Environmental Performance of Treated Wood Cooperative

Fourth Annual Report

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Executive Summary

The Environmental Performance of Treated Wood 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

The BMP verification studies have been completed for southern pine, spruce-pine-fir and Douglas-fir lumber treated with pentachlorophenol, alkaline copper quat, copper azole, chromated copper arsenate or ammoniacal copper zinc arsenate. The results suggested that BMP's had little effect on subsequent metal losses and might lead one to conclude that BMP's had no value for reducing the potential environmental footprint of treated wood. However, we believe these results are miss-leading. The long delays between treatment and exposure meant that the lumber was largely air-dried prior to exposure. Since this is one of the BMP's, all of the material was essentially subjected to a BMP prior to exposure. The variations we observed between decks were just normal differences one might find between different pieces of treated wood. We have proposed a follow-up test where decking will be treated with various preservatives and then frozen until a BMP can be applied. The materials will then be directly exposed to rainfall to simulate an actual exposure where freshly treated wood was subjected to precipitation. We expect these results to be more representative of actual practice.

We have also examined the ability of post-treatment applied deck coatings to limit subsequent metal migration from ACZA treated Douglas-fir decking. This test was initiated because we are seeing some permit writers require these coatings. Previous tests of CCA treated lumber suggested that these coatings were of limited value. We tested 6 coatings with various compositions. None of the coatings completely limited metal migration but a few did slow the initial surge in metal releases observed in previous tests. The value of these coatings; however remains questionable and any potential use of such coatings would require much more assessment to make sure that the coating actually reduces migration.

We continue to monitor PAH levels around creosote piling in our test pond. We have spent considerable time refining our analytical methods. This past year, we analyzed sediment around piling and found elevated levels of some of the 16 EPA priority pollutants immediately adjacent to the piling, but levels fell off sharply with further distance. No PAH's were detectable in the water column. These results are consistent with previous tests. We plan to install additional sediment monitoring sites around the pond along with additional piling.

We continue to locate field test sites. We have been monitoring a US Forest Service bridge west of Corvallis, OR. The bridge contains copper naphthenate treated stringers and penta treated decking. Copper and penta have been detected in the rainwater runoff, but levels of both components remain low. These results are consistent with previous field evaluations.

We have also been examining the presence of treated wood in a recycling facility in order to provide data on disposal patterns. Treated wood was almost always detected in the recycling stream, but the levels were generally low (<1 %) and not at a level that would be a concern from a regulatory perspective.

Finally, we continue to offer workshops on use of treated wood in aquatic applications. This past year, we offered the first on-line workshop. The results were promising- participants were generally positive and the on-line nature allows us to deliver content without having to travel. We will explore additional workshops this coming year.

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 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 3 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 tests have been developed on Douglas-fir, Spruce-Pine-Fir and southern pine. In each case, non-treated decking material was obtained (nominal 50 by 150 mm by 4 m long), air-seasoned or kiln dried and then cut into two 2 m long sections. One section was allocated to be treated with a given chemical using regular treatment processes, while the other was treated using a regular pressure treatment process coupled with some form of Best Management Practice to meet the WWPI Standard.

Once the treated materials were returned, the boards were sampled to determine preservative penetration and retention according to procedures described in AWPA Standard 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 a 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.

We have completed tests on BMP and non-BMP-treated Douglas-fir, southern pine and Spruce-pine-fir (SPF) decking. The Douglas-fir and SPF decking tests were only run in Corvallis, while southern pine decking was exposed at both Corvallis and Mississippi State University. The results from these tests were very mixed. In many cases, there was little or no difference in metal levels in runoff from decks with or without BMP processes. These results suggest that BMP processes have little or no value; however, we believe that there are several reasons for the lack of differences in our results that would argue for further consideration of BMP's.

The BMP's were largely developed as a result of some incidents where treated wood was transported from a plant shortly after treatment, before the chemicals in the wood had a chance to become immobilized. The lack of immobilization led to much higher chemical losses once the wood was installed in an aquatic setting. The BMP's were subjected to long vacuums and heating to accelerate immobilization before the wood left the plant to mitigate this risk. These processes have been widely recognized by

regulators and have allowed treated wood to continue to be used in sensitive environments.
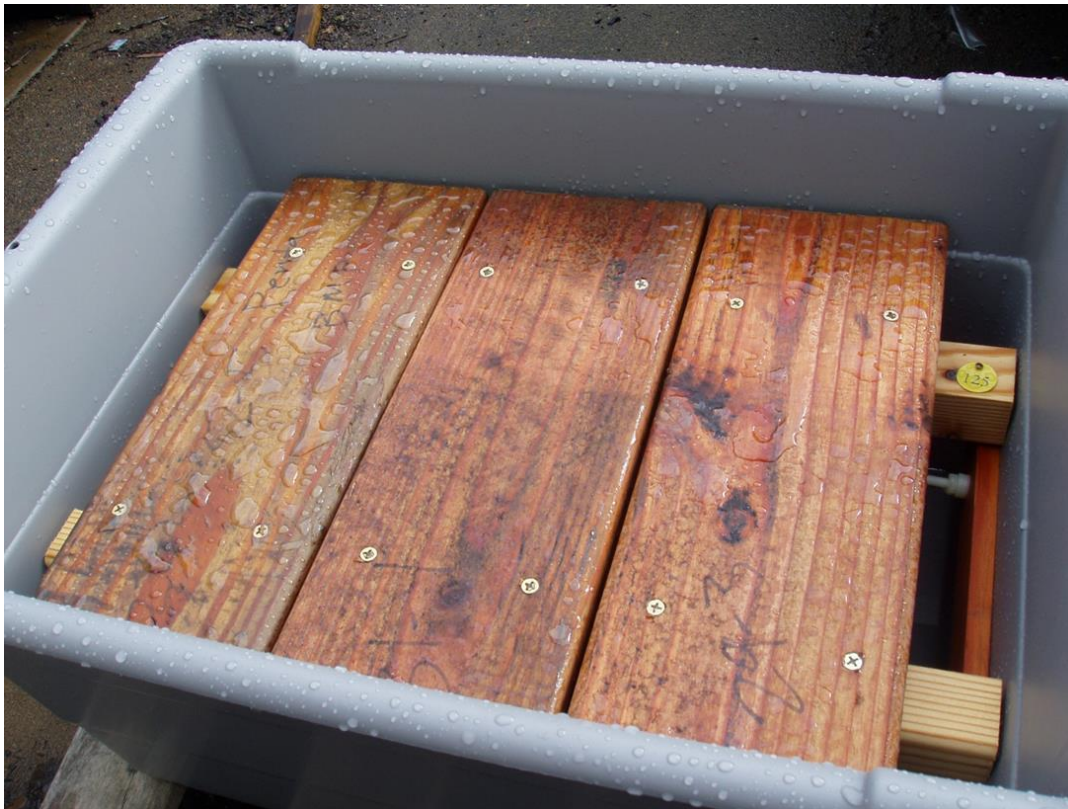

Figure 1 Examples of penta treated wood decks exposed to rainwater in Corvallis, OR.

In the case of these decking studies, however, we needed to control for the variability of wood. As a result, OSU or MSU prepared all of the decking materials and matched boards so that one part of a given board was subjected to a BMP process while the other was not. This material was sent to cooperating treaters and then returned to either university. These materials were then used to construct the test decks. This shipping led to considerable delays between treating and exposure. Furthermore, these tests were done under natural rainfall conditions and it often did not rain for some time after the decks were constructed and exposed. As a result, the decks were generally dry before the wood was exposed to the first rainfall. Air seasoning is among the processes allowed under the BMP standard. As a result, this test inadvertently tested all of the wood in a near BMP condition. The variations noted among the treatments (in some cases the so-called BMP wood lost less metal, in other cases more) were merely the result of minor differences in wood characteristics rather than the result of the processes themselves. These results suggest the need to rethink any BMP verification test to ensure that the wood is exposed as soon as possible after treatment. This approach requires much more control of the treatment process to avoid the inherent delays associated with shipping materials.

We plan to perform these tests using our controlled overhead rainfall apparatus. We described results from this system using ACZA, ACQ and CA treated Douglas-fir decking. We propose expanding this test to examine the behavior of the BMP's on southern pine and SPF treated with these materials along with pentachlorophenol and creosote.

Samples will be treated with the given preservative using only vacuum and pressure with no post-treatment BMP processes. The samples will then be [laced 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℃) to encourage air-flow and conditioned to a target moisture content below 19% over a four-week conditioning period.

-Kiln drying: The samples were placed in a steam fired kiln on stickers to enhance air flow. Samples were either dried over a three-day cycle at a dry-bulb temperature of 71.1℃ with a wet-bulb depression of 16.7℃ or a one-week kiln schedule at a dry-bulb temperature of 48.9℃ and wet-bulb depression of 5.6℃. The latter cycle limited drying, but the heat should have encouraged ammonia or amine loss. Both of the schedules resulted in wood moisture contents below 19%.

-Steaming: Samples were subjected to 1, 3 or 6 hours of steaming at 104.4℃ with stickers in between samples.

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

-Ammonia bath: Samples were soaked in aqueous 1% ammonia at 100℃ for 1 to 3 hours.

The samples were frozen 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. This helped reduce the potential for variability between boards since a portion of each was subjected to a given BMP.

Leaching test: The samples were warmed overnight before the potential for metal migration was evaluated in a specially constructed overhead leaching apparatus that applied a controlled amount of simulated rainfall at a desired temperature (Figure 2). 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℃) and a rainfall rate ranging from 0.1cm/h to 0.3 cm/h.

Figure 2 - 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 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.

Post - treated samples were placed into each holder and subjected to simulated overhead rainfall for periods up to 9 hours. Runoff water was collected in tared 50mL beakers 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 10 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 and then after 240, 300, 420 or 540 minutes.

Chemical analysis: Samples were acidified by adding 0.25 ml of 1 M nitric acid into 4.75 mL of runoff water. The samples were stored at $3℃$ 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 while the remaining samples were retained in case metal levels were elevated after 2 hours. Copper concentrations were used as a measure of BMP effectiveness.

Our next experiment with this apparatus will use southern pine and SPF lumber. All of the waterborne treatments will consist of a vacuum followed by a pressure process, but no BMP processes will be applied. The boards will be immediately cut into 12 inch long sections, placed in plastic bags and frozen until needed. The freezing should slow drying as well as any immobilization processes. Penta and creosote treatments will be performed in commercial cylinders without any post-treatment BMP procedures. These materials will then be frozen until needed

These materials will then be removed as needed, defrosted, and either tested without further treatment or subjected to a BMP process that is appropriate for that preservative system. Our intent will be to use the current BMP's as a baseline for the testing.

Table 1. Treatments to be applied to evaluate BMP processes on southern pine, Douglas-fir and spruce-pine-fir lumber.							
Species	Material	Treatment Type					
		Penta	Creosote	ACZA	CCA	ACQ	CA
Douglas-fir	Lumber	Conc.	P1/P13	Done	-	Done	Done
Southern pine	Lumber	Conc	P1/P13	-	Type B	Type D	Type B
SPF	Lumber	-	P1/P13		Type C	Type B	Type B

These materials will then be exposed to rainfall from a controlled device that allows us to deliver a specific amount of rain to a sample and then collect any subsequent runoff for analysis. As noted, we have previously used this device to assess metal losses from Douglas-fir lumber treated with the waterborne systems and found that it did show differences between BMP and non-BMP treated wood. These results will allow us to more directly compare the effects of BMP processes on preservative migration on materials that are exposed shortly after treatment. This is similar to the worst case where freshly treated materials were immediately installed and subjected to moisture.

2. Effects of coatings on migration of metals from treated wood

While all of the current models indicate that properly pressure treated wood can be used with little or no risk in most environments, that often means little to those regulating the products. One requirement that appears to be increasingly specified is that all wood be coated with an "impermeable" barrier. This is both extremely difficult to do and unlikely to last long on a surface exposed to ultraviolet light. Studies done at the Connecticut Agricultural Experiment Station showed that coatings had only minimal effects on metal losses from CCA treated southern pine decking, but there have been no follow-up studies on the effects of coatings on other preservatives. This past year, we explored the effects of various coatings on migration of metals from ACZA treated Douglas-fir lumber. Decks, similar to those described earlier were constructed using these materials, then two coats of a given coating were applied (Figure 1). The decks were then exposed to natural rainfall for 333 days. Water collected after each measurable rainfall was weighed and a small sample was acidified and analyzed for copper, zinc and arsenic by ICP. The test was run over most of one winter, an entire summer and then the beginning of the fall wet season. The goal was to determine the initial effect of the coating on metal losses and then allow the decks to be exposed to a long summer of UV exposure with little rainfall.

The coatings evaluated in this study were a polyvinyl acetate, a polyurethane, an SBR, a vinyl acryl ethylene, and a halogenated resin. Each coating contained approximately

20 % solids and was applied to 3 decks using a paint brush. The decks were exposed in Corvallis, Oregon.

The results were examined in terms of total metals released over time, metals released per area of deck and metal concentrations in water collected at a given time. The decks were exposed midway through the fall and water samples were collected from the first 12 rainfall events over 55 days (Figure 3). The decks continued to be exposed after that period, but analysis was suspended because the results indicated that metal levels in the runoff had reach a steady state. The decks were then left outside so that they were subjected to continued UV degradation. Four more collections were made in the late fall, when the rain began again, to assess the effects of additional UV exposure on the ability of each coating to affect metal migration.
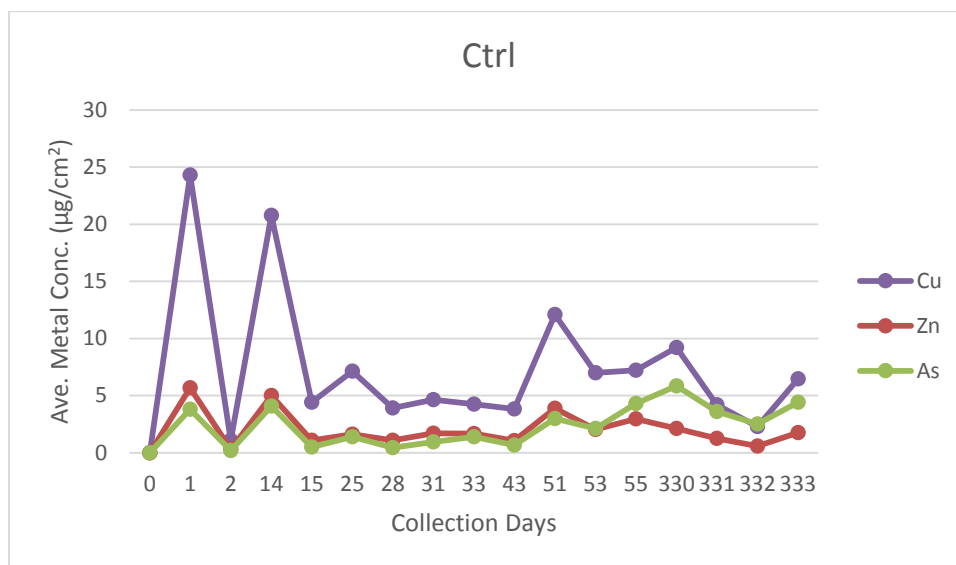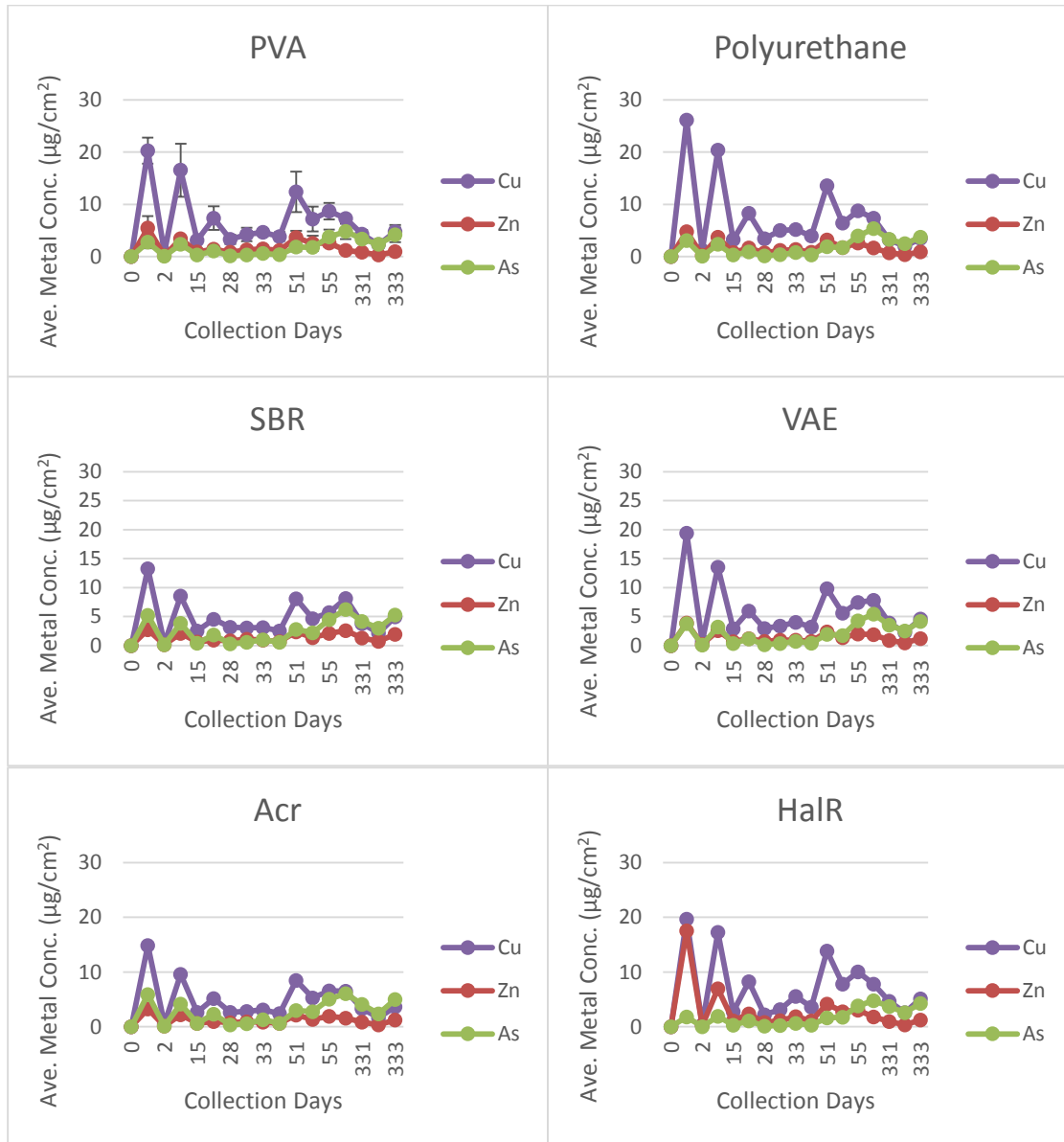

Figure 3. Copper zinc and arsenic concentrations in runoff from ACZA treated Douglas-fir decks with no supplemental coating and exposed for 333 days in Corvallis, Oregon.

Copper levels in the runoff were almost always higher than either zinc or arsenic, reflecting the much higher levels of copper present in ACZA (Figure 3). Zinc and arsenic levels tended to be similar to one another in the non-coated control decks.

Copper levels in water from the control decks ranged from 2 to 20 ppm with the two highest concentrations coming in the second and fourth rainfall events (Figure 3). Copper level in the remaining rainfall events tended to be between 1 and 10 ppm. The elevated copper levels in the early stages of exposure were consistent with the tendency for first rainfall events to dislodge surface deposits of preservative. Once these metals were lost, the losses should decrease to a lower, steady state level. There was a trend towards higher copper levels in runoff from rainfall events at 51 to 55 days. It is unclear why these levels increased.

Copper levels in water runoff from the coated decks were also elevated in the second and fourth water collections and then declined in the same manner as they did for the

control (Figure 4). However, the maximum concentrations did vary slightly with coatings. None of the coatings completely eliminated metal losses.

Zinc and arsenic levels in the runoff tended to be lower than copper although the differences were greater than the approximate 2:1:1 ratio of Cu:Zn:As in the formulation applied to the wood. Copper is believed to co-deposit with Zn in this system leading to the potential for subsequent metal losses to be more proportional. The results suggest that this is not entirely the case.

Figure 4. Copper zinc and arsenic concentrations in runoff from ACZA treated Douglas-fir decks coated with one of 6 potential deck finishes and exposed for 333 days in Corvallis, Oregon.

Cumulative copper losses from the wood over the first 55 days were again far higher than those for either zinc or arsenic, regardless of the presence or absence of a coating (Figure 5). Total copper losses were almost 40 % lower in decks receiving either the SBR or Acrylic coatings. Copper losses in decks receiving a vinyl acrylate coating were approximately 20 % lower than those for the non-coated deck. Copper losses from decks receiving the remaining coatings were similar to those for the control. Zinc and arsenic losses were generally between 15 and 25 % of those found with copper for the same coating. The similar loss patterns for these two elements suggests that their immobilization in wood is linked. In general, cumulative zinc and arsenic losses did not appear to be affected by coating with the exception of elevated zinc losses associated with the halogenated coating. It is unclear why zinc was affected by this coating.

The cumulative metal losses from the various coatings did show that some coatings were associated with decreased metal losses over time (Figures 6-8), although the initial differences appeared to be slight. These trends were also noted after the prolonged dry period. Previous studies of coating performance on Douglas-fir decking indicated that most systems provide 1 to 3 years of protection before they degrade to the point where they are no longer effective. These decks will continue to be exposed to weather and periodic water collections will be made to determine how long the differences in metal losses remain and how coating degradation affects those patterns. For the present, the results indicate that the coatings altered metal loss patterns over time, although their effects on the metal losses in the first, critical rainfall events were more difficult to discern.
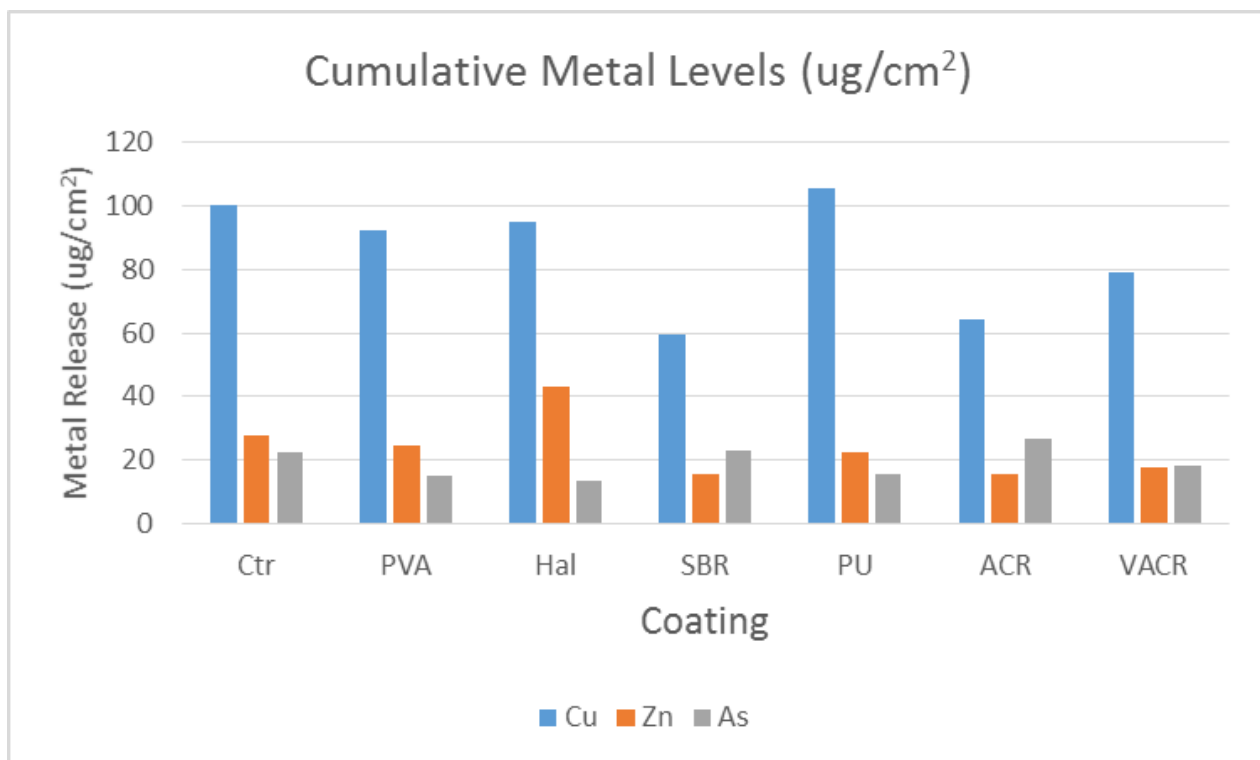

Figure 5. Cumulative metal releases from ACZA treated Douglas-fir decking exposed to natural rainfall over a 55 day period in Corvallis, Oregon.
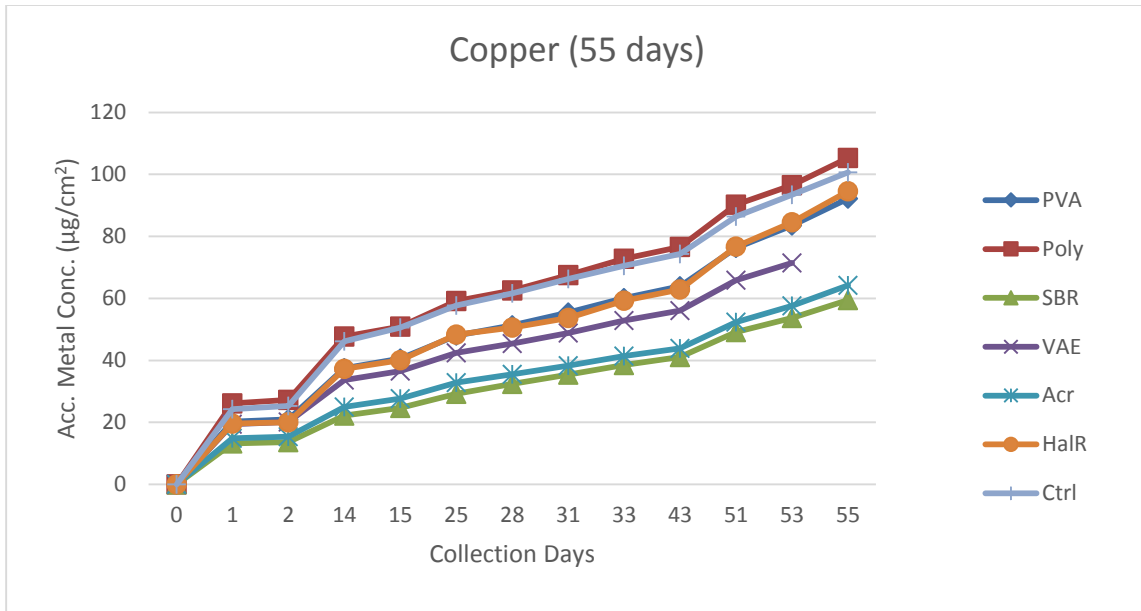
Figure 6. Cumulative copper losses from ACZA treated Douglas-fir decking exposed to natural rainfall over a 55 day period in Corvallis, Oregon
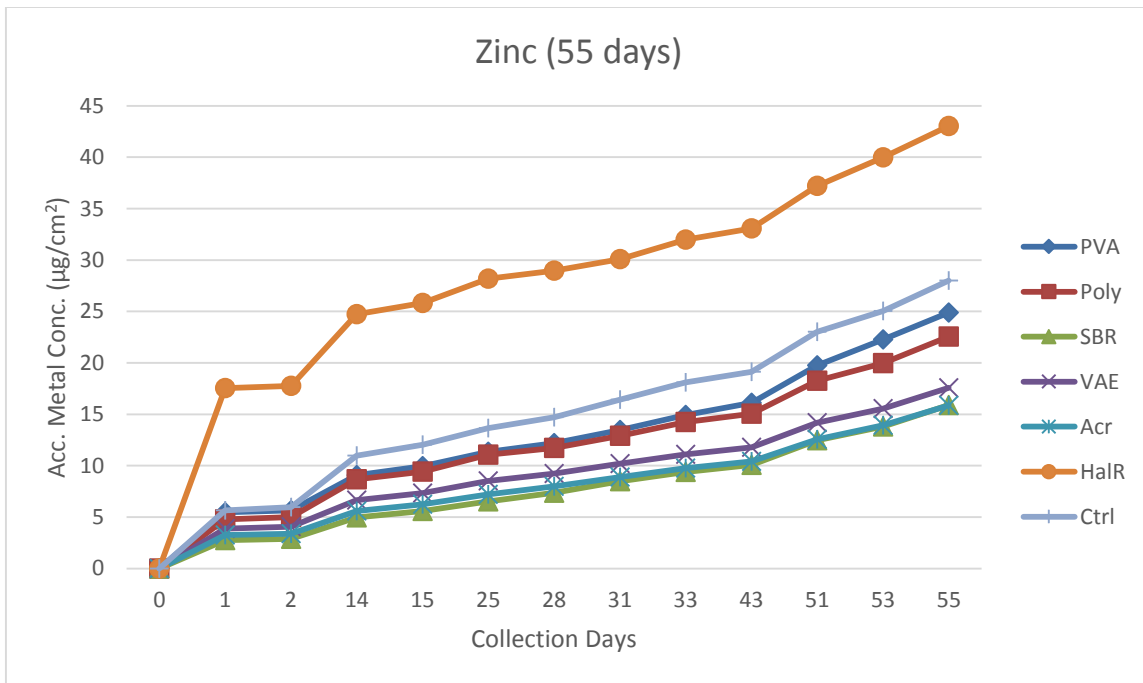

Figure 7. Cumulative zinc losses from ACZA treated Douglas-fir decking exposed to natural rainfall over a 55 day period in Corvallis, Oregon
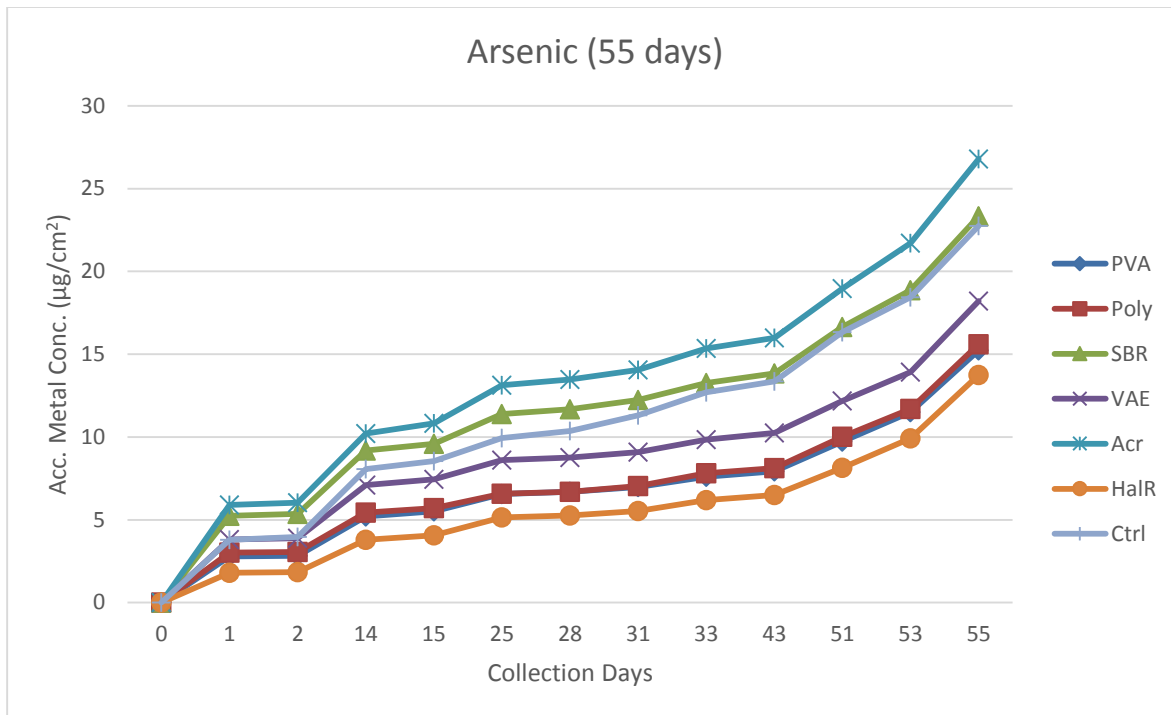
Figure 8. Cumulative arsenic losses from ACZA treated Douglas-fir decking exposed to natural rainfall over a 55 day period in Corvallis, Oregon.

In previous tests of runoff from preservative treated utility poles, we have generally observed that rainfall intensity had little effect on overall concentration of metals in the runoff. As a result, more rainfall, results in more preservative in the runoff, but the absolute concentration has not appeared to vary with rainfall level. In the current test, however, we observed a marked increase in metal concentrations with increased rainfall and this effect was observed for all three metals (Figures 9-11). Rainfall levels of 5 mm or less appeared to contain fairly low levels of metals, while there was an increase in metal concentrations in runoff from precipitation events between 5 and 10 mm and then a further jump when precipitation events were greater than 10 mm. One might expect runoff from smaller precipitation events to contain more metals because any metals on the wood surface would be readily solubilized and lost form the wood. Larger precipitation events might be expected to dilute these surface metals, resulting in lower concentrations. The opposite effect noted in these tests, suggested that rainfall intensity must be considered in models evaluating the risk of loss from treated wood exposed over aquatic environments.
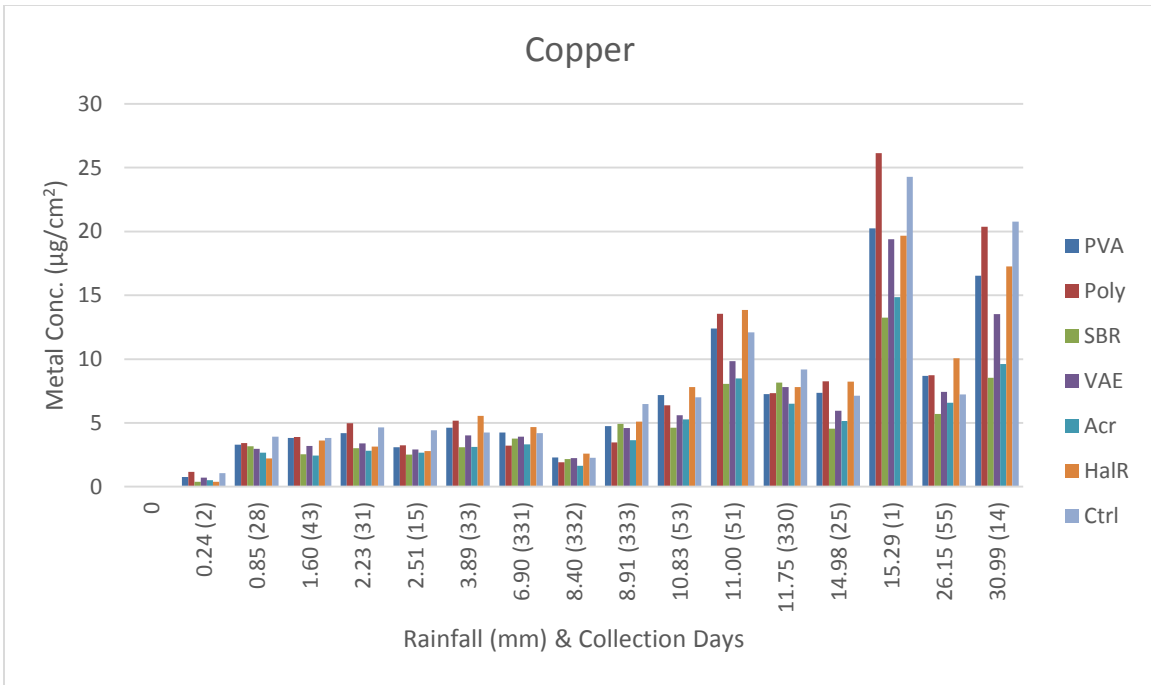
Figure 9. Relationship between rainfall intensity (as total mm of rainfall) and copper concentrations in runoff from ACZA treated Douglas-fir decking exposed to natural rainfall over a 333 day period in Corvallis, Oregon.
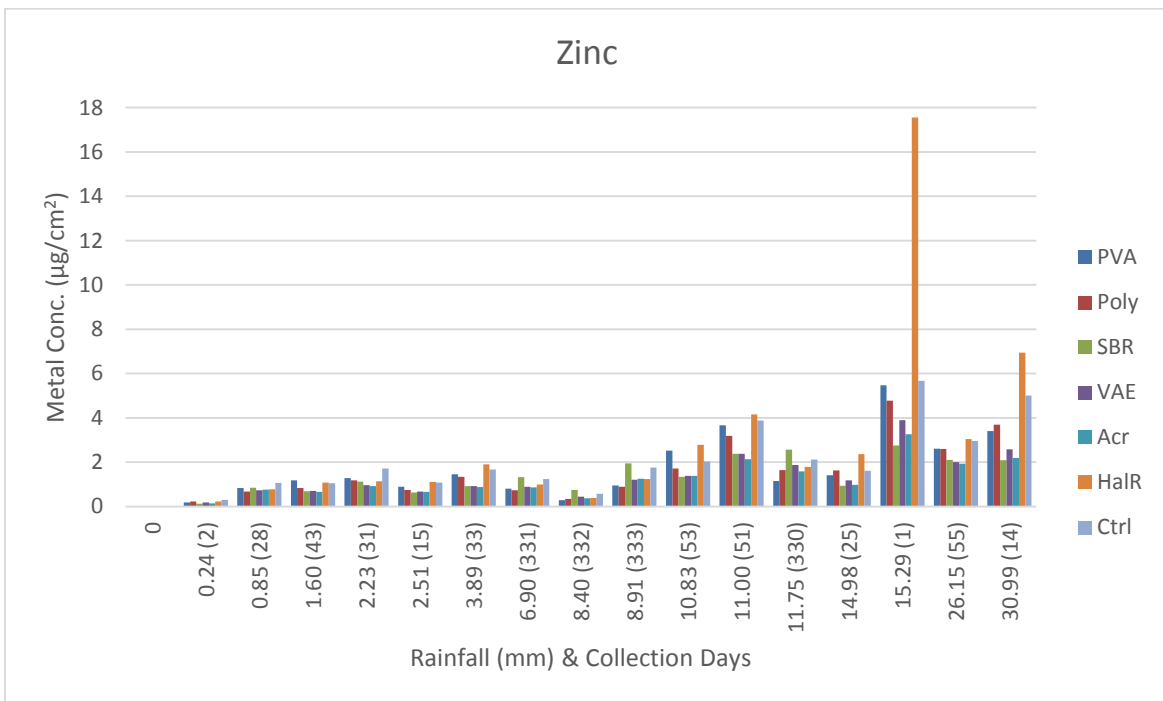

Figure 10. Relationship between rainfall intensity (as total mm of rainfall) and zinc concentrations in runoff from ACZA treated Douglas-fir decking exposed to natural rainfall over a 333 day period in Corvallis, Oregon
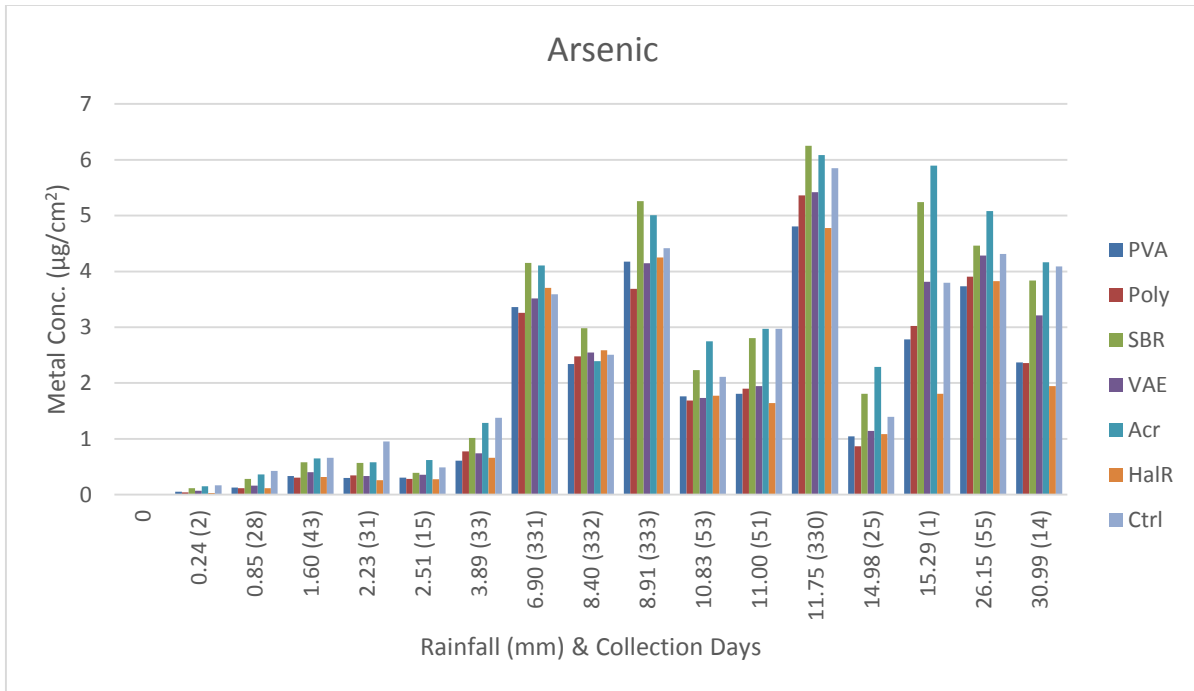
Figure 11. Relationship between rainfall intensity (as total mm of rainfall) and arsenic concentrations in runoff from ACZA treated Douglas-fir decking exposed to natural rainfall over a 333 day period in Corvallis, Oregon.

Copper levels in runoff from decks with various coatings was much higher after the first day and then gradually declined with time (Figures 12, 13). Copper levels tended to be elevated in decks without a coating as well as in decks coated with the PVA, Halogen, polyurea and vinyl acrylic systems. Copper levels were slightly lower with the SBR and acrylic coatings. Zinc levels were generally low except for the halogen coating, while arsenic levels did not appear to be affected by coating.

Copper and arsenic levels collected at day 55 were much lower than those collected at Day 1 (Figure 13). This would be typical of such exposures and reflects the loss of easily solubilized surface metal deposits. Once these are lost, the subsequent metal losses must occur by gradual diffusion of metal to the surface. This process occurs much more slowly and is reflected in the lower metal levels in the runoff. Zinc levels remained elevated in the halogenated coating.
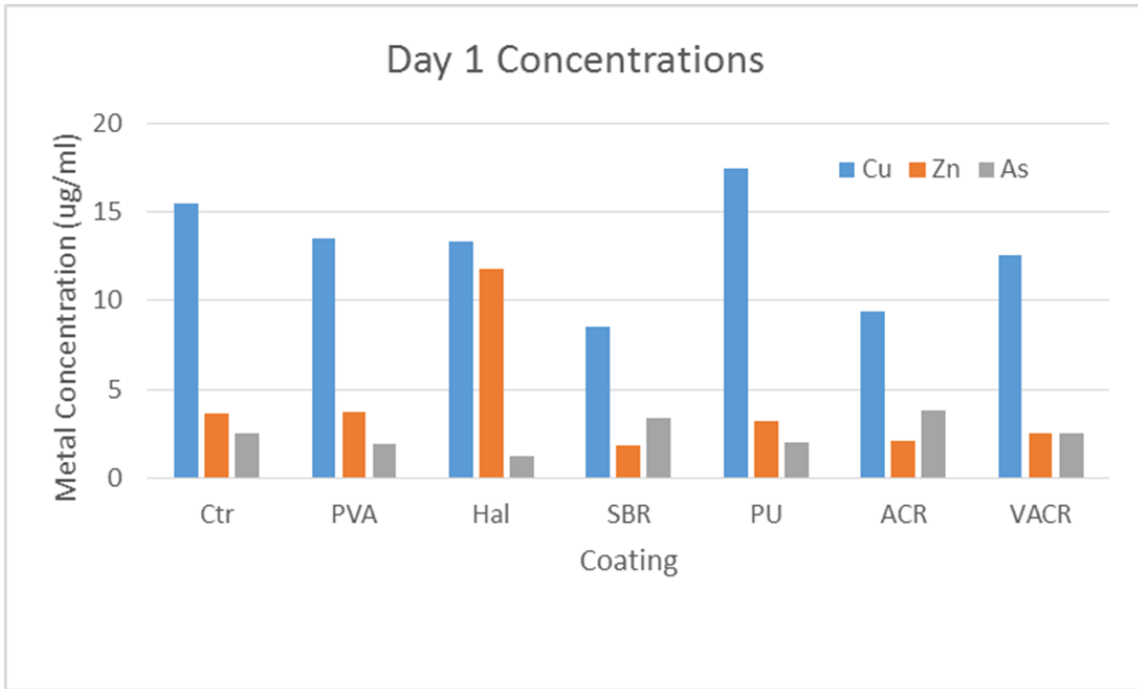
Figure 12. Metal concentrations in rainwater runoff from ACZA treated Douglas-fir decks exposed for 1 day in Corvallis, Oregon.
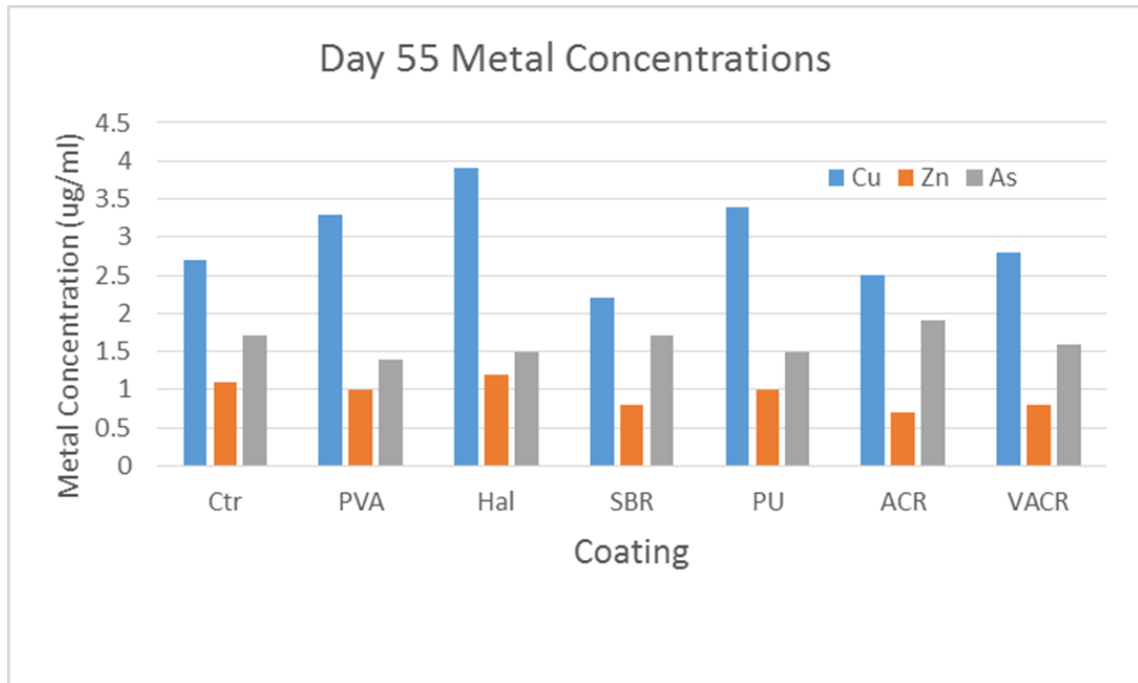

Figure 13. Metal concentrations in rainwater runoff from ACZA treated Douglas-fir decks collected on day 55 of exposure in Corvallis, Oregon.

The current results suggest that coatings can alter the overall loss of metals from treated wood, although the effects are variable. The type of coating clearly has a major influence on the results and it remains unclear how long these coatings will perform. We plan additional periodic monitoring to assess coating efficacy as measured by changes in metal losses.

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. As noted previously, we had some difficulty locating a body of water that was suitable for this test and then had some difficulty establishing uniform sediment collection methods. We finally found a freshwater pond approximately 20 km from Corvallis that was suitable for the test. We initially had difficulties with sediment sampling because the pond had a very organic layer that made it difficult to obtain uniform sediment samples over time. Instead we developed a system whereby sediment packets were created. These packets could be placed into the native sediment at selected distances from our piling and could be easily removed without disturbing the surrounding sediment. We performed a number of preliminary trials with these packets or sachets to ensure that we could recover compounds from the soil and the sachet material. This approach provided a reproducible method for sediment sampling.

We have established both ACZA and creosote treated Douglas-fir piling in the pond and placed sachets immediately adjacent to the wood, 150mm, and 300 mm away from the wood. Sachets have been removed at selected time intervals for assessment of polycyclic aromatic hydrocarbons (PAHs), or metals, depending on the piling involved. The metals were analyzed in the same manner as described for the water samples, with the exception that the sediment and sachets are acid digested prior to analysis. PAHs from the creosote treated pilings were extracted and analyzed as follows: collected sachets were frozen overnight then cut and divided into approximately three nine cm long sections (top, middle, and bottom). Each section was thoroughly homogenized and a 10 g sediment sample from a given segment was placed into a 40 mL amber glass scintillation vial. The entire sachet for each section was analyzed separately in the same manner. Twenty milliliters 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 soil 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 GS-MS operated in SIM mode. The GC conditions were: Oven temperature: 35 to 275 C, ion source

temperature: 225 C, interface temperature: 275 C. The samples were analyzed on an RXI-5ms column (0.25 mm inner diameter by 30-mm long) at a flow rate of 2.5 ml/min.

Copper levels 1 and 3 months after installation of the posts were generally at background levels 1 or 3 feet away from the post; however, levels were elevated immediately adjacent to wood (Table 2). 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 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.

Table 2. Copper, zinc and arsenic levels in sediments exposed immediately, 1 foot away and 3 feet away from an ACZA treated Douglas-fir piling 1 or 3 months after installation.				
Time (months)	Distance from pile	Metal level in soil (ppm)[a]		
		Cu	Zn	As
1	1	3.05	4.00	<0.1
	3	3.35	4.55	<0.1
3	0	117.95	57.60	0.35
	1	4.65	5.55	<0.1
	3	3.85	5.00	<0.1
[a]Values represent means of two samples per time per location				

PAHs were detected in the sediment (Table 3). We have spent a considerable amount of time this past year refining our collection and extraction procedures to improve our extraction recoveries and delineate levels for the 16 EPA priority pollutants, which we have used as our baseline. PAH's were naturally present at low levels in the native soil as well as in samples removed 1 and 3 feet away from the posts

PAH levels were elevated immediately adjacent to the posts, then declined sharply with increasing distance from the post. The soil in the sachets and the sachets themselves tended to selectively sorb PAH's from the surrounding sediment. This tendency results in a much higher probably of intercepting PAH's moving from the wood into the surrounding sediment; however, it also tended to produce slightly higher PAH levels since the sachet material was less available for microbial degradation.

These results are preliminary and further analyses are underway for sediment samples exposed for longer periods. However, we now have a reliable, reproducible method for assessing creosote component migration from treated wood.

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. Last year, we identified a bridge located near Sweet Home,

Oregon that had been treated with pentachlorophenol in oil for the decking and copper naphthenate for the laminated beams supporting the structure.

Figure 14. Photograph of the House Rock Bridge showing copper naphthenate treated laminated beams and pentachlorophenol treated decking.

Table 3. PAH's detected in sediment samples immediately adjacent, 1 and 3 feet away from creosote treated Douglas-fir posts.

PAH	PAH Level (ug/g soil)[a]								
	Adjacent			1 foot away			3 feet away		
	Top	Middle	Bottom	Top	Middle	Bottom	Top	Middle	Bottom
Naphthalene	141.4	222.6	261.2	1.0	1.2	0.8	0.8	1.0	0.5
Acenaphthalene	11.5	4.3	6.2	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1
Acenaphthene	114.8	98.6	131.3	0.3	0.6	0.4	0.1	0.3	0.3
Fluorene	113.7	63.2	83.5	0.2	0.4	0.2	0.1	0.1	0.2
Phenanthrene	309.9	193.4	346.9	0.5	0.8	1.0	0.3	0.2	0.2
Anthracene	222.9	16.8	20.3	0.5	0.7	0.9	0.2	<0.1	<0.1
Fluoranthrene	300.3	103.8	1116.7	0.2	0.3	0.4	<0.1		
Pyrene	173.0	73.5	78.1	0.1	<0.1	0.3	<0.1	0.1	0.2
Benz (α) anthracene	48.3	8.6	10.6	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01
Chrysene	54.2	7.4	10.0	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01
Benzo(j)fluoranthrene	15.6	1.9	2.7	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01
Benzo (k)fluoranthrene	15.2	1.9	2.6	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01
Benzo(α) pyrene	14.0	1.4	2.4	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01
Indeno[1,2,3-cd] pyrene	3.9	0.3	0.6	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01
Dibenz[a,h]anthracene	0.4	0.1	0.2	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01
Benzo[ghi]perylene	4.4	0.2	0.7	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01
Total PAH's	1568.9	795.3	961.9	2.9	4.3	4.3	1.5	1.9	1.5

[a]Values represent means of two soil samples per position.

The preservatives present in the runoff from the bridge were collected by constructing a collection system beneath a section of the bridge that funneled water from the surface into a large container (Figure 15). Water in the container was weighed after each rainfall event, then a sub-sample was 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 15.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 H_2SO_4 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 2 µL 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 µm 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 iso-octane between injections to minimize the risk of carryover.

The PCP standard (50 µg/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 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. 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.

Copper naphthenate in the runoff was analyzed on a copper basis 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.

Pentachlorophenol was detected in water collected from all 7 rainfall events (Figure 16). The initial penta concentrations averaged 6 ppm, then declined to less than 2 ppm after 3 rainfall events. 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 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 17). 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 presence of any surface deposited penta.

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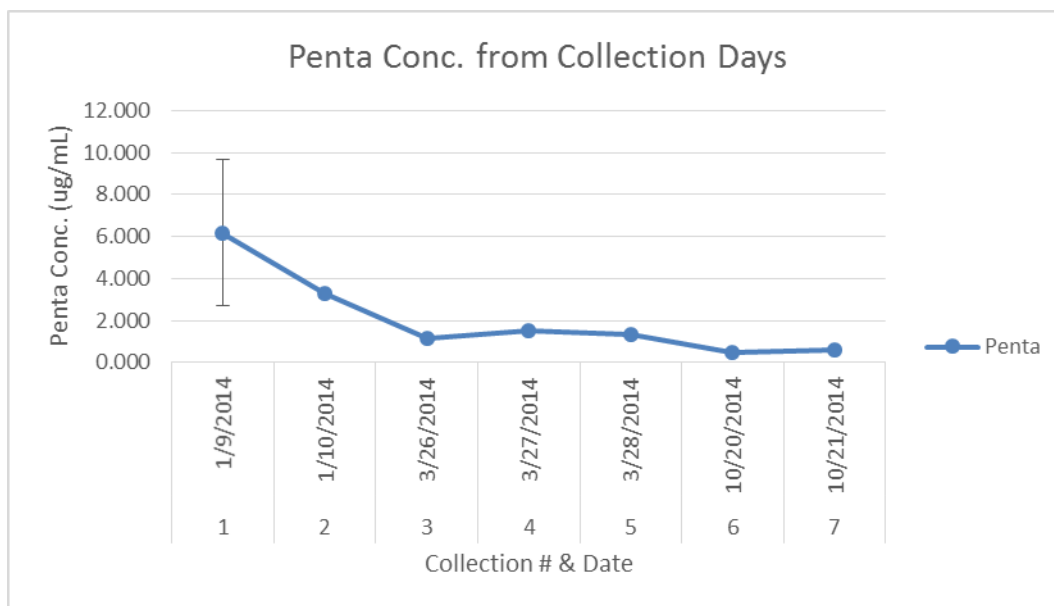

Figure 16. Pentachlorophenol concentrations in rainwater runoff collected from a section of the House Creek Bridge located near Upper Soda, Oregon.
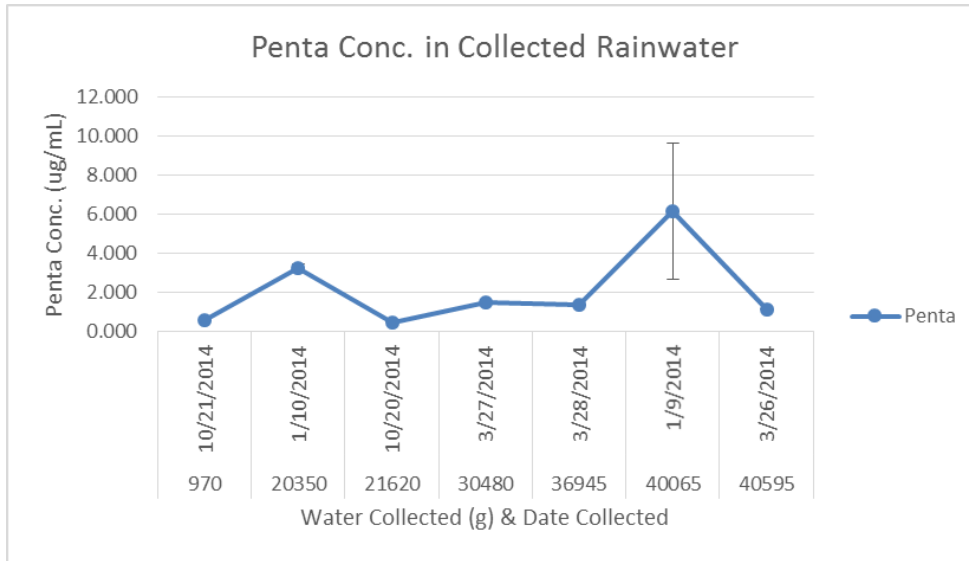
Figure 17. Concentrations of pentachlorophenol in rainwater runoff as a function of total rainwater collected from a section of the House Creek Bridge located near Upper Soda, Oregon.

Copper levels in rainwater runoff as a measure of losses from the copper naphthenate treated portion of the bridge followed trends that were similar to those found with penta in that levels were elevated for the first two collections then declined to approximately 10 ppm (Figure 18). While these levels are slightly higher than the copper levels noted in runoff from ACZA treated decking, there are few reports of copper migration from copper naphthenate treated wood. We will continue to monitor this test to determine if copper levels continue to decline over time.
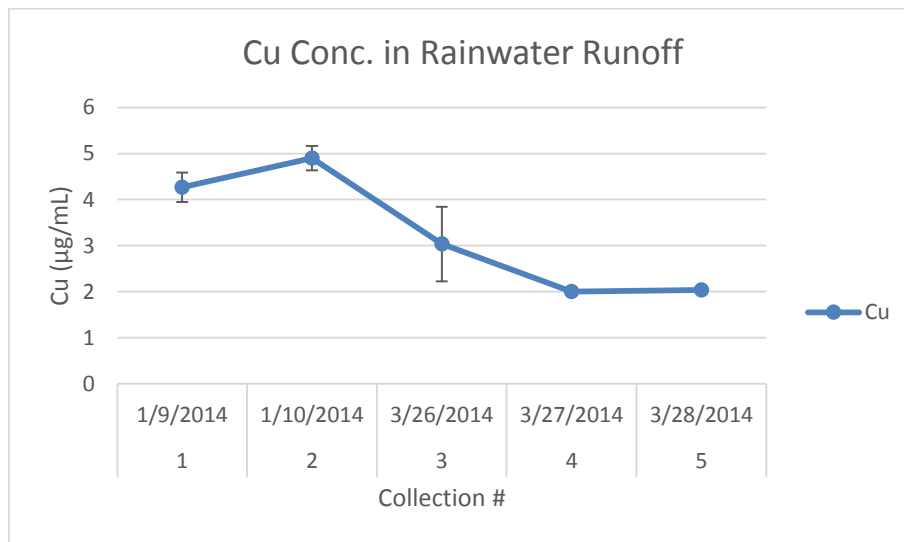

Figure 18. Copper concentrations in rainwater runoff collected at selected times from a portion of the House Creek Bridge near Upper Soda, Oregon.

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 have been 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, have participated in one planning meeting and provided comments regarding these plans. We will continue to work to help the agency shape a plan that will be representative of actual conditions and have also offered to cooperate on analysis.

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 from ACZA, CA and ACQ treated Douglas-fir 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. We have been routinely assessing the volume of treated wood entering the wood recycling facility near Corvallis, Oregon. This work has actually been underway for some time and originally started in response to reports from Florida about the amount of treated wood entering the construction and demolition facilities in that state. The levels were extremely high and led to concerns that similar levels might be entering facilities in Oregon.

The amount of treated wood has been visually assessed 168 times over a 12 year period. At each time point, the size of the entire pile was estimated. The presence of treated wood of a given dimension in the pile was then visually determined (for example 4 by 4 inches, 2 by 4 inches, etc.) and the length was estimated to the nearest 300 mm. As mentioned, treated wood was readily detected because of the distinctive brown stain and/or the presence of incisions. Depending on pile size, this allowed for visual detection 1 to 3 m inward from the outside of the pile. In addition, we estimated the relative proportions of various woody materials in the piles. The most common categories were yard debris, pallets, panels, and demolition debris. This latter categorization only began after we had performed 40 observations.

The lineal footage of each piece of dimensional material detected was then used to determine overall volume of wood using actual dimensions. Lumber for residential applications was primarily treated with chromated copper arsenate (CCA) until 2003 when this material was withdrawn from the market. Lumber is now treated with either a alkaline copper quaternary (ACQ) compound or copper azole (CA). It is not possible to visually distinguish wood treated with these three chemicals because of the brown pigments. For the purpose of determining chemical loading, we assumed that all of the wood had been treated to the American Wood Protection Association Standards ground contact retention for treatment of lumber with any of the water borne materials (6.4 kg/m^3 for ACQ or CCA or 3.3 kg/m^3 for CA) and that the entire cross section had been treated to that level. Average wood densities were then used to calculate the total amount of metal present in the material. These represented extremely conservative approaches because not all wood is treated to the ground contact retention and preservative penetration is often shallow in the species used in this region. However, since we could not visually assess treatment depth or retention, we elected to use this conservative approach. As a result, the estimates of total chemical in the wood were intentionally extremely conservative.

The most abundant materials present at the site were pallets, yard debris, and demolition debris (Figure 19). The average volume of material present at any given inspection was 338.8 cubic meters. Pallets were the most abundant material at the site (39 of 128 times), while yard debris was the most common 68 times. A variety of other materials were also present including panel trim scraps and shingles, but these represented minor volumes compared to the two most common materials.

Frequency of dominant material
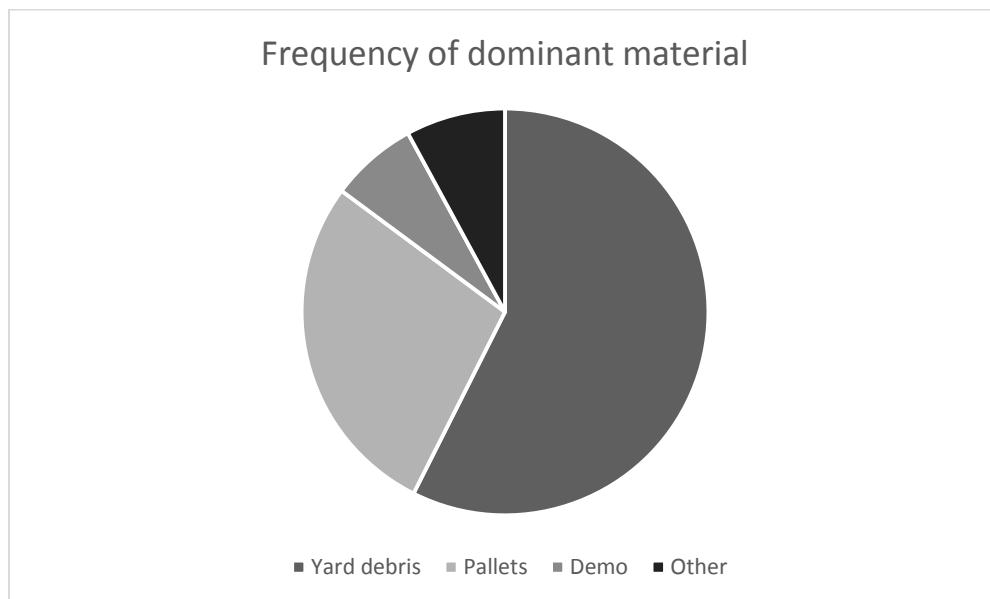
■ Yard debris   ■ Pallets   ■ Demo   ■ Other

Figure 19. Frequency of a given woody material being the dominant substrate present at the recycling center (10)
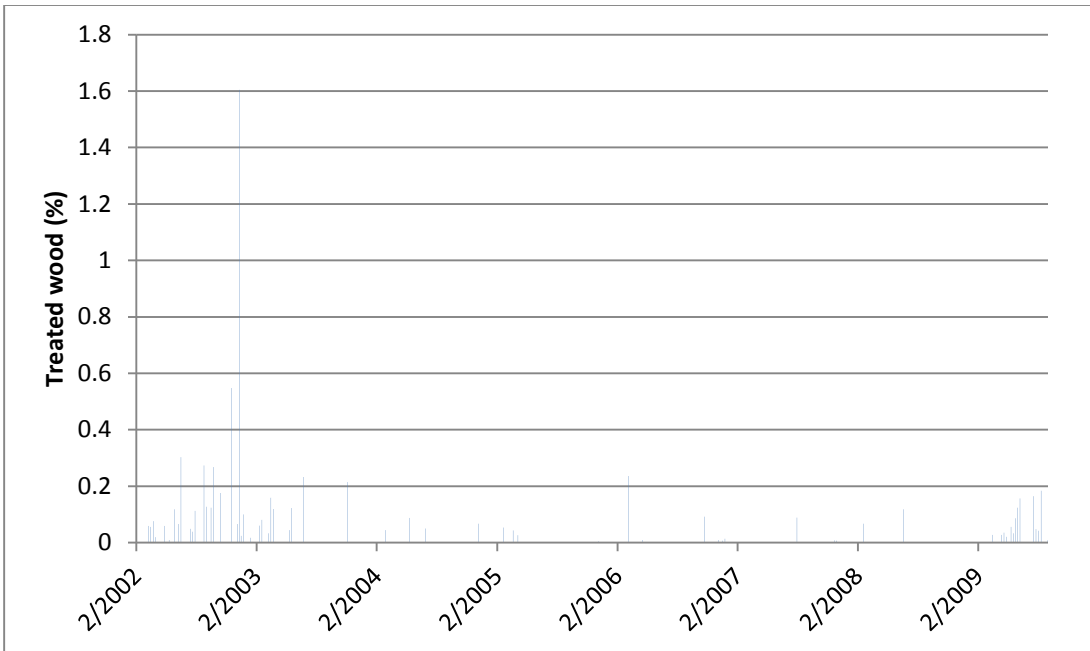
Figure 20. Percentages of treated wood detected in a recycling facility located in Western Oregon as determined by period visual surveys over a 12 year period.
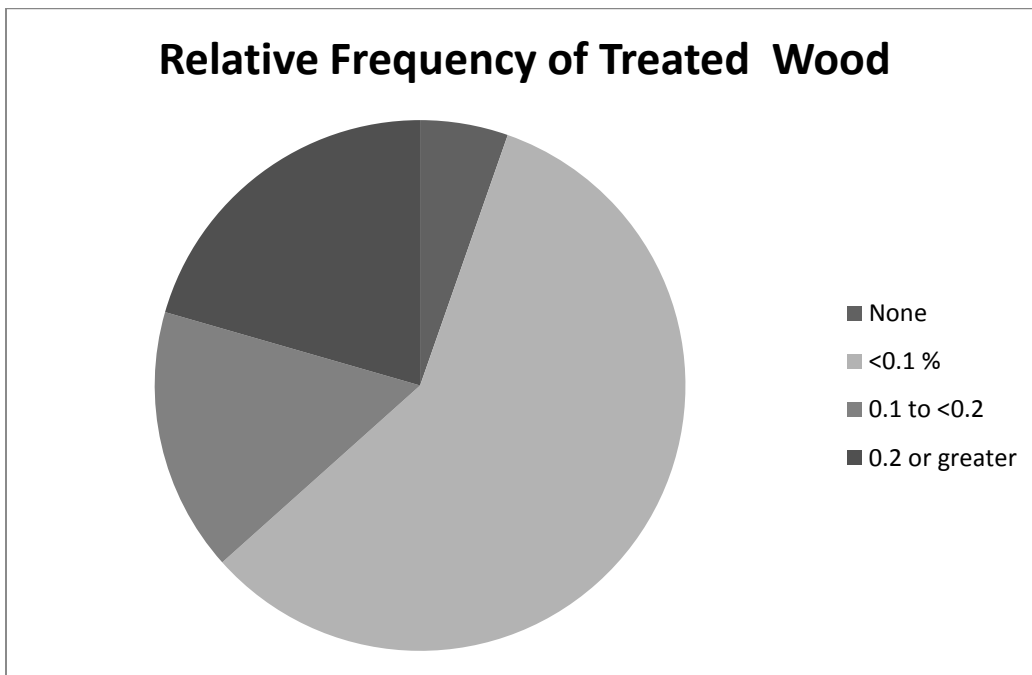

Figure 21. Frequency of different levels of treated wood in a wood recycling center in Western Oregon assessed over a 10 year period. Values are based upon 112 surveys.

Treated wood was detected in 155 out of 168 inspections or 92.3% of the samples (Figure 20). The percentages of treated wood were generally low in the samples, ranging from <0.01% to 2.0% of the estimated volume (Figure 21). Levels at or above 1% were only detected 3 times over the 12 year period. The average volume of treated wood present was 0.15% over the 12 years. Treated wood levels were > 0.2% of the volume in 20.5% of the inspections, while they were between 0.1 and 0.2% of the volumes in another 16.1% of the inspections. Treated wood represented less than 0.1% of the volume in a majority of inspections (63.4%), indicating that this material was a relatively small proportion of the recycling stream.

The results continue to indicate that treated wood does enter the recycling stream in the region, but at levels that would not raise regulatory concerns. We will continue to periodically monitor this site to ensure that this situation does not change over time.

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

We co-sponsored one workshop this past year using a webinar format. The shift to a webinar format was made because of the difficulty many potential participants have in traveling. This was our first attempt to hold an on-line workshop using Adobe Connect. The workshop was held at Oregon State University because we had the technical assistance and facilities; however, future events could be held almost anywhere.

The program was shortened to approximately 2.5 hours by eliminating some of the background on the basis for the models and time was added to more fully discuss how to use the simpler assessment tools. There were approximately 15 participants, although this counts only computers, not participants. Participants were, again, primarily federal agency people. The post-workshop survey was completed by 4 participants and it showed that most people thought the workshop was valuable (4.25/5.00). The comments mostly related to why NOAA did not accept the screening criteria. Interestingly, one commenter suggested the need for more background on the scientific basis for the models which was the topic we dropped because previous workshop participants felt that there was too much background. We will revisit this subject and plan to hold additional webinars.

We will co-sponsor another workshop February 26th in Lacey, WA. This workshop will not be on-line because of logistics of setting this up within a state facility. Instead, the goal will be to attract as many State of Washington agency people with the hope that we can begin to discuss the models and how they might be applied.