

Environmental Performance of Treated Wood Cooperative

First Annual Report

J.J. Morrell

Connie S. Love

Leann Bell

Department of Wood Science & Engineering

Oregon State University

Corvallis, Oregon



August 2011

This document contains preliminary information and was expressly prepared for use by members of the Coop Advisory Committee. Reproduction and distribution of this draft is expressly forbidden.

Advisory Committee Members

Arch Wood Protection (Bob Gruber)

Creosote Council (David Webb)

J.H. Baxter & Co. (Paul Krotts/Dick Keeley)

Osmose (James Basler)

Pentachlorophenol Task Force (John Wilkinson)

Southern Pressure Treaters Association (Carl Johnson)(Joined 2011)

Treated Wood Council (Jeff Miller)

Viance, LLC (Brian Delbrueck/Kevin Archer)

Western Wood Preservers Institute (Ted LaDoux)

Wood Preservation Canada (Henry Walthert)(Joined in 2011)

Personnel

J.J. Morrell, Professor

Leann Bell, Faculty Research Assistant

Connie S. Love, Faculty Research Assistant

Kennedy Sichamba, M.S. Graduate Student

Executive Summary

The Environmental Performance of Treated Wood Cooperative was established to improve knowledge related to the use and disposal of treated wood. In our first year, we have undertaken a number of efforts to address the five Objectives of the coop. Our primary effort has been the establishment of the BMP verification studies. Lumber and piling treated with various wood preservatives with and without Best Management Practices will be exposed to natural rainwater (for decking) or water immersion (for piling). The migration of preservative components will then be assessed. This past year, we established the BMP verification studies for Douglas-fir lumber. Migration of pentachlorophenol and copper naphthenate were consistent with previous studies and there was only a slight difference in losses between BMP and non-BMP materials. Additional tests are underway using ammoniacal copper zinc arsenate, alkaline copper quat and alkaline copper azole. The piling tests will be established this Fall.

We have also moved the Aquatic Environmental Sciences Laboratory facilities (formerly operated by Dr. Kenneth Brooks) to the OSU campus. The equipment has been partially set up and we are awaiting an opportunity to complete installation. We had elected to wait until we had the BMP verification study underway before expending effort on this project.

We have also worked cooperative with researchers at the University of Alaska to provide creosote material prepared using the BMP procedures for a study they are undertaking on the effects of treated wood on herring eggs. We anticipate further cooperation as their study develops.

The book "Managing Treated Wood in Aquatic Environments" has finally been completed and is currently at the publisher. This effort involved 14 authors and a host of chapter reviewers who all labored to produce a comprehensive review of treated wood characteristics, the regulatory environment and, most important, the current state of knowledge of the potential impacts of treated wood use in aquatic applications. This book is expected to be available by mid-August.

CONFIDENTIAL

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 and 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 for 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 (EPTWC) was established to help develop neutral 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 preservative waste wood taken out of service*

ACCOMPLISHMENTS

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

1. *Develop fundamental data on preservative migration from wood*

The main objective of the coop over the past year has been the initiation of the Best Management Practices (BMP) verification studies. The goal of these trials is to assess the effects of BMP's on the migration of preservatives from various treated wood commodities, notably decking and piling.

The first trial initiated was the BMP decking study. Untreated Douglas-fir lumber (nominal 50 mm by 150 mm by 4 m long) was obtained locally and then cut into 600 mm long sections. The sections were then randomly allocated to be treated with pentachlorophenol (Penta), copper naphthenate (CuN), alkaline copper quaternary compound (ACQ), copper azole (CA) or ammoniacal copper zinc arsenate (ACZA). The materials were end-coated with a 2 part marine grade epoxy and sent to local facilities for treatment using either BMP or non-BMP procedures. There were a few issues with the process. First, it was difficult to find a facility using non-BMP processes for copper naphthenate. As a result, only BMP processed material was included in the test. The remaining products were obtained using either BMP or non-BMP procedures. In addition, at least one product (ACZA) allows a number of procedures to be used in the BMP process. Because of sampling constraints, only one of these processes was used. We plan additional trials using a smaller scale apparatus to assess the effects of the various BMP procedures on this chemical system.

Once the treated materials were returned, the boards were sampled to determine preservative penetration and retention according to procedures described in AWWA Standard T1 and M2 (AWWA, 2010). The boards were then cut into sections that were end-sealed using epoxy to reduce the role of end-grain in preservative migration. These sections were used to construct small decks (0.412 m by 0.362 m long) each with a total surface area of 0.37976 square meters. The decks were then placed in clean bins that could capture all water running off the wood (Figure 1). The decks were exposed outdoors beginning February 17th. Only penta and CuN decks were exposed in the initial trial. Rainwater runoff was collected from each deck after each measureable rainfall event. A small sample was first collected (50 ml for Copper based systems and 250 ml for penta), then the remaining water was poured into a container and weighed. The total weight of rainwater was then recorded. The decks were then returned to the bins to await the next rainfall event. The penta and CuN decks experienced a total of 18 rainfall events before this initial trial was terminated.



Figure 1 Examples of penta and copper naphthenate treated wood decks exposed to rainwater in Corvallis, OR in BMP Deck Trial 1.

Runoff water from the CuNaph decks was acidified by adding 300 ul of concentrated nitric acid to 9.7 ml of runoff. This acidification was deemed necessary because of concerns that subsequent analysis by ion coupled plasma spectroscopy might not detect some of the copper associated with the copper naphthenate. Preliminary trials were performed where matched samples were analyzed directly, amended with 0.5 M nitric acid or microwave digested in acid. The results indicated that

simple addition of nitric acid produced higher copper levels than either direct analysis of the extract or digestion followed by analysis (Table 1). The resulting acidified solution could be stored at 5 C until a suitable batch could be collected. This method was used for all remaining samples.

Sample #	Copper Level (ug/ml)		
	No Pretreatment	0.5 M nitric acid	Microwave acid digest
11	3.8	5.4	3.5
14	4.2	6.8	3.7
17	5.7	8.3	4.3
20	3.2	6.7	3.1
23	4.9	6.3	3.4
36	2.6	4.6	1.1
Mean (SD)	4.07 (1.12)	6.35 (1.27)	3.18 (1.10)

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.

De-ionized water was added to the sample collection flask to approximately 230 mL, then 50 uL internal standard stock solution was spiked in each flask. The internal standard stock solution was 200 µg/mL ¹³C-labeled pentachlorophenol (¹³C₆H₆Cl₆, Cambridge Isotope Laboratories, Andover, MA) in methanol. Then 2.4 mL 1N NaOH was added to each flask using a pipette. A Teflon™ stir bar was placed in each flask and de-ionized water was added to bring the volume to the bottom of the neck of the volumetric 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 2.6 mL iso-octane was added to the flask from a dispenser 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 2.4 mL iso-octane. This procedure removed residual oil 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 2.6 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 2.4 mL iso-octane. This second extract was added to the first. Each sample extract was then diluted to an appropriate concentration with iso-octane containing 2 µg/mL internal standard.

High resolution gas chromatography – low resolution mass spectrometry (HRGC-LRMS) analysis was carried out by injecting 1 ml of sample into a Shimadzu HRGC-LRMS system class 5000 equipped with a Restek XTI-5 capillary column (0.25mm ID X 30 m long) composed of fused silica with a 0.25 μ m thick film of 95% dimethyl, 5% diphenyl polysilarylene.

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 °C, respectively. The oven was programmed to hold for 2 minutes at 40 °C, ramp to 80 °C at 40 °C /min, then ramp to 260 °C at 25 °C/min. The system was flushed with methanol between injections to minimize the risk of carryover.

The PCP standard (50 μ g/mL) and [$^{13}\text{C}_6$] PCP internal standard (50 μ g/mL) were 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. The selected ion for the internal standard [$^{13}\text{C}_6$] PCP was $m/z = 274$, the reference ions were 276 and 172. HRGC-LRMS auto tuning was performed with perfluorotributylamine. The calibrations were carried out with PCP concentrations of 0.1, 0.2, 0.5, 1.0, 2.0, 5.0, 10.0, and 20.0 μ g/mL; 2 μ g/mL internal standard was added for each standard solution or sample. 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) (17), as three times the standard deviation of replicate analyses of the analyte.

Both copper and penta were detected in all water samples collected from decks treated with the respective chemicals.

Copper levels in the runoff were highest at the first collection point, ranging from 13.0 to 26.5 ppm in the runoff water for the three replicate decks (Figure 2). The variations in copper levels between decks illustrate the inherent variability in wood treatment. Copper concentrations in the runoff water dropped by nearly 50 % in the second collection, were similar for the third water collection, then varied between 1 and 8.5 ppm for the remaining rainfall events. Wood is a variable material and the differences in copper levels in runoff from the three decks clearly illustrate that fact. For that reason, examining average copper concentration in the decks is a more reasonable approach to assessing impact.

The total amounts of copper released were closely related with rainfall levels (Figure 3, 4). In previous trials of pentachlorophenol treated utility poles, resulting penta concentrations in rainwater runoff tended to be very similar and this tendency also occurred with the copper.

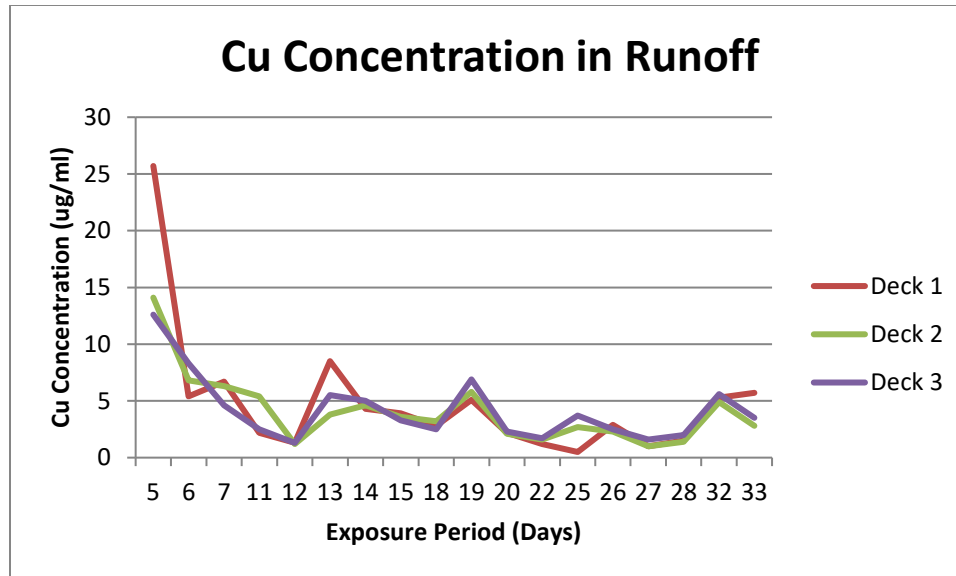


Figure 2. Copper concentrations in rainwater runoff collected over a 33 day period from copper naphthenate treated Douglas-fir decks

naphthenate. As expected, given the presence of copper in every water sample, cumulative copper releases increased steadily over time (Figure 5). The consistent relationship between rainfall amounts and metal losses makes it relatively simple to develop estimates for migration using deck surface area and total rainfall (Figure 6). Rainfall data could be collected from a weather station nearest to a site, allowing a regulator to estimate the potential total release rates for a given amount of rain. It is also clear that, aside from very high rainfalls, the greatest releases are likely to occur after the first rainfall event and then decline sharply. These results were also consistent with previous studies.

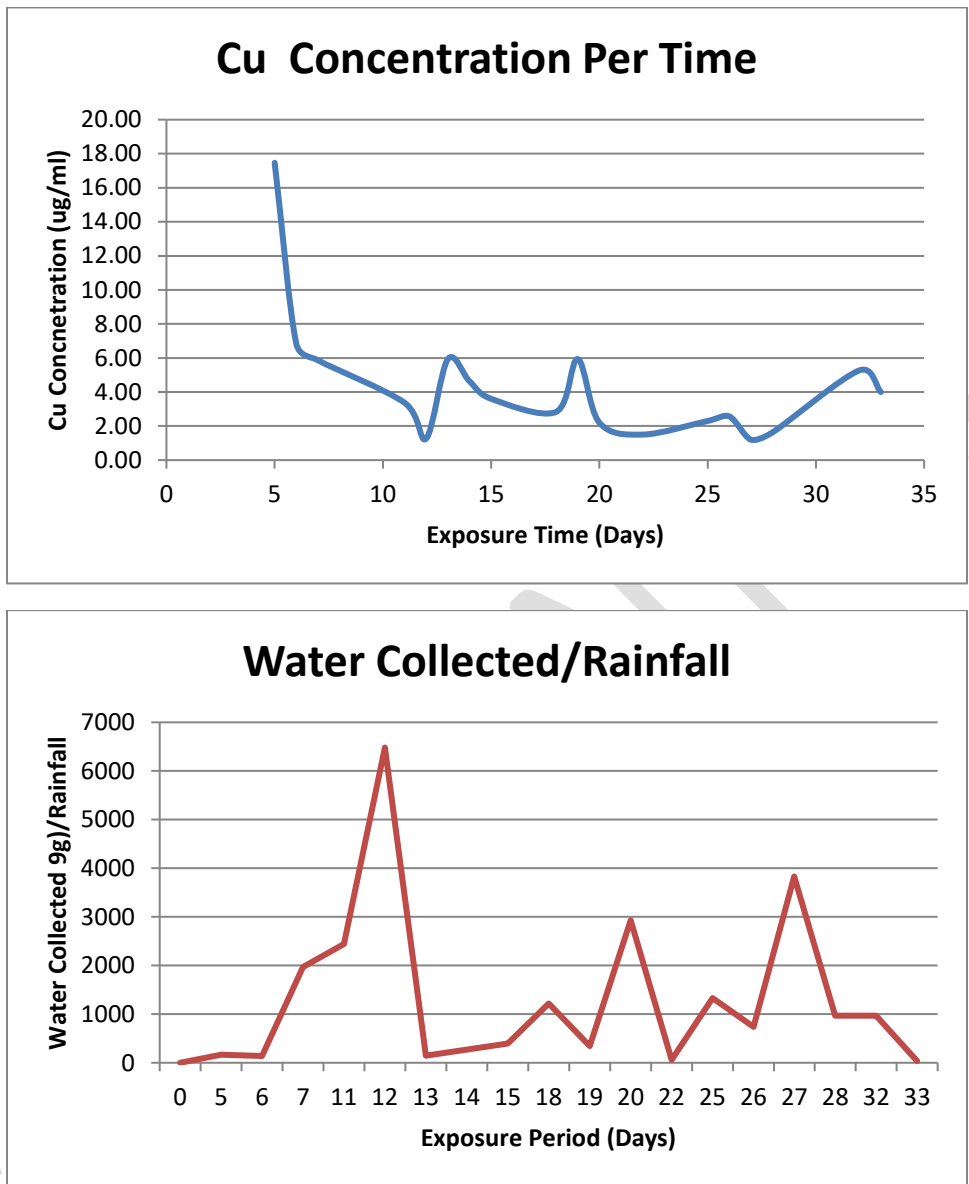


Figure 3. Average concentrations of copper in rainwater runoff collected from beneath copper naphthenate treated Douglas-fir decks after each measurable rainfall event, and the total amount of water collected from beneath each deck per event.

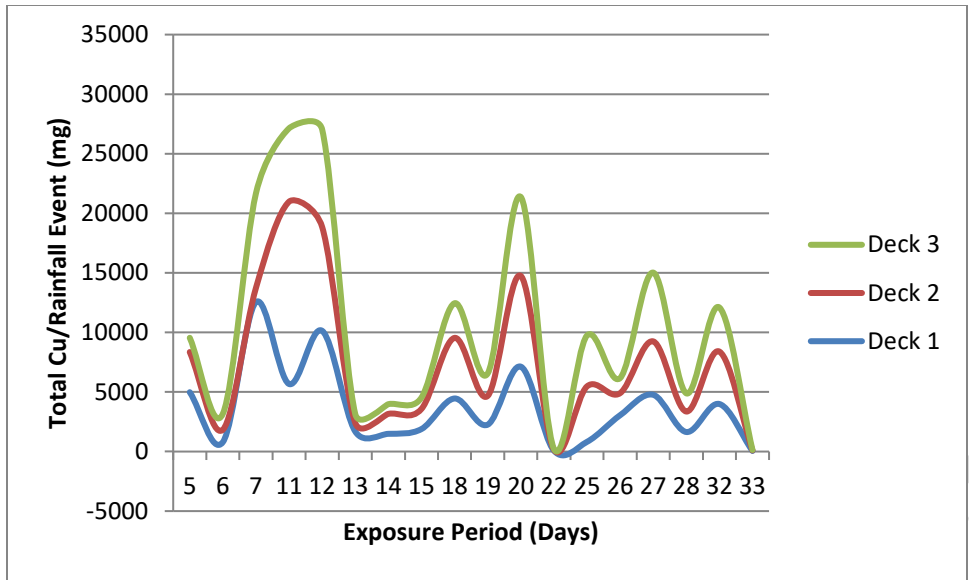


Figure 4. Total copper release from three copper naphthenate treated Douglas-fir decks exposed to natural rainfall over a 34 day period in Western Oregon

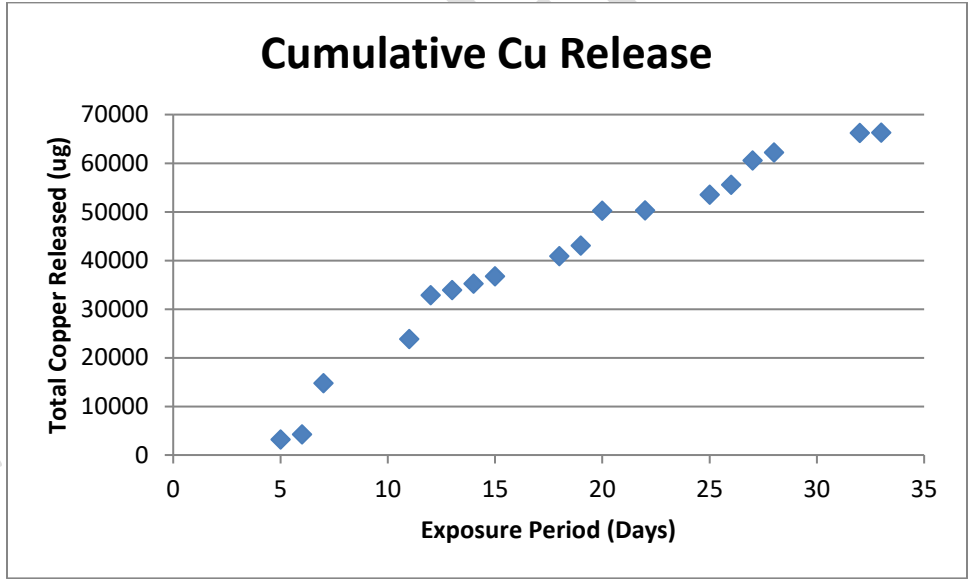


Figure 5. Cumulative copper released from copper naphthenate treated Douglas-fir decks exposed to natural rainfall for 33 days. Values represent means of 3 decks per time point.

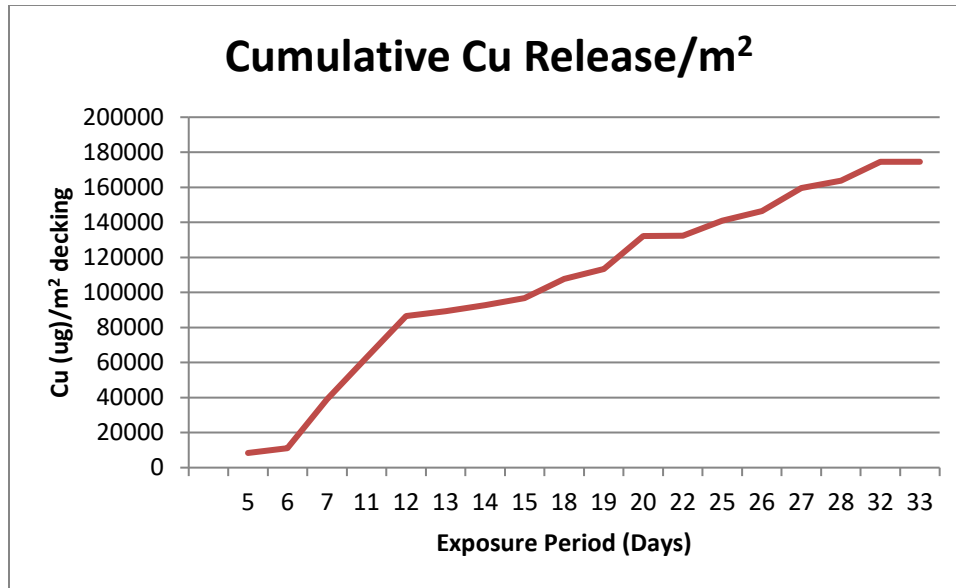


Figure 6. Cumulative copper released from beneath copper naphthenate treated Douglas-fir decks subjected to natural rainfall over a 34 day period with 18 rainfall events. Values represent means of 3 decks per time point.

Penta was also detected in every rainwater sample collected from beneath decks treated with this chemical regardless of whether or not the wood was subjected to a BMP procedure. Concentrations in runoff were highest after the first rainfall event and declined over the next 23 days. Penta levels in runoff from the non-BMP decks were between 4 and 6 ppm, while they were between 3.8 and 9 ppm for the BMP decks (Figures 7, 8). This suggests that the BMP decks actually lost more penta; however, this range is skewed by runoff from one deck that had a very high penta concentration. Penta levels in non-BMP treated decks tended to gradually decline to levels between 2 and 3 ppm. Conversely, the penta levels in the BMP treated decks rapidly dropped to the 2 to 3 ppm level. These data, while preliminary, suggest that BMP's may not appreciably alter the first emission, but they do result in more rapid declines in release rates to the background level.

Total penta releases from the decks also varied widely between the 3 decks per treatment (BMP/non-BMP)(Figures 9, 10), but they were closely related to total water collected per event (Figure 11). In previous studies, we have found that penta concentrations in runoff water from treated wood tend to be fairly steady and are related to exposed surface area, regardless of time intervals between rainfall events or rainfall amounts. These results support those observations and suggest that models incorporating rainfall amounts and surface area exposed to wetting can provide reasonably accurate estimates to total penta released into an environment.

Average cumulative penta released from the decks tended to be higher in BMP than non-BMP treated decks (Figures 12, 13); however, this difference is an anomaly resulting from the one deck in the BMP treated group that had exceptionally high

releases after the first rainfall event. The levels are very similar if this deck is removed from the analysis.

The results might lead to questions about the value of the BMP processes; however, it was clear that penta concentrations in water declined more sharply to the background level in BMP treated decking. This result makes sense when one considers that penta has very limited water solubility, but some penta will always be available on the wood surface to solubilize. The BMP procedures will to affect that solubility; however, it will reduce the amounts of surface deposits that might be available for removal during the first wetting after installation. As a result, BMP treated wood will reach the low background level more rapidly than material not subjected to these processes.

We will continue to monitor decks in Trial 2 until the end of the rainy season and will then monitor them for a short period in the Fall to determine the effects of prolonged drying on migration.

In addition, over the coming summer, we will prepare spruce-pine-fir and southern pine decking for similar exposures next Fall. Finally, we will prepare ACZA and creosote treated piling for exposure as described in the original BMP verification tests.

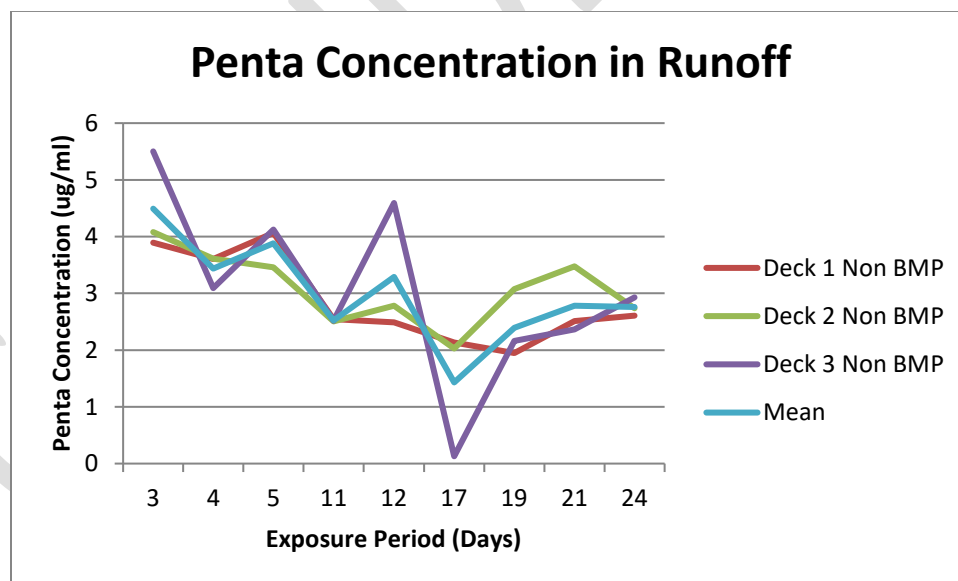


Figure 7. Penta concentrations in runoff from decks constructed using non-BMP pentachlorophenol treated Douglas-fir lumber.

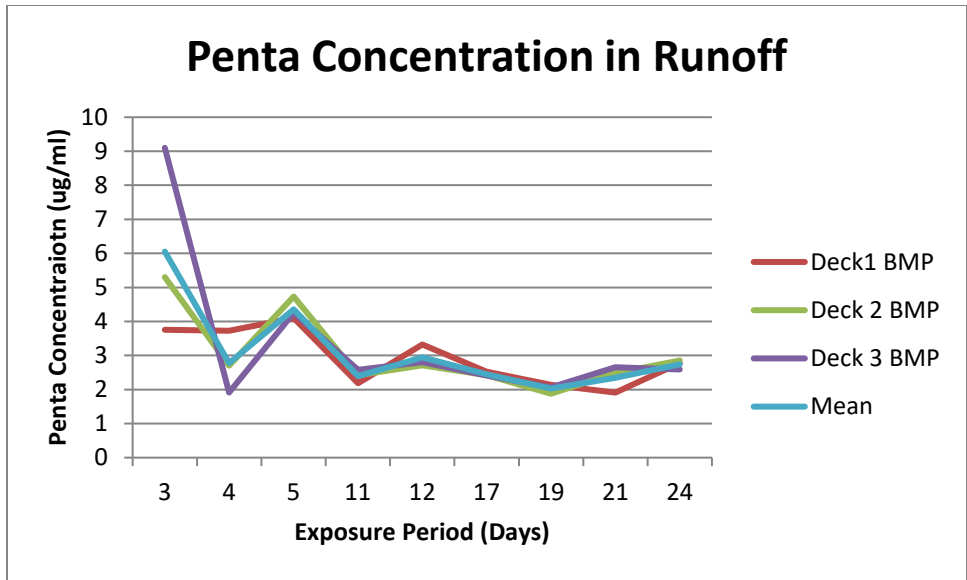


Figure 8. Penta concentrations in runoff from decks constructed using BMP pentachlorophenol treated Douglas-fir lumber.

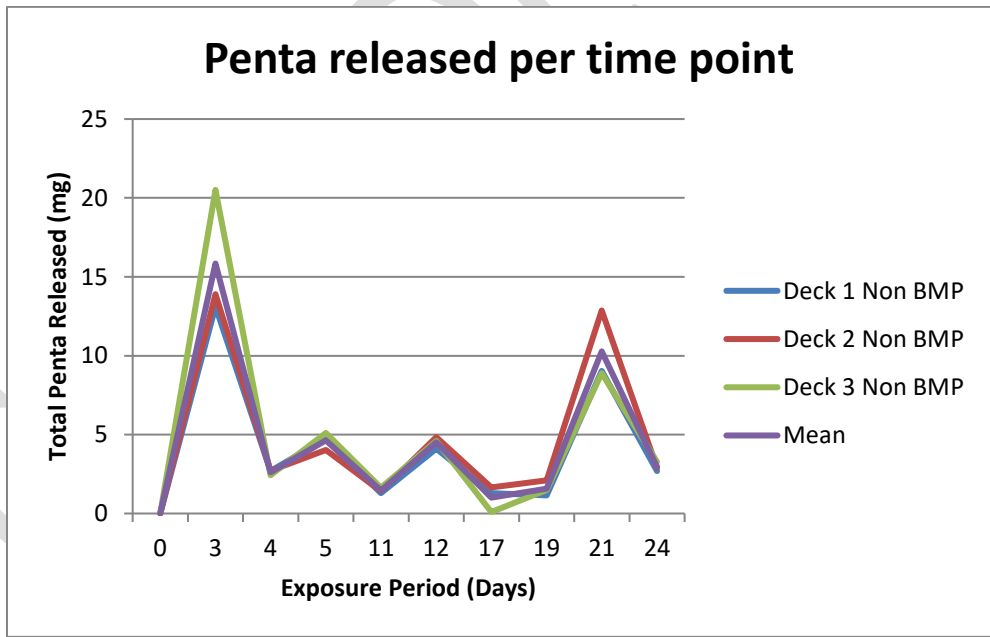


Figure 9. Penta released per time point from decks constructed using non-BMP pentachlorophenol treated Douglas-fir lumber.

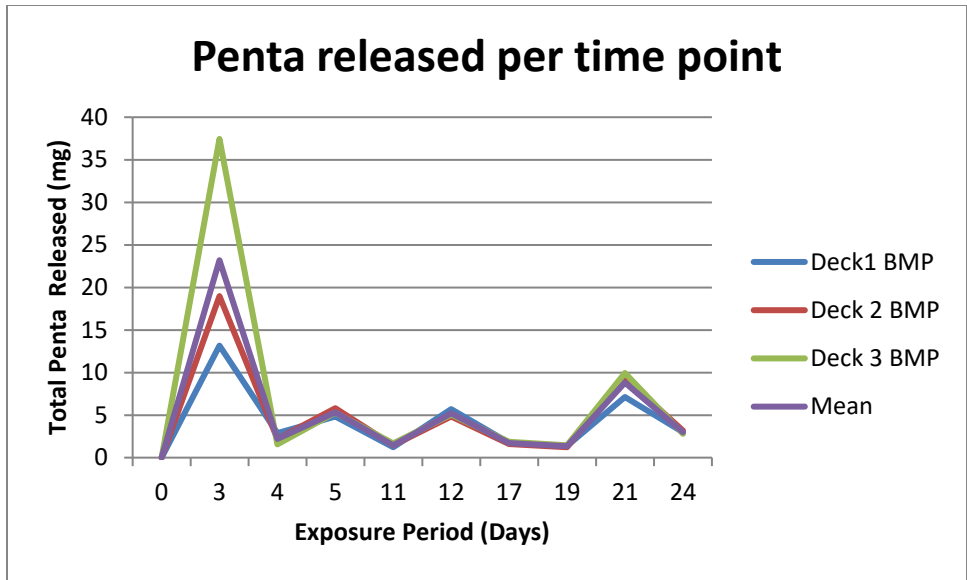


Figure 10. Penta released per time point from decks constructed using BMP pentachlorophenol treated Douglas-fir lumber.

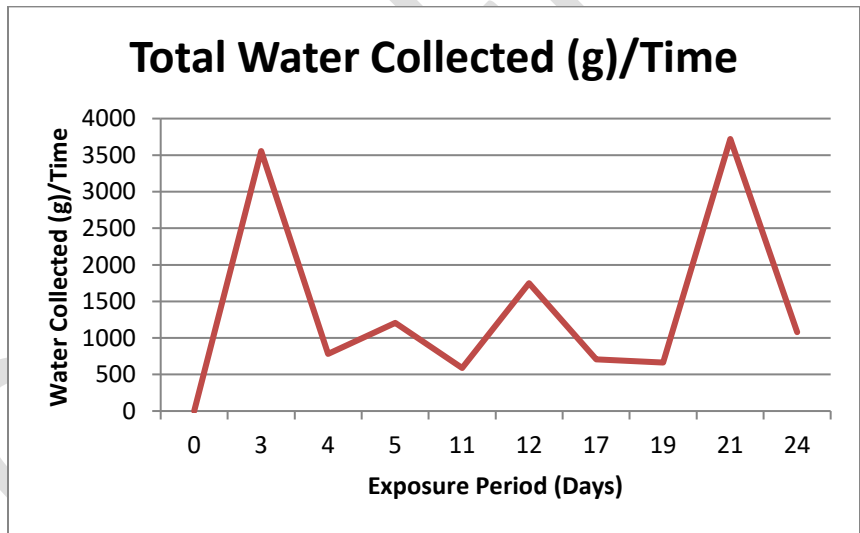


Figure 11. Total amount of rainfall water collected per event from decks constructed using BMP pentachlorophenol treated Douglas-fir lumber.

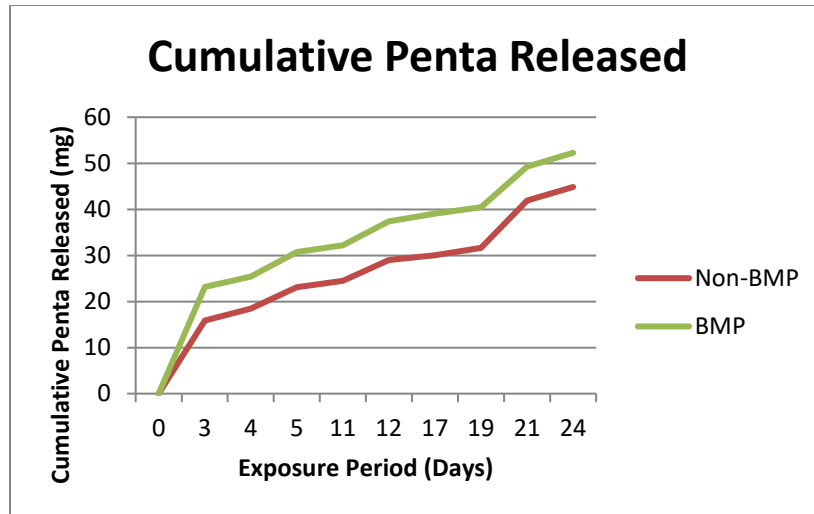


Figure 12. Cumulative penta released over a 24 day period from decks constructed using Douglas-fir lumber treated with penta using BMP and non-BMP processes.

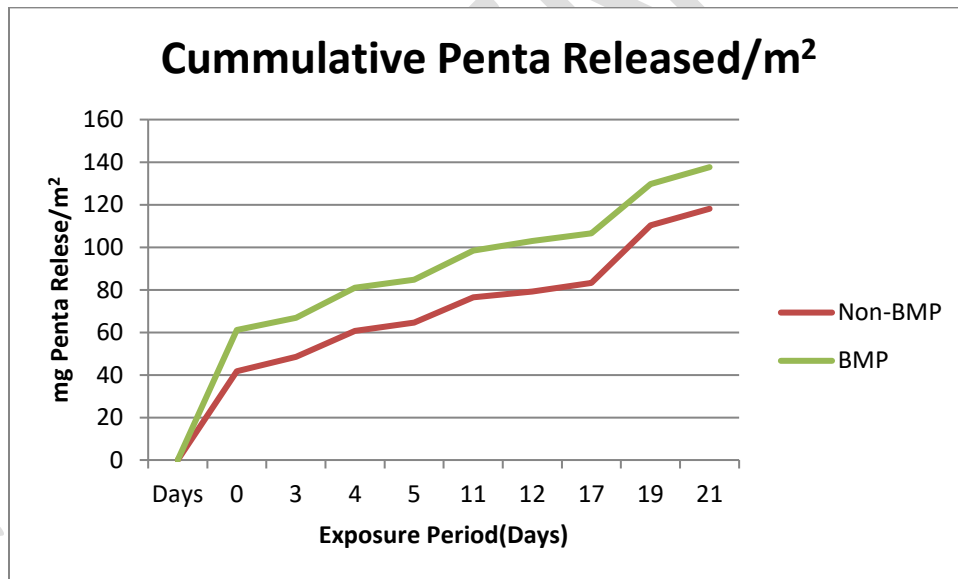


Figure 13. Cumulative penta released per square meter of deck over a 24 day period from decks constructed using Douglas-fir lumber treated with penta using BMP and non-BMP processes.

Reproducibility of Tests: A major question in these trials has been the ability to develop reproducible data. The establishment of two initial trials, each with non-BMP penta treated decks allowed us to examine the effects of different exposure periods on matched materials. Both sets of decks were cut from the same material and then treated in the same charge. The decks were exposed for approximately the same length of time but over two different periods. In both cases, there were numerous rainfall events over the exposure period. Penta levels in run the runoff were initially high in

both trials, then declined with further rainfalls (Figure 14). In both cases, there was a continued, but steady decline in water concentrations of penta. Overall penta levels released did differ between the two exposures, but this reflected total rainfall, not any differences between the two deck sets (Figure 15). The results indicate the chemical losses are consistent with rainfall totals even when the decks are exposed at different times.

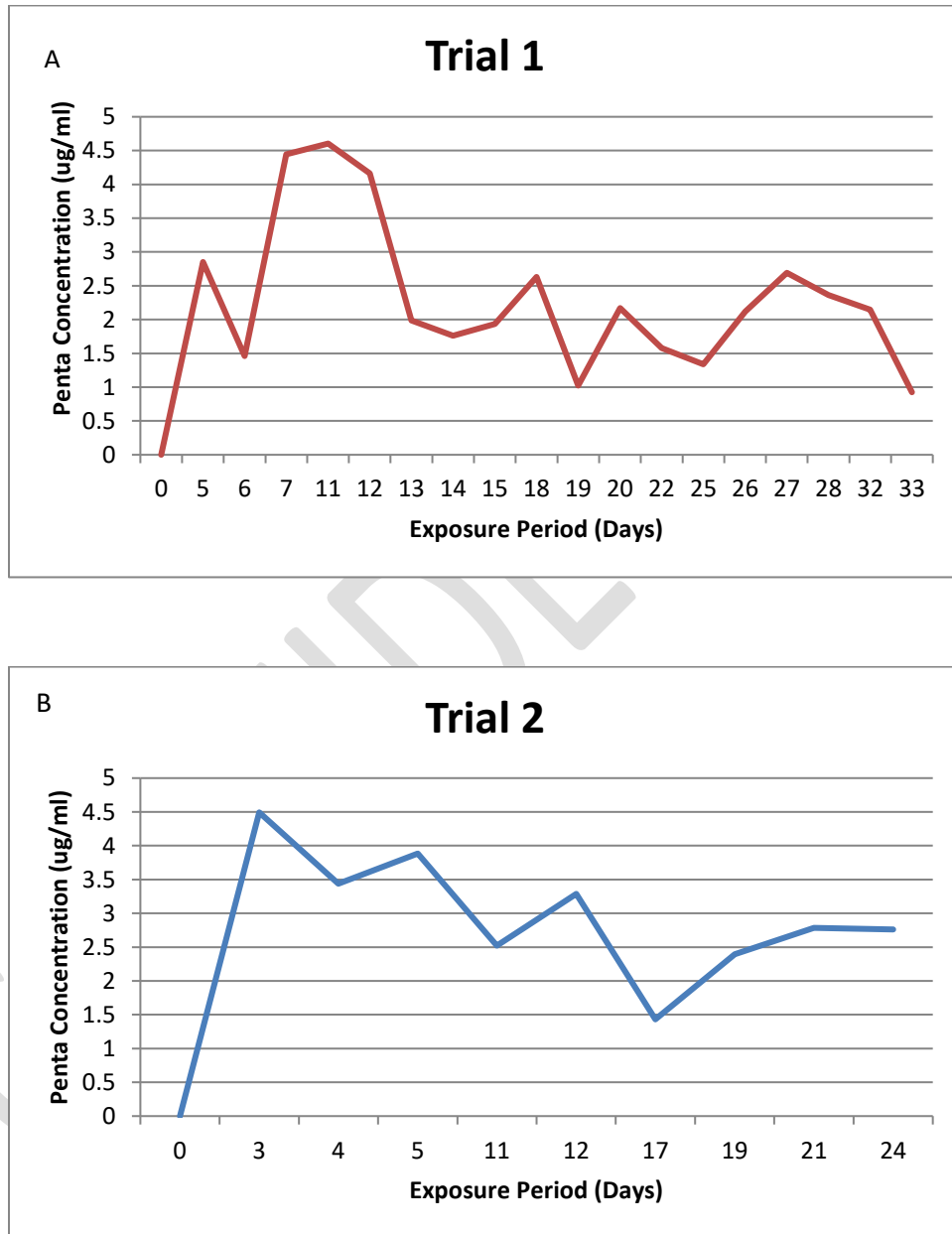


Figure 14. Penta concentrations in rainwater runoff from Douglas-fir decks pressure treated with pentachlorophenol using non-BMP procedures and exposed at two separate time periods. Values represent means of 3 decks per exposure.

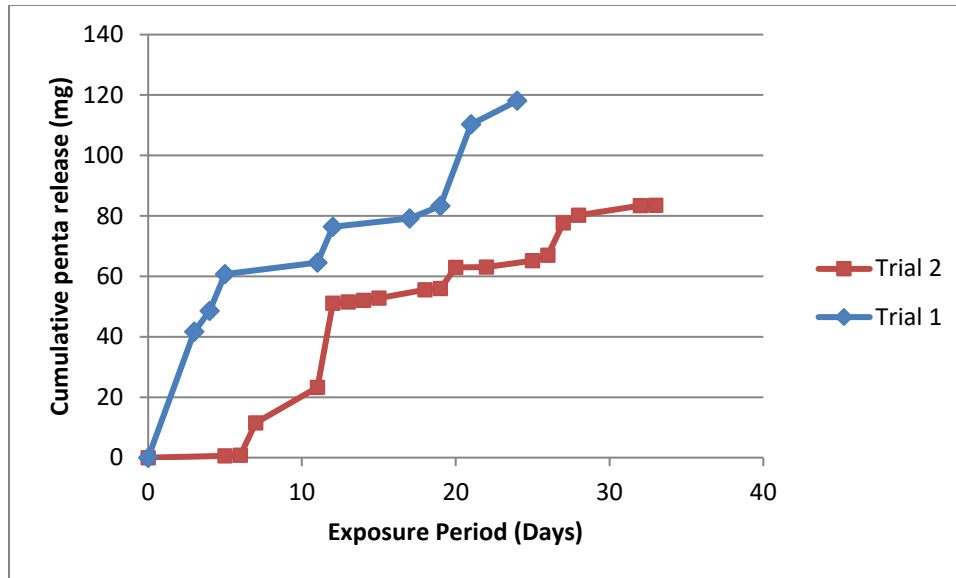


Figure 15. Cumulative penta in rainwater runoff from Douglas-fir decks treated with pentachlorophenol using non-BMP processes and exposed in two separate trials.

In the coming months, we are trying to locate a suitable pond for exposing the BMP and non-BMP treated creosote, penta and ACZA piling sections. This has proven difficult because of the size of the test and the need for some separation between samples. We had originally planned to install these materials in an estuary, but concluded that the stream flows in these sites would be too great. As a result, any releases would be diluted to the point where they were not detectable. Instead, we are seeking a pond site similar to that used by Aquatic Environmental Sciences (Montgomery Pond). We hope to have the location selected by this Fall. At the same time we need to begin to assemble materials for exposure and will be contacting area facilities to obtain the necessary treated materials.

2. Develop standardized accelerated methodologies for assessing treated wood risks

No research was undertaken under this objective. However, an important task under this objective was moving and reestablishing the aquatic lab formerly operated by Dr. Brooks. The lab equipment was moved in November 2010 and space was acquired in the Oak Creek Building on the OSU campus. We have set up some of the benches and begun to assess the tank arrangements; however, we will not set up any specific apparatus until we have tests to perform. This will allow us to concentrate our efforts on the highest priority activities.

We have also accepted a graduate student to our program starting this Fall. She will work on small scale methods for assessing BMP's. The goal will be to develop tests that

can be used to assess variables in the BMP procedures without the need to move to full scale lumber.

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

We have established linkages with Dr. Robert Perkins at the University of Alaska to assist him with establishing a study of the effects of creosote treated wood on development of herring eggs. Dr. Perkins has support from the Alaska Department of Transportation to repeat a study on this subject. We have assisted Dr. Perkins with obtaining properly treated wood and have interacted with him and his cooperators to discuss exposure methodology. We hope to continue this dialogue as Dr. Perkins undertakes the study.

4. Identify improved methods for reducing the potential for migration

No work was undertaken under this objective since we have not yet initiated trials that would show the degree of migration associated with the various BMP's. We would anticipate beginning to work on this objective in the second or third year of the cycle

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

No work has been undertaken under this objective although we are in the midst of a utility pole disposal survey and this process might be easily extended to West Coast Port and Harbor facilities.