Environmental Performance of Treated Wood Research Cooperative

2013 Annual Report

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Advisory Committee Members

Arch Wood Protection (Bob Gruber)

Creosote Council (David Webb)

J.H. Baxter & Co. (Jerry Farley/Dick Keeley)

Osmose (Mark Blattie)

Pentachlorophenol Task Force (Michael Hoffman)

Southern Pressure Treaters Association (Carl Johnson/Kevin Ragon)

Treated Wood Council (Jeff Miller)

Viance, LLC (Brian Delbrueck/Kevin Archer)

Western Wood Preservers Institute (Ted LaDoux/Dallin Brooks)

Wood Preservation Canada (Henry Walthert)

Personnel

J.J. Morrell, Professor

Connie S. Love, Senior Faculty Research Assistant

Matthew Konkler, Faculty Research Assistant

Min Ye, M.S. Graduate Student

Executive Summary

The **Environmental Performance of Treated Wood Research Cooperative (EPTW)** has been active over the past year in a number of areas under its 6 Objectives. We will address progress under each Objective.

Objective 1: *Develop Fundamental Data on Preservative Migration from Wood*

We have nearly completed the Best Management Practice (BMP) verification

test. This study was initiated to determine if there were differences in preservative migration between matched wood samples treated with the same chemical and either exposed directly or subjected to one of the BMP processes prior to exposure. Last year we reported on Douglas-fir decking treated with pentachlorophenol (penta), ammoniacal copper arsenate (ACZA), copper azole (CA) or alkaline copper quat (ACQ) as well as Spruce-Pine-Fir (SPF) decking treated with chromate copper arsenate (CCA), CA or ACQ. This past year, we examined southern pine decking treated with penta, CCA ACQ or CA. Matched decks were exposed in Oregon and Mississippi. In general, the results followed the trends noted with Douglas-fir and SPF with the largest preservative migration occurring during the first few rainfall events; however, there were differences in metal losses between decks exposed at the two sites. These differences may be attributed to rainfall rates.

The most important outcome of all the BMP tests has been the observation that there were relatively few differences in preservative losses between BMP and non-BMP treated materials. This may lead to the conclusion that BMP processes are not useful; however, there are several reasons why the results may be misleading. First, there were time delays between treatment and installation of decks exposed in these tests that could have allowed for more complete immobilization of metals than might occur if materials were installed directly after treatment. The other factor is an increasing tendency for plants to adopt elements of the BMP processes such as long post-treatment vacuums, for other purposes such as controlling drippage and improving appearance. As a result, we suspect that normal plant practices are merging with BMP's. The BMP's still have merit because they help ensure that plants meet minimum standards that are third-party verified.

In addition to the BMP verification study, we have also explored the effects of pre-washing boards on subsequent metal losses. A one day pre-wash resulted in decreases in metal levels in the subsequent runoff suggesting that some type of pre-leaching procedure might be a secondary approach to limiting metal losses, but it would also create substantial logistical problems. These data are limited to one chemical system (ACZA) and need to be repeated on other systems to determine if they are representative.

We have also examined the potential for differences in metal migration with form of precipitation. Decks were exposed to wetting using either rainfall or snow. No differences were found in metal levels for the decks indicating that longer term exposure to moisture did not result in increased metal concentrations in the runoff.

The other component of the BMP verification study is the exposure of small piling treated with ACZA or creosote. Preliminary tests indicated that we could detect PAH's in the sheen on top of the water around recently installed piling; however, PAH levels in the surrounding water were generally low. Soil analysis revealed that PAH's moved only a short distance from the pilings when exposed in a freshwater pond. We will continue to monitor these tests and install additional materials as needed.

Objective 2: *Develop Standardized Accelerated Methodologies for Assessing Treated Wood Risks*

Objective 4: *Identify Improved Methods for Reducing the Potential for Migration*

We have taken the BMP verification tests a bit farther. This test also addresses

In our initial tests described under Objective 1, we were dependent on materials treated in different plants using BMP and non-BMP processes. While the materials were matched to reduce variability, we recognize that every plant operates in a slightly different fashion and this can introduce variability. In addition, we wanted to eliminate the time lag between treatment and exposure to simulate the worst case for the use of treated wood. Douglas-fir decking was treated with CA, ACQ or ACZA with no BMP processes applied. These materials were frozen until they could be subjected to one of the processes currently listed in the BMP Standard. Even though there are specific processes used for the various chemicals, we applied every process to boards treated with each chemical to determine if there might be better approaches to the BMP's. These boards were then subjected to simulated rainfall exposure and the runoff was collected and analyzed. Metals in runoff from boards that were only air-seasoned were compared with those in runoff from boards subjected to kiln-drying, steaming, hot water baths and ammonia steaming. The results showed that BMP's had different effects on the 3 systems. Kiln drying was the most effective BMP for ACZA treated wood, while the other BMP treatments tended to be associated with higher metal levels in runoff with this preservative. Hot water or ammonia baths tended to be associated with lower metal levels in runoff from CA treated wood, while rapid kiln drying was associated with higher metal losses. Finally, metal levels in runoff from ACQ treated wood were similar regardless of the BMP process employed. These results will be used to explore specific BMP's for each system in hopes of further improvement.

Objective 3: *Work Cooperatively to Develop and Improve Models to Predict the Risk of Using Treated Wood*

We continue to cooperate with researchers at the University of Alaska. Their final report was reviewed and has been released. It showed that creosote could affect herring egg development, but not at the levels found around piling in service in Alaska. Their recommendations were for continued use of creosote treated wood, but that installation be delayed during the herring spawning season.

No work has been undertaken under Objective 5 which involves examining reuse and disposal of treated wood, although we have completed a survey of disposal practices among utilities.

Objective 6: *Deliver Educational Outreach Programs on the Proper Use of Treated Wood in Relation to the Best Management Practices*

Objective 6 addresses educating treated wood users about best practices and the

proper use. We have held a number of workshops with federal agency personnel and continue to work with agency personnel. We plan to offer our one half day course as a webinar in hopes of attracting a wider audience. These workshops will be opened to all and will help educate users about treated wood and how to use it in or near aquatic environments.

Finally, under membership, we have created an Associate Membership status. The Western Wood Preservers' Institute and Treated Wood council were instrumental in encouraging wood treaters to become Associate members. They will have access to reports and a voice on the Advisory committee but will not have voting rights should a proposed project come to a vote. We welcome our new Associate Members and look forward to their input.

Introduction

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

Membership

The EPTW Coop currently has 10 full time members; however, there was discussion over the past year about treaters being full members when they could easily obtain the same information through their respective trade associations. After considerable discussion, it was agreed to offer an Associate Membership category at a much reduce rate. Associate members will receive access to summary data and have a voice on the advisory committee, but they will not have a vote in matters related to research prioritization.

After an extensive effort by Ted LaDoux (WWPI) and Jeff Miller (TWC) the following companies agreed to join the EPTW coop as Associate members as of January 1.

Allweather Wood LLC
Amerities Holding LLC
BB & S Treated Lumber of New England
Bell Lumber & Pole
Bridgewell Resources LLC
Brooks Manufacturing Co
C M Tucker Lumber Companies LLC
Cahaba Timber Co
Coastal Treated Products Co
Conrad Forest Products
Cox Industries, Inc
Culpeper Wood Preservers
Eden Wood Preserving
Exterior Wood, Inc
Fontana Wood
Georgia Pacific LLC
Great Southern Wood Preserving, Inc
Hydrolake, Inc
International Forest Products
JH Baxter
Julian Lumber Co
Langdale Forest Products Co
Long Life Treated Wood, Inc
McFarland Cascade, a Stella-Jones Co
New South Wood Preserving LLC
Northeast Treaters, Inc
Permapost Products Co
Renewable Resource Group Inc
Royal Pacific Industries
S.I. Storey Lumber Co. Inc
Spartanburg Forest Products
Sunbelt Forest Products Corp
United Wood Treating Co
Universal Forest Products, Inc
Wheeler Lumber
William C Meredith Company, Inc
Wood Preservers, Inc

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 (Table 1). 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 Standards.

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 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.

Table 1. Preservative treatments evaluated on various wood species using the BMP's.

Wood Species	Penta	CCA	ACZA	ACQ	CA
Douglas-fir	X	-	X	X	X
Spruce-Pine-Fir	-	X	-	X	X
Southern pine	X	X	-	X	X

"-" denotes treatment not tested on that species

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

Results for the Douglas-fir and SPF were reported in the last two annual reports. This past year, we completed trials on the southern pine decks. These decks were treated in cooperation with Dr. Michael Barnes at Mississippi State University. In addition, the tests were replicated at both Oregon State and MSU. In the OSU tests, the procedures were same as those followed for Douglas-fir and SPF materials using southern pine treated with penta, CCA, ACQ or CA. The MSU tests evaluated only CCA, ACQ and CA. In addition, the collection method differed slightly. In these cases, a 50 ml water sample was collected and acidified as described; however, instead of weighing the runoff in the containers, total rainfall from a nearby weather station was used to determine the amount of rain striking the decks.

Runoff water from the CCA, CA and ACQ decks was acidified by adding 150 ul of concentrated nitric acid to 4.85 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 2). The resulting acidified solution could be stored at 5 C until a suitable batch could be collected. This method was used for all remaining samples. ICP analysis was also used to quantify chromium, zinc, or arsenic where these elements were present in the original treatment.

Table 2. Copper concentrations in matched water samples analyzed with no treatment, addition of 0.5 M nitric acid or microwave digestion in an acid solution.

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

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

De-ionized water was added to the sample collection flask to approximately 230 mL, then 50 uL internal standard stock solution was spiked in each flask. The internal standard stock solution was 200 µg/mL ^{13}C-labeled pentachlorophenol ($^{13}C_6H_6Cl_6$, Cambridge Isotope Laboratories, Andover, MA) in methanol. Then 2.4 mL 1N NaOH was added to each flask using a pipette. A Teflon™ stir bar was placed in each flask and de-ionized water was added to bring the volume to the bottom of the neck of the volumetric flask. The flasks were stirred for 1 min then allowed to stand for 30 min. This procedure converted the PCP to its sodium salt. Next 2.6 mL iso-octane was added to the flask from a dispenser and the flasks were stirred for 1 min. The solvent layer was removed with a disposable glass pipette and discarded. This iso-octane extraction was repeated with 2.4 mL iso-octane. This procedure removed residual oil and other organics from the PCP sample.

The sodium pentachlorophenate was converted back to PCP by adding 3.0 mL 1.0 N H2SO4 using a pipette. The flask was stirred for 1 min and allowed to stand for 30 min. Then 2.6 mL iso-octane was added to the flask which was stirred for 1 min to extract the PCP. The iso-octane layer was transferred to a 20 mL glass vial and the extraction repeated with an additional 2.4 mL iso-octane. This second extract was added to the first. Each sample extract was then diluted to an appropriate concentration with iso-octane containing 2 µg/mL internal standard.

High resolution gas chromatography – low resolution mass spectrometry (HRGC-LRMS) analysis was carried out by injecting 1 ml of sample into a Shimadzu HRGC-LRMS system class

5000 equipped with a Restek XTI-5 capillary column (0.25mm ID X 30 m long) composed of fused silica with a 0.25 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 $[^{13}C_6]$ 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 $[^{13}C_6]$ 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 cm^2. The LOD is defined according to the Federal Register Part 136, Appendix B, procedure (b) (17), as three times the standard deviation of replicate analyses of the analyte.

Penta treated southern pine: Penta levels ranged from 2.5 to 5.8 ppm in the first runoff from the southern pine decks and then declined to 1 to 2.5 ppm in the next collection (Figure 2). Levels then varied between 1 and 4 ppm for the remaining 8 collections. As expected, cumulative penta losses were linear over time, reflecting the tendency for concentrations to be dependent on water solubility and for some penta to always be solubilized. These results are consistent with those found for penta treated Douglas-fir where water runoff concentrations varied between < 1ppm and 4 ppm.

As with the Douglas-fir results, there was no consistent relationship between BMP treatment and penta loss. BMP processes for oilborne treatments concentrate on reducing over-treatment and minimizing the presence of surface deposits of oil on the wood. Over time, overall treatment processes have evolved to incorporate components of the BMP procedures such as heating in oil (expansion baths), post-treatment steaming and long vacuums into the normal treatment procedures to reduce the risk of bleeding in service. As a result, normal treating practices are merging with the BMP's and our results illustrate that trend.

Overall, the penta results indicate that the risk of migration from wood treated with this preservative can be readily predicted using the total exposed surface area. This could be done using a worst case assumption that all of the surface area was exposed or a more accurate approach that only considers the area that is actually wetted.

CCA Treated Southern Pine: Chromium levels in runoff from treated southern pine decks was initially low (1.8 to 3 ppm) which would be consistent with the tendency for chromium to react with wood and be reduced to the less mobile trivalent state following treatment (Figure 3). Chromium levels were generally low with continued rainfall exposure; however, there was one elevated collection after the decks had been subject to almost 50 liters of water. It is unclear why chromium levels increased so sharply at this point and then fell back for the next two col-

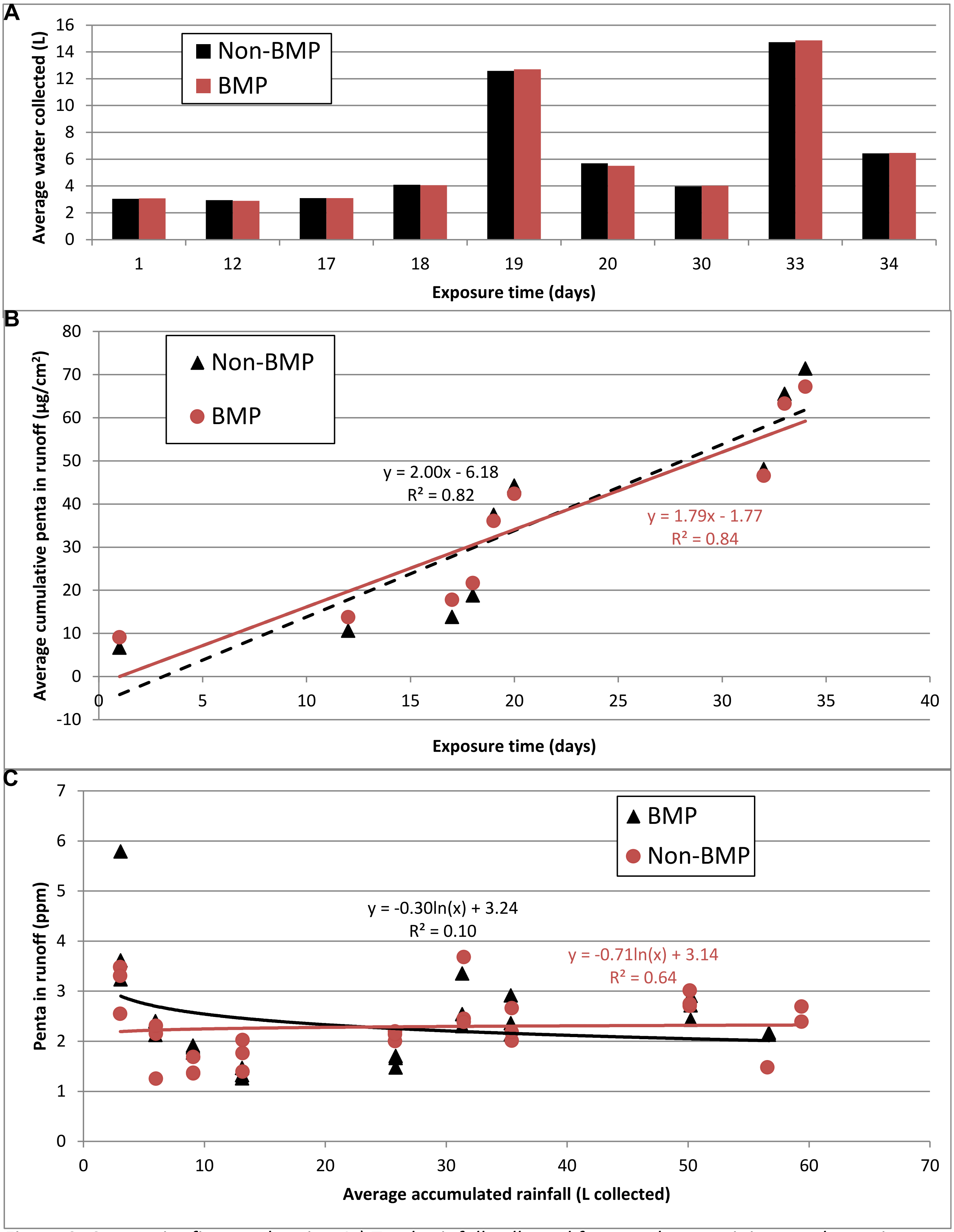

Figure 2. Composite figures showing A.) Total rainfall collected from tanks containing southern pine decking treated with penta with or without BMP Procedures and exposed to rainfall in Corvallis, OR, B.) The cumulative copper present in that rainfall and C.) The amount of penta present in rainfall at each collection point. Three deck sections were tested with BMP treated wood and three were tested with non-BMP treated wood.

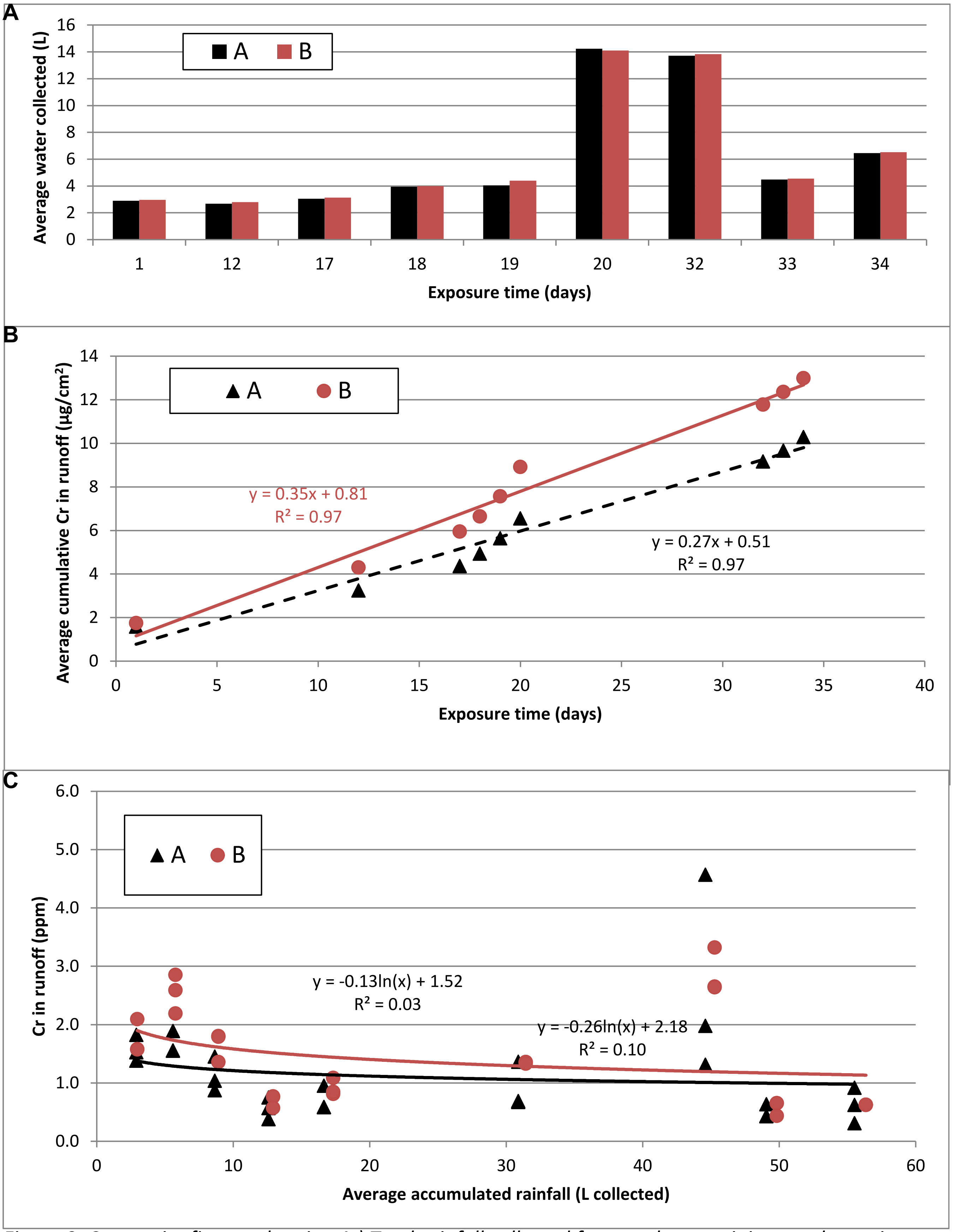

Figure 3. Composite figures showing A.) Total rainfall collected from tanks containing southern pine decking treated with CCA with or without BMP Procedures and exposed to rainfall in Corvallis, OR, B.) The cumulative chromium present in that rainfall and C.) The amount of chromium present in rainfall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

lections. The deposition of CCA is predicated on the conversion of hexavalent chromium to the trivalent state, which should not be available for migration. The results suggest that there might have been some residual chromium that migrated to the surface after continued wet/dry cycles.

Arsenic and copper levels followed similar trends with relatively low levels in runoff from the first rainfall, then a slight decline and a spike in arsenic levels in water from the seventh rainfall (Figure 4, 5). This rainfall event was among the largest in the test, but previous data indicate that rainfall amounts do not increase the concentration of metal in the runoff, just the total amount lost.

As in previous tests, there were no consistent differences in metal levels in runoff from boards treated using conventional practices or the BMP procedures. In this case, the time intervals between treatment and exposure might account for the lack of difference. These materials had to be shipped to Oregon for exposure and this process took over a month. CCA fixation is time and temperature dependent and this shipping period would be more than adequate for immobilization to occur under the ambient temperatures at the time (10 to 20 C).

CA Treated Southern Pine: Copper concentrations in rainfall runoff from copper azole treated southern pine decks ranged from 1.4 to 3.3 ppm after the first rainfall event (Figure 6). Concentrations increased slightly in runoff from the second rainfall event, then declined to less than 0.5 ppm over time. These results are consistent with those found with CA on Douglas-fir and SPF. As in previous tests, there were no consistent differences in metal levels with or without BMP processes. As noted with CCA, the long delay between treatment and exposure could help account for the lack of differences.

ACQ Treated Southern Pine: Runoff from ACQ treated southern pine decking contained copper levels that were 10 times those found in runoff from either CCA or CA treated wood. Copper concentrations ranged from 30 to 72 ppm in runoff from the first rainfall and then dropped to 16 to 28 ppm in the second rainfall (Figure 7). These levels are considerably higher than those found with the two other systems, but are consistent with the results from the Douglas-fir decks exposed last year. ACQ and CA both contain higher proportions of copper than CCA and the copper, by virtue of the absence of chromium, should be more mobile. Given these factors, it is unclear why the copper losses from the CA treated boards were so much lower. Copper levels in runoff were still elevated after the eleventh rainfall, again differing from the results found with CA or CCA treated materials.

As with the other tests on southern pine, there were no noticeable differences in copper levels in runoff from boards treated with ACQ using the BMP or non-BMP processes.

In general, the results indicate that the application of BMP processes to the various treatments had no noticeable effect on resulting losses of metals when the materials were exposed to rainfall. The results would imply that there was no value in the BMP procedures; however, caution must be exercised in this phase of the testing because of the lag between treatment and exposure. This time lag allowed any wood/metal reactions to continue and also permitted some drying to occur prior to the first rainfall exposure. While the drying after installation might have occurred in practice, one of the goals of any BMP process is to enhance immobilization when drying cannot occur. Despite the minimal effects of BMPS on the treatment/wood species combinations evaluated, the processes help ensure that materials are similarly prepared for exposure.

The waterborne southern pine treatments exposed at Corvallis were also repeated with matched materials at Mississippi State University. In this case, there were a few differences in

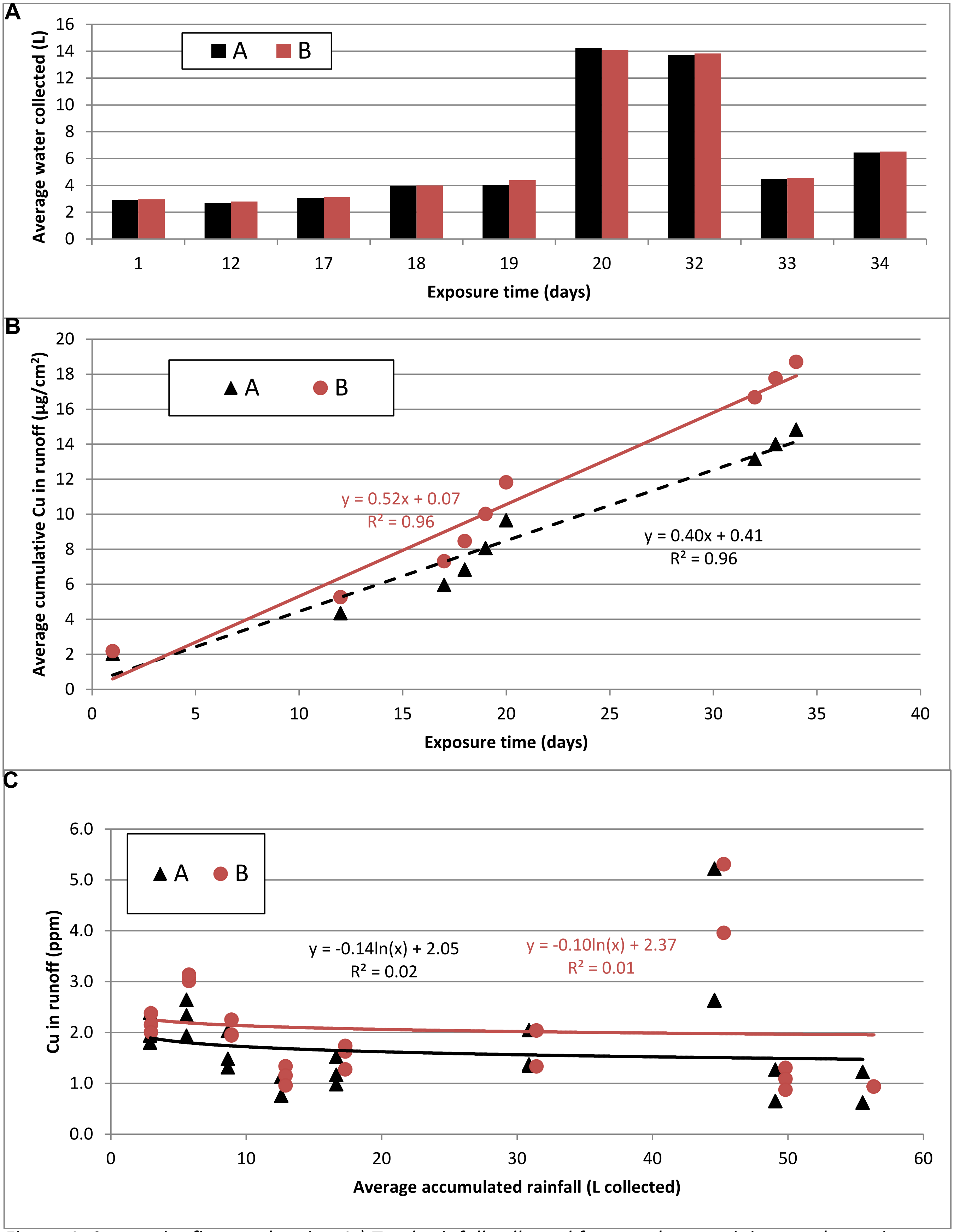

Figure 4. Composite figures showing A.) Total rainfall collected from tanks containing southern pine decking treated with CCA with or without BMP Procedures and exposed to rainfall in Corvallis, OR, B.) The cumulative copper present in that rainfall and C.) The amount of copper present in rainfall at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

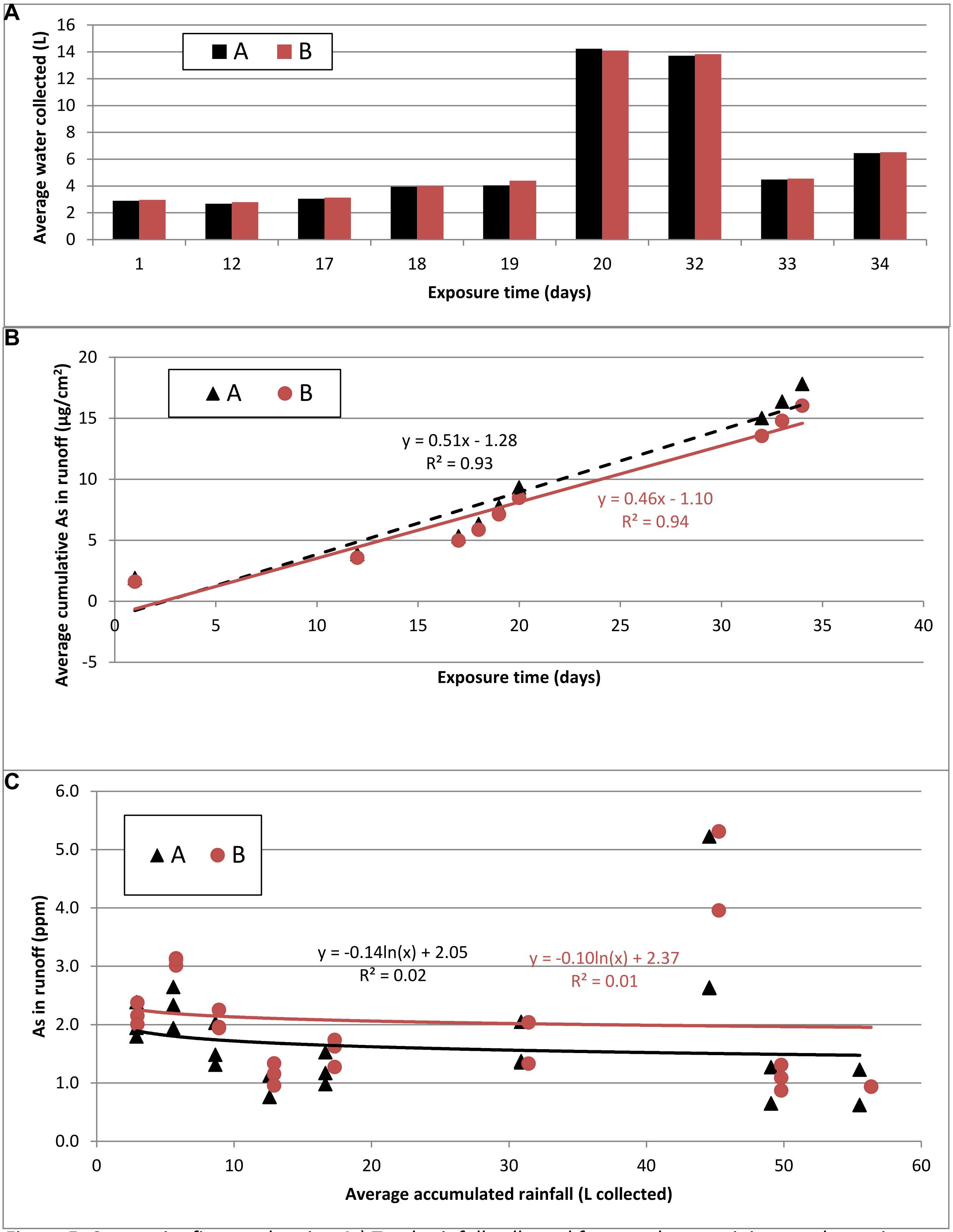

Figure 5. Composite figures showing A.) Total rainfall collected from tanks containing southern pine decking treated with CCA with or without BMP Procedures and exposed to rainfall in Corvallis, OR, B.) The cumulative arsenic present in that rainfall and C.) The amount of arsenic present in rainfall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

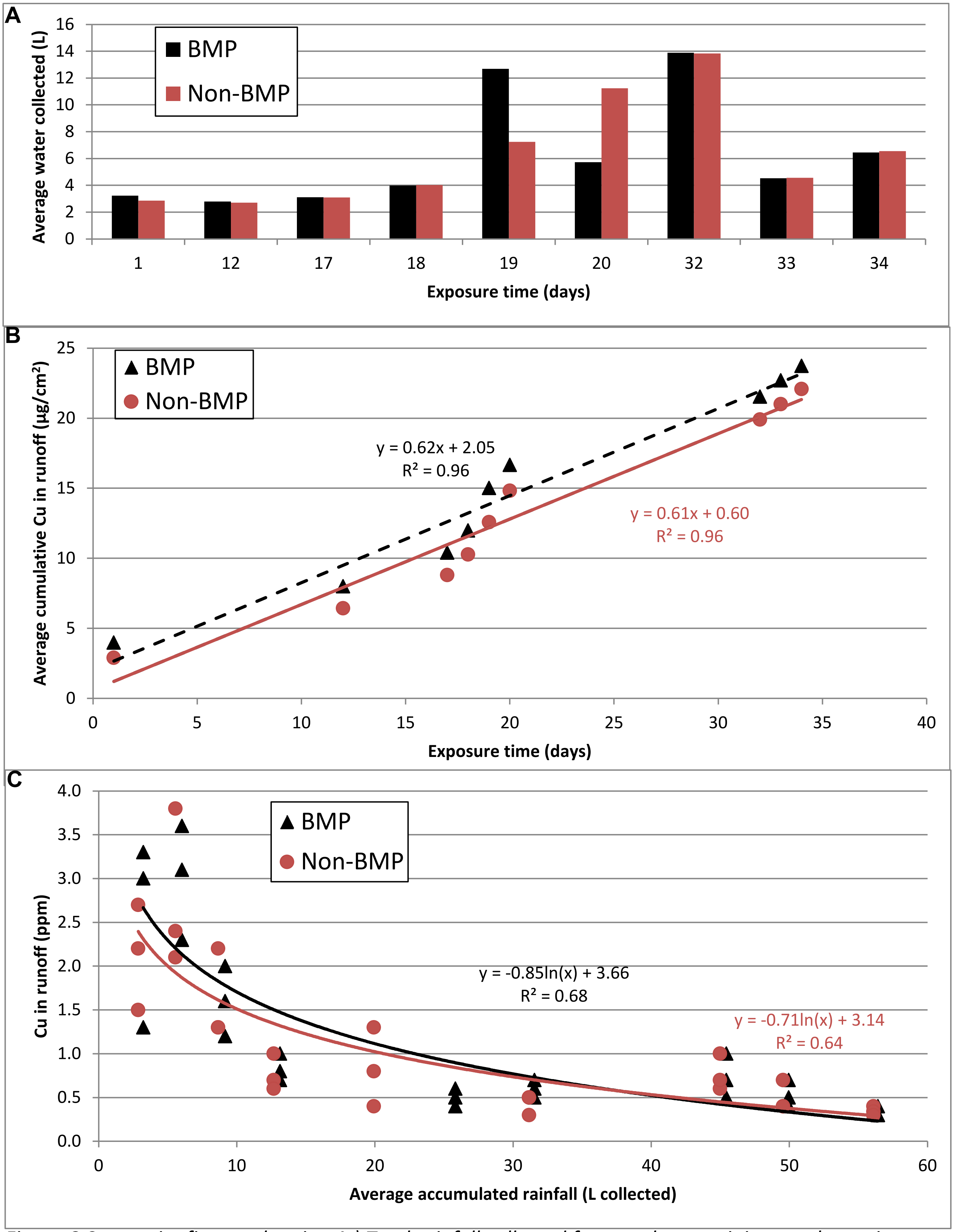

Figure 6 Composite figures showing A.) Total rainfall collected from tanks containing southern pine decking treated with CA with or without BMP Procedures and exposed to rainfall in Corvallis, OR, B.) The cumulative copper present in that rainfall and C.) The amount of copper present in rainfall at each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

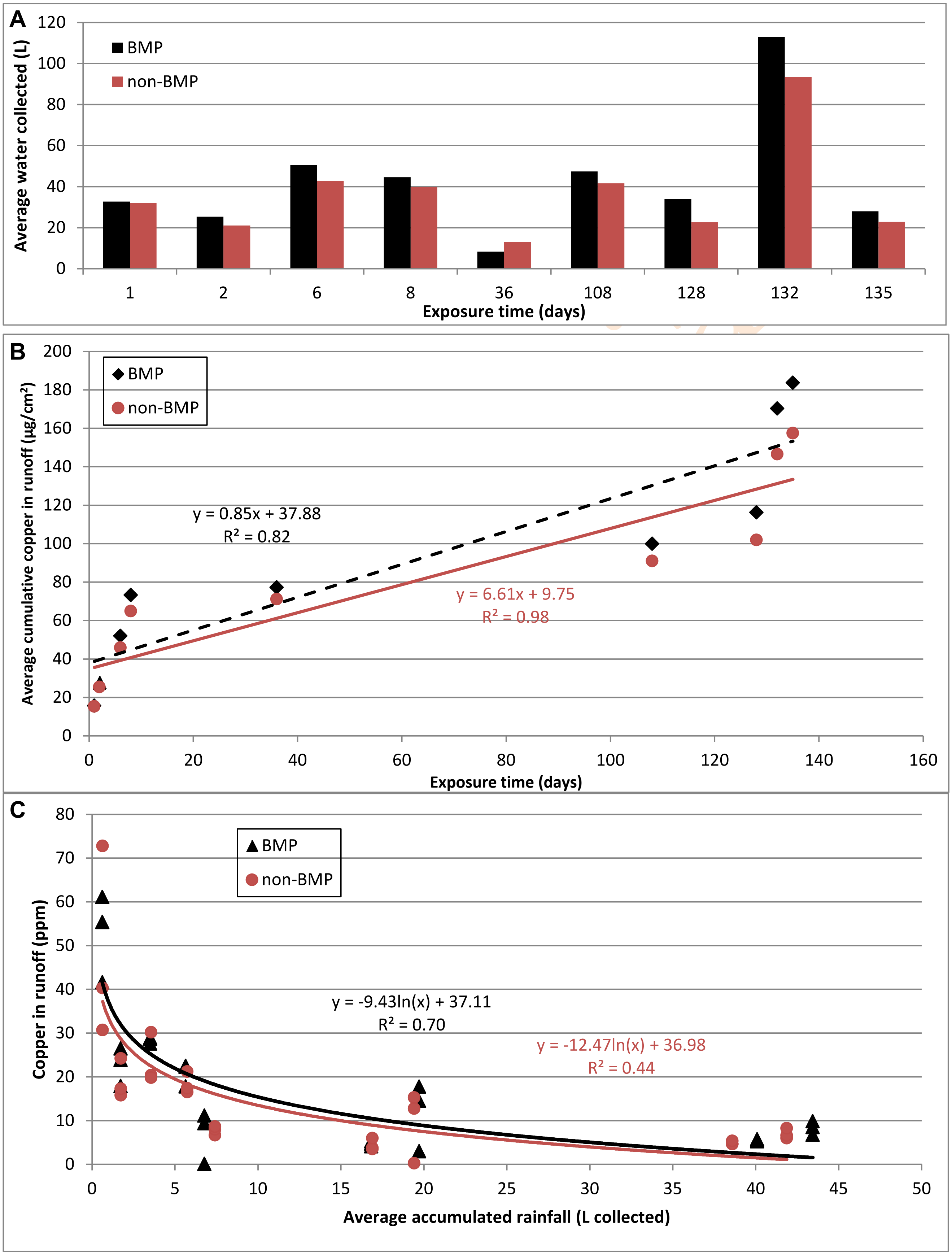

Figure 7. Composite figures showing A.) Total rainfall collected from tanks containing southern pine decking treated with ACQ with or without BMP Procedures and exposed to rainfall in Corvallis, OR, B.) The cumulative copper present in that rainfall and C.) The amount of copper present in rainfall at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

procedure. First, the water was not weighed, instead, rainfall was measured and the area exposed to rainfall was used to calculate the total amount of water collected. The samples were subjected to 9 rainfall events over a six week period (Figures 8-12). Rainfall levels tended to be shorter and more intense than those experienced at the Oregon site.

Chromium, copper and arsenic levels in runoff from the CCA treated decks exposed in Mississippi tended to be more variable than those for runoff from decks exposed in Oregon, but the overall trends were similar (Figures 8-10). Copper and chromium levels in runoff from decks treated without BMP processes were, once again, similar to those found in runoff from decks receiving a BMP process. Arsenic levels tended to be higher in the initial runoff from decks exposed in Mississippi, and remained elevated for most of the collection periods. It is unclear why arsenic levels would differ while copper and chromium levels remained similar at both sites.

Copper levels in CA treated decks exposed in Mississippi were similar to those in runoff from decks exposed in Oregon, but the levels of copper remained slightly higher even after 30 liters of rain had been collected from both sets of decking (2 ppm in MS vs 0.5 ppm in OR)(Figure 11). It is unclear why the MS decks lost slightly more copper, especially since they were exposed after a longer post treatment storage period.

Copper levels in the initial runoff from ACQ treated decks exposed in MS were much higher than those found in runoff from either CCA or CA treated materials exposed at the same site but were much lower than those found in runoff from similar decks. This is consistent with the results obtained in Oregon

Effect of Pre-leaching on Metal Losses From ACQ Treated SPF Lumber: During one of our BMP workshops, several specifiers inquired about the potential for pre-leaching treated wood to reduce the initial surge in metal losses once the material was exposed to natural rainfall. In order to examine this question, ACQ treated SPF lumber left over from the BMP verification tests was subjected to overhead wetting for one day prior to be allowed to dry. The material was used to construct three decks which were exposed to natural rainfall as described earlier. Runoff collected from these decks was analyzed and the results were compared with those obtained from the decks exposed without pre-leaching. Metal levels in runoff from the first rainfalls on the pre-leached decks were far lower than those from decks not subjected to leaching and more closely resembled the levels found after exposure to several rainfalls (Figure 14). These results suggest that some form of pre-wetting would reduce the initial metal losses from treated wood, although a system would need to be designed to ensure that the runoff from these materials did not, themselves constitute an issue.

Effect of Water State on Metal Losses From Treated Wood: While most precipitation will strike the deck in water form, some will fall as snow. Snow might have a longer wood contact period that might increase the concentration of metals in the subsequent runoff. In order to investigate this possibility, ACQ treated SPF decks were constructed and then approximately 50 mm of artificial snow was applied to the top. The snow was allowed to stand overnight, then melt. All runoff was collected and analyzed as previously described. Metal levels in the runoff from snow covered decks were similar to the levels found in decks exposed to conventional rain (Figure 14). The results suggest that water form does not alter the total metals in the subsequent runoff.

Piling tests: Small Douglas-fir piling sections (150-200 mm in diameter by 1.8 m long) were treated to target retentions of 16 pcf or 1.5 pcf with creosote or ammoniacal copper zinc arsenate, respectively, using either conventional treatment process or one of the WWPI BMP's.

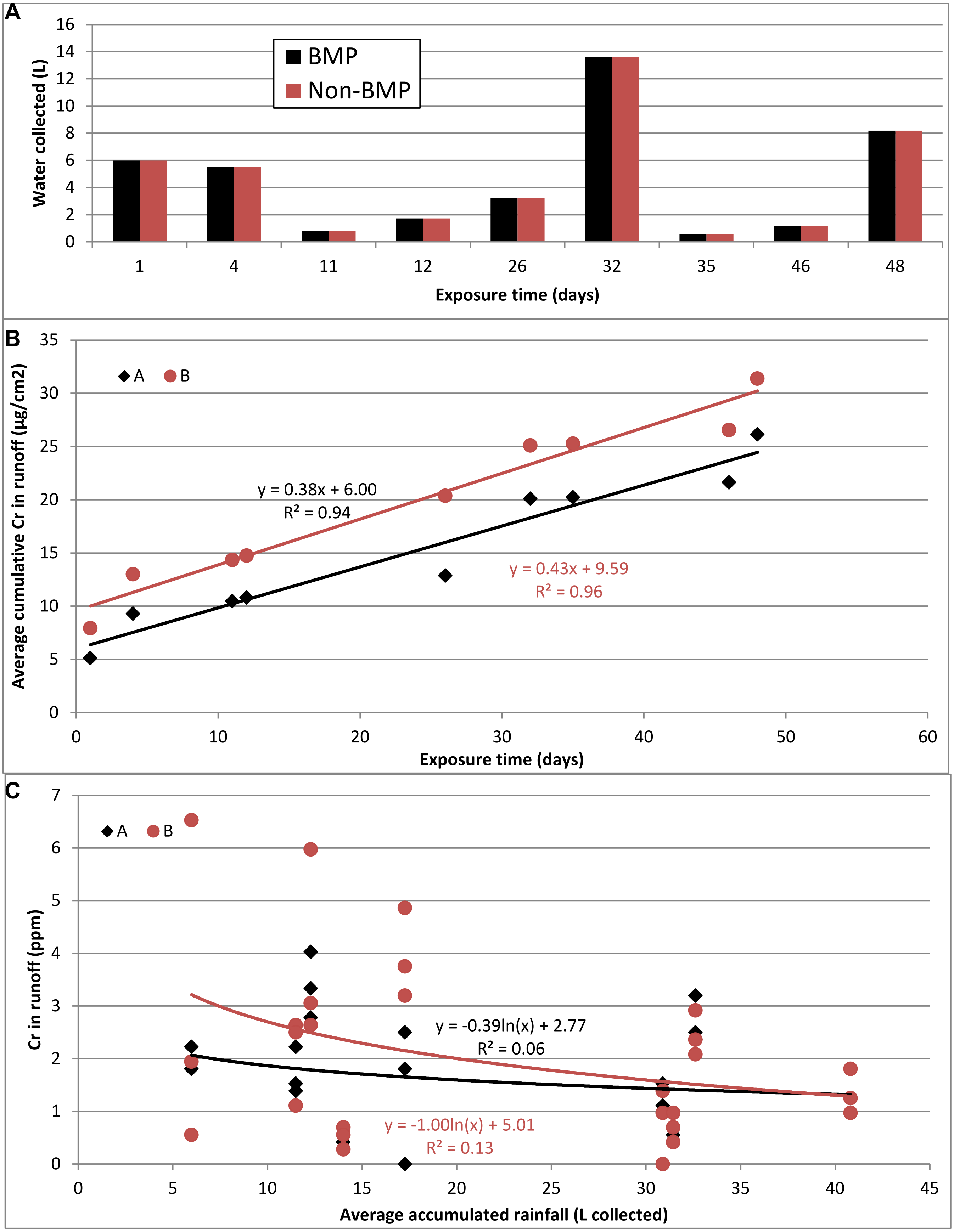

Figure 8. Composite figures showing A.) Total rainfall collected from tanks containing southern pine decking treated with CCA with or without BMP Procedures and exposed to rainfall in Starkville, MS, B.) The cumulative chromium present in that rainfall and C.) The amount of chromium present in rainfall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

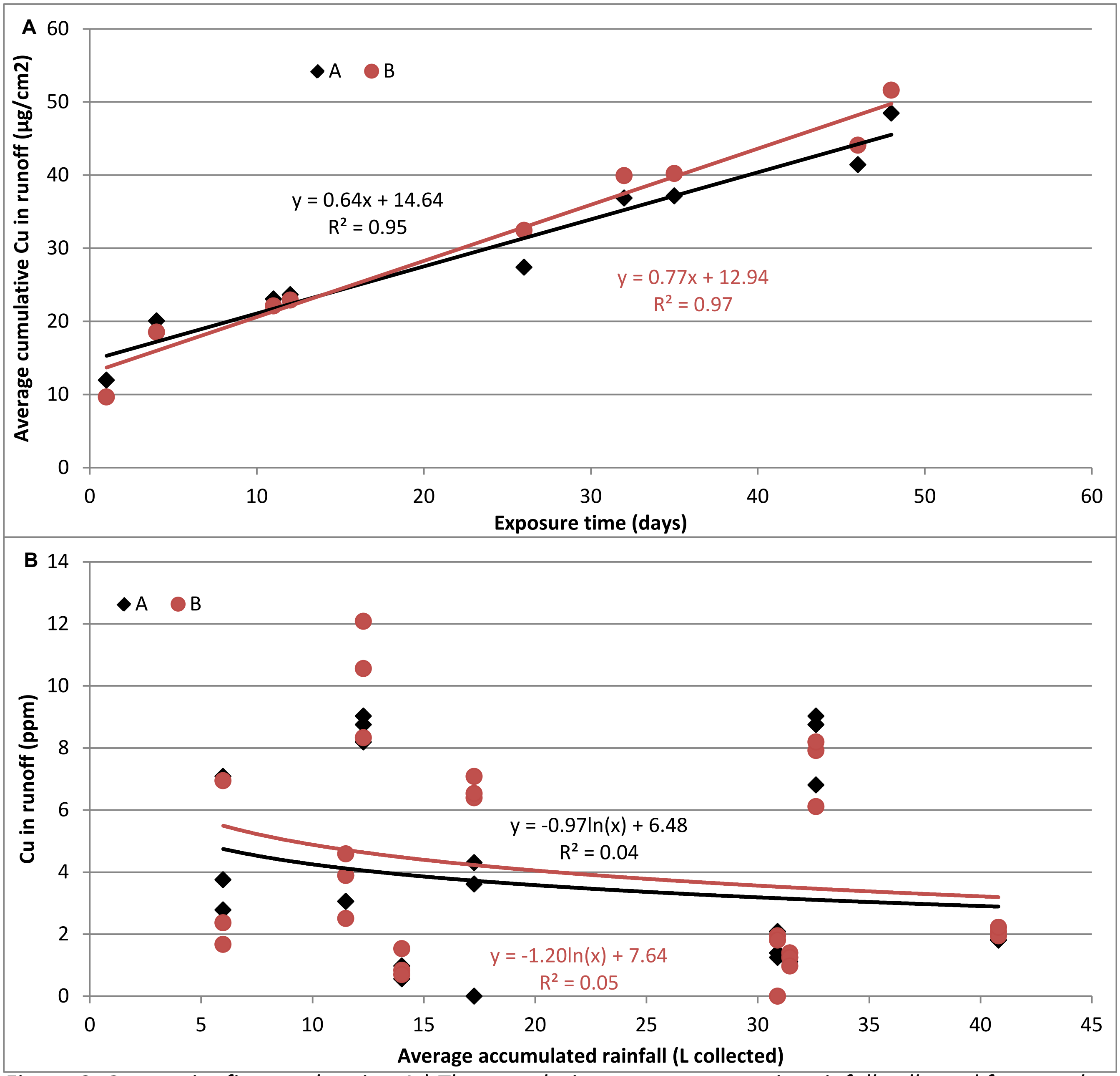

Figure 9. Composite figures showing A.) The cumulative copper present in rainfall collected from tanks containing southern pine decking treated with CCA with or without BMP Procedures and exposed to rainfall in Starkville, MS, and B.) The amount of copper present in rainfall at each collection point. Three deck sections were tested with BMP treated wood and three were tested with non-BMP treated wood. Total rainfall collected is shown in Figure 8.

The pile sections were assayed to determine preservative penetration and analyzed for retention before being placed into a pond located near Philomath, Oregon (Figure 15).

The ability of the materials to move into the sediment surrounding a post was assessed in a preliminary study by inserting packets (200 mm long by 25 mm in diameter) containing a known soil against the pile as well as 300 mm and 1.2 m from each pile. The packets were constructed of an inert plastic that did not permanently sorb metals or PAH's. These packets were used because the uneven bottom sediments present at the site made it difficult to reliably collect soil. It was felt that exposing a uniform sediment material in a controlled packet allowed for more reproducible assessment of preservative migration. In addition, these packets could be more easily retrieved and dissected to assess metal or PAH content along the pile and on

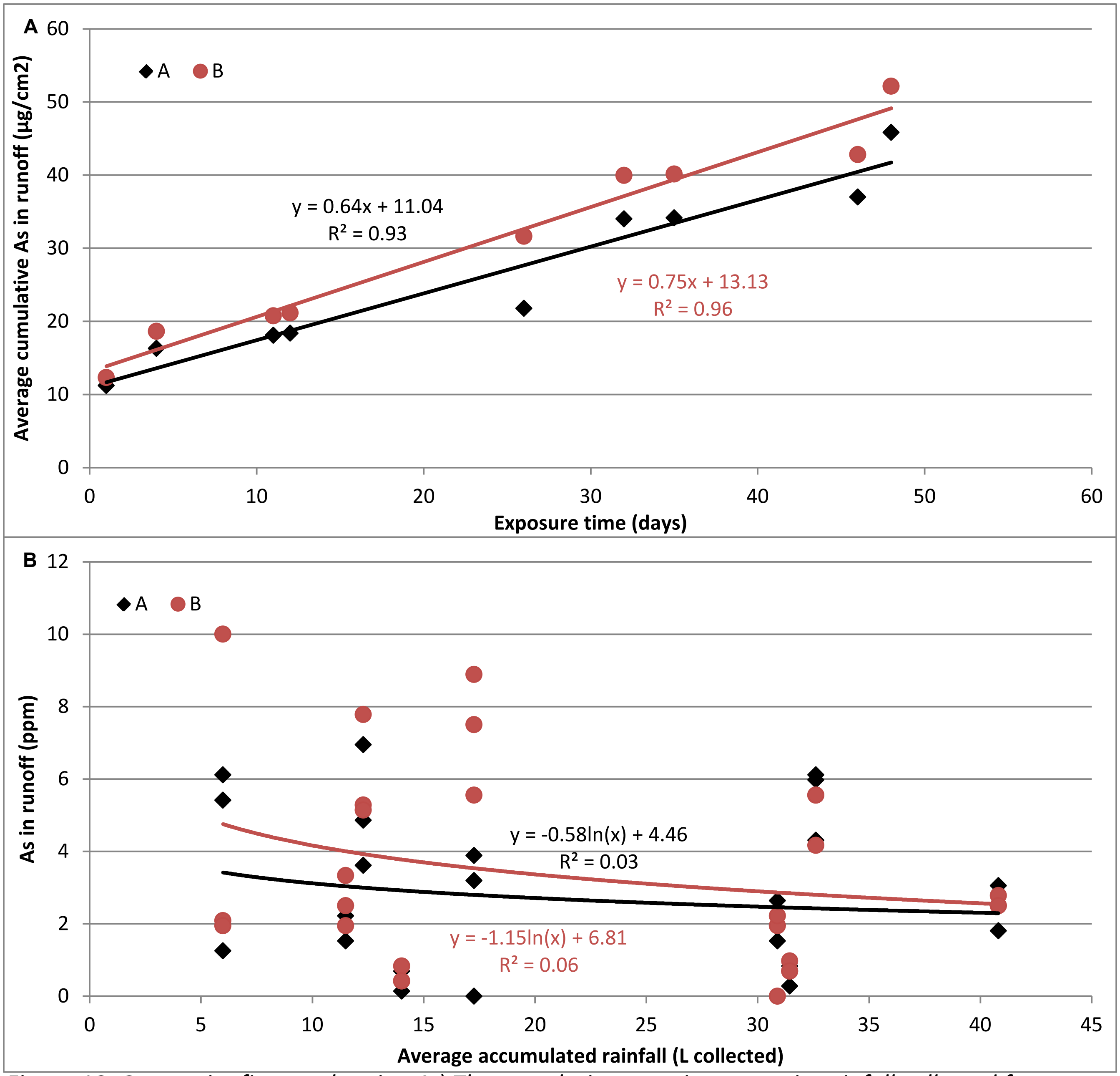

Figure 10. Composite figures showing A.) The cumulative arsenic present in rainfall collected from tanks containing southern pine decking treated with CCA with or without BMP Procedures and exposed to rainfall in Starkville, MS, and B.) The amount of arsenic present in rainfall at each collection point. Three deck sections were tested with BMP wood and three were tested with non-BMP treated wood. Total rainfall collected is shown in Figure 8.

either side of the packet. Preliminary tests showed that PAH's moved readily into the packets and we were able to obtain good recoveries of spiked PAH's from the packets. PAH's were detected on both the side in contact with the posts as well as the opposite side (Figure 16). Levels gradually increased over a 3 week exposure period indicating that material was moving from the posts into the surrounding sediment.

Based upon these data, three posts treated with either ACZA or creosote were set in the pond and soil packets were installed at multiple locations around each post. The packets were set so that they could be easily pulling from a given location with minimal disturbance.

The posts were set a minimum of 10 feet apart in such a way that any water flow past one post did not directly flow into another. Background sediment and water samples were collected

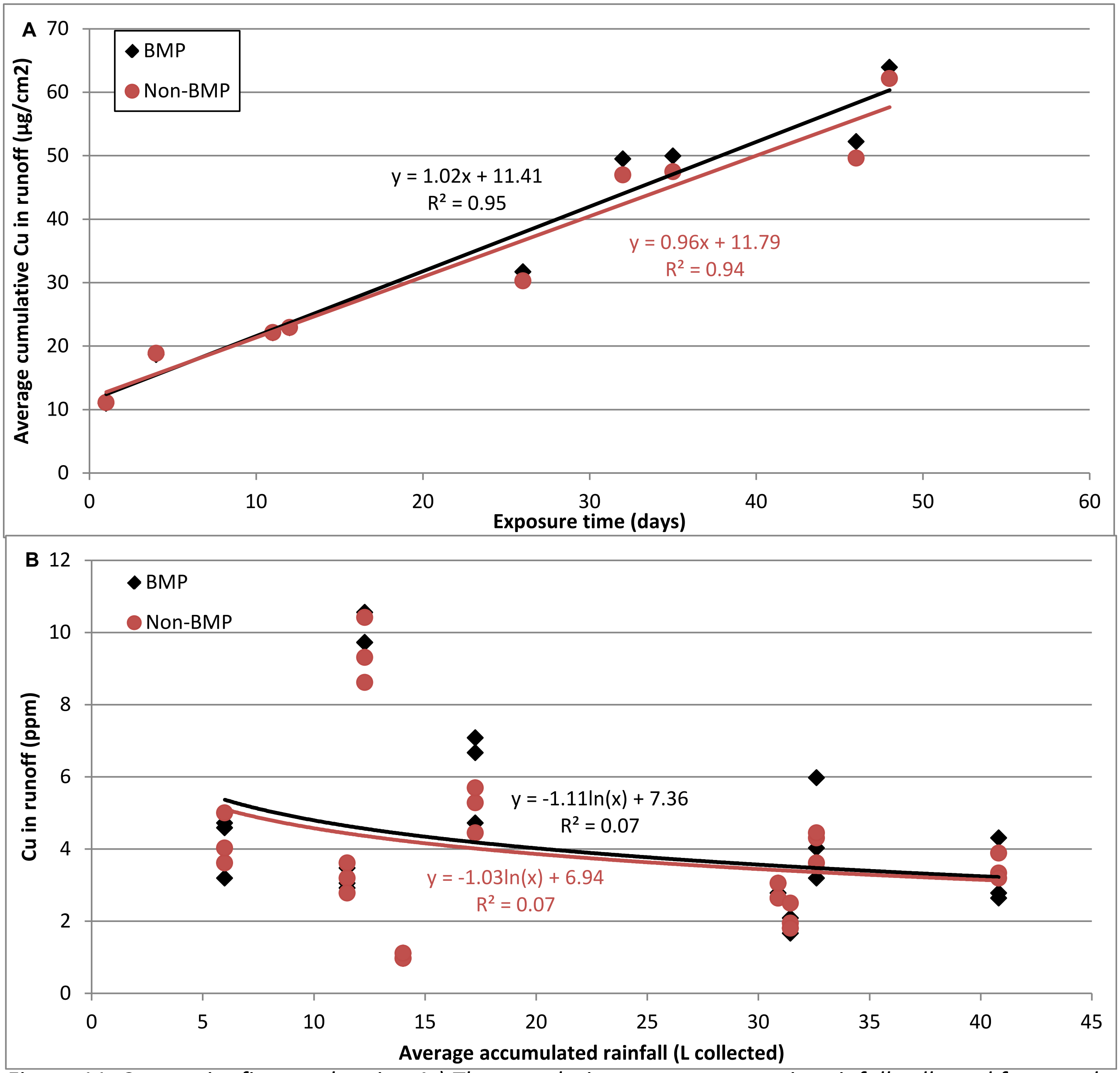

Figure 11. Composite figures showing A.) The cumulative copper present in rainfall collected from tanks containing southern pine decking treated with CA with or without BMP Procedures and exposed to rainfall in Starkville, MS, and B.) The amount of copper present in rainfall at each collection point. Three deck sections were tested with BMP treated wood and three were tested with non-BMP treated wood. Total rainfall collected is shown in Figure 8.

prior to pile installation. Water column samples collected immediately after installation and the pre-installation samples were analyzed for metals and PAH's. The metals samples were acidified with 1N nitric acid before being analyzed by ICP as previously described. One liter of each PAH sample was weighed and then 2.5 ml of methanol and 2.5 ml of the internal standard were adding. The resulting mixture was then passed through an ENVI-18 SPE disk. The disk was then eluted with two 5 ml fractions of dichloromethane and the resulting material was analyzed by GC-MS. PAH levels were quantified using the internal standards. It was not possible to quantify all possible PAH's. Instead, levels were quantified for the 16 EPA priority PAH Standards and these levels were combined for reporting purposes. Water column analysis showed that PAH's were detectable immediately adjacent to the creosote treated posts (Figure 17); however, these results must be viewed with some caution since an intentional effort was

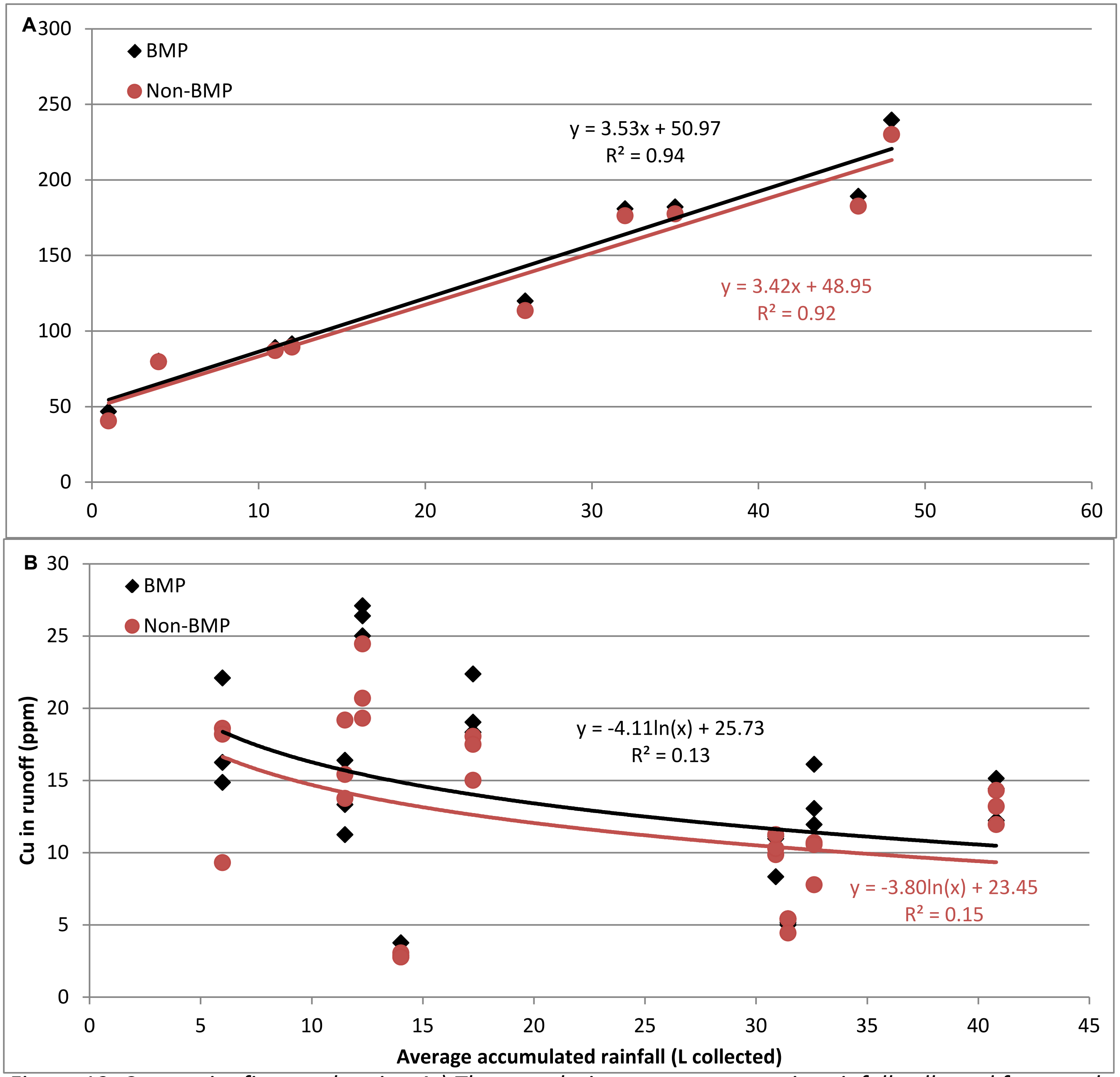

Figure 12. Composite figures showing A.) The cumulative copper present in rainfall collected from tanks containing southern pine decking treated with ACQ with or without BMP Procedures and exposed to rainfall in Starkville, MS, and B.) The amount of copper present in rainfall at each collection point. Three deck sections were tested with BMP treated wood and three were tested with non-BMP treated wood. Total rainfall collected is shown in Figure 8.

made to collect the sheen on the water surface. PAH levels away from the posts and farther below the surface were negligible.

The soil packets were removed after 1 month of exposure and were immediately frozen. The packets will be cut in half length wise so that one half represents the portion of the packet closest to the pile and the other half will be on the face away from the pile. The packets will then be cut in half so that the upper sediment and the lower sediment could be analyzed separately. These analyses are on-going and will be reported at a later date.

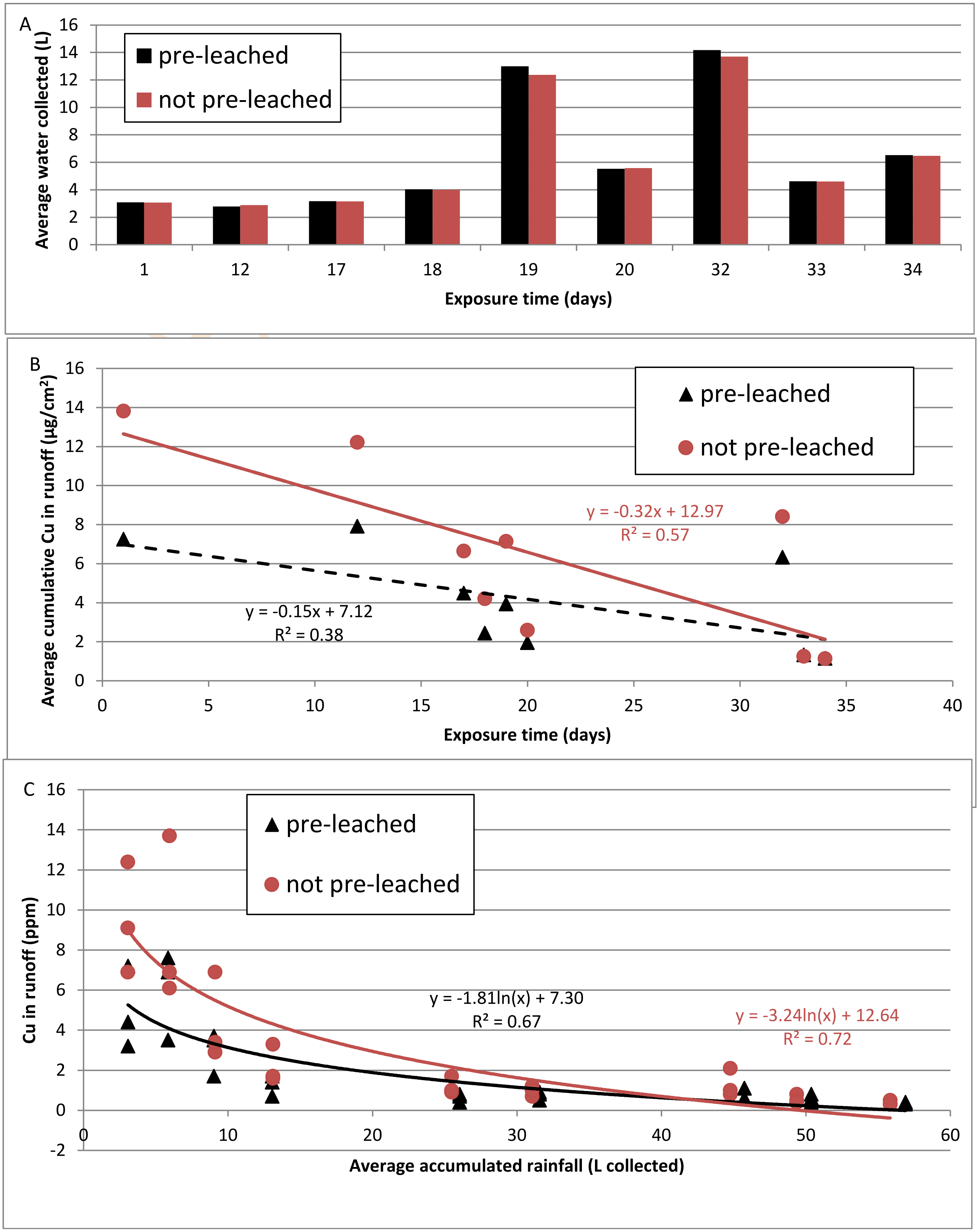

Figure 13. Composite figures showing A.) Total rainfall collected from tanks containing SPF decking treated with ACQ with or without pre-leaching before exposure to natural rainfall in Corvallis, OR, B.) The cumulative copper present in that rainfall and C.) The amount of copper present in rainfall at each collection point. Three deck sections were tested with pre-leaching and three were tested without pre-leaching.

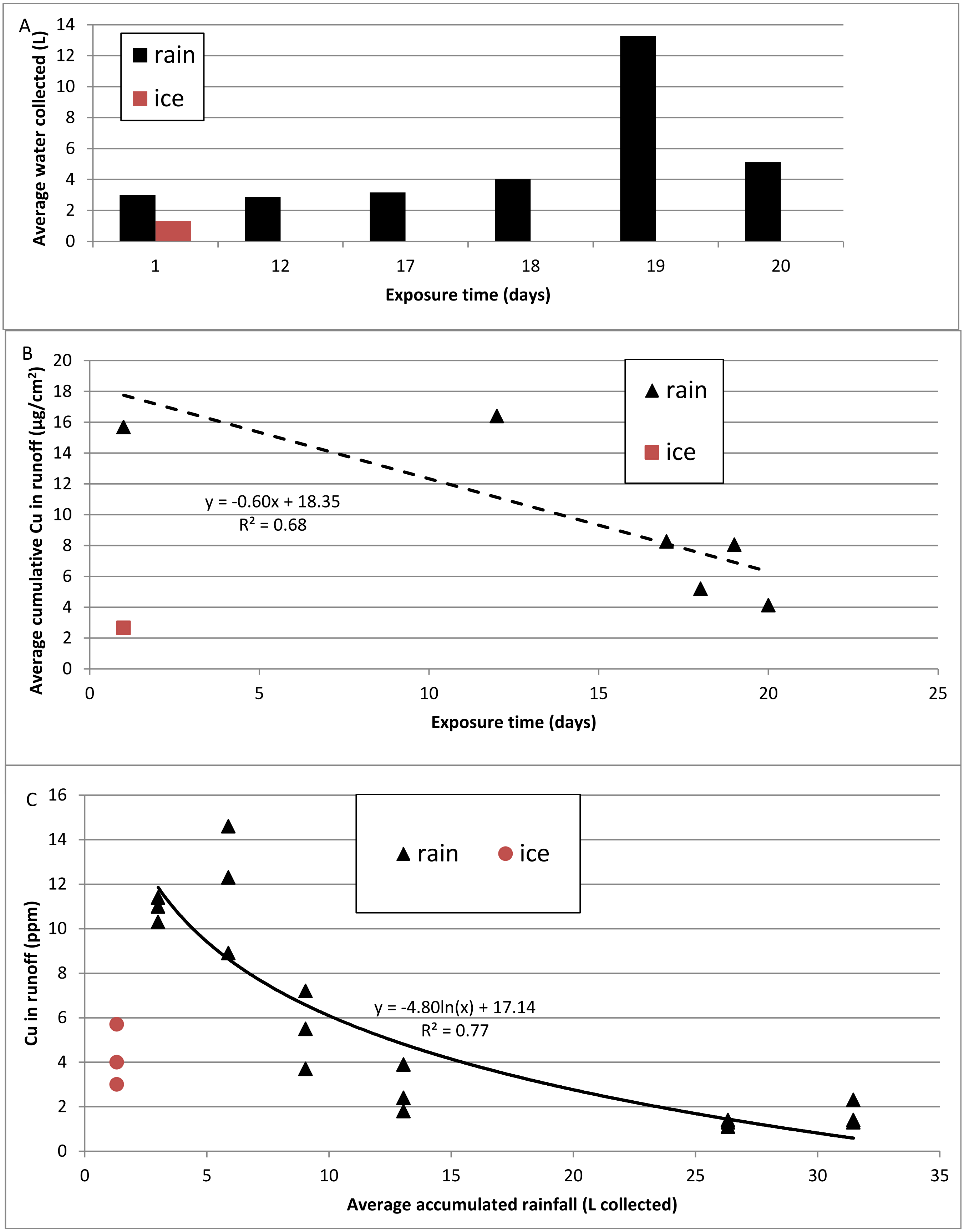

Figure 14. Composite figures showing A.) Total rainfall collected from tanks containing SPF decking treated with ACQ and exposed to either natural rainfall or simulate snow in Corvallis, OR, B.) The cumulative copper present in the leachate and C.) The amount of copper present in the leachate at each collection point.

Figure 15. A piling installed in the pond near Philomath, OR

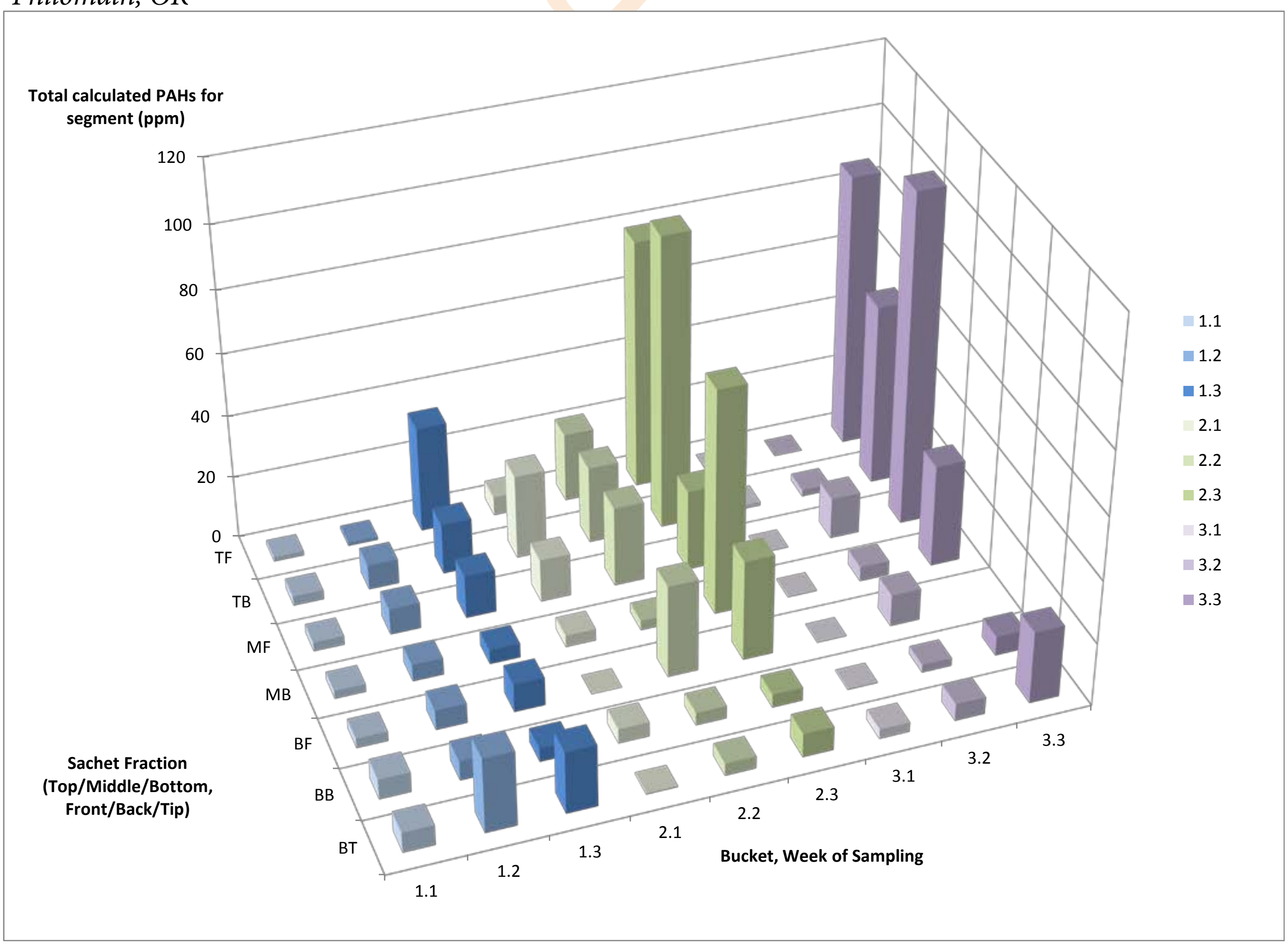

Figure 16. PAH levels in soil packets placed around Douglas-fir post sections treated with creosote and exposed in stagnant water for one to 3 weeks. Where T, M and B equal the top, middle, and bottom and F and B signify the front and back of each sachet).

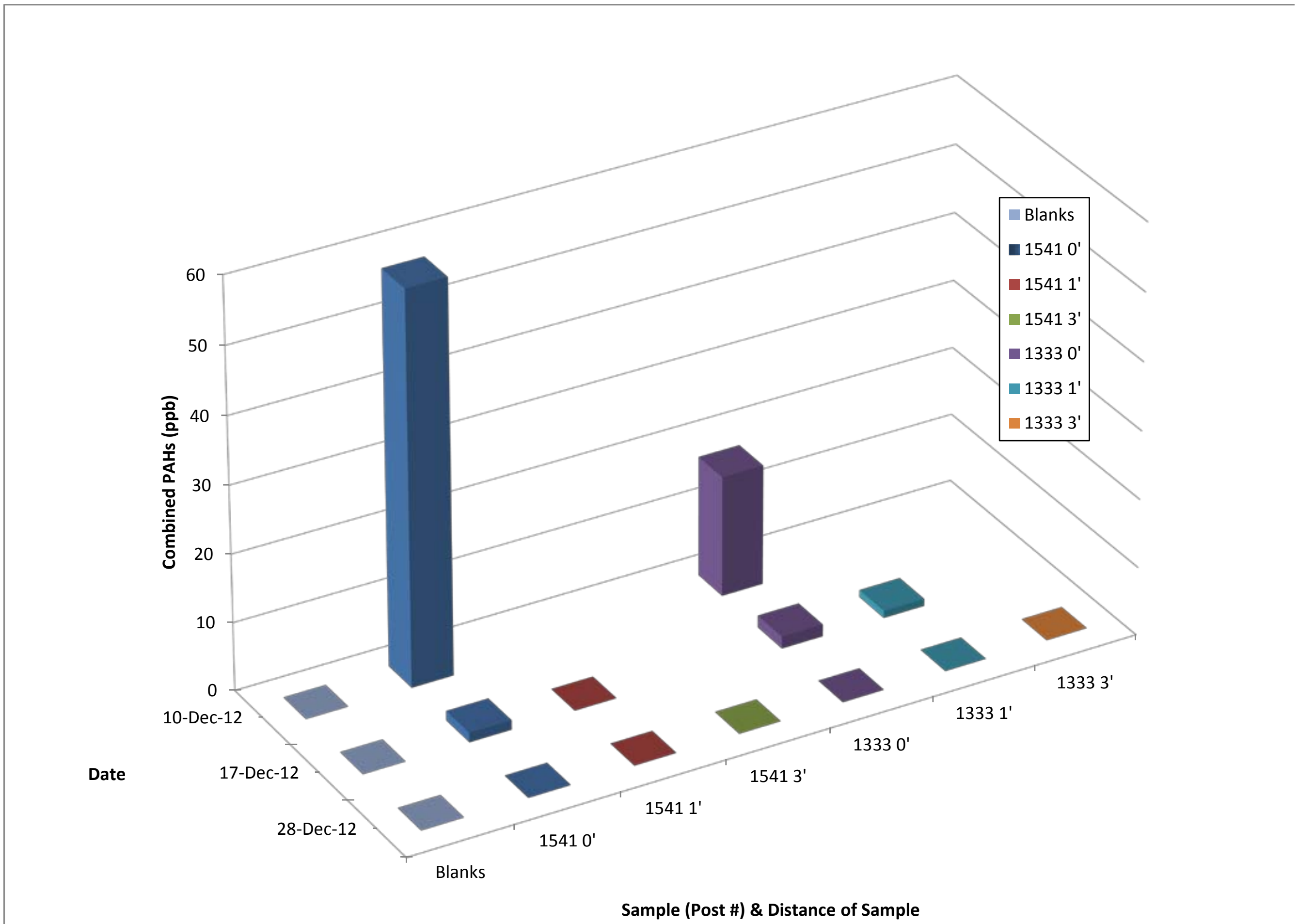

Figure 17. PAH levels in water immediately adjacent as well as 300 and 900 mm away from two creosote-treated Douglas-fir post sections that were exposed in sediment in a pond located near Philomath, OR.

2. DEVELOP STANDARDIZED ACCELERATED METHODOLOGIES FOR ASSESSING TREATED WOOD RISKS

While an array of BMP processes are allowed for the various preservatives listed in the BMP's, there are very few data on the comparative effects of the processes on metal losses. This information could be used to identify methods for improving the BMP's.

In order to investigate the possibilities, thirty Douglas-fir boards (nominally 50mm*150mm*4m long) were commercially incised to a density of 800 incisions/m^2. The lumber was conditioned to constant weight at 23℃ and 65% relative humidity before being randomly allocated to one of 5 treatment groups of six boards each (ACZA at 4.0 kg/m^3 or 6.4 kg/m^3; ACQ at 6.4 kg/m^3; or CA at 0.96 kg/m^3 or 2.4 kg/m^3). Each board was end-coated with a two-part epoxy to retard longitudinal preservative penetration.

Lumber was commercially treated to a target retention in accordance with American Wood Preservers' Association Standards U-1 and T-1 (AWPA, 2011). The goal was to complete the pressure treatment cycle without proceeding to any post-treatment vacuums or heating that might have accelerated loss of ammonia or amine and thereby hasten copper deposition. Each of the treated boards was immediately cut into ten 300 mm long sub-samples. Each sub-sample was weighed and labeled before being sealed in a plastic bag and frozen at -10℃ 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 the 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 18). Previous studies (Simonsen


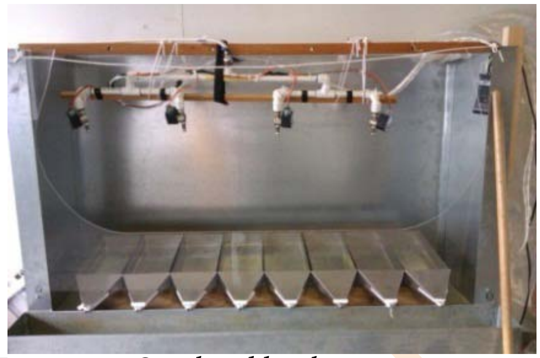

Figure 18 - Overhead leaching apparatus used to evaluate the effects of BMP procedures on migration of metals from ACZA, CA or ACQ treated wood.

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.

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 *457 mm long * 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, mostly 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 occurred at the beginning of water exposure, water samples collected over the first two hours of simulated rainfall were tested for the copper concentration while the remaining samples were retained in case metal levels were still elevated after 2 hours. Copper levels in the system over time were used as the measure of BMP effectiveness.

Data for copper levels among group means were subjected to an Analysis of Variance (ANOVA) using R statistical software. A Least Significance Difference (LSD) test was applied in conjunction with the ANOVA to assess differences. The LSD test compared every pairwise treatment group mean and identified differences between any two means. A Holm adjustment was applied along with the LSD test to adjust the p-value and reduce the risk of Type I errors.

Effects of BMPs on fixation of copper in ACZA treated wood: BMP processes varied in their ability to limit metal losses from ACZA treated boards. Copper concentrations tended to be highest in the first two water collections for all treatments, and then declined with continued rainfall (Figures 19-24). These results are consistent with numerous previous studies showing that the highest releases of copper occur during the initial exposures to wetting (Kumar et al., 1996; Brooks, 2003; Morrell et al., 2011). Copper concentrations in runoff from both ACZA retention groups were generally lowest in samples that were either air or kiln dried prior to ex-

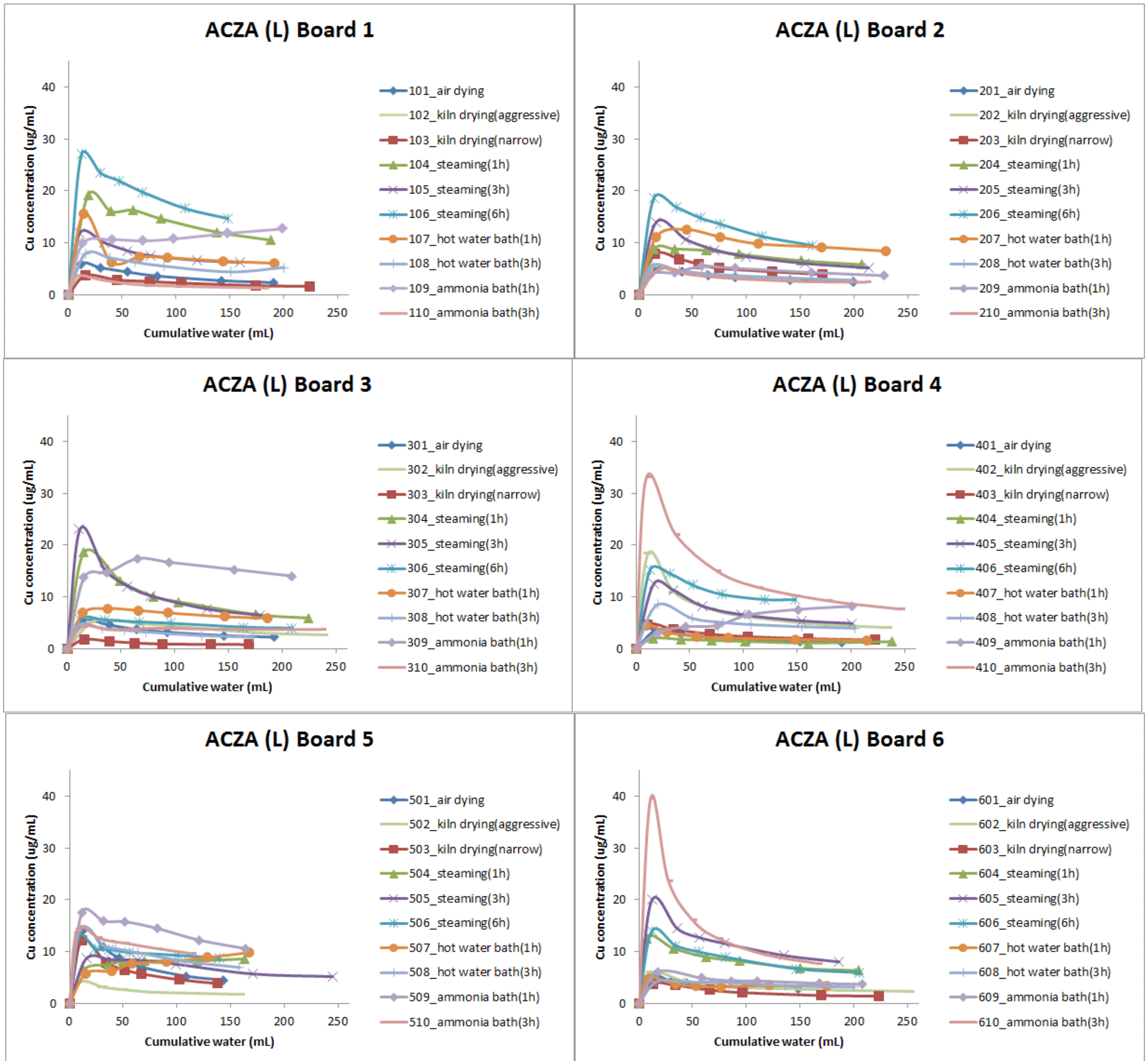

Figure 19 - Copper concentrations in simulated rainfall runoff from Douglas-fir lumber treated with ACZA to a target retention of 4.0 kg/m³ and subjected to one of the BMP procedures. Each figure represents data from a given parent board.

posure, although 1 to 3 hours of immersion in hot water was also associated with lower copper concentrations in the low ACZA retention (4.0 kg/m³) group (Figure 25-26).

Conversely, steaming for 3 or 6 hours was associated with significantly higher copper levels in the 4.0 kg/m³ ACZA retention group (Figures 25, 26). As expected, cumulative copper in the runoff increased over time and BMP treatments varied in controlling the rate of copper release (Figures 27, 28). Air drying and kiln drying groups generally had lower rates of copper release compared with other BMPs. Copper release rates in steamed or ammonia bath groups were generally higher.

Multiple comparison tests of copper concentrations in the runoff after 80 ml or 260 ml of cumulative rainfall exposure were performed using a Least Significant Difference (LSD) test (Table 3). Pairwise comparisons showed that 6 hours of steaming was associated with the highest copper levels with a mean a copper concentrations of 11.8 ug/ml in 80 ml of cumulative rainfall and 10.7 ug/ml in 260 ml of cumulative rainfall, while slow kiln drying was associated with the lowest copper levels with mean copper concentrations of 3.2 ug/ml in 80 ml of cumulative rain-

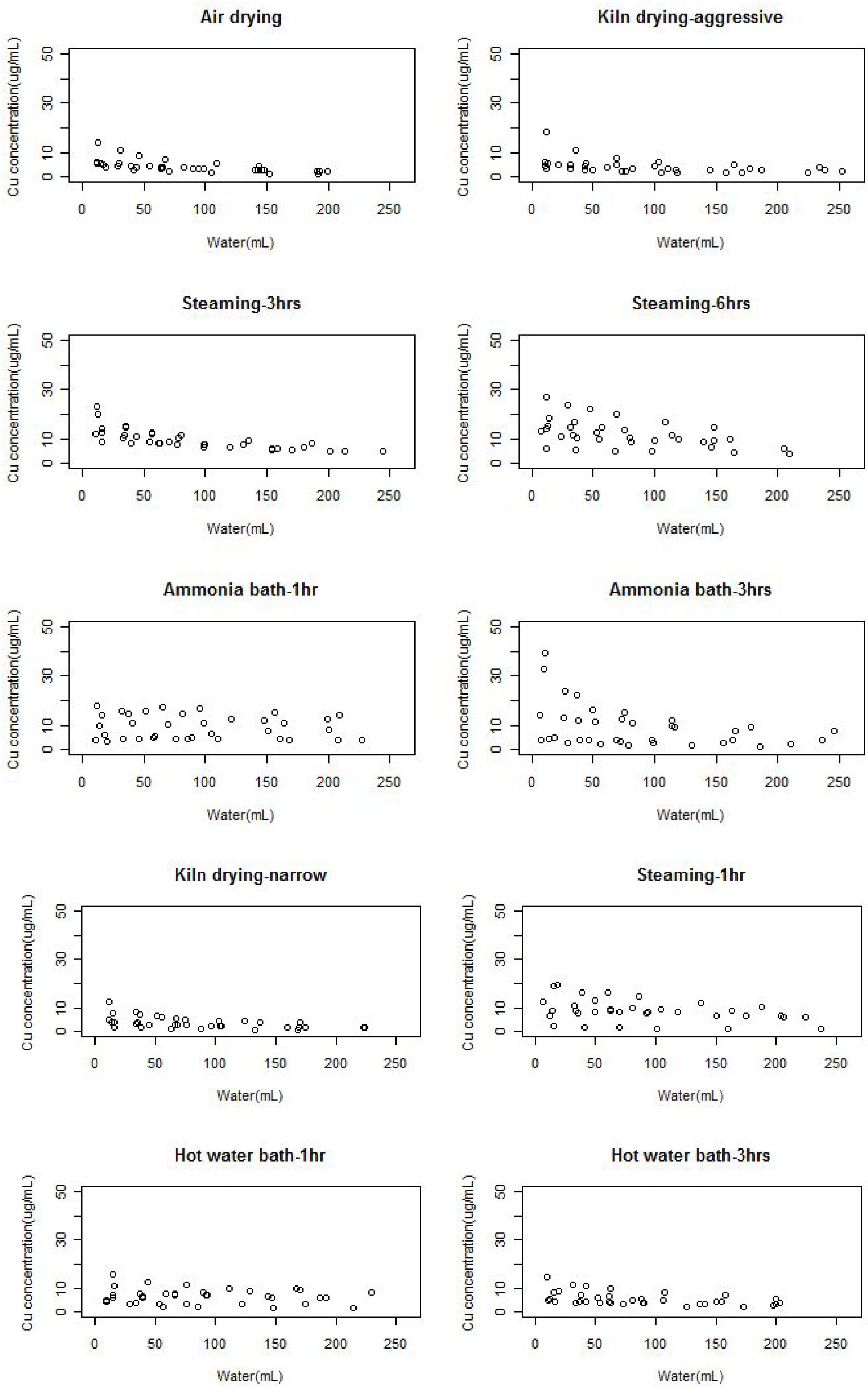

Figure 20 - Copper concentrations in simulated rainfall runoff from Douglas-fir lumber treated with ACZA to a target retention of 4.0 kg/m^3 and subjected to one of the BMP procedures. Each figure represents data from all of the runs for a given BMP process.

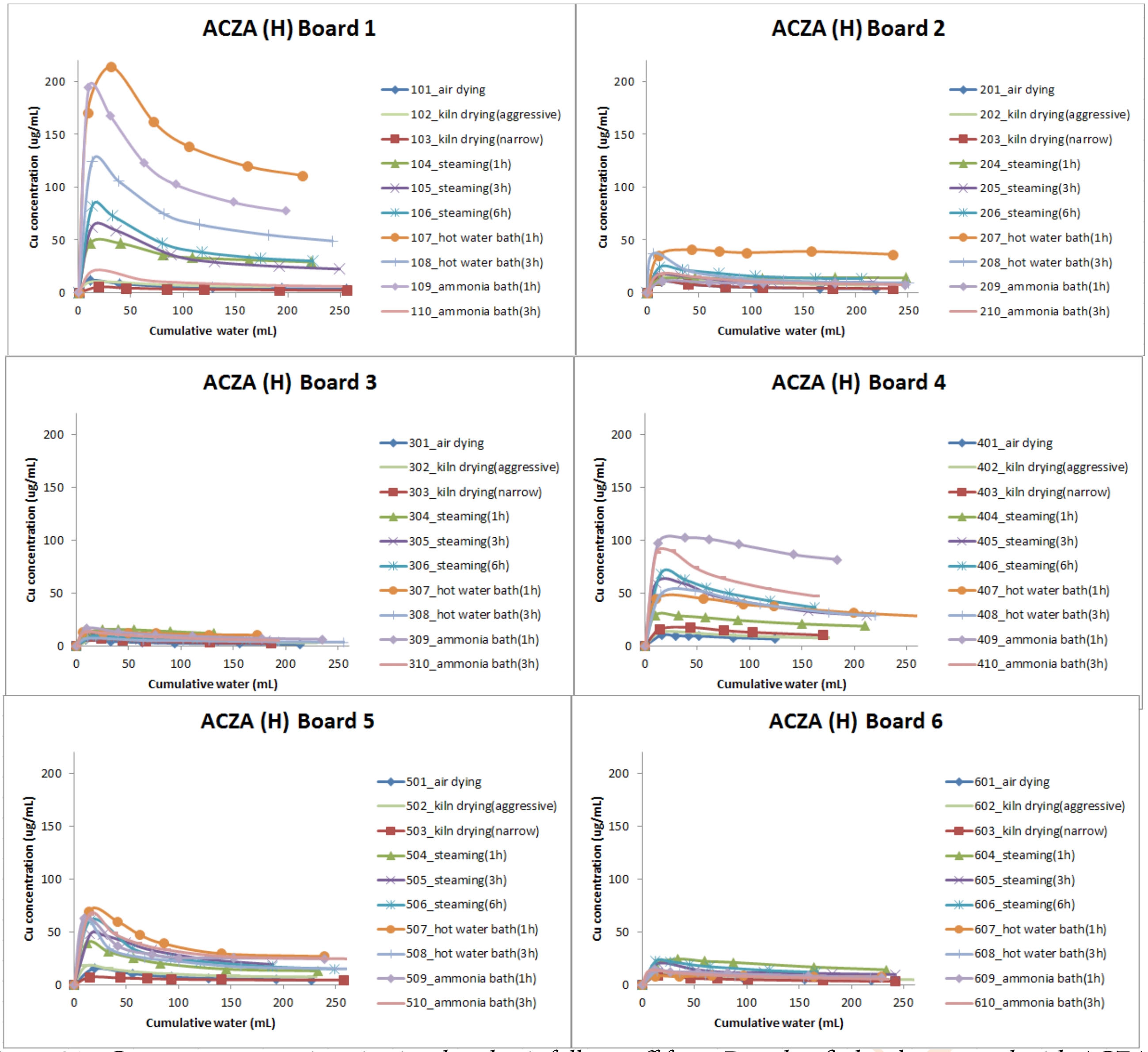

Figure 21 - Copper concentrations in simulated rainfall runoff from Douglas-fir lumber treated with ACZA to a target retention of 6.4 kg/m³ and subjected to one of the BMP procedures. Each figure represents data from a given parent board.

fall and 2.9 ug/ml in 260 ml of cumulative rainfall for the low ACZA retention (4.0 kg/m³) group (Table 3). Copper concentrations in runoff from boards steamed for 1 hour were significantly lower than those from boards subjected to 6 hours of steaming for both durations of water collection. This result suggests that longer exposure to steam may have moved more copper to the wood surface where it was more available for migration. Kiln drying tended to stabilize more copper than steaming or the ammonia bath. Changing the kiln drying cycle from slow drying to rapid drying had no significant effect on copper concentrations in the runoff for both durations of collection. Increasing hot water or ammonia bath time from 1 to 3 hours had no significant effect on copper levels in runoff.

Both air-drying and kiln drying were associated with significantly lower copper levels in the run-off from boards treated with the ACZA high retention (6.4 kg/m³) at both collection times (Table 3). Copper concentrations were less than 11 ug/ml in runoff from both the air and kiln drying groups after 80 ml of rainfall exposure. There were no significant differences in copper concentrations between steaming, hot water or the ammonia bath in the runoff after 80 ml of rainfall exposure. Mean copper concentrations in runoff from boards subjected to the other BMPs

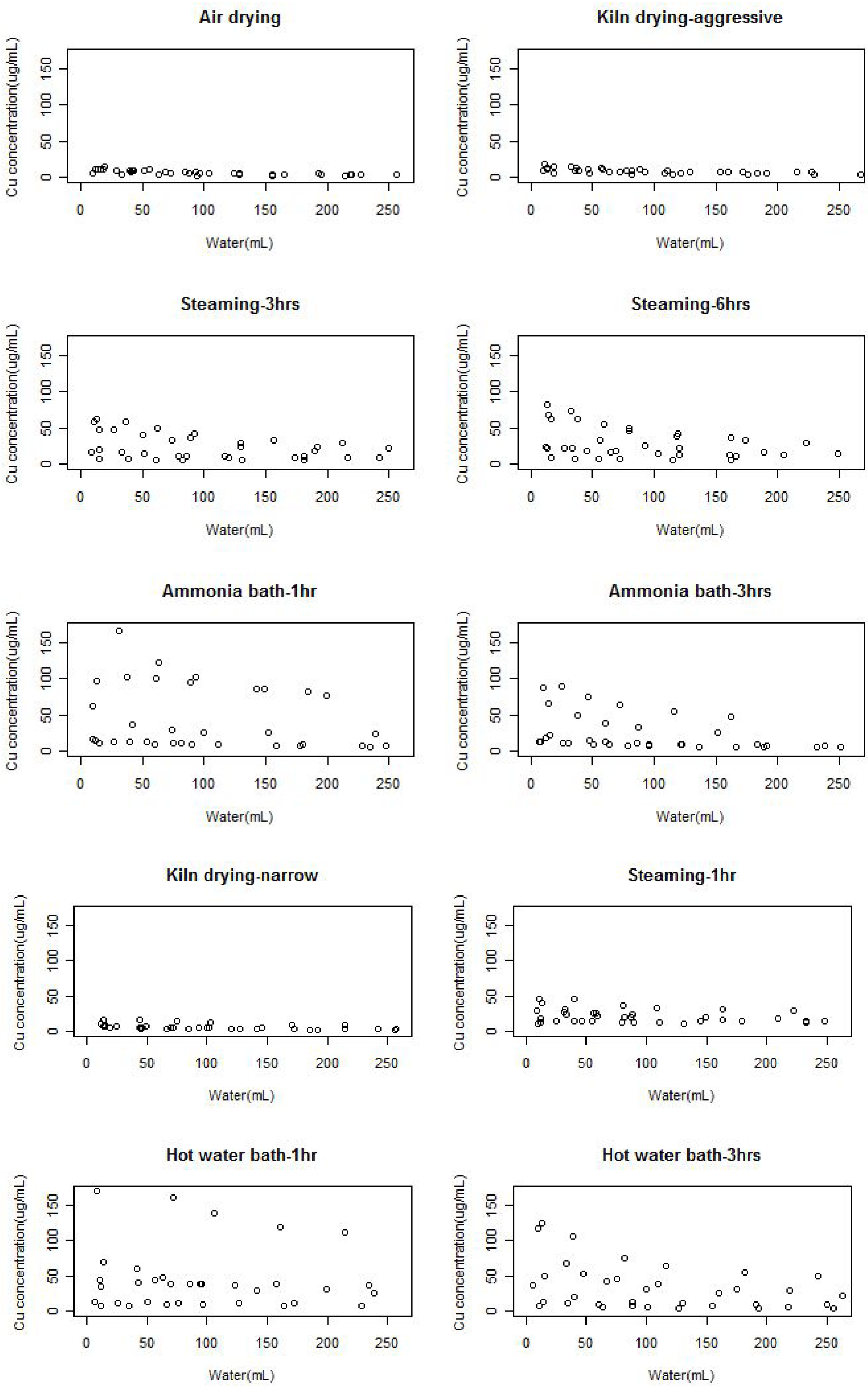

Figure 22 - Copper concentrations in simulated rainfall runoff from Douglas-fir lumber treated with ACZA to a target retention of 6.4 kg/m³ and subjected to one of the BMP procedures. Each figure represents data from all of the runs for a given BMP process.

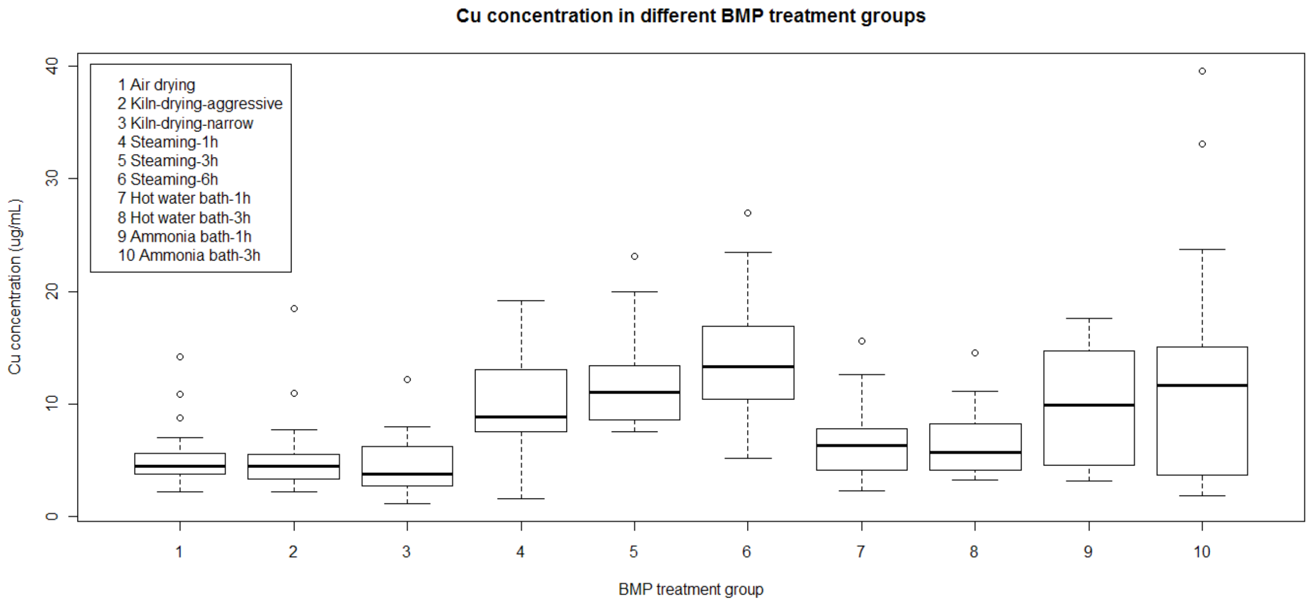

Figure 23- Box and whisker plots showing copper concentrations in first 80 ml (45-60 min of collection) of runoff from Douglas-fir lumber treated with ACZA to a target retention of 4.0 kg/m³ and subjected to one of the BMP procedures.

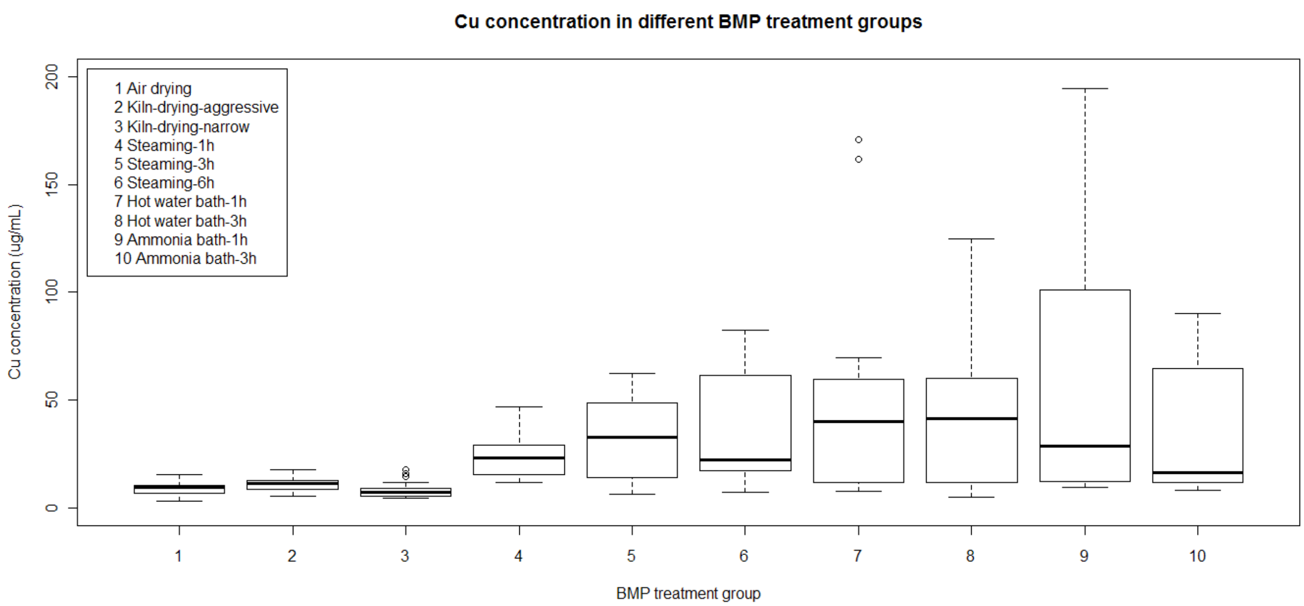

Figure 24- Box and whisker plots showing copper concentrations in the first 80 ml of runoff from Douglas-fir lumber treated with ACZA to a target retention of 6.4 kg/m³ and subjected to one of the BMP procedures.

ranged from 22~35 ug/ml over the first 80 ml of rainfall exposure. Mean copper concentrations after 260 ml of rainfall exposure were highest in the 1 hour hot water bath group (30.9 ug/ml). Copper concentrations in runoff from boards subjected to a 3 hour hot water bath (20.9 ug/ml) were significantly lower than those subjected to a 1 hour hot water bath (30.9 ug/ml). Similarly, copper concentrations in runoff from boards subjected to a 3 hour ammonia bath (26.6 ug/ml) were significantly lower than those subjected to a 1 hour ammonia bath (16.6 ug/ml). Increasing the hot water or ammonia bath time from 1 to 3 hours tended to decrease copper losses, suggesting that prolonged hot water or ammonia exposure led to the formation of more insoluble complexes with copper or that mobile copper was removed by the bath. However, increasing steaming from 1 to 6 hours did not significantly influence copper concentrations in runoff.

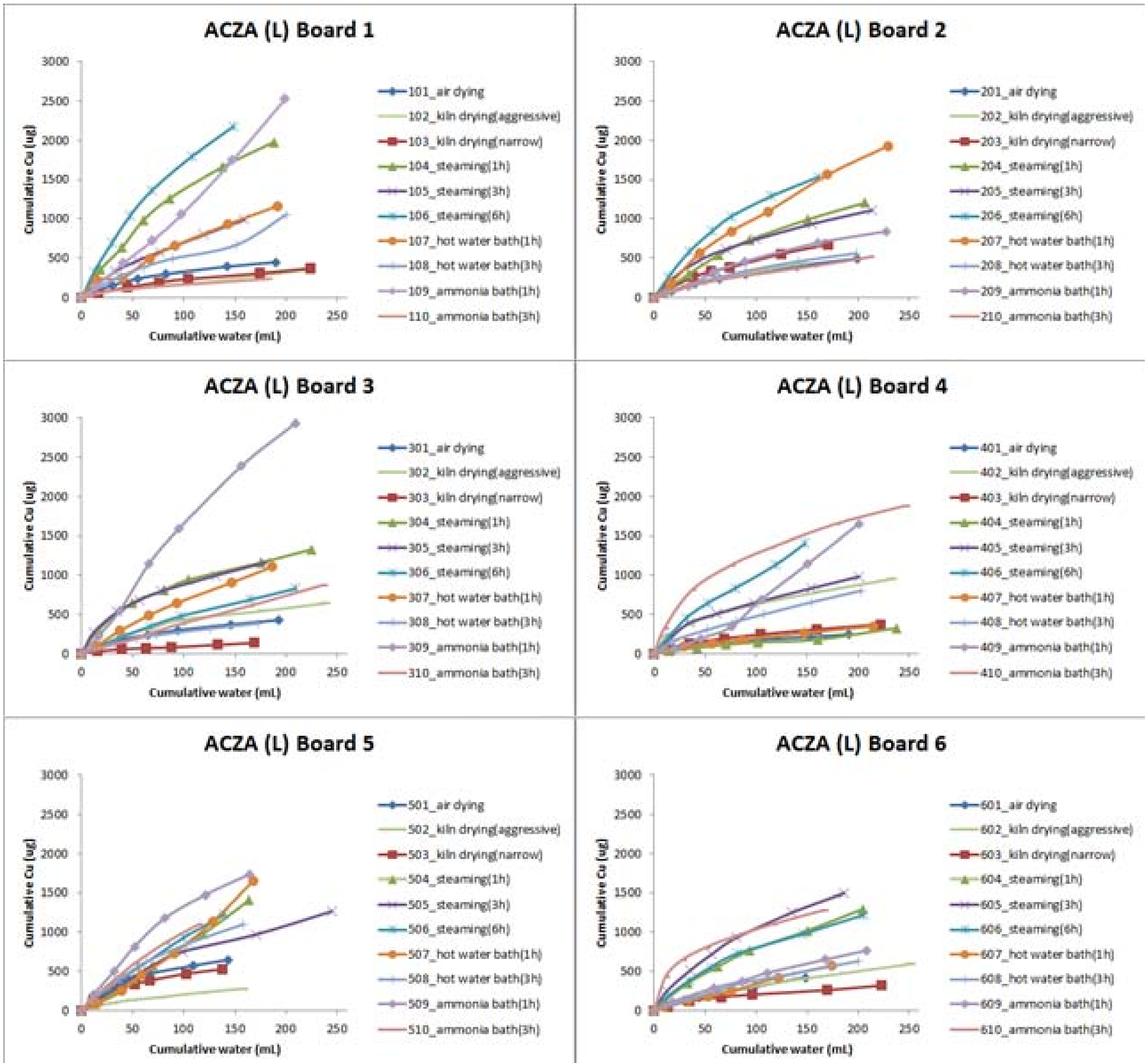

Figure 25 Cumulative copper losses in runoff from Douglas-fir lumber treated with ACZA to a target retention of 4.0 kg/m³ and subjected to one of the BMP procedures. Each figure represents data from a given parent board.

Copper concentrations in runoff from the 6.4 kg/m^3 ACZA retention group were generally higher than those in runoff from samples treated to the low target retention (4.0 kg/m^3) (Figure 12), suggesting the presence of large amounts of non-precipitated copper at higher retentions. This is consistent with previous findings that copper stabilization occurs faster at lower retentions and that higher losses of copper are associated with higher retentions (Ung and Cooper, 2005; Pasek, 2003; Ruddick, 2003). Copper migration initially occurs at or near the wood surface with losses of unfixed copper. More mobile copper is then transported by diffusion from deeper in the wood to the surface as the wood wets and dries, providing a small but steady supply for continued copper migration (Gonzalez, 2007). A comparison of copper concentrations in runoff with actual board retention showed that copper levels increased exponentially with increased copper retention (R^2=0.7365) (Figure 27). These results illustrate the benefits of BMP practices that avoid overtreatment to help minimize metal losses.

Immobilization of ACZA components in wood occurs primarily via evaporation of ammonia coupled with copper reactions with the wood. Ammonia evaporation is time and temperature

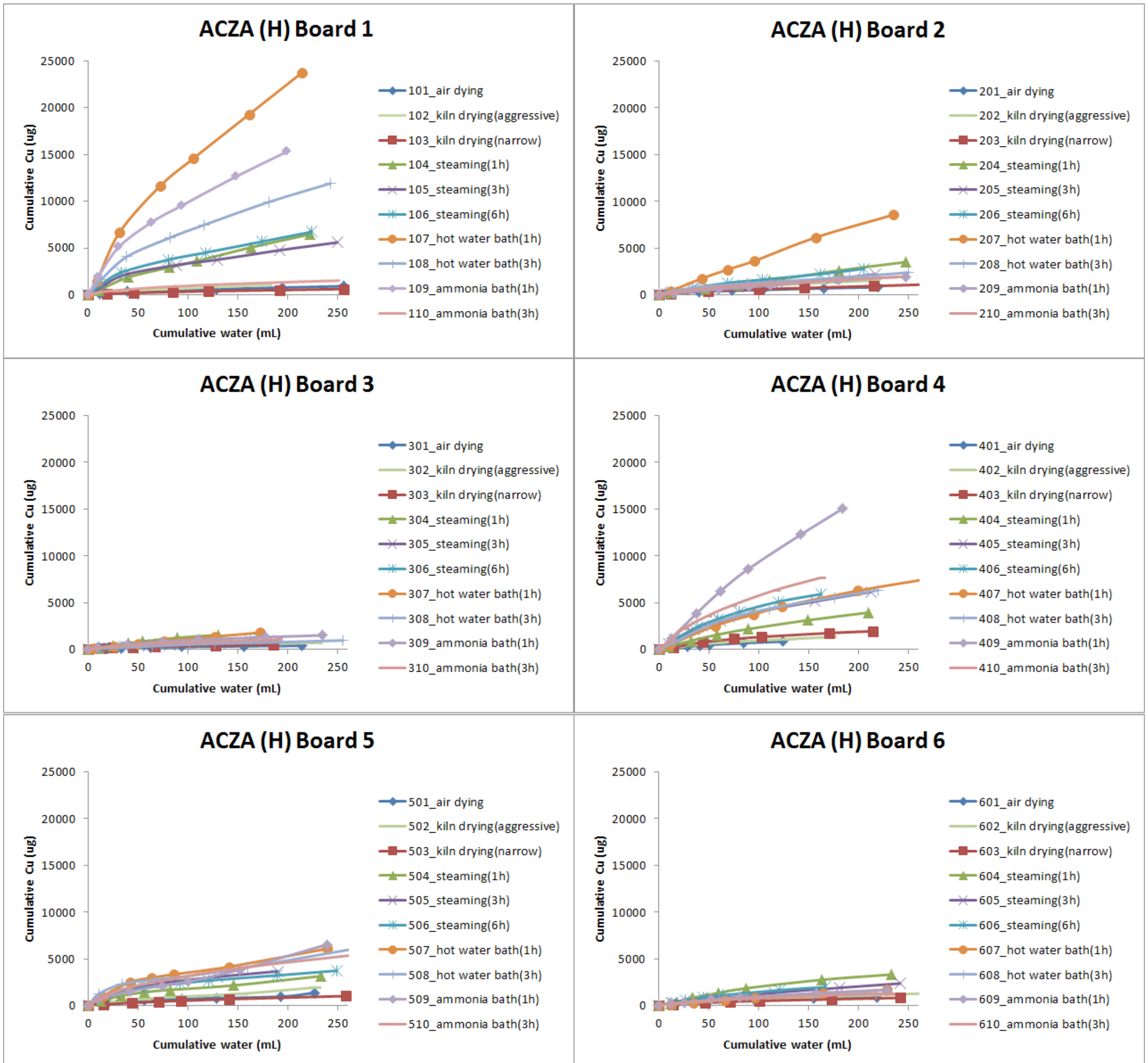

Figure 26- Cumulative copper losses in runoff from Douglas-fir lumber treated with ACZA to a target retention of 6.4 kg/m³ and subjected to one of the BMP procedures. Each figure represents data from a given parent board.

dependent (Copper, 1991; Lebow, 1992) and the BMP treatments affect this process. Except for air drying, all the other BMP treatments accelerate evaporation using some form of heating.

Both air drying and kiln drying had clear effects on copper fixation for both ACZA retentions. This is consistent with previous findings that copper immobilization was most rapid and complete with kiln drying (Kumar et al., 1996). Copper/wood interactions and losses in ammonia to the point where copper (and zinc) was immobilized can occur more completely using these approaches. The other BMP processes, especially steaming of low retention boards or a 1 hour hot water bath of high retention boards, resulted in more mobile copper. The reasons for the differences are unclear. Steaming or hot water bathes should help accelerate ammonia evaporation, but the high moisture environment appeared to slow metal immobilization. It is also possible that all of the reaction sites on the wood surface were occupied by copper or other metals and that steaming or hot water bath moved the additional copper to the wood surface where it was more available for mobilization.

Table 3 Average copper concentrations in runoff from Douglas-fir lumber treated with ACZA to a target retention of 4.0 or 6.4 kg/m3 and exposed to simulated rainfall until 80 ml or 260 ml of cumulative rainfall was collected.

BMP Treatment	Average Copper Concentration in Runoff (ug/ml)			
	$4.0\ kg/m^3$ ACZA		$6.4\ kg/m^3$ ACZA	
	80 ml of Cumulative Rainfall	260 ml Cumulative Rainfall	80 ml of Cumulative Rainfall	260 ml of Cumulative Rainfall
Air-drying	4.9 cde	3.7 ef	8.4 b	6.0 d
Kiln drying (rapid)	3.9 de	3.6 ef	10.7 b	8.3 d
Kiln drying (slow)	3.2 e	2.9 f	7.7 b	5.9 d
1 hr Steaming	6.2 bcd	6.9 bcd	22.2 a	20.5 bc
3 hr Steaming	10.4 ab	8.9 ab	25.1 a	19.2 bc
6 hr Steaming	11.8 a	10.7 a	25.6 a	22.8 abc
1 hr Hot water bath	6.1 bcde	5.7 cd	32.6 a	30.9 a
3 hr Hot water bath	5.9 bcde	5.0 de	30.8 a	20.9 bc
1 hr Ammonia bath	8.1 abc	8.0 abc	34.7 a	26.6 ab
3 hr Ammonia bath	8.0 abc	6.4 bcd	24.0 a	16.6 c

a values followed by the same letter(s) do not differ significantly from one another by a Least Significant Difference test at α=0.05 with a Holm adjustment.

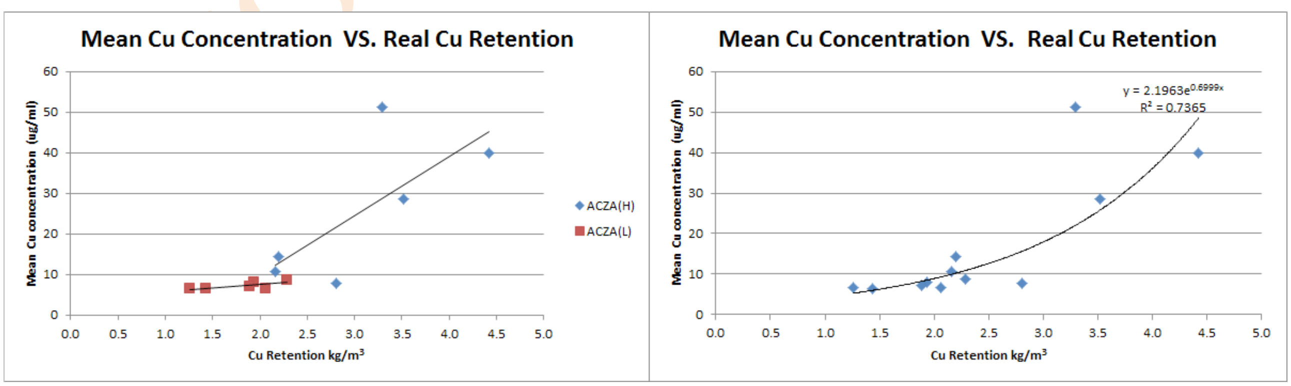

Figure 27 Relationship between actual copper retention in a board and mean copper concentration in 260 ml of simulated rainfall runoff from Douglas-fir lumber treated with ACZA to target retentions of 4.0 kg/m³ or 6.4 kg/m³. Retentions only considered the copper levels in the system.

Effects of BMPs on fixation of copper in CA treated wood: BMP processes varied in their ability to limit metal losses from CA treated boards. Copper concentrations tended to be highest in the first two or three water collections, and then declined with continued rainfall (Figures 28-31). These results were similar to those found with ACZA. Copper concentrations tended to decrease with continued rainfall exposure and generally reached a steady state after boards were subjected to 120 ml of rainfall (Figures 28, 30). Copper concentrations in both CA retention groups were generally lowest in samples that were hot water or ammonia bath treated prior to rainfall exposure. Conversely, steaming or rapid kiln drying were associated with higher

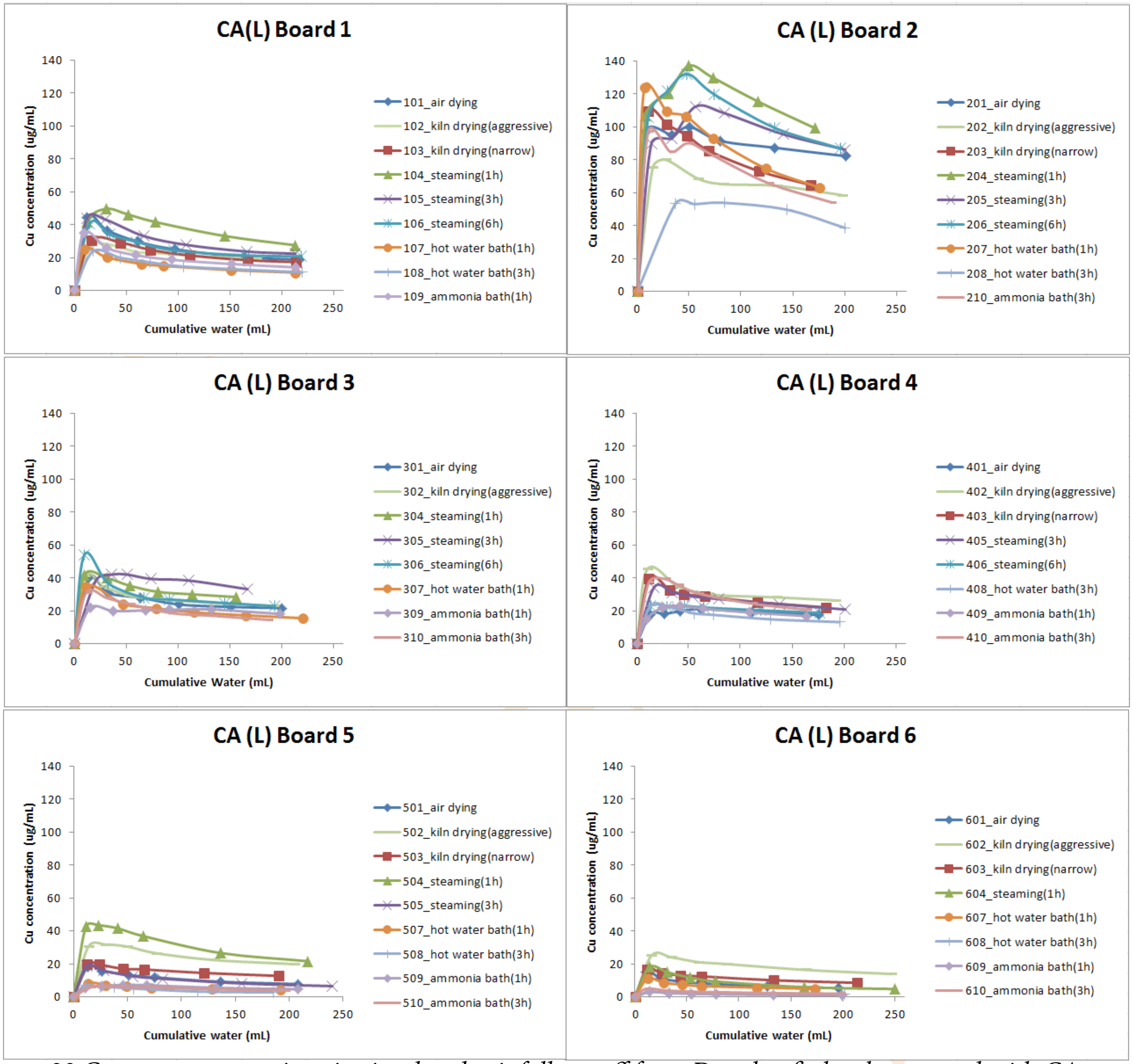

Figure 28 Copper concentrations in simulated rainfall runoff from Douglas-fir lumber treated with CA to a target retention of 0.96 kg/m³ and subjected to one of the BMP procedures. Each figure represents data from a given parent board.

copper concentrations in runoff from both CA retention groups (Figures 32-33). As expected, cumulative copper releases increased with cumulative water and the BMP treatments varied in controlling the rate of copper release (Figures 34-35).

Multiple comparison tests to investigate the effects of BMPs on copper losses from boards treated with CA after 80 ml or 260 ml of rainfall exposure were performed using a Least Significant Difference (LSD) test (Table 4). Pairwise comparisons for the low CA retention showed that 6 hours of steaming was associated with the highest copper losses with mean copper concentrations of 44.5 ug/ml after 80 ml of rainfall exposure and 37.6 ug/ml after 260 ml of rainfall exposure. However, reducing steaming time from 6 hours to 1 hour had no significant influence on copper concentrations in runoff. It appeared that instead of accelerating copper precipitation, steaming moved copper to the wood surface where it was more available for leaching. Copper levels in the runoff from a 3 hour hot water bath or a 1 hour ammonia bath were associated with significantly lower copper levels in both collection periods for the low CA

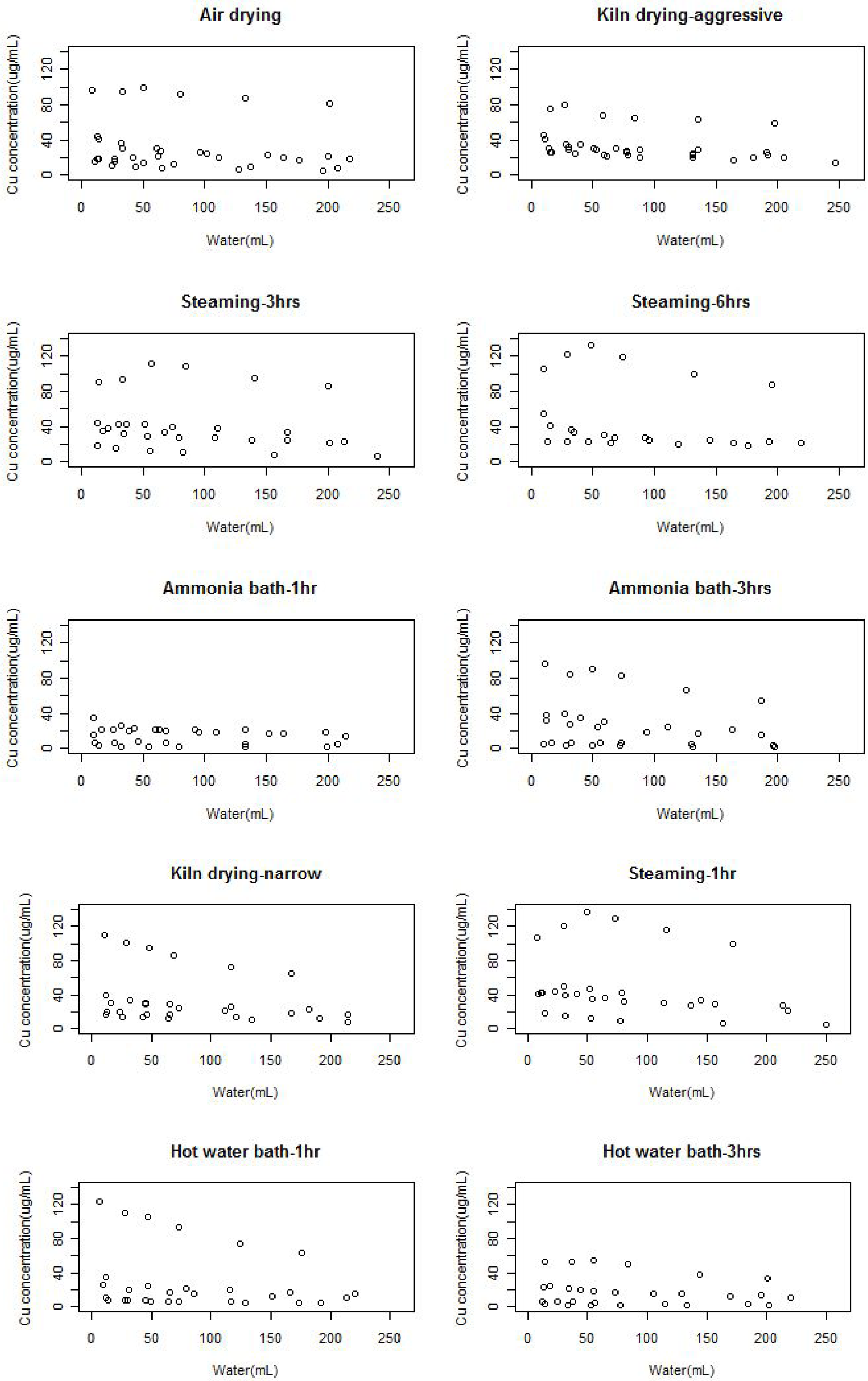

Figure 29 Copper concentrations in simulated rainfall runoff from Douglas-fir lumber treated with CA to a target retention of 0.96 kg/m^3 and subjected to one of the BMP procedures. Each figure represents data from all of the runs for a given BMP process.

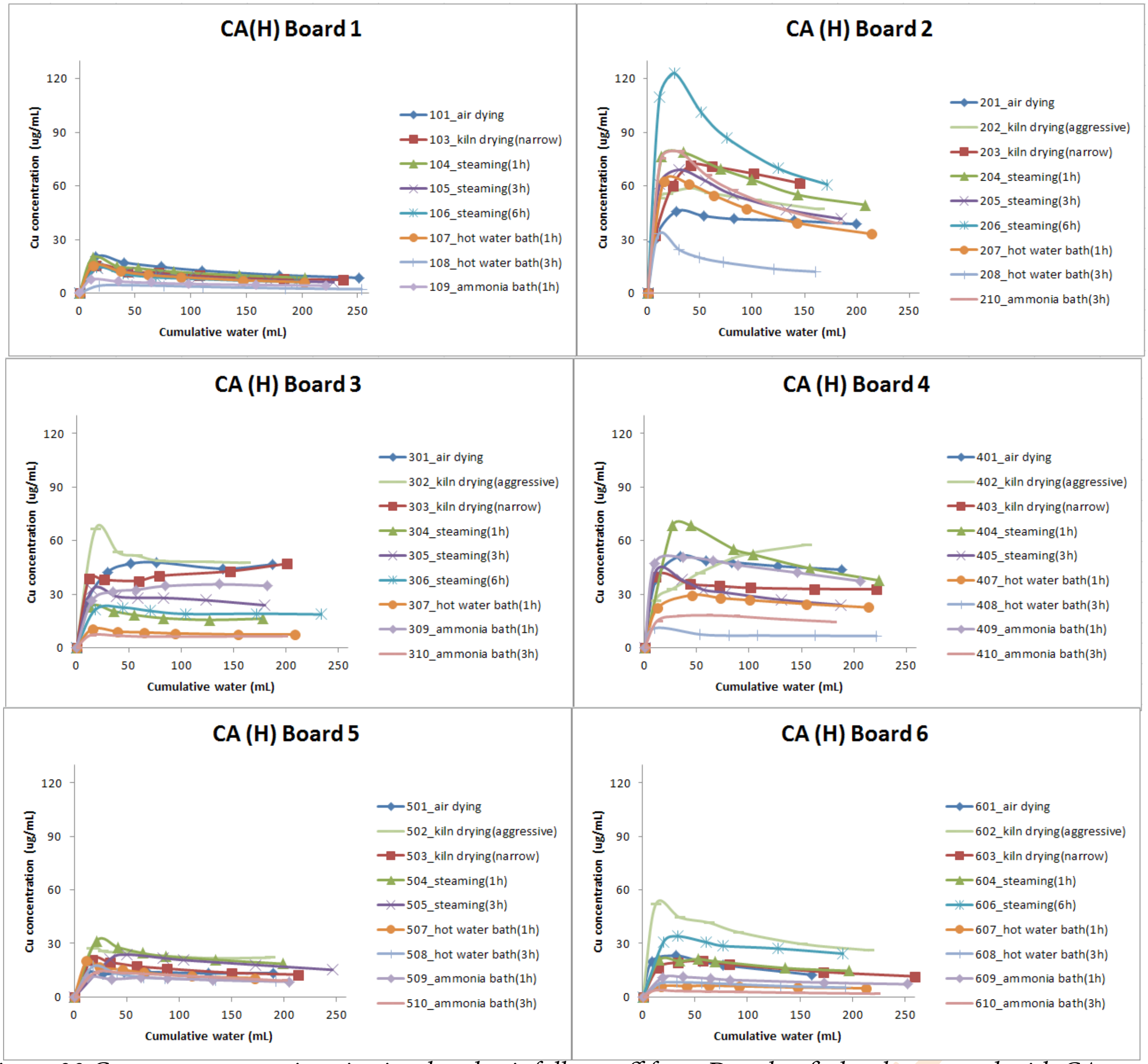

Figure 30 Copper concentrations in simulated rainfall runoff from Douglas-fir lumber treated with CA to a target retention of 2.4 kg/m³ and subjected to one of the BMP procedures. Each figure represents data from a given parent board.

retention (0.96 kg/m³) group (Table 4). Increasing hot water bath time from 1 to 3 hours significantly reduced copper concentrations in runoff in both collection periods. This was consistent with the previous studies showing that copper migration stabilized much faster during hot water exposure and the process was highly dependent on temperature and duration (Yu et al., 2009). Conversely, increasing ammonia bath time from 1 to 3 hours was associated with significantly higher copper concentrations in runoff in both collection periods. It appeared that the higher pH environment tended to help precipitate copper more quickly. However, prolonged ammonia bathes tended to have a negative effect on copper fixation, possibly because the ammonia enhanced copper movement to the wood surface where it was more available for leaching. Air or kiln drying produced the next lowest copper immobilization, followed by steaming (Table 4). There were no significant differences in copper concentrations between the two kiln dying cycles over both collection periods.

The 3 hour hot water treatment was associated with the lowest copper losses in the high CA retention (2.4 kg/m³) group with mean copper concentrations of 10.3 ug/ml after 80 ml of rainfall exposure and 8.3 ug/ml after 260 ml of rainfall exposure. Boards subjected to a 3 hour

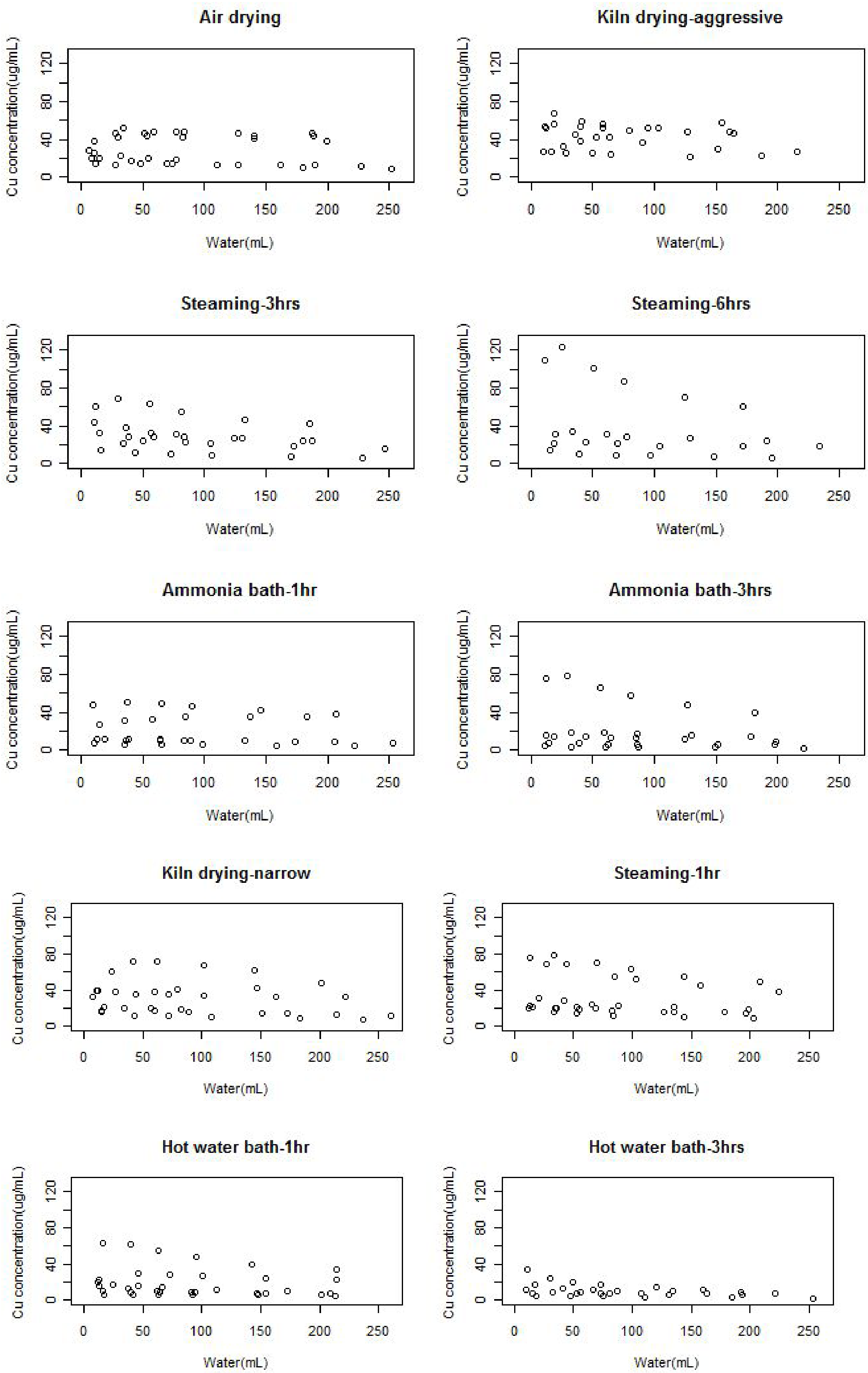

Figure 31 Copper concentrations in simulated rainfall runoff from Douglas-fir lumber treated with CA to a target retention of 2.4 kg/m³ and subjected to one of the BMP procedures. Each figure represents data from all of the runs for a given BMP process.

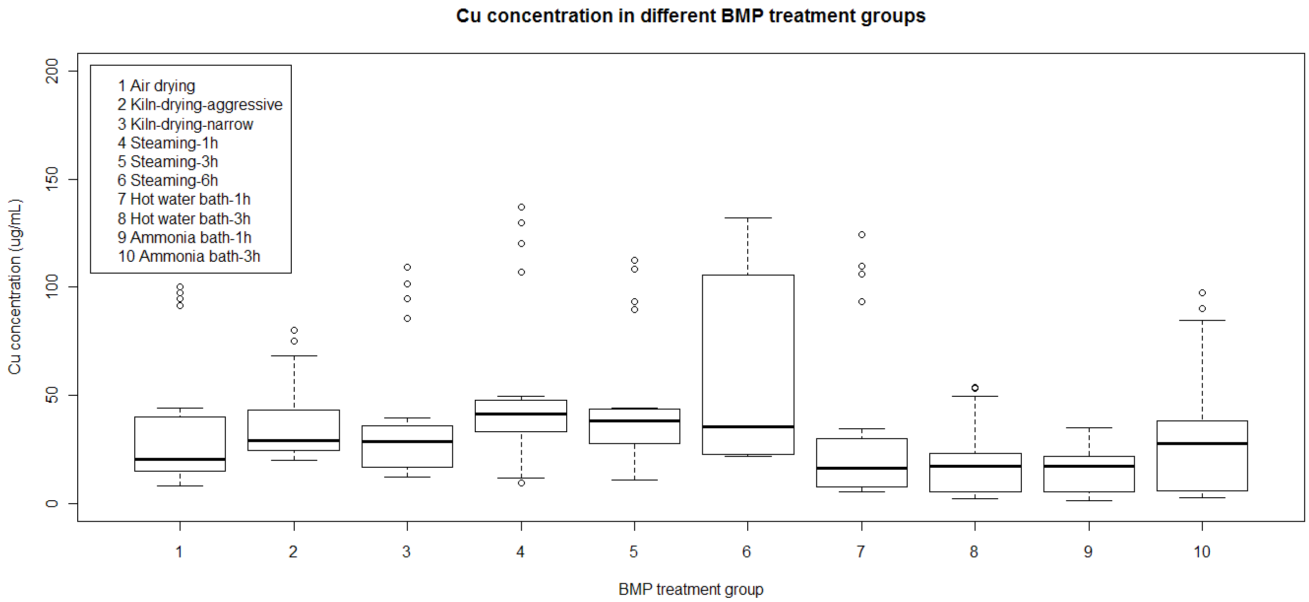

Figure 32 Box and whisker plots showing copper concentrations in the first 80 ml of runoff from Douglas-fir lumber treated with CA to a target retention of 0.96 kg/m³ and subjected to one of the BMP procedures.

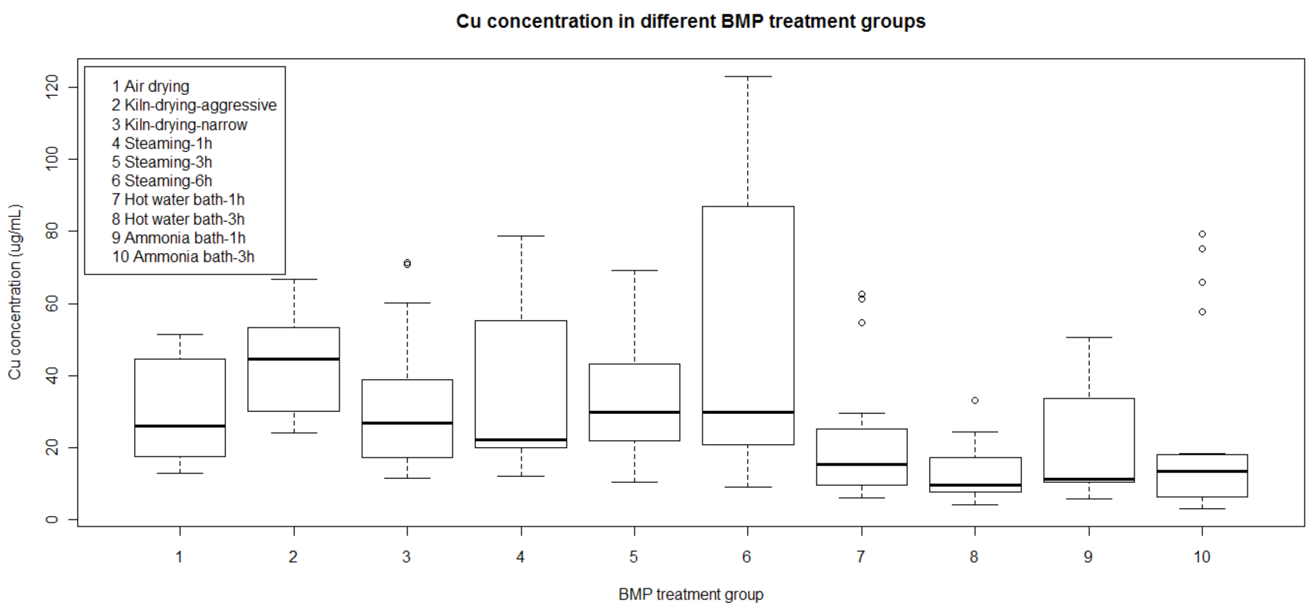

Figure 33 Box and whisker plots showing copper concentrations in 80 ml of runoff from Douglas-fir lumber treated with CA to a target retention of 2.4 kg/m³ and subjected to one of the BMP procedures.

ammonia bath, a 1 hour hot water bath or a 1 hour ammonia bath also had lower copper levels than the other BMP treatments at both collection times (Table 5). Copper losses from boards subjected to rapid kiln drying were significantly higher than those from boards air-seasoned prior to rainfall exposure after 80 ml or 260 ml of rainfall exposure. Reducing the rate of kiln drying was associated with significantly lower copper concentrations after 260 ml of rainfall exposure. Increasing steaming time from 1 to 3 or 6 hours had no significant effect on copper concentrations at either collection period. Increasing the hot water bath from 1 to 3 hours was associated with significantly lower copper concentrations after 260 ml of rainfall exposure, suggesting that added hot water exposure led to more complete copper complexation. This effect was similar to that found with the CA low retention (0.96 kg/m³) group. However, increasing ammonia bath time from 1 to 3 hours had no significant effect on copper concentrations in

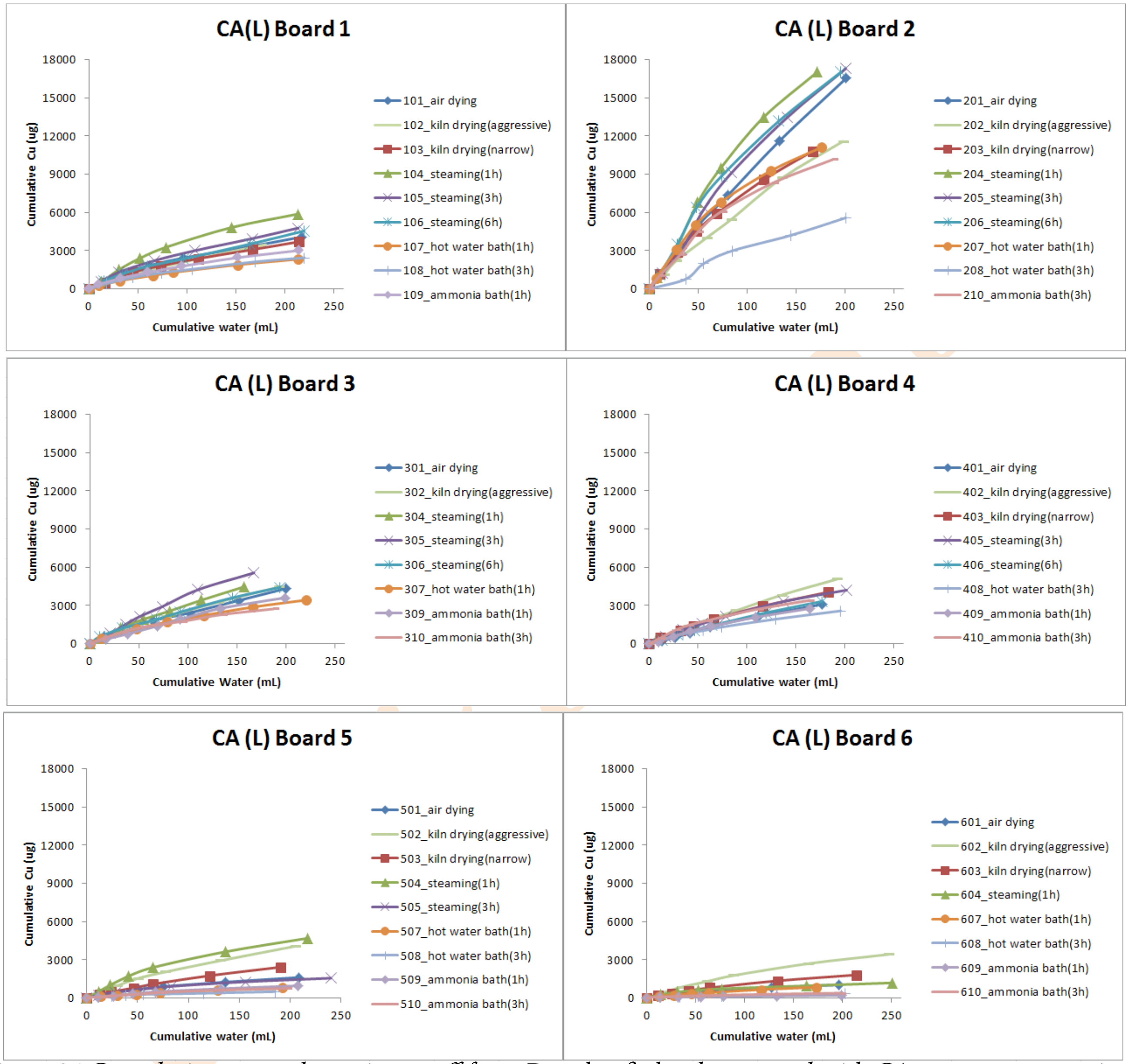

Figure 34 Cumulative copper losses in runoff from Douglas-fir lumber treated with CA to a target retention of 0.96 kg/m³ and subjected to one of the BMP procedures. Each figure represents data from a given parent board.

runoff at either collection period.

A comparison between copper concentrations in the runoff and actual board retentions showed no clear relationship with retention (R^2 = 0.2057) (Figure 36). Copper in the runoff from one board (Board 2) in the CA low retention (0.96 kg/m³) group was abnormally higher (91.1 ug/ml) than those from the other boards. The retentions were determined at 2 mm intervals from the surface were tested on three boards including the board associated with higher copper level to determine if elevated surface retentions could explain this variation (Table 5). However, there were no significant differences in retention in the outer 2 mm of the boards examined. The density of the board associated with higher copper losses was lower (412 kg/m³) than the other 5 boards treated with CA to the low target retention (Table 6) and this may have reduced copper bonding sites, leading to more copper being available for migration. The highest copper losses (55.3 ug/ml) in the CA high retention group (2.4 kg/m³) occurred in a board with the lowest density (432 kg/m³) which was consistent with the earlier observations (Figure 36; Table 6).

Copper stabilization is generally slower in wood treated with copper-amine systems than in

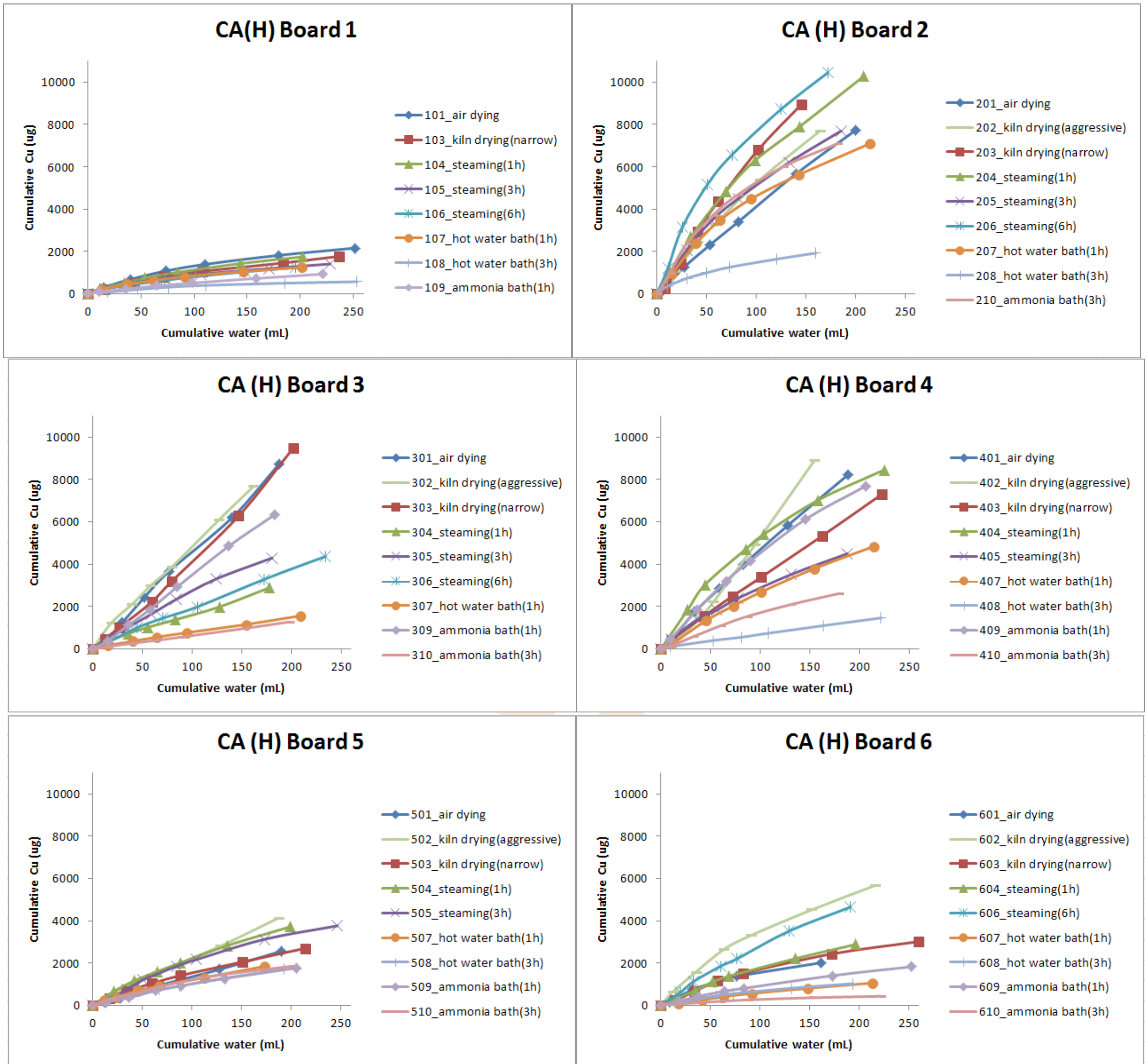

Figure 35 Cumulative copper losses in runoff from Douglas-fir lumber treated with CA to a target retention of 2.4 kg/m³ and subjected to one of the BMP procedures. Each figure represents data from a given parent board.

acidic systems. The relatively high proportion of copper in CA and the limited reaction sites in wood generally results in higher copper leaching (Dickey, 2003). Copper stabilization occurs primarily via copper reactions with acid groups in wood by neutralization of the amine, followed precipitation of the remaining copper (Jiang, 2000). The reaction is highly time and temperature dependent (Yu et al., 2009). Copper fixation on boards that were air seasoned, steamed or kiln dried prior to simulated rainfall exposure appeared to be less complete than on those that were soaked in hot water or ammonia. The high pH of the ammonia bath appeared to promote reactions with copper, possibly by enhancing the exchangability of phenolic protons in wood (Jiang, 2000). However, soaking wood in hot water or ammonia water might have also increased copper losses from the wood surface into the water, resulting in low copper levels. This would be similar to the results found with the pre-leached ACQ treated SPF decks.

Effects of BMPs on fixation of copper in ACQ (6.4 kg/m³) treated wood: BMP processes varied in their ability to limit metal losses from wood treated with ACQ to a target retention of 6.4 kg/m³ (Figures 37-38). Copper concentrations tended to be highest in the first two or three water

Table 4 - Average copper concentrations in runoff from Douglas-fir lumber treated with CA to a target retention of 0.96 or 2.4 kg/m3 and exposed to simulated rainfall until 80 ml or 260 ml of cumulative rainfall was collected.

BMP Treatment	Average Copper Concentration in Runoff (ug/ml)			
	80 ml of Cumulative Rainfall		80 ml of Cumulative Rainfall	
	24.3 cd	22.7 c	25.6 bc	24.7 b
Kiln drying (rapid)	33.2 abc	31.1 ab	41.2 a	39.9 a
Kiln drying (slow)	29.7 bc	26.0 bc	28.3 ab	24.8 b
1 hr Steaming	41.0 ab	34.9 a	29.4 ab	26.6 b
3 hr Steaming	37.1 ab	32.5 ab	29.2 ab	24.6 b
6 hr Steaming	44.5 a	37.6 a	32.5 ab	26.1 b
1 hr Hot water bath	19.6 d	16.7 d	16.3 cd	14.3 c
3 hr Hot water bath	11.2 e	10.5 e	10.3 d	8.3 d
1 hr Ammonia bath	10.0 e	9.6 e	16.2 cd	15.0 c
3 hr Ammonia bath	17.6 d	15.2 d	25.6 bc	24.7 b

a values followed by the same letter(s) do not differ significantly from one another by a Least Significant Difference test at α=0.05 with a Holm adjustment.

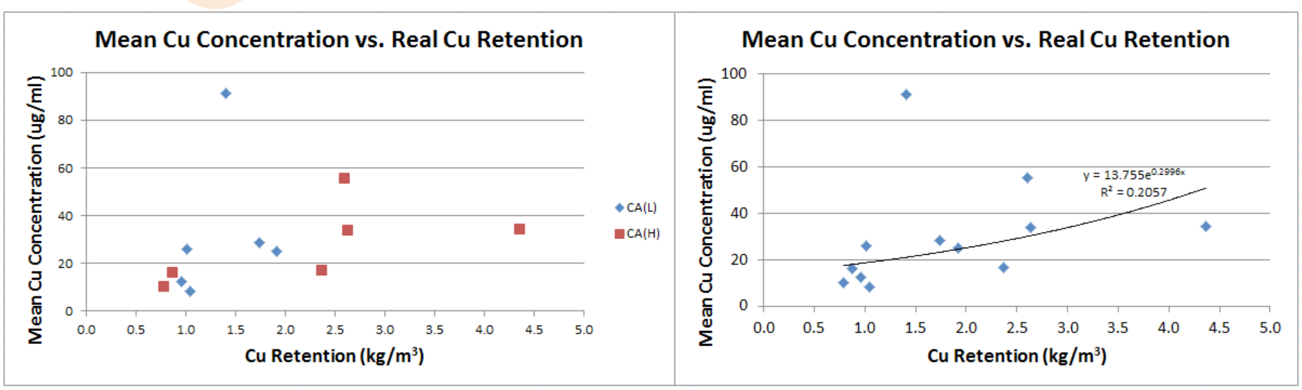

Figure 36 - Relationship between actual copper retention in a board and mean copper concentration in 260 ml of simulated rainfall runoff from Douglas-fir lumber treated with CA to target retentions of 0.96 kg/m³ or 2.4 kg/m³. Retentions only considered the copper levels in the system.

collections. Copper concentrations tended to decrease with continued rainfall and generally became steady after boards were subjected to 220 ml of rainfall (Figure 37). These results were similar to those found with ACZA or CA. Copper concentrations tended to be higher in samples that were steamed for 6 hours prior to simulated rainfall exposure and the variation of the

Table 5 Copper retentions at 2 mm increments from the surface of boards treated with CA to a target retention of 0.96 kg/m^3.

Depth(mm)	Board #	Copper (%)	Density(kg/m^3)	Cu retention (kg/m^3)
2	2	1.558	412	6.42
2	4	1.154	451	5.2
2	5	1.33	596	7.921
4	2	0.833	412	3.432
4	4	0.533	451	2.402
4	5	0.521	596	3.101
6	2	0.355	412	1.465
6	4	0.293	451	1.322
6	5	0.198	596	1.179

Table 6 Densities of boards treated with ACZA, CA or ACQ to target retentions (at approximate 19% moisture content).

Board #	Density (kg/m^3)				
	ACZA (4.0 kg/m^3)	ACZA (6.4kg/m^3)	CA (0.96 kg/m^3)	CA (2.4 kg/m^3)	ACQ (6.4 kg/m^3)
1	526	558	544	498	555
2	459	532	412	432	494
3	531	655	527	442	496
4	558	589	451	602	410
5	474	673	596	447	
6	473	586	499	516	

copper concentrations was large for samples that were steamed for 3 hours (Figures 38-39). The amount of copper in runoff tended to increase steadily with cumulative water regardless of the BMP treatment employed, but there were differences between treatments (Figure 40).

Multiple comparison tests investigated the effects of BMPs on copper losses from boards treated with ACQ to a target retention of 6.4 kg/m^3 after 80 ml or 260 ml of rainfall exposure were performed using a Least Significant Difference (LSD) test (Table 7). Steaming for 3 hours was associated with the highest copper losses with mean copper concentrations of 35.5 ug/ml in runoff after 80 ml of rainfall exposure and 22.9 ug/ml after 260 ml of rainfall exposure. Copper levels in runoff from boards subjected to a 1 or 3 hour ammonia bath (11.1 ug/ml and 12.6 ug/ml) were significantly lower than those from boards steamed for 3 hours prior to rainfall exposure, suggesting that the ammonia bath may have immobilized more copper in the wood than 3 hours of steaming. Increasing ammonia bath time from 1 to 3 hours had no significant effect on copper concentrations. There were no significant differences in copper concentrations after 80 ml of rainfall exposure among boards that were air seasoned, kiln dried, bathed in hot water or steamed regardless of the duration of treatment.

Boards that were steamed for 3 hours were still associated with the highest copper losses after 260 ml of rainfall with mean a copper concentration of 22.9 ug/ml in runoff (Table 7). Runoff from boards subjected to a 3 hour hot water bath or a 1 hour ammonia bath were associated with significantly lower mean copper concentrations than most of the other treatments except a 3 hour ammonia bath, although increasing ammonia bath time had no significant effect on copper levels. Increasing steaming time or changing kiln drying cycle had no significant effect on mean copper concentrations in the runoff. Increasing the hot water bath time from 1 to 3 hours was associated with significantly lower mean copper concentrations (18.4 ug/ml to 9.3 ug/ml) after 260 ml of rainfall exposure. This was similar to the results from previous studies on ACQ showing that hot water post-treatment helped stabilize copper and prolonged hot water exposure accelerated this process (Yu et al., 2009).

ACQ contains 67% copper oxide while ACZA contains 50% copper oxide. As a result, copper losses should be higher from ACQ treated wood. Similarly, CA contains more copper than ACQ. ACQ and CA systems used for these trials contained both ammonia and ethanolamine and copper stabilization and migration patterns should be similar. As expected, hot water and the ammonia bath seemed to have similar effects on copper in these systems. Copper-amine fixation mostly relies on the reaction between amine-copper and acid groups in wood (Jiang, 2000). It is possible that the hot water or the high pH environment helped move the amine solubilized copper deeper into the wood where there were more sites for reaction. However, steaming had a negative effect on copper that was similar to that found in the CA low retention group.

The results indicated that each BMP/preservative combination produced unique results. If we use air-seasoning as the baseline for migration, then almost all BMP's resulted in higher metal levels in runoff except for kiln drying and a 3 hour hot water bath for the low retention and the kiln drying processes at the high retention. Results were variable with CA, where fast kiln drying was associated with higher copper losses than air seasoning while the slower kiln drying process produced similar levels at either retention. Exposing wood to hot water bath or an ammonia bath resulted in much lower metal losses than air-seasoning. Finally, application of BMP processes to ACQ treated lumber produced similar results regardless of method.

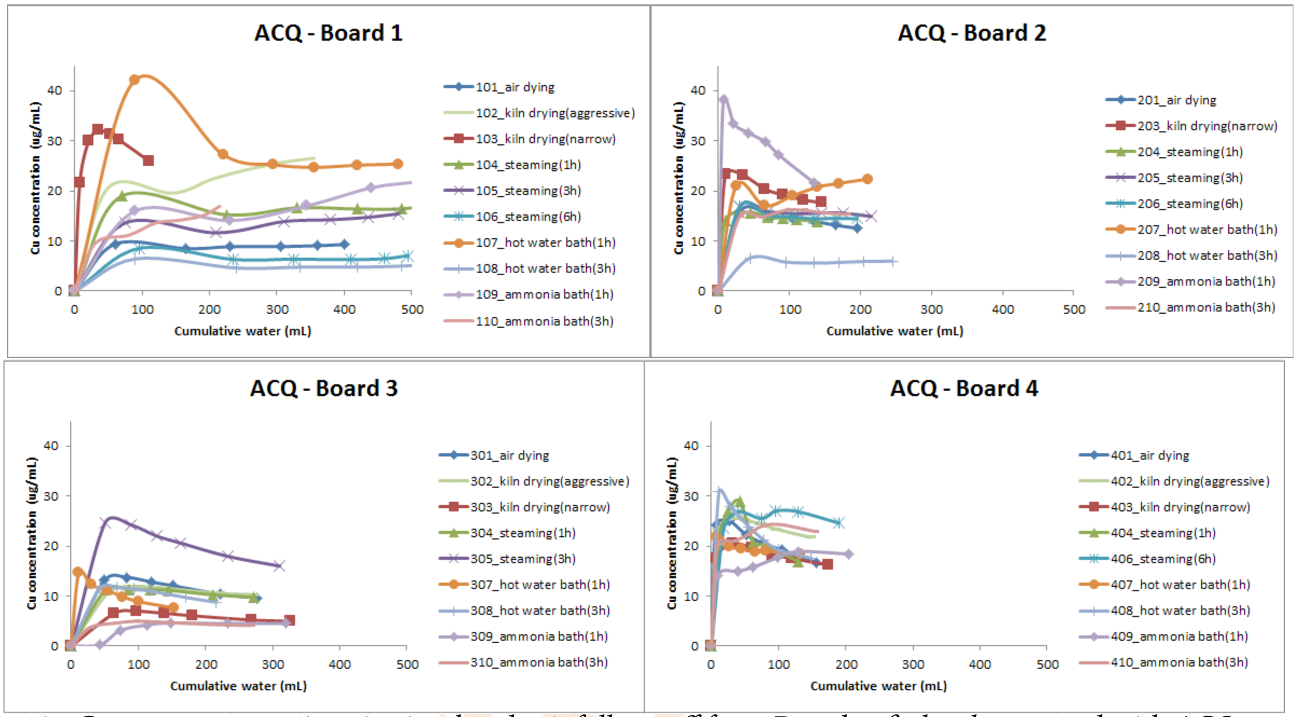

Figure 37 Copper concentrations in simulated rainfall runoff from Douglas-fir lumber treated with ACQ to a target retention of 6.4 kg/m^3 and subjected to one of the BMP procedures. Each figure represents data from a given parent board.

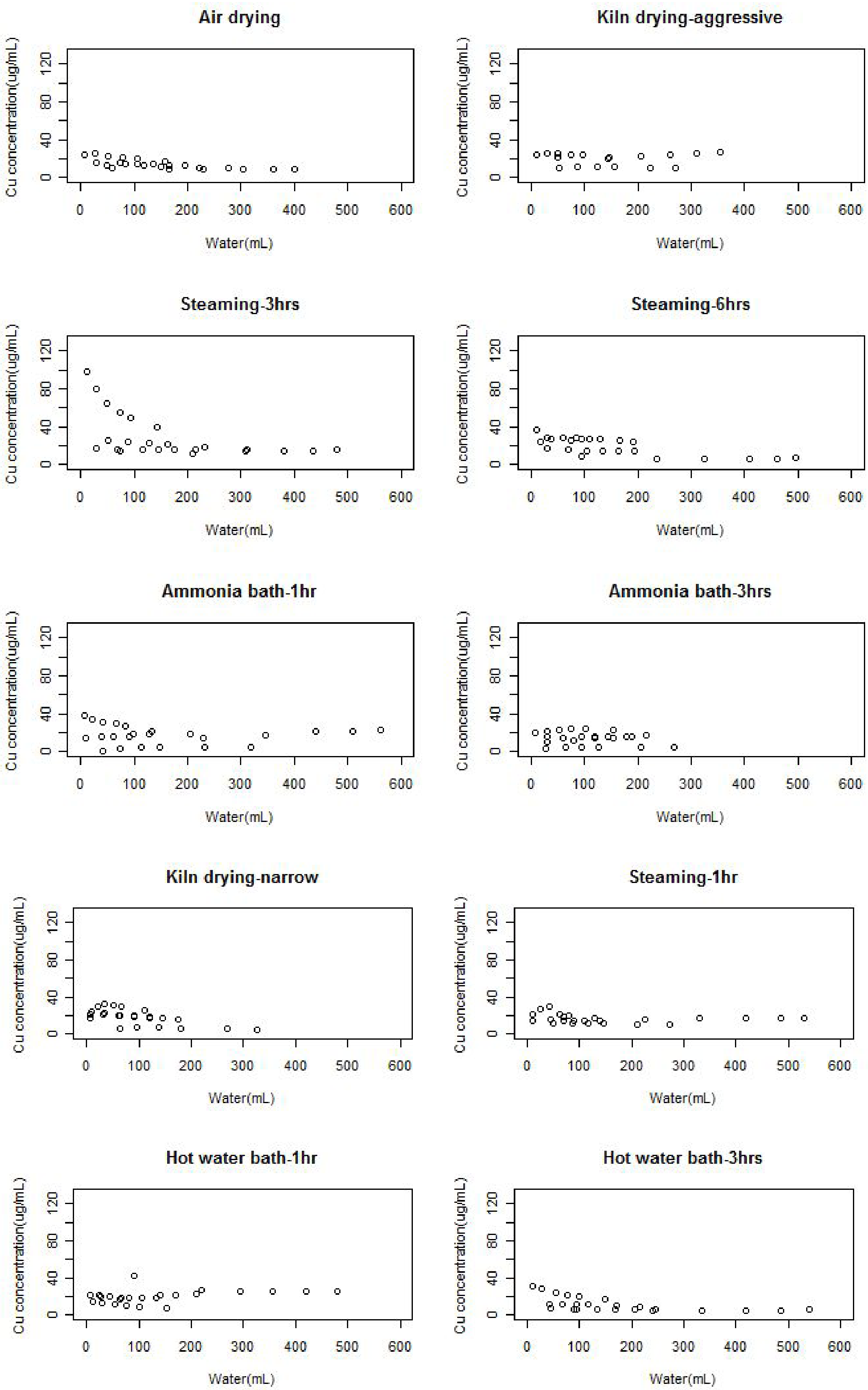

Figure 38 Copper concentrations in simulated rainfall runoff from Douglas-fir lumber treated with ACQ to a target retention of 6.4 kg/m^3 and subjected to one of the BMP procedures. Each figure represents data from all of the runs for a given BMP process.

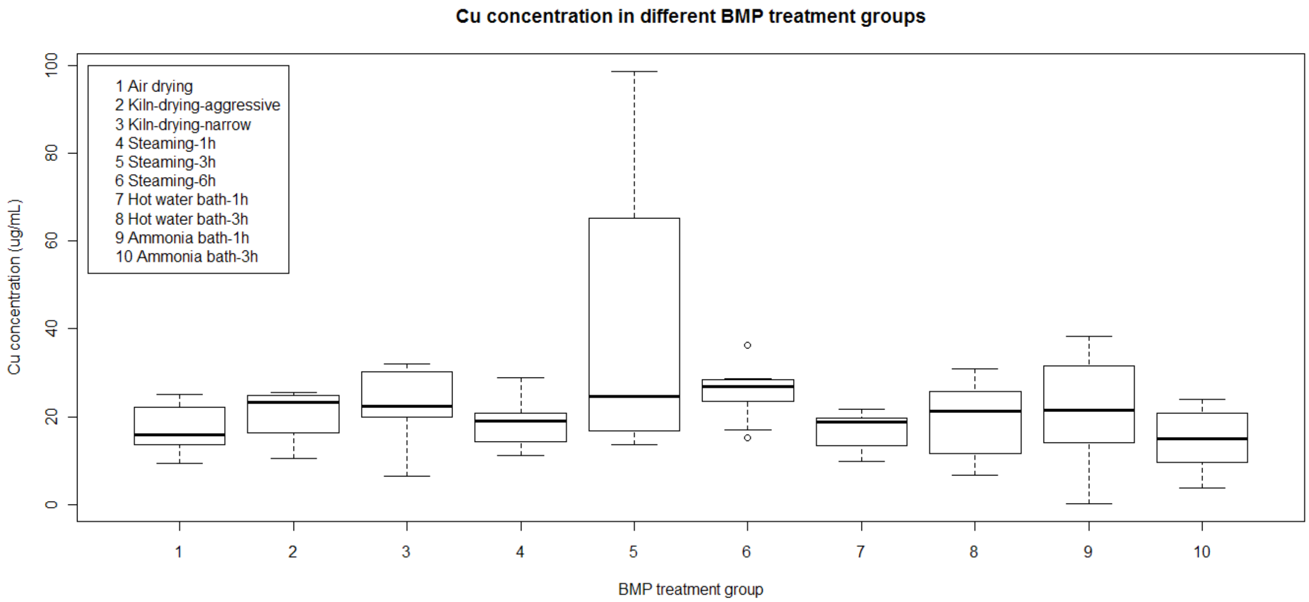

Figure39 Box and whisker plots showing copper concentrations in 80 ml of runoff from Douglas-fir lumber treated with ACQ to a target retention of 6.4 kg/m³ and subjected to one of the BMP procedures.

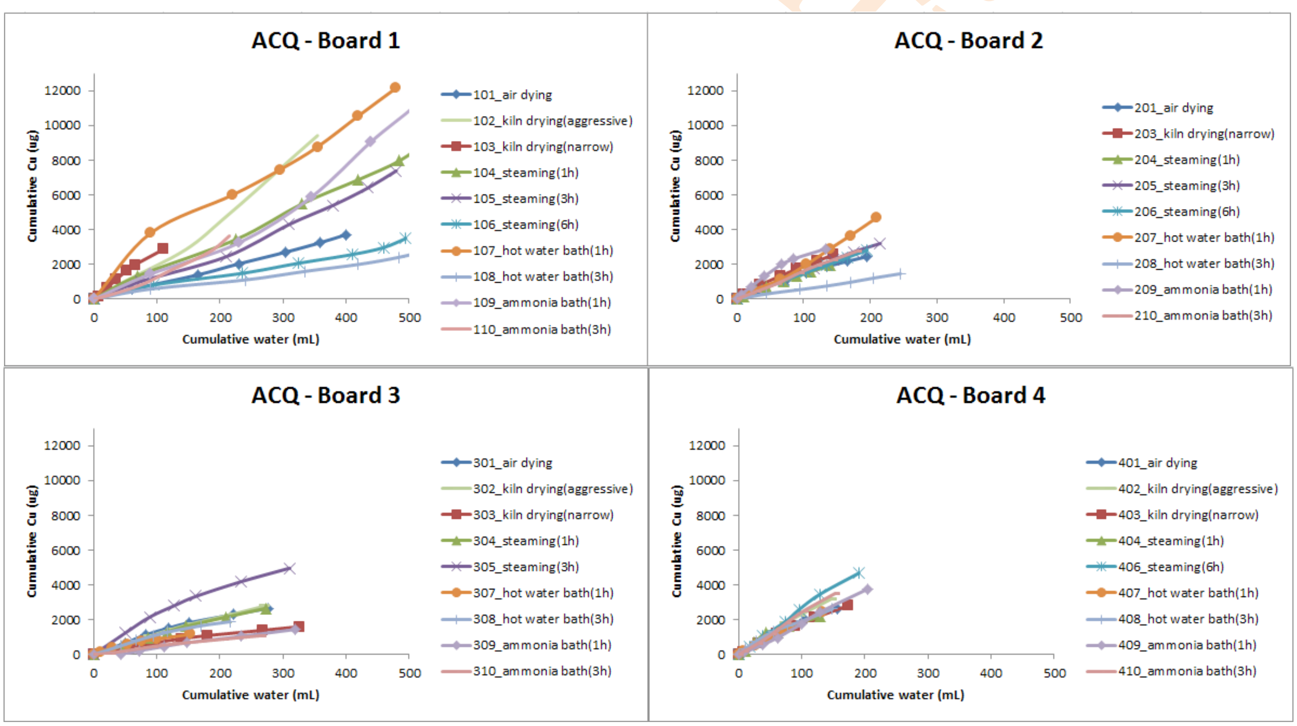

Figure 40 Cumulative copper losses in runoff from Douglas-fir lumber treated with ACQ to a target retention of 6.4 kg/m³ and subjected to one of the BMP procedures. Each figure represents data from a given parent board.

Table 7 Average copper concentrations in runoff from Douglas-fir lumber treated with ACQ to a target retention of 6.4 kg/m3 and exposed to simulated rainfall until 80 ml or 260 ml of cumulative rainfall was collected.a

BMP Treatment	Average Copper Concentration in Runoff (ug/ml)	
	80 ml (45-60 min of collection) of Cumulative Rainfall	260 ml (about 2 hours of collection) of Cumulative Rainfall
Air-drying	17.4 ab	13.4 bcd
Kiln drying (rapid)	20.7 ab	18.3 abc
Kiln drying (slow)	21.5 ab	15.8 abc
1 hr Steaming	18.4 ab	17.7 abc
3 hr Steaming	35.5 a	22.9 a
6 hr Steaming	24.3 ab	16.6 abc
1 hr Hot water bath	16.0 ab	18.4 ab
3 hr Hot water bath	16.9 ab	9.3 d
1 hr Ammonia bath	11.1 b	9.1 d
3 hr Ammonia bath	12.6 b	11.9 cd

a values followed by the same letter(s) do not differ significantly from one another by a Least Significant Difference test at α=0.05 with a Holm adjustment.

Table 8 A comparison between average actual copper retentions and target copper retentions of boards treated with ACZA, CA or ACQ.

Preservative	Copper Retention (kg/m^3)	
	Target	Actual
ACZA (4.0 kg/m^3)	1.6	2.5
ACZA (6.4 kg/m^3)	2.6	3.1
CA (0.96 kg/m^3)	0.92	1.3
CA (2.5 kg/m^3)	2.4	2.3
ACQ (6.4 kg/m^3)	3.4	3

Table 9 Effects of each BMP on copper losses as compared to air drying for boards treated with ACZA, CA or ACQ and subjected to 260 ml of rainfall.

Preservative	Target Retention	Kiln drying		Steaming			Hot water bath		Ammonia bath	
		Rapid	Slow	1 hr	3 hrs	6 hrs	1 hr	3 hrs	1 hr	3 hrs
ACZA	4 kg/m^3	Similar	Similar	Higher*	Higher	Higher	Higher	Similar	Higher	Higher
	6.4 kg/m^3	Similar	Similar	Higher	Higher	Higher	Higher	Higher	Higher	Higher
CA	0.96 kg/m^3	Higher	Similar	Higher	Higher	Higher	Lower	Lower	Lower	Lower
	2.4 kg/m^3	Higher	Similar	Similar	Similar	Similar	Lower	Lower	Lower	Lower
ACQ	6.4 kg/m^3	Similar	Similar	Higher	Similar	Similar	Similar	Similar	Similar	Similar

* Indicate that differences between air seasoning and this BMP were significantly different ($\alpha = 0.05$).

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

The final report by Dr. Robert Perkins at the University of Alaska on the effects of creosote treated wood on development of herring eggs has been published. The results were consistent and showed that, while PAH's could produce effects on herring egg development, the levels found in the natural environment were an order of magnitude below the levels that produced any measurable effects. We hope to continue this dialogue with Dr. Perkins.

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

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

We have co-sponsored 6 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.

While these programs were useful and generally received good evaluations, the attendance has been limited. We have discussed moving to a webinar format to allow participants to enroll without having to travel. We are planning to hold our first event in February of 2014.

The Program will as follows:

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

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

9:20 am Foundation for the Aquatic Risk Models - *This session very briefly outlines 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.*

10:00 am A Rapid Primer to the BMPs - Ted LaDoux/Dallin Brooks, Western Wood Preservers' Institute, Vancouver, WA - *This session gives participants an overview of why the BMP's were developed.*

10:20 am How to Use Screening Level Assessment Process and Worksheets - Neil Alongi, Maul Foster & Alongi, Portland, OR- *Teaches participants about how to use the screening level assessment process to determine the level of examination needed for a given project.*

11:00 am Model Exploration

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