was exposed was already air-dried prior to exposure; in essence, receiving one of the BMP's (air-seasoning). The BMP's 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 BMP's on migration, we moved to a smaller scale test where we could control all aspects of the process to produce more reproducible results.

We described results from this system using ACZA, alkaline copper quat (ACQ) and copper azole (CA) treated Douglas-fir decking (Ye and Morrell, 2015a,b). Spruce-Pine-Fir (SPF) samples were treated in commercial facilities located in Oregon and Washington, while the southern pine samples were treated in our experimental retort (Table 1). The use of the smaller retort was necessary because southern pine requires much shorter treatment cycles and shipping to plants outside the region would have introduced a time delay that would allow for some chemical immobilization to occur during shipping. In addition to the waterborne treatments, we have also treated SPF and southern pine samples with copper naphthenate, creosote and pentachlorophenol. Samples were treated with the given preservative using only vacuum and pressure with no post-treatment BMP processes. The samples were cut into 300 mm lengths that were placed into plastic bags and frozen (-5 °C) until needed.

Post-treatment with BMP's: The frozen samples were defrosted before being subjected to one of nine treatments listed in the Western Wood Preservers Institute Best Management Practices requirements. The methods were applied to sub-samples of each board treated with a given chemical even though we recognize that not all of these processes are currently listed as BMP's for all chemicals.

-Air-drying: Samples were placed on stickers at ambient temperature (20-25°C), 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°C and wet-bulb depression of 5.6°C. This cycle limits drying, but the heat should encourage 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 104.4°C with stickers in 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°C for 1 or 3 hours.

-Ammonia bath: Samples were soaked in aqueous 1% ammonia at 100°C for 1 and 3 hours.

The samples were frozen (-5 °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 a portion of each board being subjected to a given BMP.

Leaching test: The samples were thawed overnight before the potential for preservative migration was evaluated in a specially constructed overhead leaching apparatus that applies 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 was operated at room temperature (20~28°C) 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 BMP procedures on migration of metals from ACZA, CA or ACQ treated wood.

The apparatus (1.5 m wide * 0.6 m long * 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.

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 water 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 two hours. Preservative retention in the samples was determined using either net solution uptake for the southern pine samples treated with waterbornes or by x-ray fluorescence for both southern pine and SPF samples. Penta and creosote analysis are underway.

Chemical analysis: Samples from waterborne preservatives were acidified by adding 0.15 mL of 1 M nitric acid into 4.85 mL of runoff water. The samples were stored at 4°C until they could be analyzed for residual metal, mainly copper, using a Perkin Elmer Optima 3000DV inductively-coupled plasma optical emission spectrometer with a diode array detector (ICP). Since most of the chemical migration occurs at the beginning of water exposure, 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 collect additional rainfall exposures. Copper concentrations were used as a measure of BMP effectiveness, although chromium, zinc and arsenic were also measured where those metal were present in a preservative system. Retentions were high for CCA treated southern pine but slightly below the targets for ACQ and CA (Table 2). SPF retentions were just above the target for ACZA, but well below that level for CCA, ACQ and CA. Cross cuts of the samples illustrate the poor penetration. The SPF boards were treated as full length samples that were then cut for exposure. Even with incising, the samples were poorly treated (Figure 2).

Table 1. Treatments applied to evaluate BMP processes on southern pine, Douglas-fir and spruce-pine-fir lumber.

Species	Treatment Type						
	CuNaph	Penta	Creosote	ACZA	CCA	ACQ	CA
Douglas-fir	-	Conc.	P1/P13	Done	-	Done	Done
Southern pine	Done	Conc	P1/P13	-	Type C	Type D	Type B
SPF	Done	-	P1/P13	Done	Type C	Type B	Type B

Metal levels in runoff from CCA treated southern pine were generally low. Copper levels tended to be higher than those for arsenic or chromium except for the non-BMP-treated controls, although there were some exceptions (Figure 3, Table 3). Copper levels tended to be lowest in the air and kiln dried samples as well as those subjected to 1 or 3 hours of ammonia steaming. The effects of the ammonia steaming were surprising given the acidic nature of CCA. Interestingly, prolonged steaming (1 to 6 hours) was associated with the highest copper levels in the first 15 minutes of rainfall runoff. It is unclear whether prolonged steaming results in migration of additional metal to the wood surface, but minimizing steaming to optimize amine loss while limiting such migration might be one approach for enhancing the efficacy of this BMP. The one hour hot water bath was also associated with elevated copper levels in the runoff, but these levels declined with an additional 2 hours of exposure suggesting that the heat was affecting deposition. Copper levels declined sharply after the first 15 minutes of rainfall for all the BMP processes, which is consistent with previous reports indicating that the initial rainfall poses the most critical risk for CCA treated wood in aquatic environments (Brooks, 2011).

Arsenic levels were generally low in runoff from the CCA treated boards regardless of BMP process (Figure 3, Table 4). Air and kiln drying were associated with the lowest arsenic levels in rainwater runoff. The highest arsenic levels were found in boards receiving no BMP treatment as well as those subjected to either 1 to 6 hours of steaming or 1 and 3 hours of a hot water bath. Arsenic levels in runoff from boards

subjected to the other BMP treatments tended to be well below 1 ppm and continued to decline over the 2 hour rainfall period.

Chromium is the most critical component in CCA because its reduction from the hexavalent to trivalent state drives the simultaneous deposition of copper and arsenic in the wood. This so-called “fixation” sharply reduces the potential for migration of all three metal components. Chromium reduction can occur naturally as this metal reacts with the wood, but it can also be accelerated using heat and many users of CCA in colder climates have installed fixation chambers to accomplish this task using either direct steaming or hot water baths. The chromium reduction process is then dependent on the amount of time the wood is heated.

Chromium levels were elevated in rainwater runoff from boards that received no BMP treatment prior to exposure (Figure 3, Table 5). Chromium concentrations in rainwater runoff from non-BMP treated boards averaged 12.4 ppm in the first 15 minutes and only declined to 6.7 ppm after 2 hours of exposure. These results indicate that considerable amounts of non-reduced chromium remained near the surface of the boards where it could be removed during the exposure. Chromium levels in rainwater runoff from boards that received a BMP treatment were generally below 0.7 ppm in runoff from the first 15 minutes of rainfall regardless of the process employed. This is consistent with the relatively rapid rate of chromium reduction following treatment and the use of heat for most of the BMP's. Chromium levels continued to decline with increased rainfall exposure in BMP treated materials until the end of the 2 hour test. The results illustrate the benefits of a BMP process for immobilizing chromium in CCA treated wood.

Table 2. Target and actual retentions of CCA, ACZA ACQ or CA in southern pine 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	-	7.26 (0.29)
Petna	8	-	7.87 (0.23)	-
Creosote	160	-	-	-

^aValues represent means of 8 samples for the net uptake and 3 replicates for the XRF (x-ray fluorescence) retentions. Figures in parentheses represent one standard deviation.





B



C

Figure 2. Photos showing poor preservative penetration in SPF boards treated with CCA (A), CA (B) or ACQ (C).

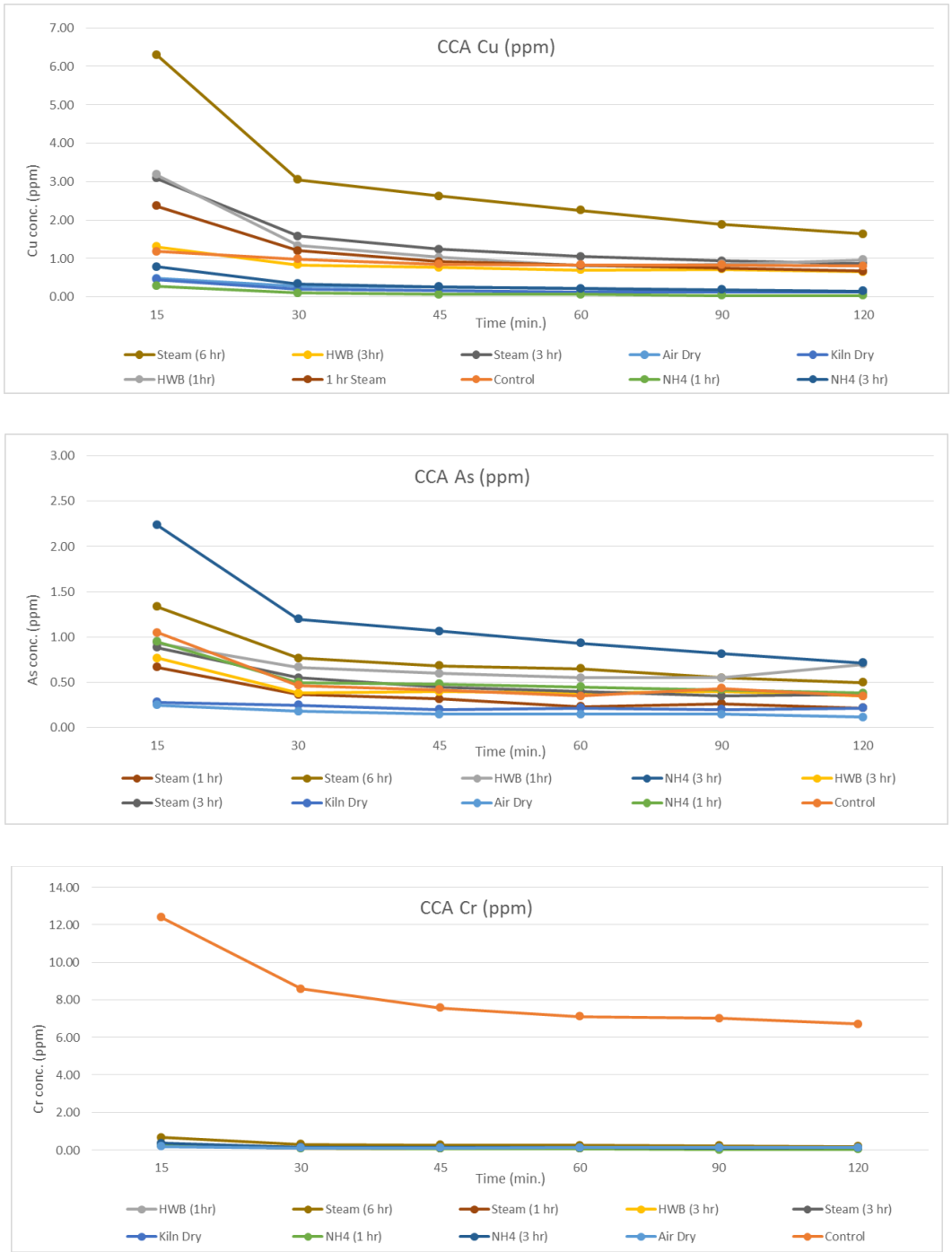


Figure 3. Copper, arsenic and chromium concentration in runoff from CCA treated southern pine sapwood lumber subjected to various BMPs and exposed to simulated rainfall for 2 hours.

Table 3. Effect of post-treatment BMP processes on copper concentrations in runoff from simulated rainwater applied to CCA treated southern pine boards.						
BMP Process	Copper Concentration in Runoff (ppm) ^a					
	15 min	30 min	45 min	60 min	90 min	120 min
Air Dry	0.48 (0.45)	0.28 (0.33)	0.25 (0.26)	0.22 (0.17)	0.15 (0.18)	0.15 (0.18)
Control	1.18 (0.48)	0.98 (0.33)	0.85 (0.23)	0.83 (0.23)	0.83 (0.26)	0.80 (0.25)
HWB (1hr)	3.18 (2.04)	1.33 (0.56)	1.03 (0.37)	0.80 (0.48)	0.85 (0.31)	0.97 (0.47)
HWB (3 hr)	1.30 (0.42)	0.83 (0.31)	0.77 (0.32)	0.70 (0.24)	0.72 (0.27)	0.65 (0.20)
Kiln Dry	0.45 (0.31)	0.20 (0.09)	0.17 (0.05)	0.13 (0.05)	0.12 (0.08)	0.12 (0.08)
NH4 (1 hr)	0.28 (0.13)	0.10 (0.06)	0.07 (0.05)	0.07 (0.05)	0.03 (0.05)	0.03 (0.05)
NH4 (3 hr)	0.78 (0.86)	0.33 (0.38)	0.27 (0.32)	0.22 (0.25)	0.18 (0.21)	0.15 (0.20)
Steam (1 hr)	2.37 (0.85)	1.20 ((0.58)	0.92(0.46)	0.82 (0.39)	0.75 (0.36)	0.67 (0.30)
Steam (3 hr)	3.08 (1.96)	1.58 (0.95)	1.23 (0.77)	1.05 (0.63)	0.93 (0.55)	0.87 (0.48)
Steam (6 hr)	6.30 (2.27)	3.05 (0.96)	2.62 (1.35)	2.25 (1.11)	1.88 (0.92)	1.63 (0.87)

^aValues represent means of 8 replicates per time per BMP process.

Table 4. Effect of post-treatment BMP processes on arsenic concentrations in runoff from simulated rainwater applied to CCA treated southern pine boards.						
BMP Process	Arsenic Concentration in Runoff (ppm) ^a					
	15 min	30 min	45 min	60 min	90 min	120 min
Air Dry	0.25 (0.26)	0.18 (0.26)	0.15 (0.21)	0.15 (0.23)	0.15(0.19)	0.12 (0.15)
Control	1.05 (0.58)	0.47 (0.23)	0.42 (0.27)	0.35 (0.24)	0.43 (0.20)	0.35 (0.20)
HWB (1hr)	0.93 (0.36)	0.67 (0.31)	0.60 (0.30)	0.55 (0.24)	0.55 (0.12)	0.70 (0.28)
HWB (3 hr)	0.77 (0.30)	0.38 (0.23)	0.40 (0.21)	0.38 (0.19)	0.40 (0.18)	0.35 (0.14)
Kiln Dry	0.28 (0.28)	0.25 (0.18)	0.20 (0.17)	0.22 (0.17)	0.20 (0.15)	0.22 (0.17)
NH4 (1 hr)	0.95 (0.28)	0.50 (0.11)	0.48 (0.15)	0.45 (0.14)	0.42 (0.17)	0.38 (0.13)
NH4 (3 hr)	2.23 (1.01)	1.20 (0.45)	1.07 (0.45)	0.93 (0.38)	0.82 (0.40)	0.72 (0.32)
Steam (1 hr)	0.67 (0.14)	0.37 (0.14)	0.32 (0.10)	0.23 (0.08)	0.27 (0.10)	0.22 (0.15)
Steam (3 hr)	0.88 (0.70)	0.55 (0.39)	0.45 (0.39)	0.40 (0.23)	0.35 (0.23)	0.37 (0.22)
Steam (6 hr)	1.33 (1.14)	0.77 (0.57)	0.68 (0.61)	0.65 (0.62)	0.55 (0.60)	0.50 (0.50)

^aValues represent means of 8 replicates per time per BMP process.

Table 5. Effect of post-treatment BMP processes on chromium concentrations in runoff from simulated rainwater applied to CCA treated southern pine boards.						
BMP Process	Chromium Concentration in Runoff (ppm) ^a					
	15 min	30 min	45 min	60 min	90 min	120 min
Air Dry	0.18 (0.04)	0.10 (0.06)	0.10 (0.06)	0.12 (0.04)	0.12 (0.04)	0.12 (0.04)
Control	12.38 (4.58)	8.58 (4.01)	7.57 (4.12)	7.12 (4.00)	7.02 (4.14)	6.70 (3.96)
HWB (1hr)	0.33 (0.16)	0.15 (0.08)	0.12 (0.04)	0.08 (0.04)	0.10 (0.00)	0.13 (0.08)
HWB (3 hr)	0.27 (0.12)	0.13 (0.05)	0.12 (0.04)	0.12 (0.04)	0.12 (0.04)	0.10 (0.00)
Kiln Dry	0.25 (0.21)	0.10 (0.09)	0.10 (0.09)	0.10 (0.09)	0.08 (0.08)	0.07 (0.05)
NH4 (1 hr)	0.25 (0.15)	0.08 (0.04)	0.07 (0.05)	0.07 (0.05)	0.02 (0.04)	0.03 (0.05)
NH4 (3 hr)	0.35 (0.20)	0.13 (0.05)	0.13 (0.05)	0.12 (0.08)	0.10 (0.06)	0.12(0.08)
Steam (1 hr)	0.24 (0.11)	0.10 (0.06)	0.07 (0.05)	0.07 (0.05)	0.07 (0.05)	0.07 (0.05)
Steam (3 hr)	0.28 (0.12)	0.15 (0.05)	0.10 (0.00)	0.10 (0.00)	0.08 (0.04)	0.08 (0.04)
Steam (6 hr)	0.67 (0.72)	0.30 (0.30)	0.27 (0.27)	0.23 (0.24)	0.22 (0.24)	0.18 (0.16)

^aValues represent means of 8 replicates per time per BMP process.

Copper levels in rainwater runoff from CA treated southern pine samples tended to be much higher than those found with CCA treated lumber of the same species (Figures 3, 4). These levels reflect, in part, the much higher amounts of copper present in this preservative system, but they also reflect differences in how the metals are deposited in the wood. Small amounts of copper in all three systems (CCA, CA and ACQ) can react directly with the wood. In CCA, the remaining copper forms complexes with chromium and arsenic to become leach resistant. Copper is immobilized around the amine or ammonium components in ACQ or CA. As a result, copper tends to remain more mobile in these systems, leading to slightly higher copper losses, particularly at the start of any rainfall exposure.

Copper levels in runoff from copper azole treated southern pine samples tended to be elevated for control samples that had not been subjected to a BMP process as well as those that were either air-dried or immersed in a hot water bath for 3 hours (Table 6). Copper levels ranged from 3.4 to 7.8 ppm in the remaining samples subjected to various BMP processes. Copper levels generally declined over the 2 hour rainfall period, although the 3 hour hot water immersion was associated with the highest copper levels in runoff over the entire test. Copper levels fell sharply over time in runoff from samples subjected to kiln drying, ammonia baths or steaming as well as the 1 hour hot water immersion. Interestingly, copper levels in runoff remained elevated for samples

that were air-dried, suggesting that some heat associated BMP process might be more valuable than air-drying for amine-based systems.

Table 6. Effect of post-treatment BMP processes on copper concentrations in runoff from simulated rainwater applied to CA treated southern pine boards.						
BMP Process	Copper Concentration in Runoff (ppm) ^a					
	15 min	30 min	45 min	60 min	90 min	120 min
Air Dry	18.11 (9.05)	11.98 (6.67)	10.46 (5.85)	10.37 (5.46)	9.12 (4.97)	8.02 (3.98)
Control	18.15 (9.00)	9.54 (6.44)	7.62 (4.82)	6.32 (4.04)	5.77 (4.26)	4.48 (3.55)
HWB (1hr)	6.10 (2.89)	3.10 (1.70)	2.84 (2.13)	2.19 (1.28)	1.93 (1.05)	1.71 (1.34)
HWB (3 hr)	17.23 (8.13)	14.64 (9.95)	14.23 (8.99)	13.21 (7.18)	11.10 (3.65)	10.93 (4.23)
Kiln Dry	3.44 (1.27)	1.45 (0.52)	1.23 (0.51)	1.16 (0.59)	1.15 (0.42)	0.95 (0.21)
NH4 (1 hr)	6.09 (3.12)	3.07 (1.36)	2.53 (0.97)	2.33 (1.28)	2.21 (1.43)	1.97 (1.49)
NH4 (3 hr)	6.89 (2.05)	2.91 (0.84)	2.10 (0.73)	1.71 (0.42)	1.51 (0.41)	1.41 (0.40)
Steam (1 hr)	5.65 (1.96)	2.51 (1.16)	2.05 (0.86)	1.82 (0.80)	1.86 (0.84)	1.59 (1.06)
Steam (3 hr)	4.53 (2.03)	2.22 (1.13)	1.76 (0.89)	1.62 (0.68)	1.34 (0.58)	1.28 (0.62)
Steam (6 hr)	7.83 (2.15)	3.62 (0.98)	2.60 (0.57)	2.26 (0.69)	2.11 (0.69)	1.79 (0.48)

^aValues represent means of 8 replicates per time per BMP process.

Copper levels in runoff from ACQ treated Southern pine were extremely high in samples that did not receive any BMP treatment (Figure 5, Table 7). Copper levels were lower, but still elevated in rainwater runoff from materials that were subjected to air drying, a 1 hour hot water bath, kiln drying or 1 to 6 hours of steaming. Copper levels tended to be lowest in samples subjected to the 3 hour hot water bath as well as either of the ammonia treatments. As with the other preservatives, metal levels declined over the 2 hour rainfall exposure, although levels remained elevated in the control samples as well as the air and kiln dried samples at the end of that period. Metal levels in runoff from samples exposed to the other treatments ranged from 1.9 to 3.6 ppm at the end of the 2 hour period.

These results indicate that specific BMP treatments have value for the different preservatives. They also suggest that prolonged heat application may not markedly alter the resulting potential for metal loss from some systems. This could allow for reductions in BMP process time without adversely affecting the environmental outcome.

Table 7. Effect of post-treatment BMP processes on copper concentrations in runoff from simulated rainwater applied to ACQ treated southern pine boards.

BMP Process	Copper Concentration in Runoff (ppm) ^a					
	15 min	30 min	45 min	60 min	90 min	120 min
Air Dry	18.09 (3.33)	14.00 (3.68)	11.55 (2.78)	10.25 (2.75)	9.22 (2.31)	8.00 (1.76)
Control	47.84 (24.72)	23.72 (10.12)	18.30 (7.68)	16.53 (6.27)	13.48 (4.54)	12.04 (3.66)
HWB (1hr)	15.34 (4.58)	5.26 (2.92)	4.76 (1.37)	4.07 (1.81)	3.71 (1.76)	3.04 (1.03)
HWB (3 hr)	8.48 (1.65)	3.48 (1.25)	2.67 (0.96)	2.49 (0.86)	2.18 (0.80)	1.89 (0.69)
Kiln Dry	15.83 (5.00)	12.27 (4.06)	10.76 (3.38)	9.73 (2.77)	9.06 (2.76)	8.16 (2.35)
NH4 (1 hr)	8.11 (5.32)	3.34 (2.00)	2.65 (1.63)	2.49 (1.54)	2.19 (1.56)	1.97 (1.34)
NH4 (3 hr)	7.28 (1.40)	3.64 (1.26)	2.85 (1.14)	2.26 (0.75)	1.94 (0.73)	1.66 (0.63)
Steam (1 hr)	15.57 (5.02)	6.82 (2.55)	5.32 (1.78)	4.80 (1.56)	3.92 (1.43)	3.56 (0.99)
Steam (3 hr)	13.92 (4.49)	6.89 (3.23)	5.65 (2.86)	4.63 (2.38)	3.80 (1.79)	3.33 (1.41)
Steam (6 hr)	13.68 (8.95)	4.70 (3.12)	3.81 (1.53)	3.22 (1.33)	2.74 (1.08)	2.46 (1.06)

^aValues represent means of 8 replicates per time per BMP process.

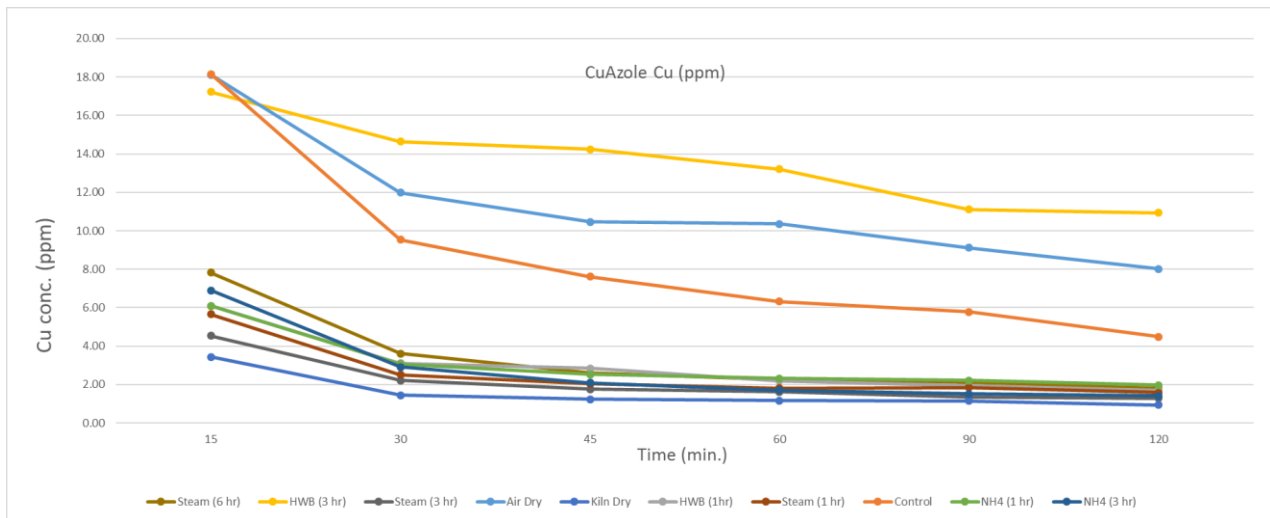


Figure 4. Effect of BMP processes on copper concentrations in runoff from CA treated southern pine lumber.

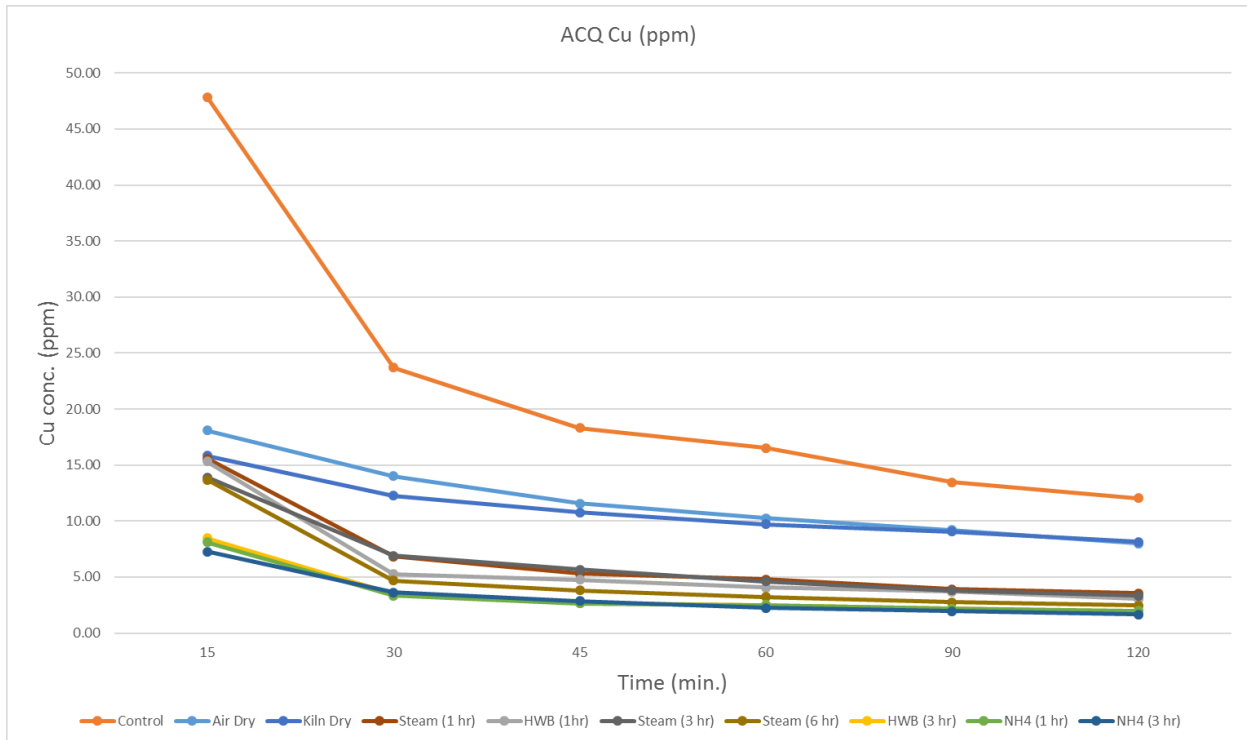


Figure 5. Effect of BMP processes on copper concentrations in runoff from ACQ treated southern pine lumber.

B. Effects of BMP processes on preservative losses from round timbers immersed in water.

A second component of the BMP verification process was to assess the potential migration of preservatives from round-timbers with and without BMP treatments. Doulgas-fir posts (125 to 150 mm in diameter by 1.8 m long) were treated with either ACZA or creosote to the northern retentions for each system (24 kg/m for ACZA or 384 kg/m for creosote). One half of the posts were subjected to a BMP treatment while the others were provided without this process

The posts were set in a freshwater pond located approximately 20 km southwest of Corvlalis, OR. In our initial trials, we found that the sediment at this pond was far too inconsistent to allow for regular sampling. Instead, we created sediment packets that could be placed in the actual sediment at selected distances away from each post. The packets (200 mm long by 25 mm in diameter) or sachets contain a known soil that is heat sealed into an inert plastic mesh. The mesh allows water to move through the

sediment, but contains the material for later analysis. Preliminary tests indicated that the mesh material did accumulate PAH's and, to a lesser extent metals, but the sachets provided a uniform sediment media that could be easily removed for sampling.

We have established ACZA and creosote treated Douglas-fir piling in two separate tests, three or 42 months ago. The former test was installed because we felt our PAH recovery ability has improved and we wanted to confirm that premise. In the initial test, two creosote treated posts were installed, while 4 posts have been installed in the more recent test. The initial ACZA test consisted of 2 posts installed approximately 31 months ago. We also installed 5 more ACZA posts at the same time as the new creosote study. The results for the first sediment sampling for the more recent test are not yet available.

Sachets removed at selected time intervals have been used to assess polycyclic aromatic hydrocarbons (PAHs) or metals, depending on the posts involved. The metals were analyzed in the same manner as described for the water samples, with the exception that the sediment and sachets were acid digested prior to analysis. PAHs from the creosote treated posts were extracted and analyzed as follows: collected sachets were frozen until analysis. Upon analysis the sachets were thawed and the sediment was separated from the sachet. Three 10 g subsamples were taken from the homogenized sediment and placed into 40 mL amber glass scintillation vials. The sachet material was split into two sections and analyzed separately from the sediment but in the same manner. Twenty mL of a 2:2:1 acetone:ethylacetate:isooctane mixture was added to the scintillation vials. The vials were vigorously agitated for 5 minutes to ensure that the sediment was in intimate contact with the 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 the supernatant was removed and added to a solid phase extraction (SPE) microcentrifuge tube, and agitated further for 5 minutes. These dual procedures were used to precipitate polar compounds, lipids, fatty acid, sterols and other compounds that would interfere with the PAH analysis. The tube was then

centrifuged one last time for 5 minutes and a 1 mL aliquot of the supernatant was removed for analysis by GC-MS.

The samples were analyzed using a Shimadzu QP2010S GC-MS operated in scanmode, m/z range 50-300, with a splitless injection. One μL of sample was injected and analysis was performed with the following GC conditions: Oven temperature: 70 hold for 2 min. then ramping to 265 at 10 $^{\circ}\text{C}$ a min. and hold at 265 $^{\circ}\text{C}$ for 15.5 min until Benzo(ghi)perylene elutes (total run time 37 min.), ion source temperature: 225 $^{\circ}\text{C}$, interface temperature: 275 $^{\circ}\text{C}$, injection temperature 275 $^{\circ}\text{C}$. 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.

Background copper, zinc and arsenic levels in the sachet soil averaged 2.89 ppm (SD= 1.22), 3.74 ppm (sd= 1.30) and 0.97 ppm (sd=1.09), respectively.

Copper levels in sachets removed 1 and 3 months after post installation were generally at background levels 300 and 900 mm away from the post; however, levels were elevated immediately adjacent to wood 3 months after installation (Table 8). Arsenic was generally below the detection limit (0.1 ppm) except immediately adjacent to the posts at 3 months and even this level was below 1 ppm. The presence of elevated metal levels immediately adjacent to the treated wood is consistent with previous reports as is the sharp drop-off in levels with increasing distance from the wood. These posts will continue to be sampled over time to establish long term release data.

Zinc and copper levels were elevated immediately adjacent to the posts 31 months after installation. Metal levels declined 300 mm away, but were still slightly above the background levels as well as 300 mm away, but declined to near background levels 900 mm from the post. This drop off is consistent with previous reports showing that metal migration is largely confined to a narrow zone around a treated wood sample and does not change appreciably over time. Arsenic remains at very low levels except immediately adjacent to the posts where it had increased sharply over the 28 month interval between sampling. The results indicate that all three metals migrate away from

the posts into the surrounding sediment but the extent of migration is limited and declines sharply with distance away from the treated wood source.

Table 8. Copper, zinc and arsenic levels in sediments exposed immediately, 300 and 900 mm away away from an ACZA treated Douglas-fir piling 1 to 31 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

^aValues represent means of two samples per time per location. BDL= below the detection limit (<0.1 ppm)

Fifteen of the 16 PAH's we evaluated were detected in one or more sachets sampled in the test installed in 2013, while only 12 were detected in the more recent test installed in October, 2016 (Tables 9, 10). Two PAH's were combined with other PAH's because they eluted so closely from one another that they were difficult to accurately separate.

Naphthalene was detected at very low levels (~0.9 ppm) in sachets exposed at the inlet of the pond (Table 9). This PAH was present at elevated levels immediately adjacent to the post, but declined sharply 300 mm away. Slightly elevated levels were detected 900 mm away at 32 months after installation, but these levels had declined to background levels at 42 months. Naphthalene can represent a high percentage of creosote, but it is also one of the more easily biodegradable components. as a result, it should be rapidly degraded as it moves out of the wood. This PAH is also difficult to quantify because of its high volatility. The results at 42 months support that premise.

The other components present at elevated levels (>5 ppm) immediately adjacent to the posts included acenaphthene, fluorine, fluoranthrene, and pyrene which were all well above background levels at all three sampling times (Table 9). PAH levels immediately adjacent to the posts tended to remain elevated over the 42 month exposure period for

all of these PAH's, but did not appear to be increasing. Benzo(α)anthracene/chrysene and Benzo(j,k) fluoranthrene levels were also elevated immediately adjacent to the post at the 18 month sampling point, but then declined to near or below the 5 ppm level. These levels were still well above the background levels for either compound. Levels of all of the same PAH's 300 and 900 mm away were sharply lower than those found adjacent to the post and tended to be similar to those found in the background sediment. Levels of benzo(j,k)fluoranthrene and benzo(α)pyrene were also elevated immediately adjacent to the posts but not at all sampling times. Levels of these compounds also declined sharply 300 and 900 mm from the posts, indicating that either migration was limited or that microbial decomposition was occurring at a rate similar to any migration.

The results indicate that PAH's are migrating into the surrounding sediment over time, but the migration is very limited. We will continue to sample these materials until we run out of sachets.

Only 12 PAH's were detected around posts exposed for only 3 months (Table 10). The three that were detected in the older test, but not in this one were present at the lowest levels in the older test and at levels similar to the background levels. As in the earlier test, naphthalene, acenaphthylene, acenaphthalene, fluorine, phenanthrene/anthracene, fluoranthrene and pyrene were present at elevated levels (>5 ppm) immediately adjacent to the posts. Benzo(α)anthracene/chrysene was present immediately adjacent to the posts at a concentration of 2.79 ppm, but then declined sharply away from the post. The remaining PAH's were present at very low levels approaching background.

PAH levels 300 mm from the posts declined sharply and approached background levels in most cases except for naphthalene, which was slightly above that level. PAH levels continued to decline 900 mm away from the posts, suggesting that, as with the older test, any migration was either limited or the PAH's were degrading at rates that were similar to the rate of migration. Either way, the results show that PAH migration from the posts into the surrounding sediment is extremely limited.

Table 9. Concentrations of 13 PAH's in sediment at selected distances from creosote treated Douglas-fir posts exposed in freshwater for 42 months.

PAH	Concentration (ug/g sediment) ^a											
	Control			0 m			0.3 m			0.9 m		
	18 m	32 mo	42 mo	18 m	32 mo	42 mo	18 m	32 mo	42 mo	18 m	32 mo	42 mo
Napthalene	0.42	0.87	ND	49.58 (22.08)	45.89 (31.66)	50.50 (10.71)	1.30 (1.40)	1.01 (0.28)	0.36 (0.330)	0.46 (0.05)	1.61 (0.35)	0.33 (0.31)
Acenaphthylene	ND	0.23	ND	4.20 (3.00)	1.93 (0.91)	2.01 (1.01)	1.10 (1.55)	0.31(0.28)	ND	ND	0.10 (0.01)	0.03 (0.04)
Acenaphthene	0.37	1.01	ND	45.16 (17.48)	34.70 (9.48)	41.37 (5.50)	1.43 (2.02)	1.08 (0.87)	0.23 (0.16)	ND	0.61 (0.18)	0.88(0.11)
Fluorene	0.38	0.73	ND	28.57 (12.59)	21.74 (4.26)	25.76 (2.09)	1.14 (1.61)	0.64 (0.69)	0.23 (0.19)	ND	0.16 (0.01)	0.09 (0.12)
Phenanthrene	1.36	0.75	0.18	81.08 (30.86)	29.93 (0.99)	45.75 (30.62)	2.66 (2.77)	0.69 (0.28)	1.22 (0.27)	0.81 (0.14)	0.47 (0.01)	1.46 (0.42)
Fluoranthrene	0.62	0.62	ND	55.41 (37.75)	26.03 (7.52)	27.76 (7.76)	1.28 (1.41)	0.50 (0.51)	0.39 (0.35)	0.19 (0.27)	0.39 (0.30)	0.32 (0.07)
Pyrene	0.52	0.48	ND	35.90 (22.91)	18.02 (5.74)	18.17 (5.92)	1.25 (1.41)	0.38 (0.38)	0.26 (0.22)	0.16 (0.23)	0.28 (0.25)	0.20 (0.25)
Benz(α)anthracene &Chrysene	0.80	0.12	ND	17.31 (11.53)	4.03 (2.22)	5.08 (1.03)	2.16 (3.05)	0.08 (0.11)	ND	ND	ND	ND
Benzo (j,k)fluoranthrene	ND	0.15	ND	6.99 (4.19)	2.50 (1.31)	1.44 (0.58)	2.33 (3.05)	0.09 (0.13)	ND	ND	ND	ND
Benzo (α)pyrene	ND	0.30	ND	3.57 (2.27)	2.96 (2.91)	0.69 (0.32)	1.26 (1.77)	ND	ND	ND	ND	ND
Indeno(1,2,3 cd)pyrene	ND	0.40	ND	1.12 (0.01)	0.65 (0.39)	ND	1.38 (1.80)	ND	ND	ND	ND	ND
Dibenzo (a,h) anthracene	ND	0.50	ND	0.54 (0.76)	0.39 (0.08)	ND	1.29 (1.82)	ND	ND	ND	ND	ND
Benzo(g,h,i)perylene	ND	0.51	ND	1.25 (0.01)	0.55 (0.30)	1.34 (1.89)	ND	ND	ND	ND	ND	ND

^aValues represent triplicate analyses of sediment from two piling at each time point. Figures in parenthesis represent one standard deviation.

Table 10. Concentrations of 10 PAH's in sediment at selected distances from Douglas-fir posts treated to the northern marine retention and exposed in freshwater for 3 months.

PAH	PAH Concentration (ug/g sediment) ^a			
	Control	Adjacent	0.3 m	0.9 m
Naphthalene	ND	10.92 (2.92)	1.61 (2.34)	0.28 (0.08)
Acenaphthylene	ND	0.57 (0.06)	0.02 (0.04)	ND
Acenaphthene	ND	10.87 (3.05)	0.99 (1.64)	0.85 (1.41)
Fluorene	ND	8.37 (2.44)	0.62 (0.84)	0.60 (0.90)
Phenanthrene	0.18	22.22 (8.43)	1.35 (0.86)	1.76 (1.31)
Fluoranthrene	ND	14.60 (2.73)	0.61 (0.85)	0.53 (0.70)
Pyrene	ND	9.33 (2.12)	0.35 (0.50)	0.29 (0.45)
Benz(α)anthracene & Chrysene	ND	2.79 (1.00)	0.07 (0.14)	0.13 (0.25)
Benzo (j,k)fluoranthrene	ND	0.98 (0.40)	ND	0.10 (0.20)
Benzo (α)pyrene	ND	0.25 (0.22)	ND	ND

^aValues represent triplicate analyses of samples removed from 4 piling. Values in parentheses represent one standard deviation. ND= not detected. Indeno (1,2, 3 c,d) pyrene, dibenz(a,h)anthracene and benzo (ghi) perylene were not detected.

The results support limited migration of PAH's into the sediment surrounding the posts. One aspect of these results that must be considered is the method of PAH capture. The sachets allow for repeated sampling of a defined soil media; however, we have also observed that the mesh material tends to capture a disproportionately higher quantity of PAH's than the sediment. We suspect this is because the PAH's continue to degrade in the sediment, but may not be as accessible to the microflora on the mesh. As a result, we suspect that our PAH levels (which include both the mesh and sediment extractions) are somewhat higher than would be present were we to only sample the sediment. The resulting values will tend to be higher than if only sediment was evaluated.

We will continue to sample both the ACZA and creosote treated posts - however, the results to date support the premise that migration of components from treated wood in these environments is extremely limited.

Concentration of Pentachlorophenol and Copper Naphthenate in Rainwater Runoff from a bridge in Western Oregon

We have worked to establish field trials evaluating preservative migration from various treated wood commodities. Two years ago, we identified a bridge located near Sweet Home, Oregon that had been constructed with decking treated with pentachlorophenol in oil and laminated beams treated with copper naphthenate for supporting the structure (Figure 6). The House Rock Bridge spans the South Santiam River in the Willamette National Forest. Unfortunately, we did not learn about the bridge until it had been in service for several weeks and had been subjected to several rainfall events; however, we have been able to monitor the bridge since that time.



Figure 6. Photograph of the House Rock Bridge showing copper naphthenate treated laminated beams and pentachlorophenol treated decking.

The preservatives present in the runoff from the bridge were examined by constructing a rainfall runoff collection system beneath a section of the bridge that funneled water from the surface into a large container (Figure 7). Water in the container was weighed after each rainfall event, then 3 300 mL sub-samples were taken for later analysis. The total area of treated wood from which the runoff was collected was measured so that we could later determine preservative loss per square cm of wood surface area.

The penta runoff samples had to be processed immediately because of concerns about sample degradation. The rainwater runoff samples were collected in tared 250 mL glass volumetric flasks and weighed (nearest 0.1 g). The remainder of the water was weighed to determine total runoff after each rainfall event.



Figure 7. System used to collect water from the House Rock Bridge located near Upper Soda, Oregon.

2.5 mL 1N NaOH was added to each flask using a pipette. A Teflon™ stir bar was placed in each flask. The flasks were stirred for 1 min then allowed to stand for 30 min. This procedure converted the PCP to its sodium salt. Next 2.5 mL iso-octane was added to the flask and the flasks were stirred for 1 min. The solvent layer was removed with a disposable glass pipette and discarded. This iso-octane extraction was repeated with 2.5 mL iso-octane. This procedure removed residual oils and other organics from the PCP sample.

The sodium pentachlorophenate was converted back to PCP by adding 3.0 mL 1.0 N H₂SO₄ using a pipette. The flask was stirred for 1 min and allowed to stand for 30 min. Then 2.5 mL iso-octane was added to the flask which was stirred for 1 min to extract the PCP. The iso-octane layer was transferred to a 20 mL glass vial and the extraction

repeated with an additional 2.5 mL iso-octane. This second extract was added to the first.

High resolution gas chromatography – low resolution mass spectrometry (HRGC-LRMS) analysis was carried out by injecting 1 μL of sample into a Shimadzu HRGC-LRMS system class 5000 equipped with an RXI-5ms column (0.25 mm inner diameter by 30-mm long) at a flow rate of 1.0 ml/min.

The carrier gas was helium (grade 5) at a flow rate of 1.2 mL/min and the system was operated in the splitless mode. The injector and detector temperature were 250 and 280 $^{\circ}\text{C}$, respectively. The oven was programmed to hold for 2 minutes at 40 $^{\circ}\text{C}$, ramp to 80 $^{\circ}\text{C}$ at 40 $^{\circ}\text{C}/\text{min}$, then ramp to 260 $^{\circ}\text{C}$ at 25 $^{\circ}\text{C}/\text{min}$. The system was flushed with iso-octane between injections to minimize the risk of carryover.

The PCP standard (50 $\mu\text{g}/\text{mL}$) was scanned and identified using the National Institute of Science and Technology (NIST) Mass Spectral Library #107 software. The retention time for PCP was 9.70 min. The selected ion for PCP quantitative analysis was $m/z = 266$, the reference ions were 264 and 268. HRGC-LRMS auto tuning was performed with perfluorotributylamine. The calibrations were carried out with PCP concentrations of 4, 12, 20, 40, & 100 $\mu\text{g}/\text{mL}$. A five point calibration was employed, i.e., for each single batch a minimum of 5 consecutive standards were selected depending on the range of concentration of the samples.

The volume of water collected was measured by weight. A density of 1.00 g/mL was assumed for water. The limit of detection (LOD) of this method was estimated to be 0.025 ng/mL cm^2 . The LOD is defined according to the Federal Register Part 136, Appendix B, procedure (b), as three times the standard deviation of replicate analyses of the analyte.

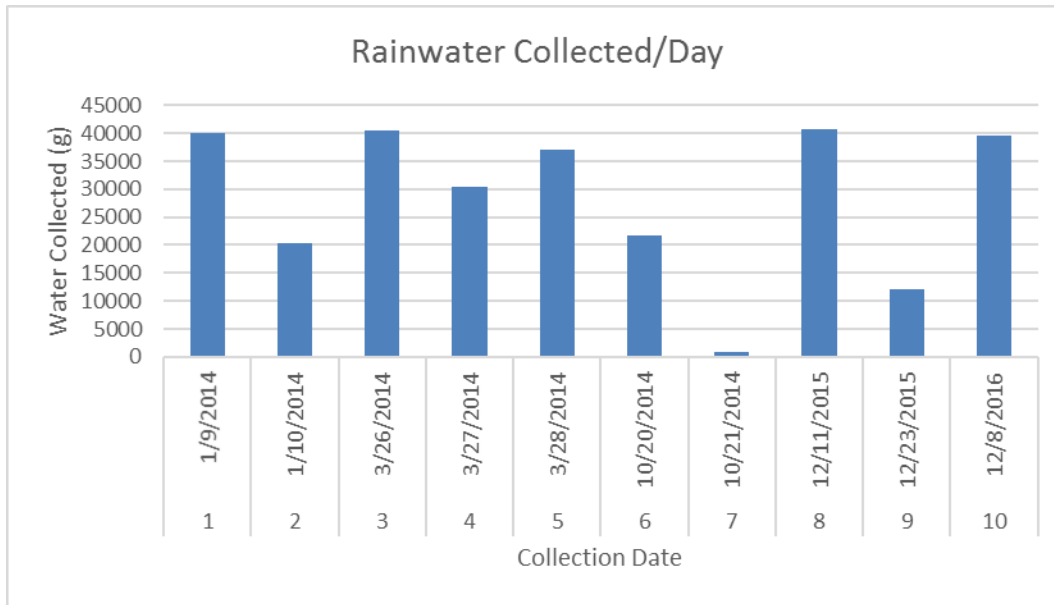


Figure 8. Amounts of water collected from the House Rock Bridge after various rainfall events.

Copper naphthenate in the runoff was analyzed on a copper basis as described previously by collecting a sub-sample of the runoff, acidifying this sample and then analyzing this sample by ICP. The results were expressed on a copper metal basis.

Rainfall amounts varied widely over the 10 collections from a low of 970 mL to over 40,000 mL (Figure 8). The bridge is located in the foothills of the Cascade Mountain Range and rainfall is normally steady, but light. Typical total daily precipitation might total 25 mm even though it rained all day. This precipitation pattern might be expected to result in near continuous wetting of exposed surfaces, which should facilitate solubilization and eventual loss of preservatives near the wood surface.

Pentachlorophenol was detected in water collected from all 10 rainfall events (Figure 9). The initial penta concentrations averaged 6 ppm, then declined to less than 2 ppm after 3 rainfall events. Concentrations declined even further to less than 1 ppm in the 6th and 7th collections but then rose sharply to 8.7 ppm in the 8th collection. The reasons for this sharp increase are unclear. Concentrations declined slightly to 5.7 ppm in the 9th collection which was made only 13 days after the eighth collection. The bridge had not been sampled since that time. Concentrations in a more recent collection made one year later averaged 0.4 ppm. It is unclear why concentrations rose so sharply in the prior

two collections, but the more recent analysis is consistent with those found previously. It is important to note that these water collections were not continuous over time because of the logistics of setting up and collecting water. As a result, the site received a number of rainfall events between individual water collections. However, previous studies of penta runoff from stored utility poles have shown that penta levels in water runoff are more a function of solubility than time or rainfall intensity once any surface deposits of chemical have been removed.

The relative insensitivity of penta to repeated rainfall exposure reflects the high concentrations of penta available near the wood surface coupled with the low water solubility of this biocide. Penta solution concentrations in most wood treatments range from 5 to 9 % in some type of hydrocarbon solvent. Assuming minimal loss of solvent following treatment, this translates to a concentration of 50,000 ng of penta/kg in a 5 % treatment solution. This leaves an abundant amount of penta available near the wood surface for potential interaction with precipitation. Penta has a water solubility of approximately 14 $\mu\text{g/g}$ of water at 20 °C. The temperature of the rainwater in the current collections would range from 5 to 8 °C, further reducing the amount of penta that can be solubilized as precipitation strikes the wood. The lower concentrations of penta found in the runoff for several collections were perplexing and suggest that other factors such as interactions with leaves and other detritus on the deck may have resulted in the loss of some penta. Penta levels in two of the three most recent collections were again elevated at 8.7 and 5.7 $\mu\text{g/mL}$ of water, but declined at the most recent assessment to 0.4 $\mu\text{g/mL}$ of water.

The lack of an effect of total rainfall at a given collection point on penta concentration can be seen by the lack of effect of increased water collection on concentration (Figure 10). The exception was the first water collection, which coincided with a very heavy rainfall, but would also have been expected to have a higher penta concentration by virtue of the potential presence of any surface deposited penta. The lack of consistency is also illustrated by the fact that one of the lowest penta concentrations and the highest concentration both occurred with water collection levels greater than 40 liters of collected precipitation. Our previous studies of stored utility poles suggested that penta

concentrations in runoff ranged from 3 to 8 ppm regardless of the amount of precipitation to which the poles were stored (Love and Morrell, 2014; Morrell and Chen, 2008, Morrell et al., 2010). This premise also appears to hold with the bridge deck. As a result, the effects of any preservative loss become more dependent on the characteristics of any receiving body of water coupled with the total amount of treated wood exposed to precipitation. The current study collects rainfall from an area representing 14% of the total area of treated wood in the bridge.

We will continue to periodically monitor this bridge to determine how weathering might affect penta migration.

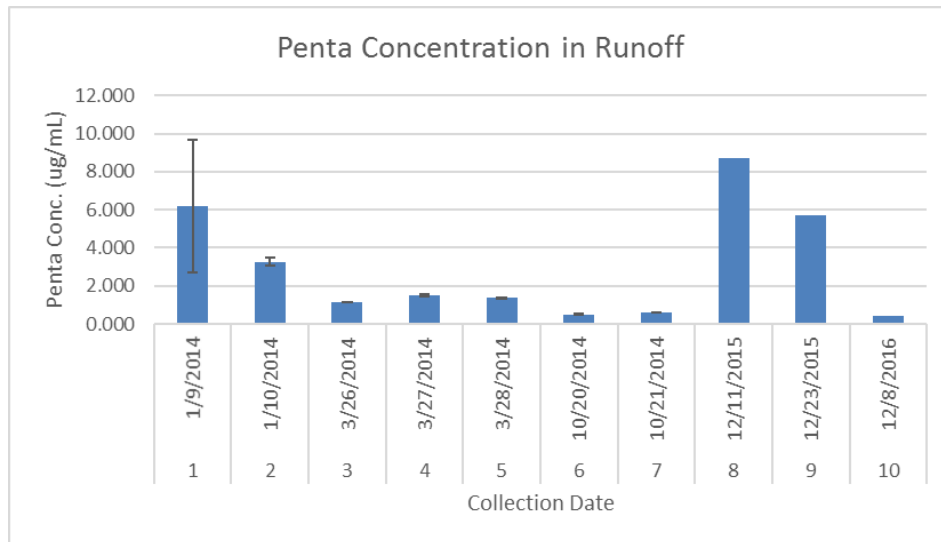


Figure 9. Pentachlorophenol concentrations in rainwater runoff collected from a section of the House Rock Bridge located near Upper Soda, Oregon.

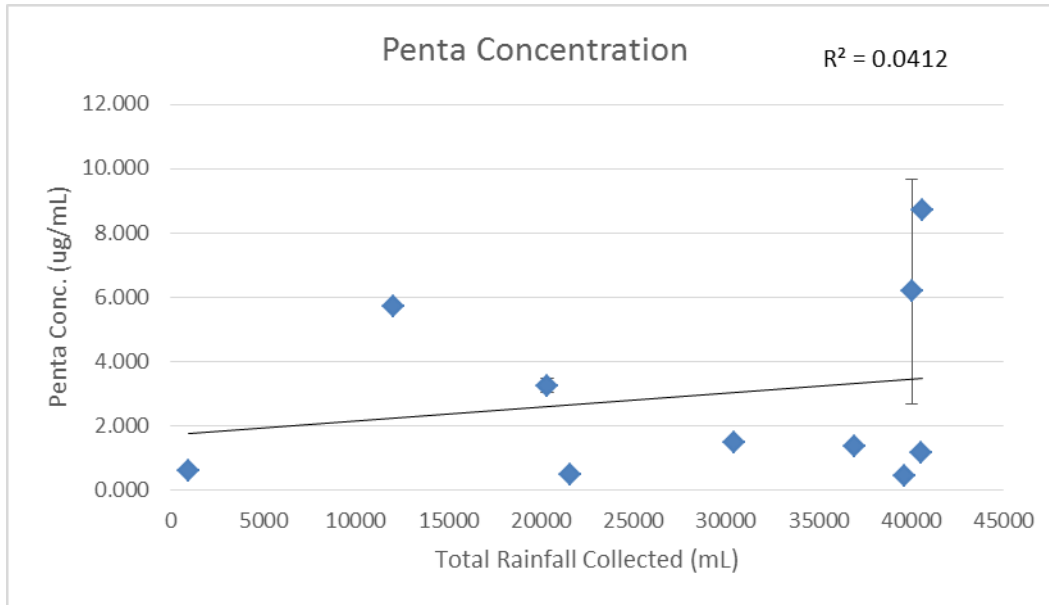


Figure 10. Concentrations of pentachlorophenol in rainwater runoff as a function of total rainwater collected from a section of the House Rock Bridge located near Upper Soda, Oregon.

Copper levels in rainwater runoff, as a measure of losses from the copper naphthenate treated portion of the bridge, followed trends that were initially similar to those found with penta. The copper analysis for the most recent sampling is still in process.

Copper concentrations were elevated for the first two collections then declined to approximately 10 ppm (Figure 11), but there was little relationship between metal losses and rainfall intensity (Figure 12). While these levels were slightly higher than the copper

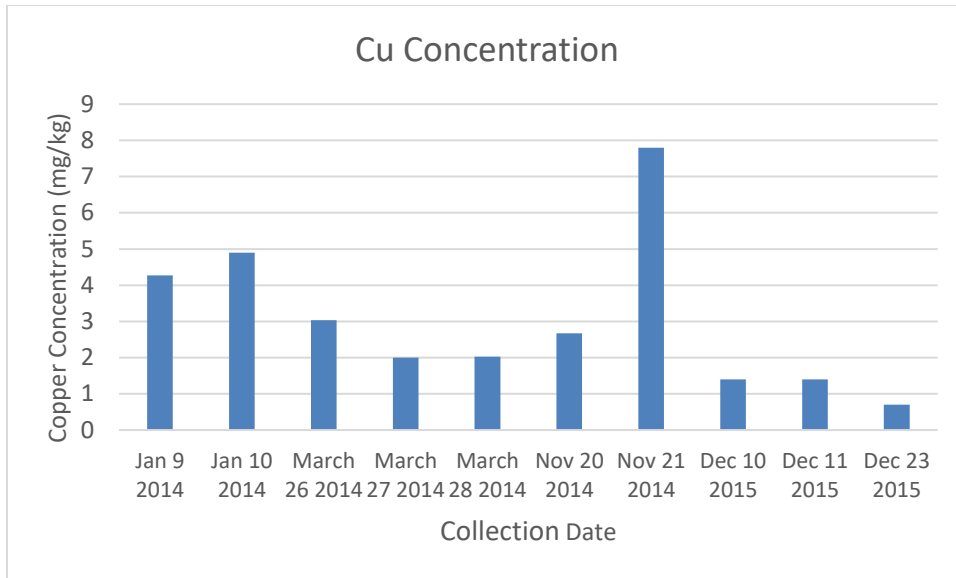


Figure 11. Copper concentrations in rainwater runoff collected at selected times from a portion of the House Rock Bridge near Upper Soda, Oregon.

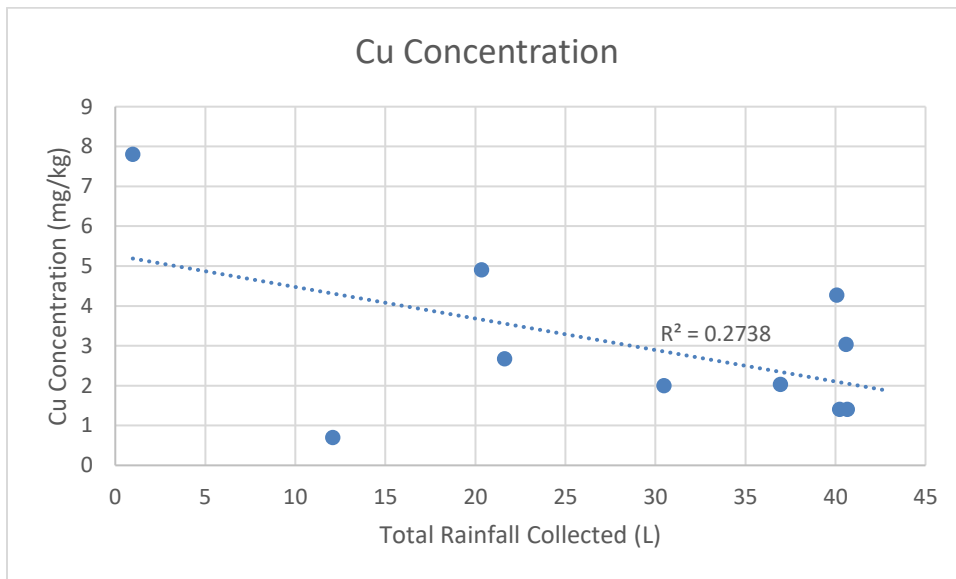


Figure 12. Copper concentrations in rainwater runoff collected at selected times from a portion of the House Rock Creek Bridge near Upper Soda, Oregon as a function of total rainwater runoff collected.

levels noted in runoff from copper naphthenate treated poles, there are few reports of copper migration from copper naphthenate treated wood. Over time, however, the levels

of copper and penta in the runoff tended to deviate suggesting that there was little relationship between losses of the two chemicals (Figure 13). We will continue to monitor this test to determine if copper levels continue to decline over time.

Table 11. Concentrations of copper and pentachlorophenol in rain water runoff collected at various times from the House Rock Bridge near Upper Soda, Oregon.			
Date Collected	Total Runoff (L)	Runoff Concentration (mg/kg)	
		Pentachlorophenol	Cu Naphthenate
1/9/2014	40.07	6.18 (3.49)	4.27 (0.32)
1/10/2014	20.35	3.26 (0.21)	4.90 (0.26)
3/26/2014	40.60	1.17 (0.01)	3.03 (0.81)
3/27/2014	30.48	1.51 (0.05)	2.00 (0)
3/28/2014	36.49	1.36 (0.03)	2.03 (0.06)
11/20/2014	21.62	0.51 (0.01)	2.67 (0.58)
11/21/2014	0.97	0.61 (0.02)	7.80 (0.35)
12/10/2015	40.2	-	1.40 (0)
12/11/2015	40.66	8.73 (0.14)	1.40 (0)
12/23/2015	12.09	5.72 (0.04)	0.73 (0.02)
12/15/2016	39.68	0.43 (0.03)	NA

^aValues represent triplicate analysis at each collection point.
^bSamples lost. Values represent means of 3 replicates per time point

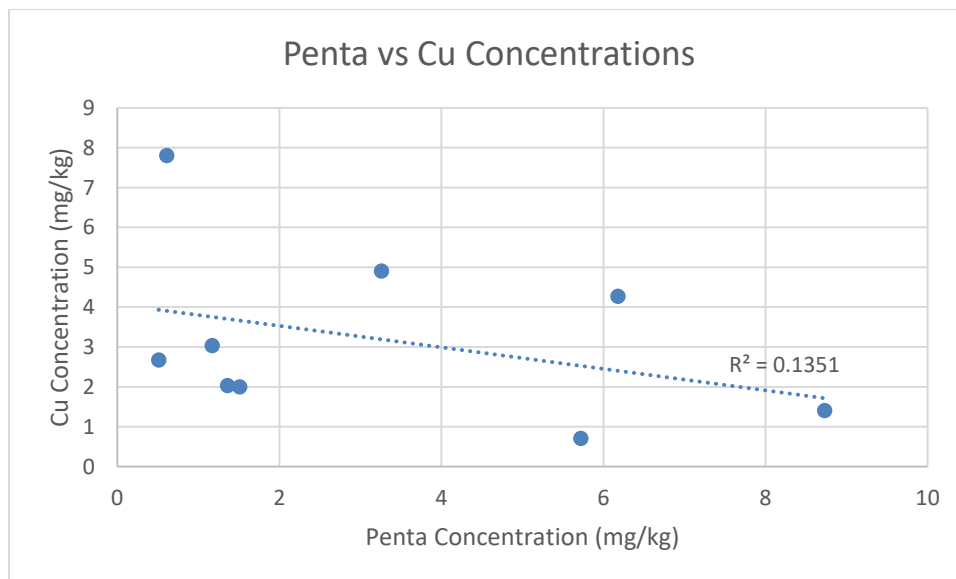


Figure 13. Relationship between pentachlorophenol and copper concentrations in rainwater runoff from the House Rock Bridge near Upper Soda, Oregon.

Implications: Developing data on the absolute amounts of chemical migrating from a structure is useful, but it must be placed in context with the potential impacts of the chemical on the receiving body of water. We used a stream gauge located at Cascadia State Park approximately 13 miles downstream from the bridge as the basis for our estimates of concentrations of penta and copper that developed in the receiving river beneath the bridge. Data for stream flow were taken as the high and low flow in liters per day for each collection period (Tables 11). The bridge area from which the water was collected represented 14% of the bridge surface area and all of the water was assumed to leave the bridge and enter the water. This value was multiplied to estimate migration from the entire bridge. All faces of the treated wood were considered to be capable of contributing to preservative migration. This was a bit of an over-estimate because there were short banks next to the bridge abutments that might capture some runoff. The resulting value was then used to calculate a potential penta concentration in the stream from the bridge using either high or low water flow values.

Penta levels in river ranged from 0.009 ng/L to a high of 5.182 ng/L (parts per trillion) over the 10 collection periods when low flow at each sampling time was considered (Table 12). These values decreased to 0.006 to 3.701 ng/L when the high flow for that collection point was used. Copper levels in the river downstream from the bridge would be 0.216 to 5.498 ng/L using the low flow rate and 0.083 to 1.649 ng/L for the high flow condition (the data for the most recent collection have not yet been processed).

We do not have regular copper concentration data for this river, but the Brook's Risk Assessment model uses an assumed 1.5 $\mu\text{g Cu/L}$ of water as a baseline copper level (1500 ng/L)(Brooks, 2011). While it would be difficult to completely assess the toxicity of added copper in this river, it is possible to look at the proportional increase in copper levels in the receiving water with varying precipitation levels. The highest copper concentration in runoff was 2.809 ng/L which would represent a 0.19% increase in background copper levels. In most other cases, the changes were less than 0.05% under the low stream flow condition and less than that at the higher flow rates. While one can argue that any change in copper concentrations could influence behavior, the

levels noted herein would generally fall within the range of error for most analytical methods given the variability in flow conditions and collection methods.

Clearly, there should be no background penta in the river above the bridge. Thus any penta introduced from the bridge would need to be examined alone. The highest level of penta estimated to be in the stream below the bridge was 5.18 ng/L when the collection was made during a period of lower stream flow. The Risk Assessment Model uses a value of 9.8 µg/L (9.8 ppb) as a minimum effects threshold (Brooks, 2010). The highest level detected in our 10 collections would translate to 0.0052 µg/L, far below the level of concern in the model.

Table 12. Average pentachlorophenol and copper concentrations below the House Rock Bridge as determined by the total amount of chemical migrating from the bridge and low/high stream flows.								
Collection Date	Total Chemical Released (mg) ^a		Water Flow (ML/Day)		Low Flow Concentration (ng/L)		High Flow Concentration (ng/L)	
	Penta	Cu	Low Runoff	High Runoff	Penta	Cu	Penta	Cu
1/9/2014	1768.8	1222.1	3131.6	3792.2	0.565	0.466	0.390	0.322
1/10/2014	473.9	712.3	3669.9	4428.3	0.129	0.107	0.194	0.161
3/26/2014	339.3	878.7	1590.3	2201.9	0.213	0.154	0.553	0.399
3/27/2014	328.7	435.4	2202.0	4403.8	0.149	0.075	0.198	0.099
3/28/2014	354.5	529.1	4403.4	12722.2	0.081	0.028	0.120	0.042
11/20/2014	78.8	412.3	146.8	489.3	0.537	0.161	2.809	0.843
11/21/2014	4.2	54.0	489.3	685.0	0.009	0.006	0.110	0.079
12/10/2015	- ^b	402.0	489.3	685.0	-	-	0.822	0.587
12/11/2015	2535.4	406.6	489.3	685.0	5.182	3.701	0.831	0.594
12/23/2015	580.3	63.0	489.3	685.0	1.186	0.847	0.129	0.092
12/15/2016	121.9	- ^c	489.3	685.0	0.249	0.178	-	-

^aValues represent triplicate analysis at each collection point. ML= megaliters and ng= nanograms.
^bSamples lost.
^cSamples still being analyzed

The results indicate that preservative migration from the House Rock Bridge is well below the minimum effects levels. It is, however important to note that the river over which this bridge crosses has some exceptional characteristics in that there is little or no risk of migration during the warmer summer months when the flow is quite low and

precipitation is minimal, while stream velocities during the cooler winter months when rainfalls are heavier are such that any materials moving into the water are rapidly diluted.

We will continue to sample this bridge periodically as it ages to determine if this aging process affects preservative migration characteristics.

C. Effects of coatings on migration of metal components from ACZA treated marine piling

Port Authorities in many locations are returning to the use of preservative treated pilings in place of concrete, but still have some concerns about the potential for preservative migration from these products. This is particularly true in ports where prior activities, notably ships with copper based anti-fouling coatings, have resulted in an excess of copper in water and sediment. One possible solution for limiting additional copper input would be to coat pilings with impermeable barriers to limit preservative migration. Salt water presents an especially rigorous environment for coatings; the risk of debris or ships damaging the wood surface further limits their application. However, a number of polyurea-based coatings have been developed for this application and are currently required in several California ports. While these barriers have been reported to be effective, there are relatively few data demonstrating their effectiveness. In this report, we describe preliminary evaluations of polyurea coated pilings treated to the marine retention (2.5 pcf or 40 kg/m³) with ammoniacal copper zinc arsenate (ACZA).

Materials and Methods: ACZA treated Douglas-fir pilings with and without a ~125 or 250 mil thick polyurea coating from the butt to the tip were received from Thunderbolt Wood Treating (Riverbank, CA) as 1.8 m long by 250-300 mm diameter sections (Figure 14). The coating was only on the vertical surfaces, not the cross sections. Four sections were coated and three were left uncoated. Pilings were buried to a depth of 600 mm in soil in 208 L Nalgene tanks and the tanks were filled with artificial seawater to a depth of 600 mm so that the base of the pile was in sediment, but the remaining 600 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 levels. Coated pilings were installed November 20, 2015, while the non-coated pilings were installed January 27, 2016, but both sets of materials were exposed to the same conditions after installation.

Sediment samples were removed immediately adjacent to pilings, oven dried and ground to a fine powder for acid extraction. Resulting extracts were analyzed for copper, zinc and arsenic by Ion Coupled Plasma Spectroscopy (ICP). Water was gently agitated to more evenly distribute any metal, care was taken not to disturb the sediment, a 20 mL sample of water was removed and acidified with nitric acid and analyzed for metal content by ICP. Initial sampling was frequent (daily, then weekly), but then decreased as trends became evident. Detection limits for copper, zinc, and arsenic via this method were <0.05 mg/kg for all three metals.

Results and Discussion: Sediment analyses are still on-going. This report will only discuss the water column sampling for the first 282 days of immersion.

Water column: 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 352 day exposure period. Results illustrate the ability of these coating to contain metallic elements in salt water.

Metal levels in non-coated piling exposed in the same manner have steadily increased over the 282 day exposure (Table 13, 14; Figure 15) although there has been some variation in levels with prolonged exposure as a result of less frequent sampling. The overall trend, however, had been steadily upwards with the possible exception of the 3 most recent collections that suggests that a plateau has 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 increase sharply shortly after immersion as residual metals on the wood surface are solubilized (as reviewed in Morrell et al., 2011). These pilings were subjected to post-treatment Best Management Practices according to procedures described in the Western Wood Preservers Institute (WWPI) Guidelines

(WWPI, 2012). While these processes reduce the presence of surface deposits and help ensure immobilization of metals, the lack of any noticeable surge is interesting, although not pertinent to the current test (Ye and Morrell, 2015).

Sediment Metal Levels: Sediment analysis after 309 and 340 days of exposure show that metal levels have remained exceedingly low in the sediment around the coated samples. These results agree closely with the water column analysis and indicate that the coating is restricting potential metal movement.

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

Table 13 Residual copper, zinc and arsenic in sediment surrounding non-coated and polyurea coated ACZA treated Douglas-fir. ^a				
Treatment	Exposure Time (Days)	Metal Concentration (ug/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)

^aValues represent means of 3 or 4 samples per time point. Figures in parentheses represent one standard deviation.



Figure 14. Example of polyurea coated piling in exposure tanks

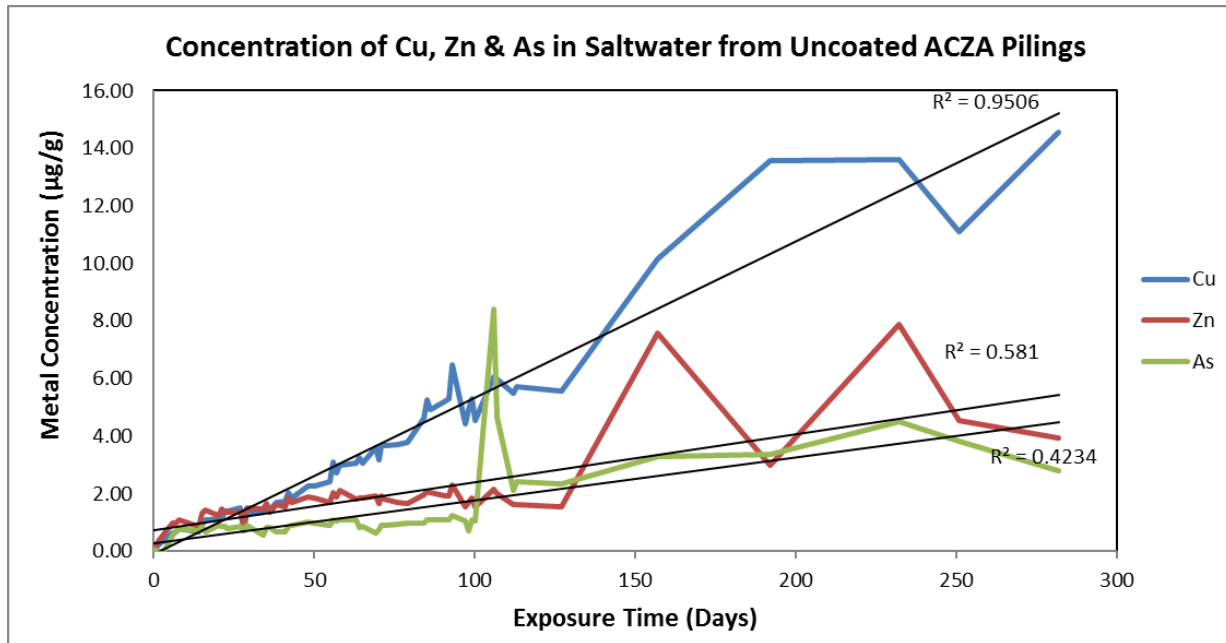


Figure 15. Copper, zinc and arsenic levels in salt water samples removed over a 282 day period from tanks containing ACZA treated Douglas-fir piling

Conclusions: The polyurea coating has completely inhibited the migration of copper zinc and arsenic 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. Further assessments are planned.

2. 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 the small scale BMP verification procedures, the sachets used to detect preservative migration in aquatic environments, and our efforts to quantify the levels of PAH's in the water column that have been described earlier. Our intent is to publish the results of these tests in peer-reviewed journals and, once they are accepted in that venue, to move to make these methods standards under the appropriate organizations.

Table 14. Concentrations of copper, zinc and arsenic in synthetic seawater surrounding ammoniacal copper zinc treated Douglas-fir piling without a coating.

Days of Exposure	Metal Levels (mg/kg)		
	Cu	Zn	As
1	0.16 (0.02)	0.29 (0.10)	< 0.05
2	0.27 (0.05)	0.43 (0.15)	< 0.05
3	0.36 (0.10)	0.58 (0.17)	< 0.05
6	0.63 (0.17)	0.97 (0.19)	0.54 (0.07)
7	0.67 (0.05)	0.95 (0.21)	0.68 (0.13)
8	0.76 (0.08)	1.08 (0.17)	0.77 (0.17)
14	0.67 (0.54)	0.84(0.70)	0.48 (0.39)
15	0.95 (0.03)	1.32 (0.32)	0.59 (0.48)
16	1.08 (0.14)	1.41 (0.32)	0.65 (0.13)
20	1.14 (0.11)	1.22 (0.21)	0.88 (0.11)
21	1.12 (0.33)	1.46 (0.25)	0.84 (0.08)
22	1.37 (0.12)	1.35 (0.16)	0.84 (0.10)
23	0.94 (0.78)	0.92 (0.76)	0.53 (0.42)
27	1.50 (0.14)	1.35 (0.20)	0.87 (0.12)
28	0.79 (0.65)	0.91 (0.76)	0.49 (0.38)
29	1.30 (0.29)	1.48 (0.32)	0.88 (0.04)
34	1.35 (0.21)	1.46 (0.23)	0.55 (0.30)
35	1.56 (0.29)	1.64 (0.21)	0.81 (0.11)
36	1.43 (0.40)	1.33 (0.25)	0.83 (0.06)
38	1.70 (0.30)	1.63 (0.21)	0.67 (0.25)
41	1.73 (0.32)	1.53 (0.15)	0.67 (0.06)
42	2.03 (0.35)	1.83 (0.23)	0.87 (0.06)
43	1.83 (0.06)	1.70 (0.26)	0.90 (0.10)
48	2.27 (0.23)	1.90 (0.36)	1.00 (0.10)
50	2.27 (0.12)	1.83 (0.29)	0.88 (0.19)
55	2.40 (0.52)	1.70 (0.17)	0.90 (0.10)
56	3.10 (0.69)	2.03 (0.06)	1.07 (0.12)
57	2.70 (0.62)	1.90 (0.35)	1.03 (0.06)
58	2.97 (0.40)	2.10 (0.17)	1.07 (0.12)
63	3.07 (0.25)	1.80 (0.17)	1.07 (0.15)
64	3.27 (0.81)	1.83 (0.06)	0.82 (0.01)
65	3.07 (0.58)	1.83 (0.06)	0.86 (0.10)
69	3.60 (0.78)	1.93 (0.21)	0.65 (0.32)
70	3.17 (0.64)	1.67 (0.29)	0.73 (0.13)
71	3.68 (0.82)	1.93 (0.27)	0.89 (0.09)
72	3.67 (0.88)	1.81 (0.25)	0.89 (0.08)
76	3.71 (0.99)	1.68 (0.26)	0.94 (0.06)
79	3.79 (1.18)	1.65 (0.44)	0.95 (0.09)
84	4.61 (1.53)	1.95 (0.53)	0.96 (0.07)
85	5.28 (1.90)	2.07 (0.68)	1.10 (0.08)
86	4.93 (1.39)	2.05 (0.57)	1.08 (0.19)
91	5.23 (2.37)	1.94 (0.59)	1.10 (0.08)
92	5.30 (2.36)	1.94 (0.61)	1.10 (0.13)
93	6.48 (2.57)	2.29 (0.92)	1.23 (0.12)
97	4.44 (1.88)	1.55 (0.44)	1.03 (0.09)
98	4.93 (2.36)	1.68 (0.52)	0.71 (0.12)
99	5.32 (2.38)	1.85 (0.76)	1.09 (0.17)
100	4.53 (1.88)	1.53 (0.38)	1.05 (0.10)
157	10.17 (1.50)	7.57 (5.44)	3.28 (1.14)
192	13.55 (7.21)	2.97 (0.54)	3.37 (0.72)
232	13.60 (3.69)	7.88 (3.62)	4.52 (1.73)
251	11.10 (3.68)	4.53 (1.88)	3.83 (0.06)
282	14.54 (5.47)	3.94 (0.06)	2.81 (0.40)

Values represent means of 3 replicates per time point except for the 187 day sampling point when one vial was lost. Figures parentheses represent one standard deviation.

3. Work cooperatively to develop and improve models to predict the risk of using treated wood in various applications

There has been no additional activity in cooperation with Dr. Robert Perkins at the University of Alaska.

We were actively engaged with the State of Washington regarding a study for creosote migration from railroad ties in the Puget Sound area. We, along with a number of other companies and associations, participated in one planning meeting and provided comments regarding these plans. The study, however, was never undertaken because of the difficulty in identifying a site that was agreeable to all participants.

4. Identify improved methods for reducing the potential for migration

No work was undertaken under this objective; however, the studies undertaken to evaluate the effects of the various BMP's on metal migration treated Douglas-fir and southern pine lumber have provided valuable information on the effects of the BMP's on metal migration from wood treated with the various preservative systems. We intend to use these data to explore improved methods for reducing metal losses

5. Evaluate the environmental impacts and identify methods for reuse, recycling and/ or disposal of preservative waste wood taken out of service

We have continued to examine treated wood entering the recycling stream. The Recycling 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 system that meets their safety concerns, while allowing us access to the materials in a timely fashion.

6. Deliver educational outreach programs on the proper use of treated wood in relation to the Best Management Practices

We held one meeting with the U.S. Army Corp of Engineers in Portland. These workshops are useful for exposing those who have oversight on the use of treated wood

to wood treatment, the model premise and give them some hands-on experience with the model; however, their reach is limited. They are also useful because they help identify concerns among potential users of treated wood and the models that can be addressed through the coop.

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