Environmental Performance of Treated Wood Cooperative

Second Annual Report

J.J. Morrell Connie S. Love Jason Schindler Department of Wood Science & Engineering Oregon State University Corvallis, Oregon



December 2012

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 Treater's Association (Carl Johnson) Treated Wood Council (Jeff Miller) Viance, LLC (Brian Delbrueck/Kevin Archer) Western Wood Preservers Institute (Ted LaDoux) Wood Preservation Canada (Henry Walthert)

Personnel

J.J. Morrell, Professor Connie S. Love, Senior Faculty Research Assistant Jason Schindler, Faculty Research Assistant Min Ye, M.S. Graduate Student

EXECUTIVE SUMMARY

The Cooperative works to address six objectives related to the use of treated wood in or near aquatic environments. Progress on each objective will be summarized sequentially.

Objective 1 addresses developing fundamental data on the migration of preservatives from treated wood. The majority of the work on the cooperative over the past year has taken place under this objective via the BMP verification study. Decking of Douglas-fir or Spruce-pine-fir was treated with penta, ACZA, ACQ, CA, or CCA (depending on species) using BMP and non-BMP procedures. Small posts of the same species have been treated with creosote or ACZA, again using BMP and non-BMP procedures. The decking has been exposed to natural and simulated rainfall and the resulting runoff was collected and analyzed. The results indicate that the decks released higher quantities of metals during the first few rainfall events, but then these releases fell to background levels. This trend is consistent with previous tests. Metal or penta levels in the runoff varied widely between decks and, interestingly, there were few noticeable differences between BMP and non-BMP treated materials of the same species. All of these materials were treated in commercial facilities. We believe that the lack of difference has occurred because general plant practices have evolved to the point where most plants are already incorporating many BMP procedures into every treatment. As a result, the differences have become less noticeable. We still recommend BMP procedures be used because they provide the consumer with a system for verifying that BMP's have been applied to treated materials. This reduces the risk of improper treatments that could lead to environmental contamination. We have also prepared southern pine decking treated with penta, CCA, ACQ or CA and plan to evaluate the effects of BMP's on this material in the coming months.

In addition to the decking tests, we performed preliminary tests on the posts which serve as simulated piling. We initially had difficulty identifying a suitable pond for exposure. Our initial trials indicate that release rates from individual posts are extremely low and we used these trials to work out the logistics of water column and sediment sampling. We will proceed with full scale trials this Fall.

Objective 2 addresses developing standardized methods for assessing treated wood risks. We have an MS student working on examining the potential for using an overhead simulated rainfall device to assess the efficacy of the BMP procedures for waterborne treatments. Douglas-fir lumber was treated with ACZA, ACQ or CA with no applied BMP procedures. The wood was then frozen until needed. These samples were allowed to warm and then subjected to the various BMP procedures listed in the WWPI guidelines. These materials will then be exposed to simulated rainfall in an overhead leaching apparatus later this year to determine how the various procedures affect migration.

Objective 3 involves working to develop and improve the risk models. We have had very little activity under this objective over the past year. We anticipate more activity as we develop the BMP verification data.

Objective 4 seeks to improve methods for reducing preservative migration. We will move to address this objective in the coming year as we develop data on the effects of the various BMP's in the simulated rainfall device described under Objective 2.

Objective 5 examines the potential uses for treated wood taken out of service. While we have not been highly active under this objective, we are working on two ancillary projects. The first examines the amounts of treated wood entering the recycling stream. We have been surveying treated wood occurrence in a large regional wood waste recycling center. Treated wood

levels have been consistently low at the facility. The other effort involves collecting wood from various depths in a municipal waste facility. The wood was collected while methane gas collection wells were being drilled. The materials have been collected, categorized and prepared for chemical analysis so that we can determine the relative rates of decomposition of wood under these landfill conditions. The results will help in developing improved life cycle assessments that more fully account for the length of time carbon from wood is sequestered at the end of its useful life.

Objective 6 involves developing educational outreach programs. We delivered three outreach programs this year on the use of treated wood in aquatic applications in cooperation with the WWPI. These efforts took place from May 29 to 31 in Portland, Springfield and Prineville, Oregon. The attendees were primarily federal agency personnel and the goal was to acquaint them with the BMP procedures, the Brooks models and the approaches they could take to avoid the use of the full models for specifying treated wood. The participant comments were generally favorable, but there was frustration with the inability to avoid consultations that slowed projects to the point where alternative materials had to be used in order to time constraints and possible loss of funding over budget years. We have discussed how to deliver workshops to broader audiences and will need to use web-based systems to deliver the program to remote locations. We will pursue this with the federal agencies. There was also discussion about the potential for delivering this type of program to transportation and port officials in California as well as other agencies in Canada.

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 should help improve the surface qualities of treated wood, there are little data demonstrating the benefits of these procedures. 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

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 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 2 years 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 2 x 4 Douglas-fir lumber (nominal

50 mm by 150 mm by 4 m long) was obtained locally and then cut into 2 ft (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 BMP and 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 the American Wood Protection Association (AWPA) Standards T1 and M2 (AWPA, 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 mm by 0.362 mm 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). 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.

Runoff water from the CuNaph, CA, ACQ and ACZA decks was acidified by adding 300 µl 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, particularly with 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 number of samples was collected. This method was used for all remaining samples. Ion coupled plasma spectroscopy (ICP) analysis was also used to quantify chromium, zinc, or arsenic where these elements were present in the original treatment.

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. The extraction procedure is detailed in Appendix A.

In addition to the initial tests on Douglas-fir, we have established similar trials using Spruce-Pine-Fir (SPF) East and West that were treated with either Copper azole (CA) or alkaline copper quaternary compound (ACQ). The materials were shipped to a treating facility near Vancouver, B.C. where they were cut to length and allocated to be treated with either CA or ACQ with or without a BMP process. The materials were treated and then shipped to OSU where they were cut into pieces for inclusion in the deck test. Additional samples were set aside for later assessment of preservative penetration and retention. Penetration was assessed on a visual basis while retention was determined by removing a 0 to 15 mm assay zone from each piece, grinding this material to pass a 20 mesh screen and analyzing the resulting material by



Figure 1 Examples of penta treated wood decks exposed to rainwater in Corvallis, OR.

x-ray fluorescence spectroscopy. The materials were then exposed to natural rainfall and the water was collected in the same manner as described for the Douglas-fir samples.

The tests were performed in 4 separate trials and results from each test will be described separately (Table 2).

Table 1. Copper concentrations in matched water samples analyzed with no treatment, addition of 0.5 M nitric acid or microwave digestion in an acid solution.

5							
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)				

Table 2. Characteristics of tests used to characterize preservative migration from BMP and non-BMP treated wood of selected species.								
Test	Chemicals Tested	Wood Species	Time period	Total Rainfall (mm)	#Rainfall Events	Aver- age High Temp (C)		
1	Copper naphthe- nate and penta- chlorophenol	Douglas-fir	2/17/2011- 3/22/2011	111	16	10.1		
2	Pentachlorophe- nol	Douglas-fir	3/25/2011- 6/13/2011	134	20	16.1		
3	ACZA, copper azole and ACQ	Douglas-fir	6/27/2011- 7/26/2011	236 ¹	10	25.0		
4	Copper azole, ACQ, CCA and pentachlorophe- nol	Douglas-fir	3/9/2012- 4/2/2012	173	10	10.5		
	Copper azole, ACQ and ACZA	spruce						
1. Water was from the municipal supply delivered by garden sprinkler.								

Trial 1: Trial 1 consisted of Douglas-fir boards treated with either copper naphthenate (CuN) using a BMP process or pentachlorophenol (Penta) in a light solvent using BMP or non-BMP processes. The results of these trials were briefly discussed in the First Annual Report, but we have had time to further analyze our results.

The copper naphthenate data are presented for only 33 days, when copper levels in the runoff were consistently below 1 ppm. There were 16 rainfall events over the 33 day exposure period with a total of 23 liters of water collected. The largest rainfall occurred in the third storm event after approximately 12 days of exposure, but most of the other precipitation events were small, with less than 1 liter of water collected from each deck.

Copper levels in the runoff from all but one collection were below 5 ppm and most were less than 1 ppm (Figure 2). There was no evidence of an initial spike in copper levels in the runoff,

suggesting that the initial wetting did not liberate an excess of copper naphthenate residue from the wood surface. The relatively stable copper concentrations in the runoff resulted in a steady increase in cumulative copper release with increasing rainfall. These results differ from those with waterborne copper based biocides where there is typically a sharp increase in copper migration in the first rainfall event. The differences likely reflect the much lower water solubility of copper naphthenate and suggest that BMP's that limit the presence of surface deposits and reduce the risk of bleeding can markedly reduce the potential for wholesale loss of chemical from the wood. However, the wood will continue to lose small amounts of copper over time in proportion to the water solubility of the formulation. This pattern is extremely helpful for predicting the potential migration of chemical from a given structure.

The penta trial was run for 80 days and the results are presented using data from two separate analyses of the same samples (Figure 3B). Both sets of data are included because the analytical chemist changed in the midst of this test and the results from the first chemist tended to be slightly higher than those found when the same samples were reanalyzed by the other chemist. The results from the first analyses were 6-7 ppm higher in a given sample than those from the second analysis of the same sample; however, we have no explanation for these deviations. We considered the possibility that the samples degraded while in storage. Although the penta is clearly unstable in the collected water, we have seen no evidence in prior tests that it will degrade in storage once it has been extracted from the water. In addition, penta levels in subsequent trials were slightly lower than the second set of analysis, suggesting that these results were more reliable. As a result, further discussion will be based upon the results from the second analyses.

There were 20 rainfall events over the 80 day test period with a total of nearly 39 liters of water collected per deck. There were 4 heavy rainfall events with collections greater than 2 liters per deck and one of these resulted in over 6 liters of collected water. Half of the remaining rainfall events resulted in less than 1 liter of water being collected.

Cumulative penta levels tended to gradually increase over time, although there was one sharp rise in cumulative release after 31 days of exposure that corresponded to the largest rainfall event. Penta concentrations in runoff ranged from less than 1 ppm to one sample that contained over 6 ppm, but most samples contained 1 to 3 ppm. These results are consistent with previous tests of penta migration from stored utility poles and again indicate that migration from oil-borne systems is more closely related to water solubility and will tend to be low, but consistent over time. It was also evident that there was little difference in cumulative penta migration for BMP and non-BMP treated wood. The lack of a clear cut effect of BMP processing on subsequent preservative losses was initially perplexing; however, we now believe that the lack of difference reflects a gradual trend on the part of treating facilities to adopt many of the BMP procedures as standard plant operating practices since these practices will help to reduce the risk of preservative loss during in-plant storage and this helps decrease the potential for plant storm water to contain excess levels preservative. Whatever the reason, plant practices appear to be approaching those recommended for BMP's and this should produce treated wood with a lower risk of preservative migration.

Trial 3: Trial 3 consisted of Douglas-fir lumber treated with ACQ, CA or ACZA to the above ground retention as specified in AWPA Standard U1/T1 with or without a BMP process (AWPA, 2010). The test was performed for 29 days; however, since this test was initiated during our drier summer months, the samples were artificially watered (Table 2). The samples were subjected to approximately 41 I of water over the test period delivered in 10 rainfall events (Figures 4-8). Most of the events delivered less than 4 liters of water per deck, but there was some variability in levels delivered to BMP and non-BMP decks because the sprinkler spary

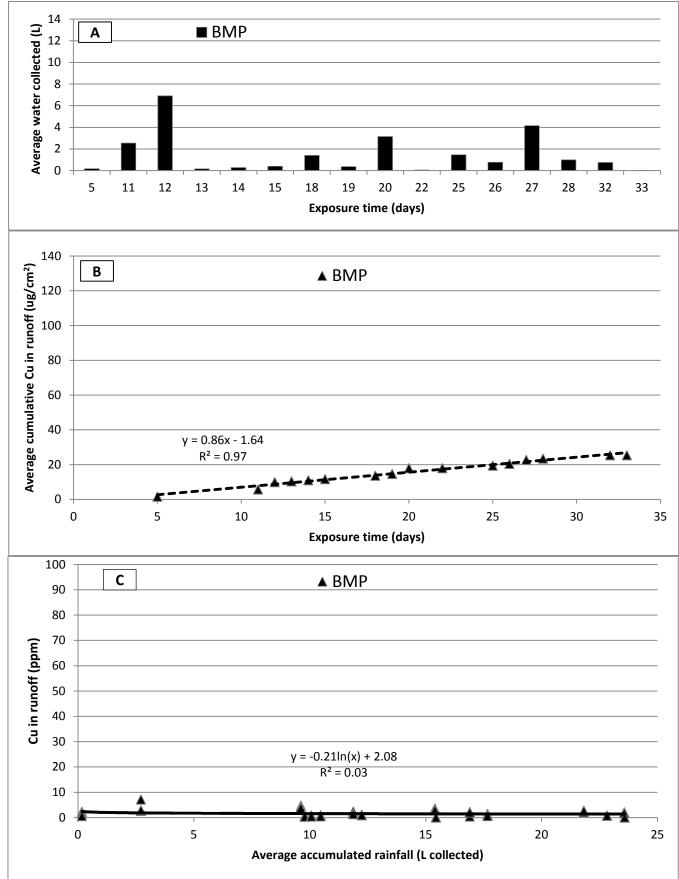


Figure 2. Composite figures showing A.) Total rainfall collected from tanks containing Douglas-fir decking treated with copper naphthenate with BMP Procedures and exposed to rainfall, B.) The cumulative copper present in that rainfall and C.) The amount of copper present in rainfall at each collection point. Three deck sections were tested with BMP wood.

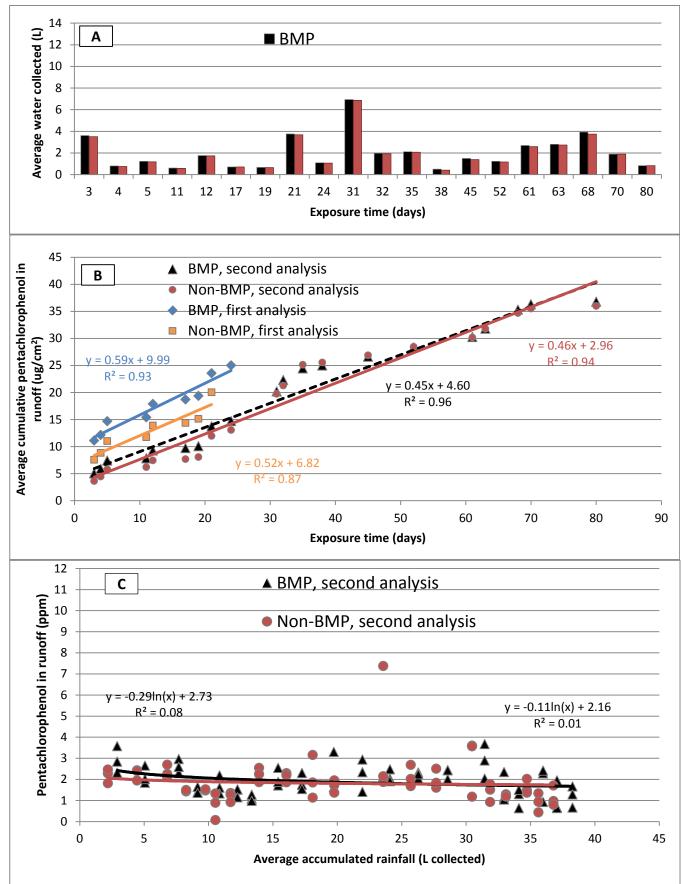


Figure 3. Composite figures showing A.) Total rainfall collected from tanks containing Dougas-fir decking treated with penta with or without BMP Procedures and exposed to rainfall, B.) The cumulative copper present in that rainfall and C.) The amount of penta present in rainfall at each collection point. Three deck sections were tested with BMP wood and three were tested with non-BMP treated wood.

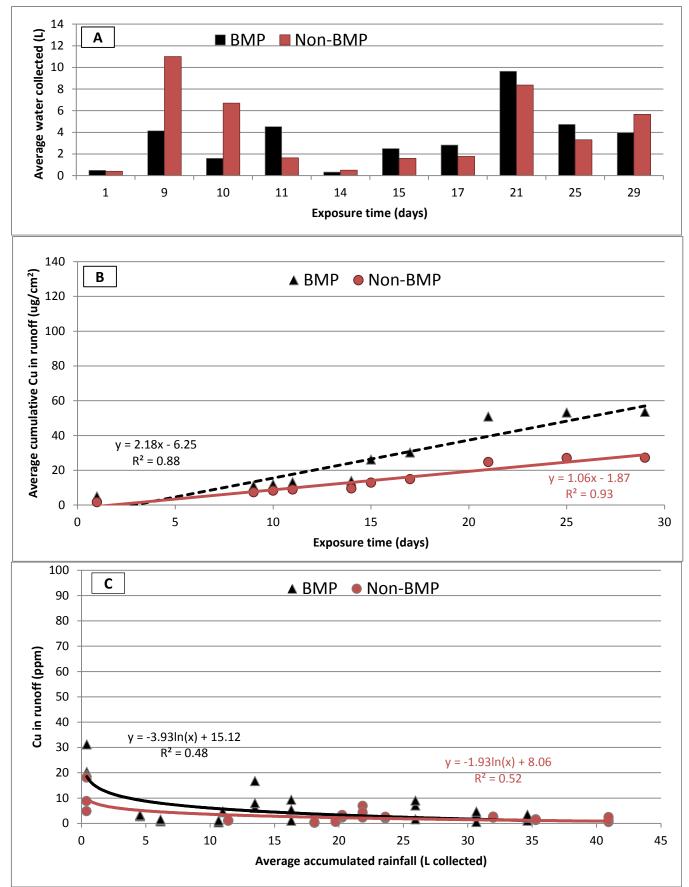


Figure 4. Composite figures showing A.) Total rainfall collected from tanks containing Douglas-fir decking treated with ACQ with or without BMP Procedures and exposed to rainfall, B.) The cumulative copper present in that rainfall and C.) The amount of copper present in rainfall at each collection point. Three deck sections were tested with BMP wood and three were tested with non-BMP treated wood.

did not fall evenly on all decks.

As expected, decks treated with ACQ steadily lost copper over the 41 day exposure (Figure 4). Average cumulative copper losses after the first rainfall event tended to be consistently higher from BMP treated decks with cumulative losses at 41 days being nearly twice as high from BMP treated materials. It is unclear why the BMP material tended to lose more copper, especially since this effect emerged with increasing rainfall. BMP related effects would be expected to occur early in the exposure process. Copper concentrations at each rainfall event were highest immediately after exposure and then declined sharply thereafter. Copper levels had largely reached a steady state release rate around 1 ppm by Day 10, although there were periodic spikes in copper level, particularly with the BMP treated material.

Copper levels in runoff from CA treated decks also tended to be higher in the BMP treated materials with increasing exposure time (Figure 5). The overall levels of copper migration were also much higher from the ACQ treated decks, reflecting the much higher loadings of copper used with this system. As with the ACQ, it is unclear why the BMP treated wood tended to lose more copper. Copper concentrations in the runoff were very high after the first 2 rainfall events, then declined. The sharp rise in copper levels in runoff at the first rainfall followed by an equally sharp decline with further wetting is consistent with the presence of highly soluble copper deposits on the wood surface. Once these deposits are removed, the overall copper losses become relatively small.

Copper losses from ACZA treated wood were initially elevated, then declined rapidly in a manner similar to that found with CA, (Figure 6). Unlike CA or ACQ; however, there was little difference in copper levels with BMP and non-BMP treated wood. ACZA goes through a complex series of reactions between the copper and zinc as the ammonia volatilizes. These reactions have the potential to immobilize more copper. In addition, ACZA contains less copper than either of the other two systems tested.

Zinc levels in the runoff were much lower than those for copper, reflecting the lower proportion of zinc in the original treatment solution, but the trends of a high initial concentration followed by a sharp decline were similar to those found with copper (Figure 7). As with the copper, there were no noticeable differences between zinc levels in BMP and non-BMP treated materials. Arsenic levels in the runoff followed a trend that was similar to that observed with zinc and copper, but the levels were much lower (Figure 8). Low arsenic levels in runoff are consistent with previous tests. Lebow studied ACZA deposition in wood suggested that copper and zinc interact to immobilize arsenic. The disproportionately low arsenic levels (in composition to the balance in the original treatment) in the runoff seem to support this premise.

Trial 4: This set included Douglas-fir samples treated with either ACZA or penta and Spruce pine fir treated with ACQ, CA, or CCA (Table 2). The Douglas-fir samples were residual material from Trials 1 and 3 and were included as comparative references. This sample used natural rainwater, compared with samples exposed in Trial 3, which used city water. The decks were exposed to 51 liters of rainfall over a 21 day period. Most events produced collections less than 2 liters, but there were 4 heavy rainfall events where 6 to 12 liters of water was collected (Figure 9). Decks tended to collect different levels of water, possibly as a result of differences in moisture content at the start of each rainfall.

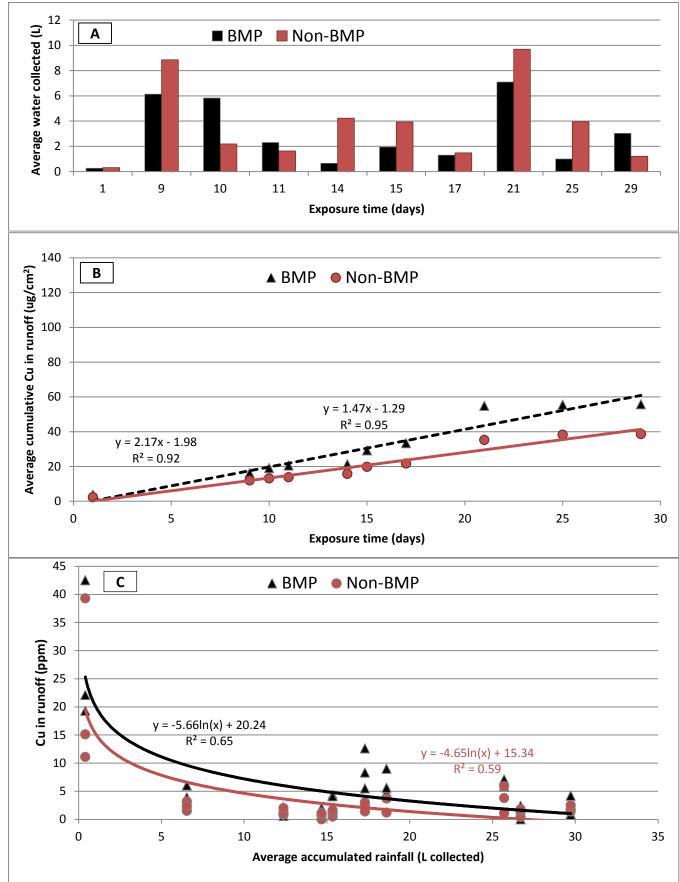


Figure 5. Composite figures showing A.) Total rainfall collected from tanks containing Douglas-fir decking treated with CA-B with or without BMP Procedures and exposed to rainfall, B.) The cumulative copper present in that rainfall and C.) The amount of copper present in rainfall at each collection point. Three deck sections were tested with BMP wood and three were tested with non-BMP treated wood.

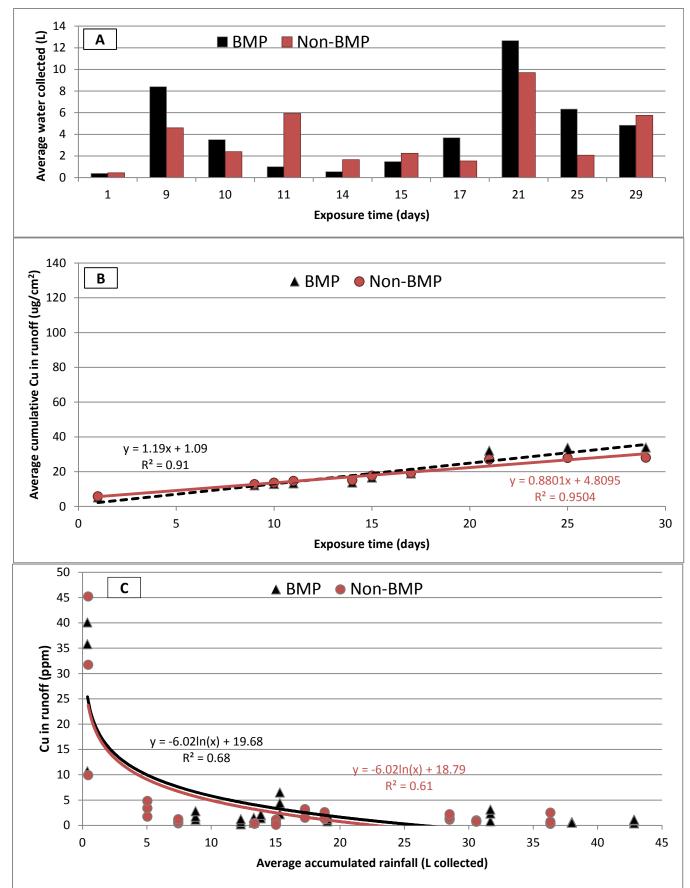


Figure 6. Composite figures showing A.) Total rainfall collected from tanks containing Douglas-fir decking treated with ACZA with or without BMP Procedures and exposed to rainfall, B.) The cumulative copper present in that rainfall and C.) The amount of copper present in rainfall at each collection point. Three deck sections were tested with BMP wood and three were tested with non-BMP treated wood.

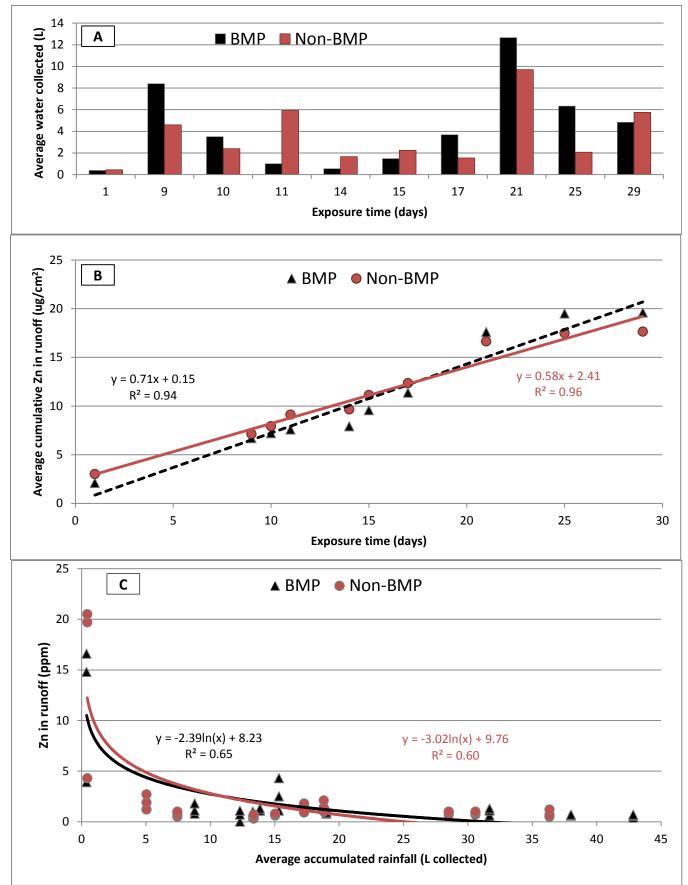


Figure 7. Composite figures showing A.) Total rainfall collected from tanks containing Douglas-fir decking treated with ACZA with or without BMP Procedures and exposed to rainfall, B.) The cumulative zinc present in that rainfall and C.) The amount of zinc present in rainfall at each collection point. Three deck sections were tested with BMP wood and three were tested with non-BMP treated wood.

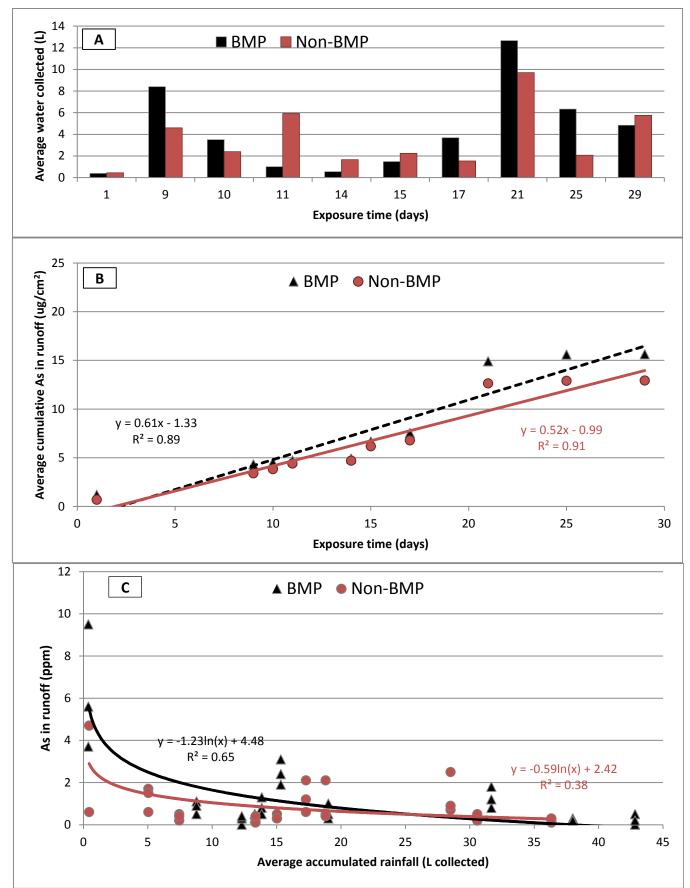


Figure 8. Composite figures showing A.) Total rainfall collected from tanks containing Douglas-fir decking treated with ACZA with or without BMP Procedures and exposed to rainfall, B.) The cumulative arsenic present in that rainfall and C.) The amount of arsenic present in rainfall at each collection point. Three deck sections were tested with BMP wood and three were tested with non-BMP treated wood.

found in Trial 3 immediately after exposure and then fell to background levels within 20 days (Figure 9). There were no noticeable differences between BMP and non-BMP treated materials in cumulative copper losses.

Zinc losses from ACZA treated boards were approximately one half those for copper, which is consistent with the amounts of each metal in the preservative system (Figure 10). Levels dropped off sharply and were at background levels (1-2 ppm) after the second rainfall event. Once again, there were no differences in zinc levels in runoff from BMP and non-BMP treated materials

Arsenic levels in the runoff from the sample material was slightly elevated in runoff from the first rainfall (1-2 ppm vs <1 ppm), but there were no differences between BMP and non-BMP treated materials and levels quickly fell to background levels (Figure 11). The overall results for ACZA from this trial indicate that the materials experienced slightly lower metal losses after the first rainfall and that there were no noticeable differences between BMP and non-BMP treated materials.

Copper levels in runoff from ACQ and CA treated Douglas-fir decks exposed to natural rainfall were similar to those found with simulated rainfall from Trial 3 (Figures 12 and 13).

Metal losses in runoff from Spruce-Pine Fir (SPF) samples treated with ACQ were elevated after the first rainfall event, but then rapidly declined thereafter and had reached near background levels by the fourth rainfall event (Figure 14). Two of these rainfalls were extremely heavy (6 to 10 liters of water collected), which might have hastened the decline. As with ACZA, there was no noticeable difference in metal levels in runoff from BMP and non-BMP treated wood. The initial copper losses represented over 25 % of the total copper losses measured over the 21 day test period and illustrate the importance of the limiting losses in the first rainfall.

Copper levels in runoff from the first rainfall from SPF decks treated with Copper Azole were about one half of those found with ACQ on the same material (Figure 15) and then rapidly declined with continued rainfall. Cumulative copper releases were similar to those found with ACQ, suggesting that the systems behaved similarly despite the slight variation in initial release rate. Once again, the BMP procedures were not associated with any noticeable differences in copper loss.

CCA is no longer used for treatment of materials used in residential applications but it is used for commercial or industrial structures. Copper levels in runoff from CCA treated SPF were negligible, even after the first rainfall event (Figure 16). Copper levels remained low in most collections, although copper levels in one collection from a BMP treated deck approached 10 ppm after the second rainfall. The low copper release rates are consistent with the ability of copper to react with chromium to become less mobile. As with ACQ and CA, there were no noticeably differences in copper levels in runoff from BMP and non-BMP treated materials.

Interestingly, chromium levels were slightly elevated in runoff from the first rainfall from the CCA treated SPF, but then declined to background levels in the second rainfall (Figure 17). Chromium levels were <0.5 ppm in the runoff. Once again, there were no differences in chromium levels between BMP and non-BMP treated materials.

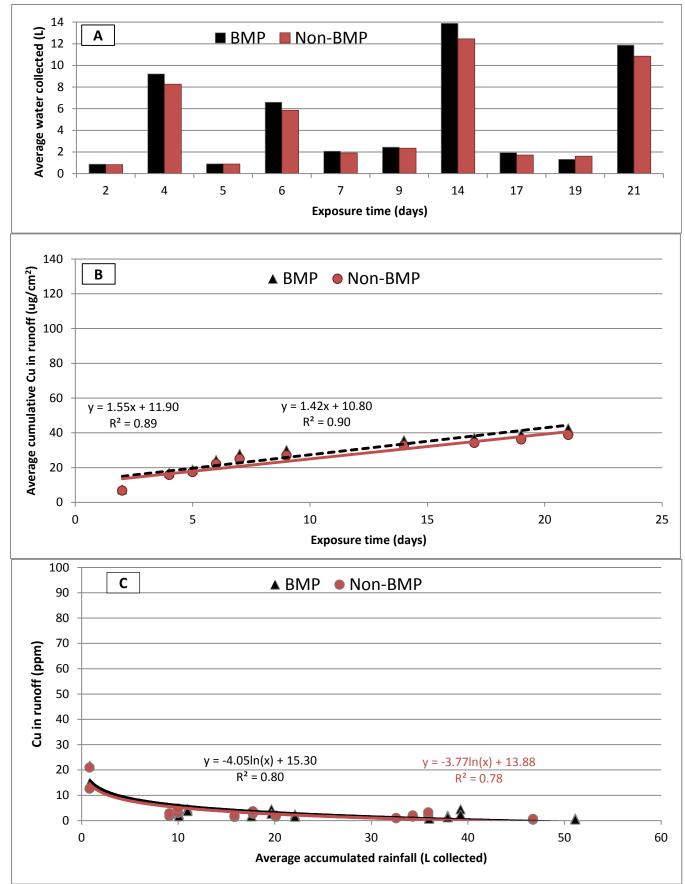


Figure 9. Composite figures showing A.) Total rainfall collected from tanks containing Douglas-fir decking treated with ACZA with or without BMP Procedures and exposed to rainfall, B.) The cumulative copper present in that rainfall and C.) The amount of copper present in rainfall at each collection point. Three deck sections were tested with BMP wood and three were tested with non-BMP treated wood.

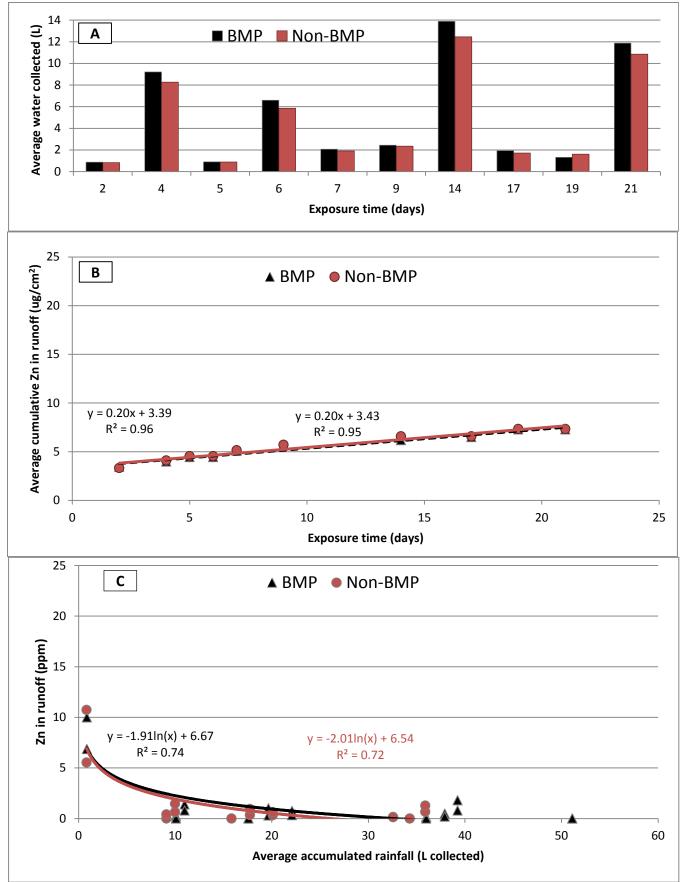


Figure 10. Composite figures showing A.) Total rainfall collected from tanks containing Douglas-fir decking treated with ACZA with or without BMP Procedures and exposed to rainfall, B.) The cumulative zinc present in that rainfall and C.) The amount of zinc present in rainfall at each collection point. Three deck sections were tested with BMP wood and three were tested with non-BMP treated wood.

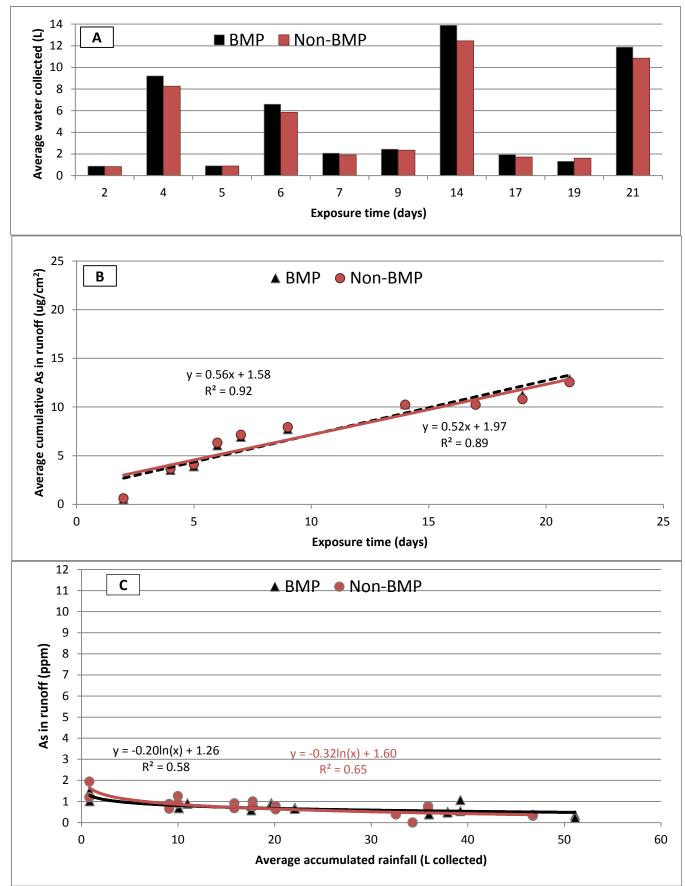


Figure 11. Composite figures showing A.) Total rainfall collected from tanks containing Douglas-fir decking treated with ACZA with or without BMP Procedures and exposed to rainfall, B.) The cumulative arsenic present in that rainfall and C.) The amount of arsenic present in rainfall at each collection point. Three deck sections were tested with BMP wood and three were tested with non-BMP treated wood.

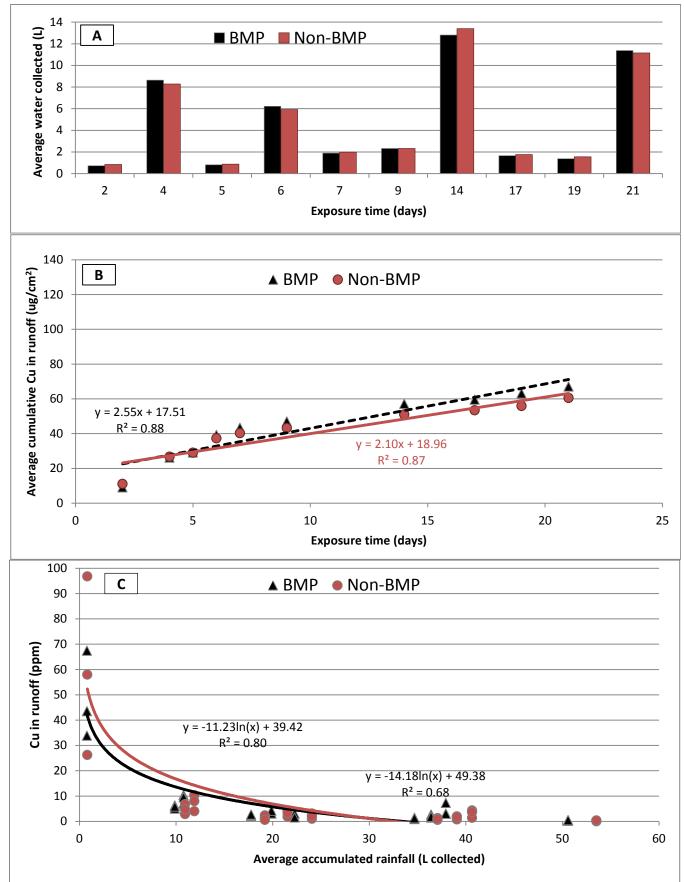


Figure 12. Composite figures showing A.) Total rainfall collected from tanks containing Douglas-fir decking treated with ACQ with or without BMP Procedures and exposed to rainfall, B.) The cumulative copper present in that rainfall and C.) The amount of copper present in rainfall at each collection point. Three deck sections were tested with BMP wood and three were tested with non-BMP treated wood.

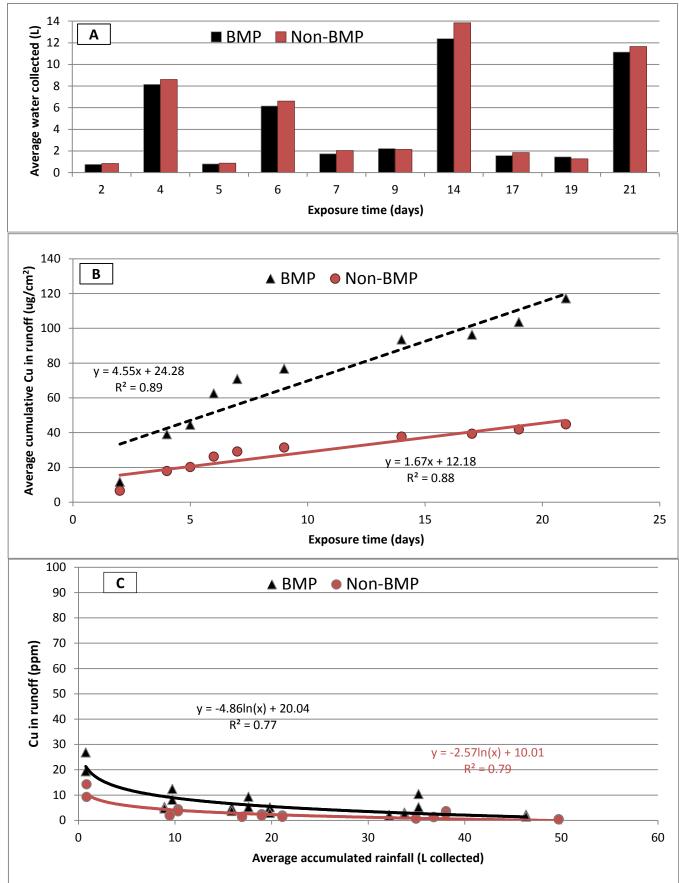


Figure 13. Composite figures showing A.) Total rainfall collected from tanks containing Douglas-fir decking treated with CA-B with or without BMP Procedures and exposed to rainfall, B.) The cumulative copper present in that rainfall and C.) The amount of copper present in rainfall at each collection point. Three deck sections were tested with BMP wood and three were tested with non-BMP treated wood.

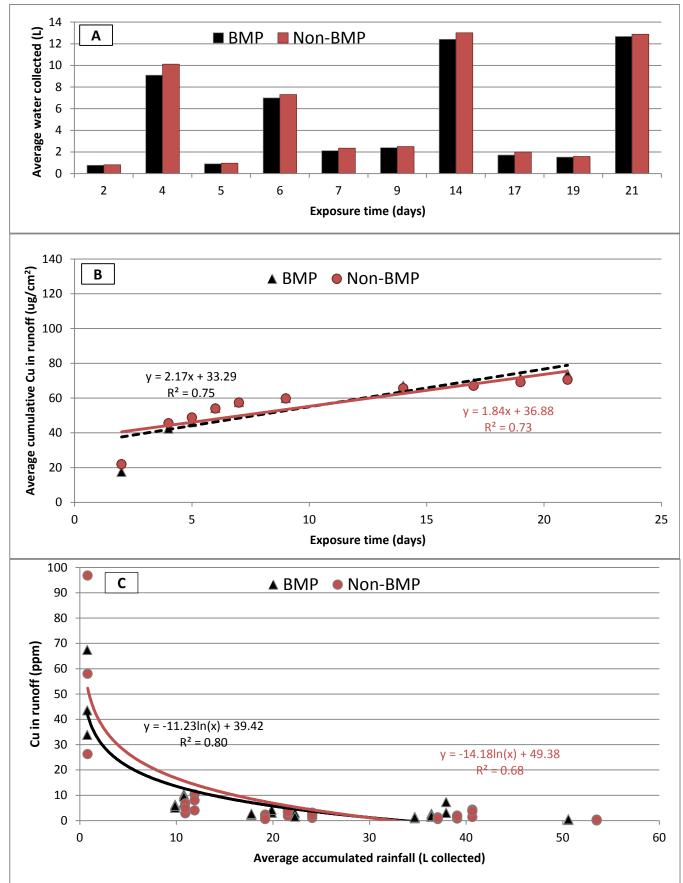


Figure 14. Composite figures showing A.) Total rainfall collected from tanks containing spruce decking treated with ACQ with or without BMP Procedures and exposed to rainfall, B.) The cumulative copper present in that rainfall and C.) The amount of copper present in rainfall at each collection point. Three deck sections were tested with BMP wood and three were tested with non-BMP treated wood.

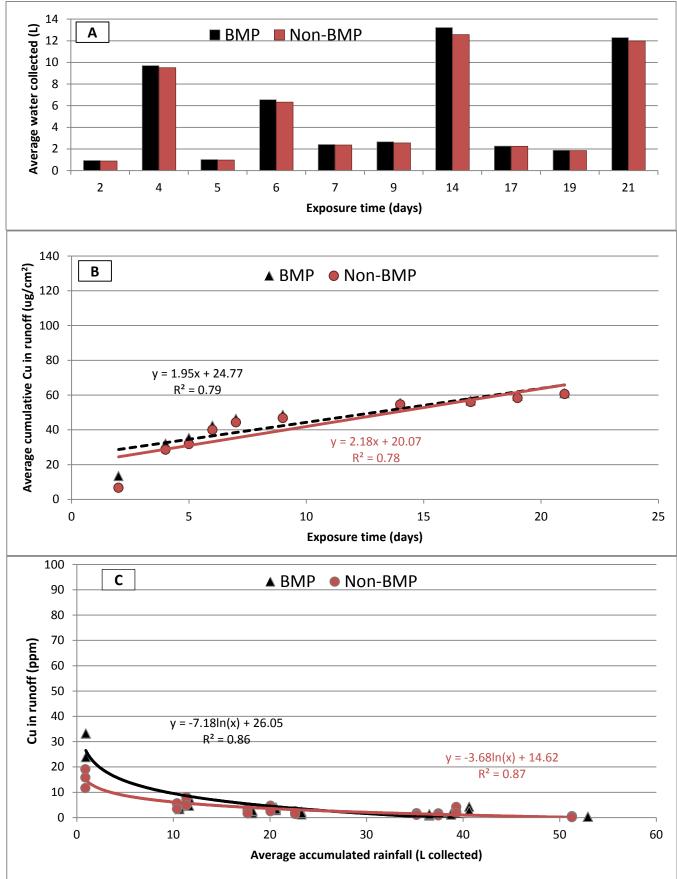


Figure 15. Composite figures showing A.) Total rainfall collected from tanks containing spruce decking treated with CA-B with or without BMP Procedures and exposed to rainfall, B.) The cumulative copper present in that rainfall and C.) The amount of copper present in rainfall at each collection point. Three deck sections were tested with BMP wood and three were tested with non-BMP treated wood.

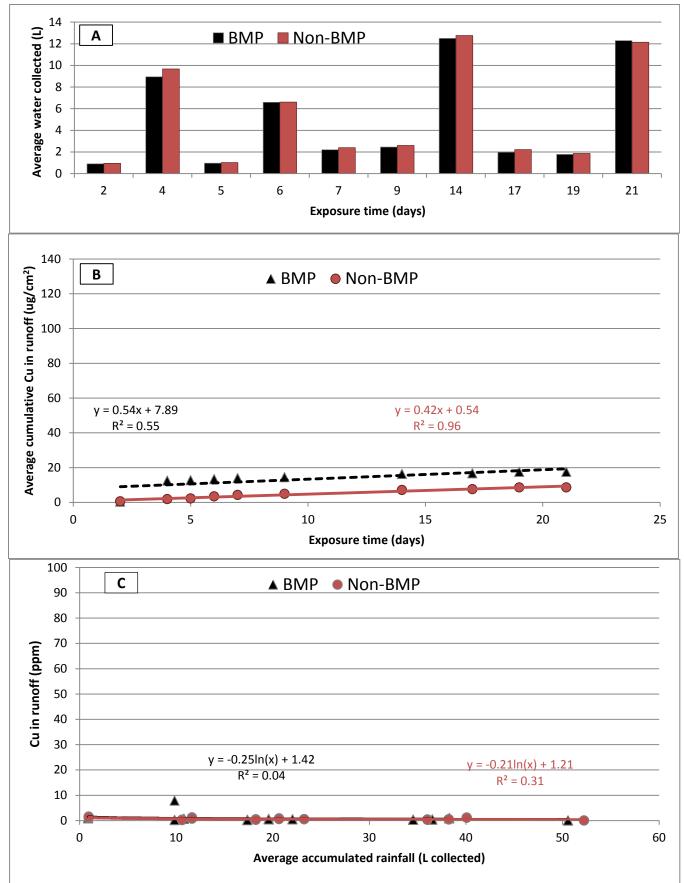


Figure 16. Composite figures showing A.) Total rainfall collected from tanks containing spruce decking treated with CCA with or without BMP Procedures and exposed to rainfall, B.) The cumulative copper present in that rainfall and C.) The amount of copper present in rainfall at each collection point. Three deck sections were tested with BMP wood and three were tested with non-BMP treated wood.

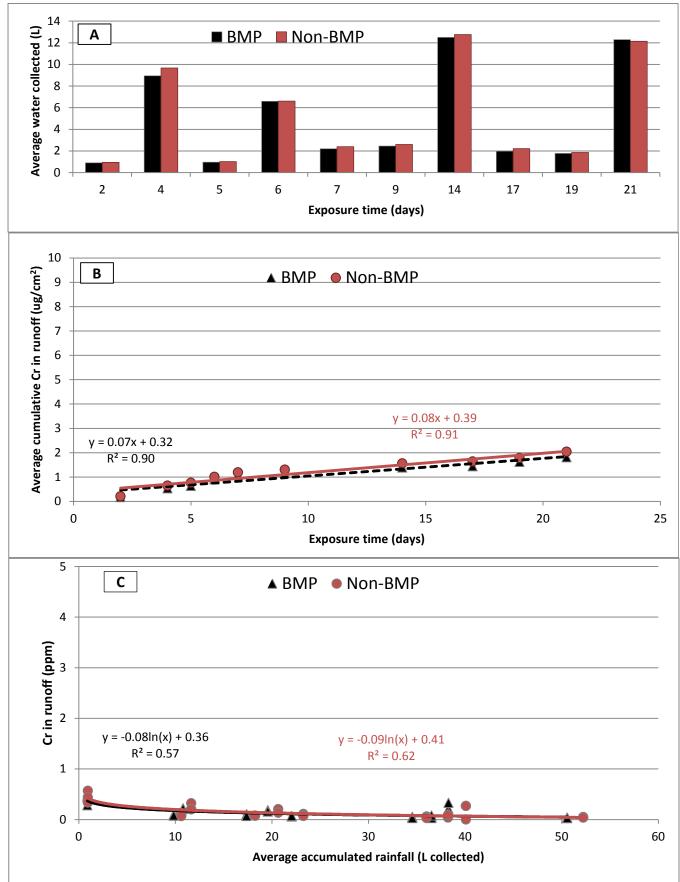


Figure 17. Composite figures showing A.) Total rainfall collected from tanks containing spruce decking treated with CCA with or without BMP Procedures and exposed to rainfall, B.) The cumulative chromium present in that rainfall and C.) The amount of chromium present in rainfall at each collection point. Three deck sections were tested with BMP wood and three were tested with non-BMP treated wood.

As with chromium, arsenic levels were slightly elevated in the first runoff collected, approaching 1 ppm, and then declined (Figure 18). Arsenic levels remained near or below 1 ppm for virtually all of the runoff samples tested, but then declined to near the detection limit (0.1 ppm) in the final collection. CCA fixation has been extensively studied and these previous studies showed that chromium reacts with the wood as it is reduced from hexavalent to the trivalent state. As these reactions proceed, copper and arsenic are immobilized in various metal complexes that sharply reduce mobility of the metals. Our deck tests illustrate the effect of this fixation process on reduced migration of both copper and arsenic.

The final decks exposed in Trial 4 were Douglas-fir decks treated with penta using the BMP procedures. These materials were matched to those used in Trial 1 and had been stored under cover until needed. Penta levels in runoff from first runoff from the Trial 4 penta treated materials ranged from 1.5 to 3.0 ppm (Figure 19). The levels gradually declined over time and were less than 1 ppm after the decks had been subjected to 65 liters of rainfall. These levels were approximately one half of those found in Trial 1 (Figure 3). Cumulative penta migration was slightly higher in Trial 1 when accounting for the total amount of rainfall to which each deck was exposed. Decks in Trial 1 were only subjected to 38 liters of rainfall over 80 days, while the decks in Trial 4 received the same amount of precipitation in only 14 days. Cumulative penta migration at these time points was 40 ug/cm² for the Trial 1 and 28 ug/cm² for Trial 4. Some of this variation can be attributed to the inherent variability of wood and it receptivity to treatment; however, it is also clear that results can vary between trials. As a result, model inputs may have to use broader ranges of release rates to account for this variation.

Overall Observations: In general, the results are similar to those from previous studies. In most cases, elevated levels of preservative were found in runoff from the first rainfall and then these levels declined sharply with further precipitation. While there were differences in levels with different preservatives, they were not consistent. Most importantly, no consistent relationship was found between preservative levels in runoff and the use of a BMP procedure.

The BMP's were developed to reduce the potential environmental impacts of using treated wood. They recognized that the greatest risk associated with using treated wood occurred at the time of installation. They also reflect the importance of minimizing excess preservative on the wood surface. The procedures incorporated into the BMP's were, therefore, designed to reduce the presence of preservative deposits on the wood while limiting the potential for over-treatment. Many of the processes included in the BMP's, however, are also common to most treating operations. For example, steaming of oil-based systems is commonly used to relieve internal pressure at the end of the treatment process to reduce the risk of bleeding, but it also helps to remove surface deposits. Similarly, long vacuums can be used to remove excess preservative from wood treated with both oil and water-based solutions, thereby reducing drippage on the drip pad. These same processes, however, also help produce cleaner wood with fewer surface deposits. The vacuums also help facilitate loss of the amines that solubilize copper, thereby hastening copper immobilization within the wood. We suspect that overall changes in regular plant processes have resulted in much of the regularly produced treated wood being well on its way to meeting the BMP requirements. While this might suggest that the BMP's have little value, the presence of verifiable process standards has considerable value to the intended consumer since it provides a means for confirming that treatments have been properly applied. This reduces the risk that poorly prepared materials will enter the market pur-

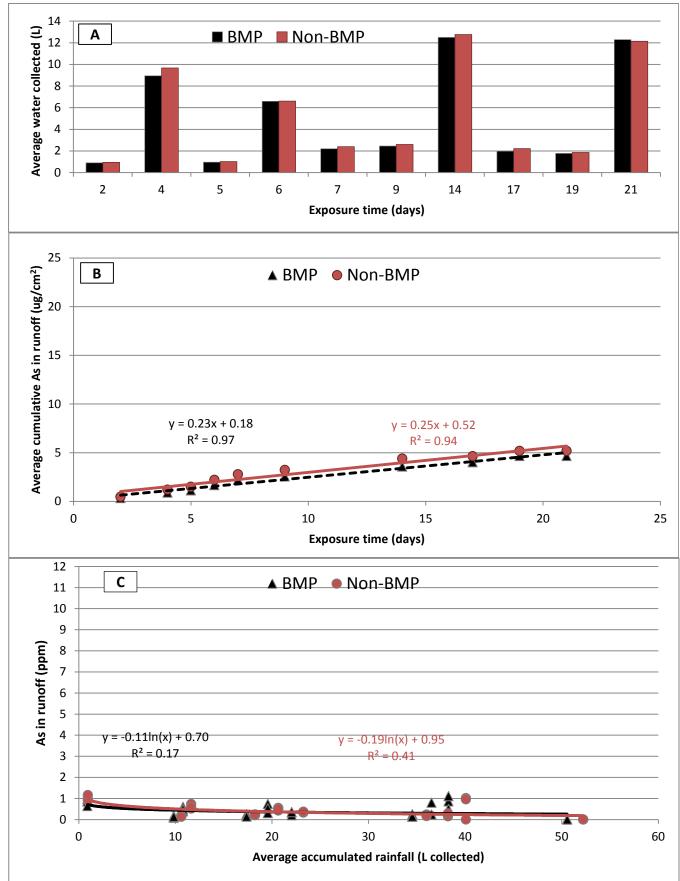


Figure 18. Composite figures showing A.) Total rainfall collected from tanks containing spruce decking treated with CCA with or without BMP Procedures and exposed to rainfall, B.) The cumulative arsenic present in that rainfall and C.) The amount of arsenic present in rainfall at each collection point. Three deck sections were tested with BMP wood and three were tested with non-BMP treated wood.

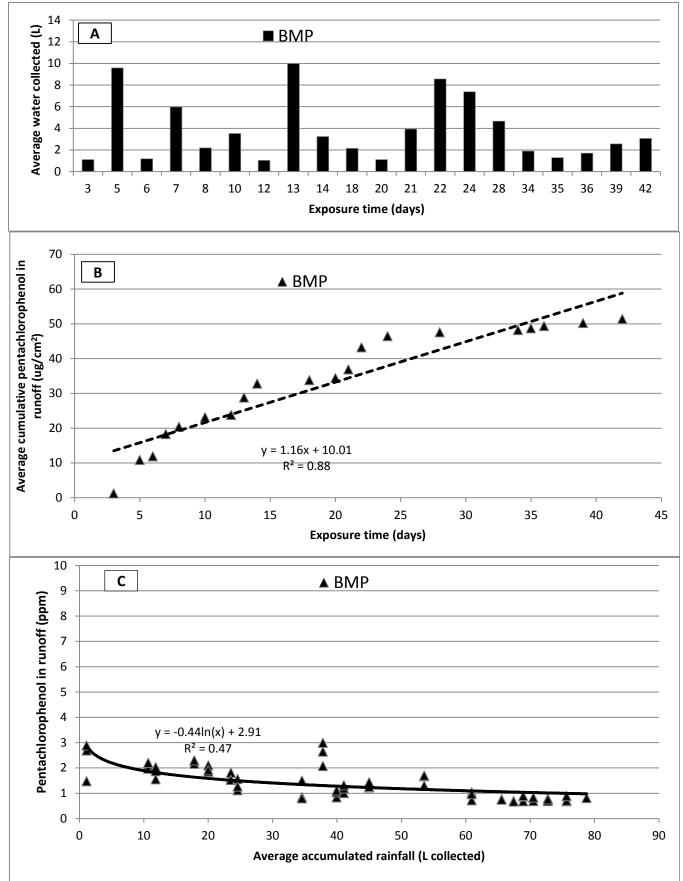


Figure 19. Composite figures showing A.) Total rainfall collected from tanks containing Dougas-fir decking treated with penta with BMP Procedures and exposed to rainfall, B.) The cumulative penta present in that rainfall and C.) The amount of penta present in rainfall at each collection point. Three deck sections were tested with BMP wood..

porting to be BMP treated.

We are awaiting arrival of the southern pine lumber for exposure in similar trials and will report on these results in future reports.

2. Develop standardized accelerated methodologies for assessing treated wood risks

No research was undertaken under this objective in the past year.

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

We continue our linkages with Dr. Robert Perkins at the University of Alaska to assist him with his 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, have interacted with him and his cooperators to discuss exposure methodology and most recently assisted him with sampling methodology for assessing creosote retentions in his samples. We hope to continue this dialogue as Dr. Perkins completes his studies.

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 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.

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

This past year, we co-sponsored 4 workshops with WWPI on the use of the Risk Models for Using Treated Wood in Aquatic Environments. The workshops were primarily directed at Federal Agency staff who were trying to use treated wood and were intended to help educate them about both the full model developed by Dr. Kenn Brooks and the screening criteria developed as an addendum to this model.

The first workshop was held on the OSU campus in August of 2011 and attracted 26 attendees. The participants were primarily Federal Agency staff; however, none were biologists and this was a major criticism from the participants. The comments about the workshop content were largely positive, although there were a few comments about wanting more specific examples that were related to preservatives being used by the agencies.

In December, we met with the State Director of the BLM and the Regional Forester for the Forest Service in Portland to discuss how we could hold workshops that attracted both engineers and biologists. They agreed to support attendance at such workshops and we worked to develop three workshops to be held in Portland, Eugene, and Prineville. The events were

held at agency facilities to make it as easy as possible to attend. The Workshops were held in Portland, Eugene and Prineville, Oregon on May 29-31 (Appendix B). Two were held at BLM facilities while the Portland workshop was held at the OSU Foundation Center. While the total attendance was only 31, it consisted of a broader mixture of biologists and engineers including personnel from the Forest Service, Bureau of Land Management and the Corp of Engineers. More importantly, NOAA sent participants to both the Portland and Eugene Workshops. We also changed the format slightly and Dr. Kenn Brooks altered his presentation to remove large portions of the discussion related to creosote since neither agency uses this preservative.

Post-conference evaluations of the workshop were generally positive, although a number of participants felt that they did not need an extensive session on the background data supporting the models. This could allow to us shorten this part of the workshop and reduce the overall session to a half day.

There have been requests for similar workshops in other western regions as well as by contractors in California. The primary limitation for this would be cost; however, it might be possible to deliver these workshops to remote locations via video conference or other suitable technologies. The primary short-coming of these approaches is the loss of intimacy that can encourage questions. However, it is clearly not economical to offer these workshops to small audiences.

We plan to meet with the BLM and Forest Service to discuss the next steps in working with these groups. We will also explore reaching out to other groups in California..

APPENDIX A PROCEDURES USED TO SEPARATE PENTACHLOROPHENOL FROM RAINWATER SAMPLES

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 (${}^{13}C_{6}H_{6}CI_{6}$, Cambridge Isotope Laboratories, Andover, MA) in methanol. Then 2.4 mL 1N NaOH was added to each flask using a pipette. A TeflonTM 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 H_2SO_4 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 Fm 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 µg/mL) and [¹³C₆] PCP internal standard (50 µg/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 [¹³C₆] PCP was m/z = 274, the reference ions were 276 and 172. HRGC-LRMS auto tuning was performed with perfluorotributlyamine. 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 µg/mL; 2 µg/ 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 cm². 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.

APPENDIX B EXAMPLE OF THE PROGRAM USED FOR THE "USE OF RISK MODELS FOR TREATED WOOD" WORKSHOPS

The Program was as follows:

9:00 am Wood Treating and Why We Have BMP's - Jeff Morrell, Oregon State University, Corvallis, OR

This session gave participants a basic idea about the chemicals used for wood treatment and the treatment process used to deliver them into the wood.

<u>9:20 am Foundation for the Aquatic Risk Models - Kenn Brooks, Aquatic Environmental Sciences, Port</u> <u>Townsend, WA</u>

This session outlined the basic issues associated with the use of treated wood in or over aquatic environments and the assumptions used to build the Excel Risk Assessment Models.

10:30 am A Rapid Primer to the BMPs - Ted LaDoux, Western Wood Preservers' Institute, Vancouver, WA

This session gaves participants an overview of why the BMP's were developed.

<u>11:00 am</u> How to Use Screening Level Assessment Process and Worksheets - Neil Alongi, Maul Foster & Alongi, Portland, OR

Participants learned about the screening level assessment process to determine the level of examination needed for a given project.

<u>12:45 pm</u> Overview of Models and Their Use - Kenn Brooks, Aquatic Environmental Sciences, Port Townsend, <u>WA</u>

This session introduced participants to the Excel Risk Assessment Models and is presented in two parts.

2:00 pm Model Exploration

In this session each participant was given an opportunity to explore the model at their leisure and encouraged to use real life projects as part of the training.