Environmental Performance of Treated Wood Cooperative

Seventh Annual Report

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Personnel

Matthew Konkler, Faculty Research Assistant

J.J. Morrell, Professor

Executive Summary

The Environmental Performance of Treated Wood Research Cooperative was established to improve knowledge related to the use and disposal of treated wood. The Coop has been active in a number of areas; progress on each will be reviewed below.

We have completed all of the waterborne BMP tests with the exception of the two micronized copper azole formulations. These were not in the AWPA standards at the time we initiated these tests. Southern pine lumber will be treated with these materials so that we can begin BMP tests. The remaining trials show that BMP processes do differ in their ability to limit metal migration. Similar trials with pentachlorophenol treated material show that steaming reduces subsequent penta losses. Finally, tests on steaming of creosote treated wood show that longer steaming periods produce a more beneficial effect. All of these data will be used to modify the current BMP processing guidelines to make sure that the most appropriate processes are coupled with each preservative system. Further trials are also planned with copper naphthenate treated SPF and southern pine. These materials are already on hand. Field trials in our test pond continue to show that metal and PAH levels are elevated immediately adjacent to the treated wood, but decline within 0.3 to 0.9 m away. These results are consistent with previous trials.

Field trials on a bridge containing both penta and copper napthehnate treated wood are largely complete. Both preservatives were detected in runoff, however, modeling these data with available stream flow measurements indicated that the levels never approached the minimum effects levels. The results also illustrate how the model can be used to predict the risk of exceeding minimum effects levels under varying stream conditions. We are seeking additional projects to monitor and have worked with an East Coast treater to establish several sites in Maryland.

Trials of polyurea coatings continue to show that the barrier is highly effective at limiting metal migration into surrounding seawater. We have also damaged the coating to evaluate how much damage can occur before metal levels become a concern and necessitate repair. We will continue to apply increasing amounts of damage to identify a threshold.

We are now hosting the Aquatic Model on our website, following its update by WWPI. We have had a number of inquiries about how to use the model and have participated in one workshop in Oakland. While further workshops are planned, efforts are also underway to create videos so that the materials can be more widley distributed without the need for extensive travel. In general, users find the new model much easier to work with.

INTRODUCTION

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

OBJECTIVES

The overall goal of the EPTWC is to develop knowledge that improves the ability to use and dispose of treated wood in a safe and environmentally sensitive manner. This goal is being addressed through the following objectives:

1. *Develop fundamental data on preservative migration from wood*
2. *Develop standardized accelerated methodologies for assessing treated wood risks*
3. *Work cooperatively to develop and improve models to predict the risk of using treated wood in various applications*
4. *Identify improved methods for reducing the potential for migration*
5. *Evaluate the environmental impacts and identify methods for reuse, recycling and/ or disposal of preserved wood that is removed from service*
6. *Deliver educational outreach programs on the proper use of treated wood in relation to the Best Management Practices (BMP’s)*

ACCOMPLISHMENTS

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

1. Develop fundamental data on preservative migration from wood

A. Evaluate the effects of BMP’S on preservative migration patterns

In previous reports, we have described efforts to develop data on the effects of the BMP’s on preservative migration. The results have been mixed. In some cases, the results suggest a benefit for using these practices, but many tests suggest that BMP’s have little effect. We believe these results occurred because most of the material that was exposed was already air-dried prior to exposure; in essence, receiving one of the BMP's (air-seasoning). The BMP's were originally developed in response to situations where freshly treated wood was taken out of the cylinder, transported to a site and then installed in projects where it was subjected to nearly immediate rainfall or soaking (WWPI, 2011). To work around this problem and examine the real effect of BMP's on migration, we moved to a smaller scale test where we could control all aspects of the process to produce more reproducible results under worst case conditions.

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

Post-treatment with BMP's: The frozen samples were defrosted before being subjected to one of nine treatments listed in the Western Wood Preservers Institute Best Management Practices requirements. The methods were applied to sub-samples of each board treated with a water-based 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. No supplemental airflow was supplied.

-Kiln drying: The samples were placed in a steam-fired kiln on stickers to enhance air flow. Samples were dried over a one-week kiln schedule at a dry-bulb temperature of 48.9℃ and wet-bulb depression of 5.6℃. This cycle limited drying, but the heat encouraged ammonia or amine loss. Wood moisture contents in these samples were below 19% when subjected to overhead leaching.

-Steaming: Samples were subjected to 1, 3 or 6 hours of steaming at 104.4℃ with stickers in between samples. Steaming was performed in an autoclave where steam entered the vessel and was allowed to exit so that pressure remained near atmospheric.

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

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

The samples were frozen (-5 °C) after being subjected to a given BMP until needed. Each treatment was replicated on one section cut from each board treated with a given preservative to help reduce the potential for variability between boards. This resulted in a portion of each board being subjected to a given BMP.

Leaching tests: The samples were thawed overnight before testing. The potential for preservative migration was evaluated in a specially constructed overhead leaching apparatus that applied a controlled amount of simulated rainfall at a desired temperature (Figure 1). Previous studies (Simonsen et al, 2008) have shown that migration is independent of both temperature and rainfall rate so the device was operated at room temperature (20~28℃) and a rainfall rate ranging from 0.1 cm/h to 0.3 cm/h.

Figure 1 - Overhead leaching apparatus used to evaluate the effects of BMP procedures on migration of metals from ACZA, CA or ACQ treated wood.

The apparatus (1.5 m wide * 0.6 m long * 0.9 m) was constructed with stainless steel and a plastic panel and had eight 152 mm wide x 457 mm long x 51 mm high sample holders. Holders were placed on a shelf with a 4.5° incline from the horizontal to allow water to flow down the wood. Simulated rainfall was produced by four spray nozzles connected to a deionized water supply. The rate of water spray was controlled by a small pump and an electronic controller. A pressure gauge near the spray nozzles also helped control flow.

BMP-treated samples were placed into each holder and subjected to simulated overhead rainfall for 2 hours. Previous tests had shown that metal levels in runoff drop off sharply to a steady state by this time. Runoff water was collected in tared 250 mL Erlenmeyer flasks that were weighed after rainfall exposure to determine the total volume of water applied per board for each time period. The weight of water was recorded and 4. 85mL of each water sample was placed into a vial. Water was collected at 15-minute intervals for the first hour then at 30-minute intervals for two hours. Preservative retention in the samples was determined using either net solution uptake for the southern pine samples treated with waterbornes or by x-ray fluorescence for both southern pine and SPF samples.

Chemical analysis: Water runoff from samples treated with waterborne preservatives was acidified by adding 0.15 mL of 1N nitric acid into 4.85 mL of leachate.

The samples were stored at 4 ^{0}C until they could be analyzed for residual metal using a Perkin Elmer Optima 3000DV inductively-coupled plasma optical emission spectrometer with a diode array detector (ICP). Water samples collected over the first two hours of simulated rainfall were tested for copper, zinc, chromium or arsenic (depending on the treatment). The exposed wood samples were frozen and retained in the event we needed to perform additional rainfall exposures. Copper concentrations were used as a measure of BMP effectiveness, although chromium, zinc and arsenic were also measured where those metals were present in a preservative system.

Retentions were high for CCA treated southern pine, but slightly below the targets for ACQ and CA (Table 2). SPF retentions were just above the target for ACZA, but well below that level for CCA, ACQ and CA. Cross cuts of the samples illustrate the poor penetration. The SPF boards were treated as full length samples that were then cut for exposure. Even with incising, the samples were poorly treated (Figure 2).

Table 2. Target and actual retentions of CCA, ACZA ACQ or CA in southern pine or SPF lumber used to evaluate the BMP processes.

Treatment	Target Retention (kg/m^3)	Retention (kg/m^3)^a		
		Southern Pine		SPF
		Net Uptake	XRF	XRF
CCA	6.4	5.92(1.07)	9.46 (0.33)	2.43 (0.18)
ACQ	6.4	6.18 (0.25)	5.86 (0.07)	0.52 (0.04)
CuA	2.4	2.50 (0.92)	2.37 (0.04)	0.73 (0.03)
ACZA	6.4	Not tested	-	7.26 (0.29)
Penta	8	-	7.87 (0.23)	-
Creosote	160	-	-	-

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

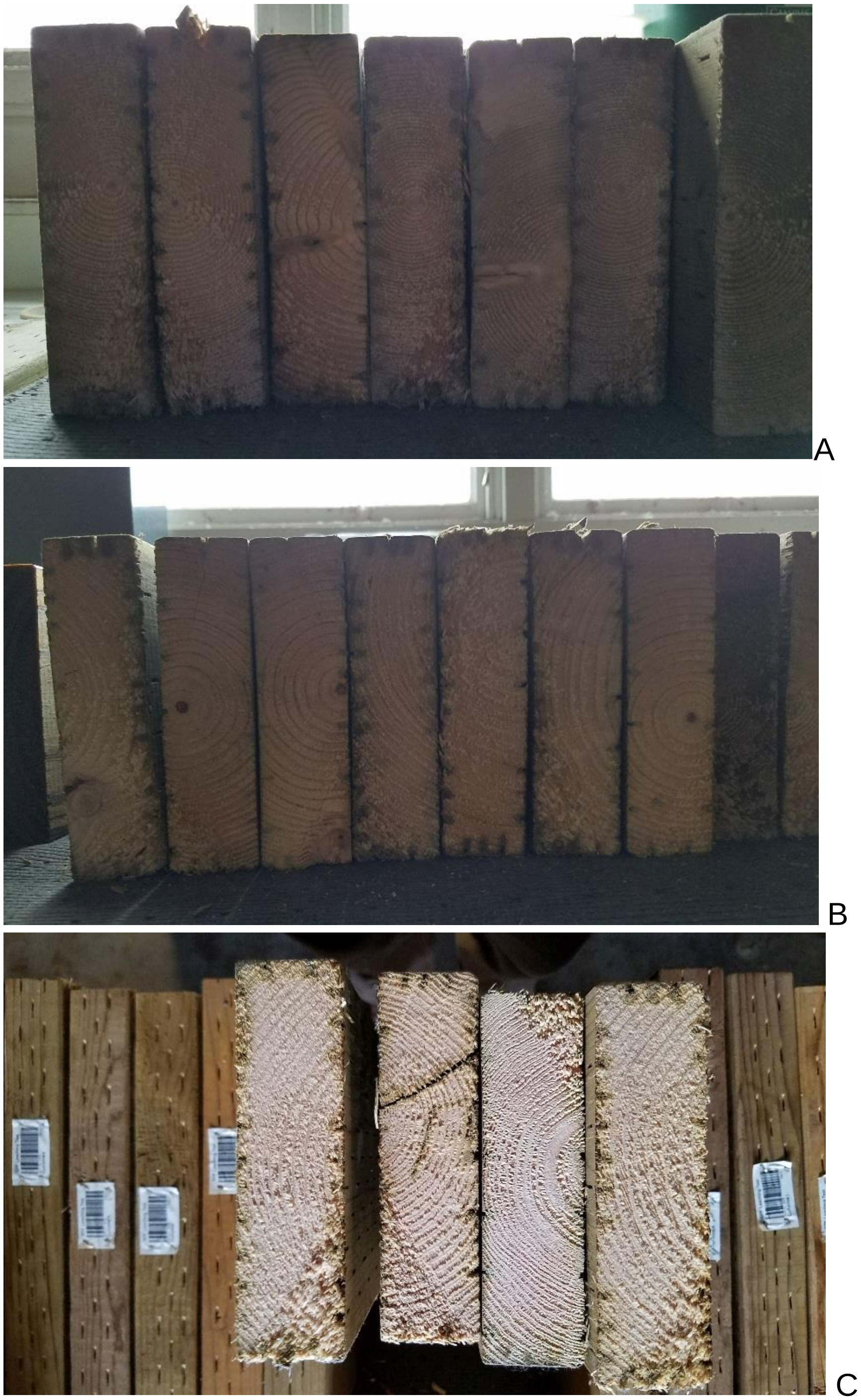


Figure 2. Photos showing poor preservative penetration in SPF boards treated with CCA (A), CA (B) or ACQ (C).

Copper Levels in Rainfall from Copper Azole (CA) Treated Wood: Retention levels in SPF were considerably lower than those for SYP, reflecting the much higher permeability of SYP.

Copper levels in rainwater runoff from SPF treated CA samples tended to be higher in non-BMP treated samples than from nearly all of the samples receiving a BMP process. The one exception was the one hour steam treatment, where copper levels were similar. Copper levels were generally higher immediately after the start of the simulated rainfall and then declined by approximately 50% after the first 15 minutes of rainfall. Levels declined further to approximately 25% of the initial levels at the end of the two hour rainfall period. These results are consistent with previous tests and indicate that the largest metal releases occur during the first rainfall. Copper levels in runoff from air or kiln dried lumber were approximately half of those found in the non-BMP treated material. Metal levels in runoff from samples subjected to a one hour ammonia bath were the lowest of those found with all of the BMP's.

Copper levels in runoff from CA treated southern pine lumber were much higher than those found with SPF, partially reflecting the higher overall retentions in the wood. Copper levels in the first 15 minutes of runoff were similar for southern pine samples that received no BMP or were air or kiln dried. These results were surprising since moisture removal should result in copper immobilization in the wood. It is unclear if freezing after treatment or after BMP processing affected copper mobility. Copper levels in runoff from CA treated SYP subjected to steaming, hot water immersion or ammonia baths were all much lower than those found for the non-BMP or dried materials. Copper levels were generally below two ppm in runoff from these samples after two hours of rainfall, while they were 4.5 to 10.9 ppm in runoff from samples not receiving BMP's or those that were air-or kiln dried. It is unclear why air or kiln drying, which should immobilize metals, did not affect copper to the same degree as the other processes.

Copper levels in CA treated Douglas-fir were also elevated compared with the SPF treated samples. It is important to note that the samples were treated separately and at different times and this could account for some of the differences. Thus, it is probably most useful to examine these data in terms of the relative effects of BMP's rather than the absolute differences between wood species. The Douglas-fir samples also did not have a non-BMP control treatment; instead air drying was used as the comparator.

Copper levels in runoff from air-dried CA treated Douglas-fir lumber were similar to those found for air-dried southern pine, while those from kiln dried samples were nearly double the air-dried levels (Figures 3, 5, 9). The application of hot water or an ammonia bath had a slight effect on copper levels in runoff, while steaming appeared to increase copper levels in the first 15 minutes of runoff from the samples. These results would seem to negate the value of a BMP in Douglas-fir lumber

Copper Levels in Rainfall from Ammoniacal Copper Quaternary (ACQ) Treated Wood: Retention levels in ACQ treated wood were extremely variable ranging from a low of 0.52 kg/m^3 in SPF to 5.86 kg/m^3 in southern pine. It is unclear why the levels were so low in the SPF, although penetration was also limited.

Copper levels in rainwater runoff from ACQ treated SPF were also extremely low, especially from the BMP treated materials averaging 2.79 µg/mL in rainwater collected in the first 15 minutes of rainfall (Figure 7). Copper levels were higher in rainwater collected from samples subjected to almost every other BMP except one hour in a hot water bath and the two ammonia washes. These results clearly reflect the low initial retentions in the boards.

Copper levels in rainwater runoff from southern pine boards not subjected to any BMP were almost 20 times higher than those found with the SPF samples and were more in line with expectations (Figure 4). Copper levels declined by 50% after the first 15 minutes of simulated rainfall and then an additional 50% after 120 minutes. The non-BMP treated sample results are consistent with previous studies showing a relatively large surge of chemical loss followed by an equally sharp drop-off as surface deposits are removed. Copper levels in ACQ treated Douglas-fir and southern pine followed similar trends with regard to the effects of BMP's although the effects were more consistent in southern pine (Figure 7, 10).

Exposure of samples to 1 to 6 hours of steaming produced dramatic reductions in copper levels in southern pine, but less of an effect on Douglas-fir. Increased steaming periods did not appear to improve copper immobilization in ACQ treated southern pine. There was also little evidence that the process had any effect on long-term losses from Douglas-fir since copper levels in runoff collected after 120 minutes of rainfall differed little from that collected in the first 15 minutes.

The use of an ammonia bath appeared to have the greatest effect on copper losses for southern pine and only a slight effect on Douglas-fir. The differences between the two species are surprising. These tests were performed at different times, but used the same apparatus and procedures.

<u>Copper Losses from Chromated Copper Arsenate (CCA) Treated Lumber</u>: CCA remains an important preservative in industrial applications. Reduction of chromium from the hexavalent to trivalent state after treatment initiates a series of reactions that sharply reduce the risk of metal migration from the wood.

CCA was evaluated on both SPF and southern pine, but not Douglas-fir since this species is notoriously resistant to CCA (Figures 5, 12, 14). CCA retentions averaged 9.46 kg/m^3 in southern pine boards, but only 2.43 kg/m^3 in SPF. The differences again reflect the overall resistance of SPF to preservative treatment. Chromium levels in rainwater runoff were extremely high in tests of non-BMP treated materials and declined quickly with the various BMP processes. Although not discussed further here, it is important to understand that mobility of both arsenic and copper is closely related to the degree of chromium reduction.

Copper levels in runoff from CCA treated SPF boards tended to be very low, even in the first 15 minutes of rainfall on non-BMP treated boards. These levels declined with additional rainfall exposure. Application of BMP's to CCA treated SPF produced variable results. Copper levels were lower in runoff from boards subjected to air-drying, kiln drying, or an ammonia bath. Both air and kiln drying should have facilitated chromium reduction, thereby hastening copper immobilization. The effect of ammonia on the system is unclear. CCA is a strongly acidic system and pH is further reduced as fixation occurs. It is unclear why ammonia would have improved that process. The remaining post-treatment BMP's were associated with slightly higher levels of copper in the runoff, suggesting that they had little effect on copper, although they clearly influenced chromium reduction.

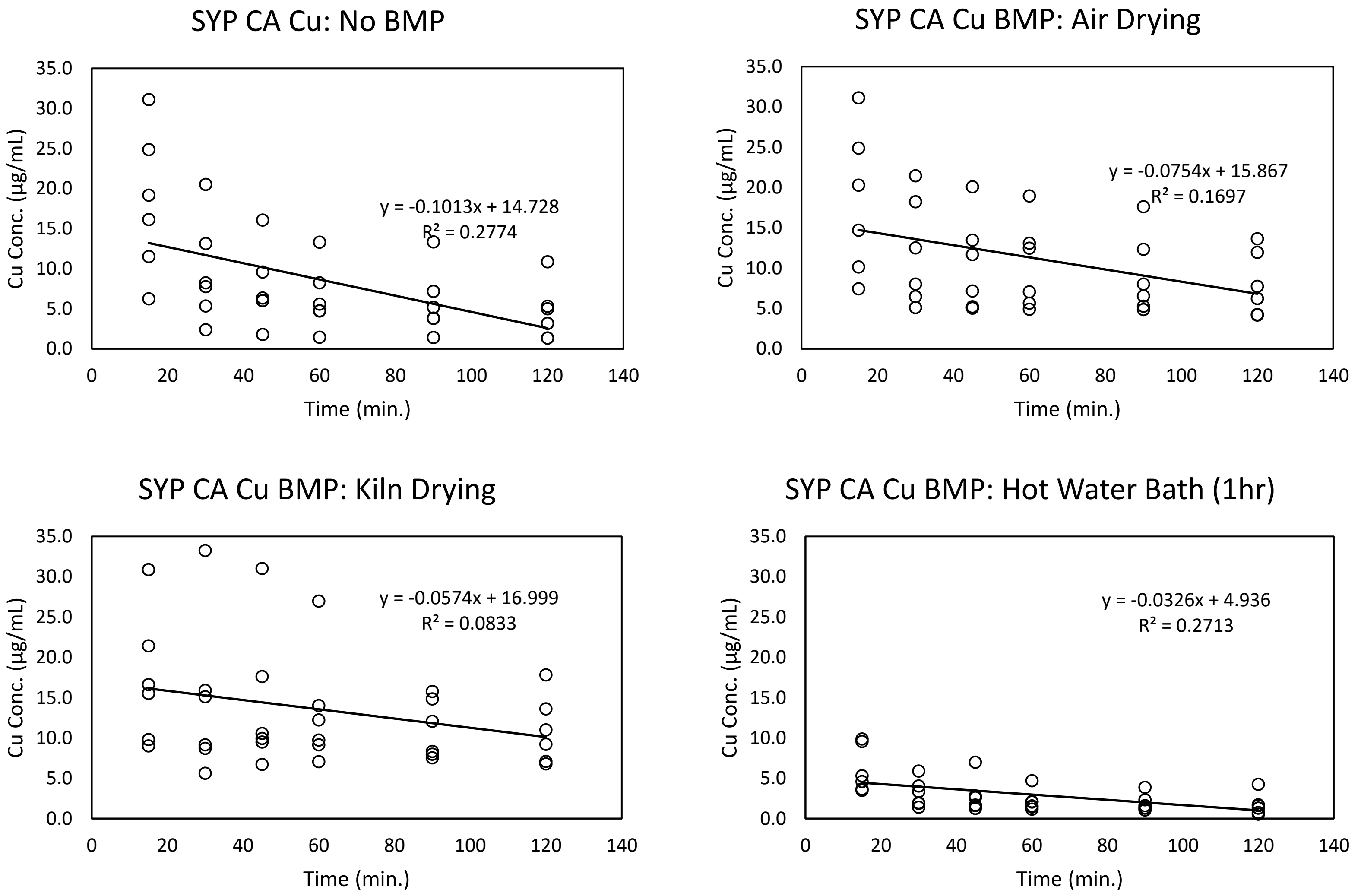
Copper levels in CCA treated southern pine were similar to those found in runoff from CCA treated SPF even though retentions were much higher in southern pine. As with SPF, copper levels were fairly low in runoff from non-BMP treated boards, but levels declined only slightly over the 120 minute rainfall exposure. Copper levels were about 50% lower in samples subjected to either air or kiln drying, illustrating the benefits of allowing drying to encourage chromium reduction. Once again, the ammonia treatments were both associated with reduced copper levels in rainwater runoff. The remaining BMP's had little effect on copper levels in runoff, although, as noted with SPF, they should have important effects on chromium reduction. Thus, while BMP processes did not markedly reduce copper losses, they did affect chromium and this process ultimately reduces the environmental footprint of CCA.

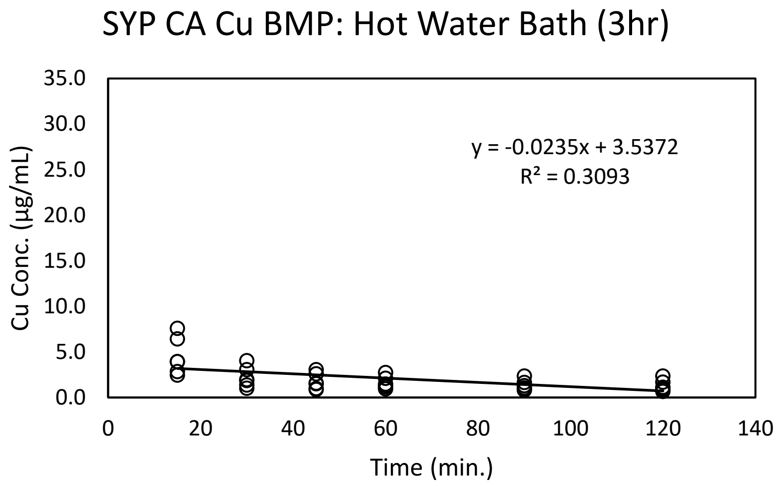
Copper levels in Ammoniacal Copper Zinc Arsenate (ACZA) Treated Wood: ACZA was developed as an alternative to other copper-based systems for treatment of Douglas-fir and other refractory wood species. Unlike CCA, the copper in ACZA is solubilized using high pH that also helps solubilize zinc and arsenic. The system precipitates when the ammonia or amine systems evolve from the wood, leaving various copper, arsenic and zinc complexes that are resistant to leaching.

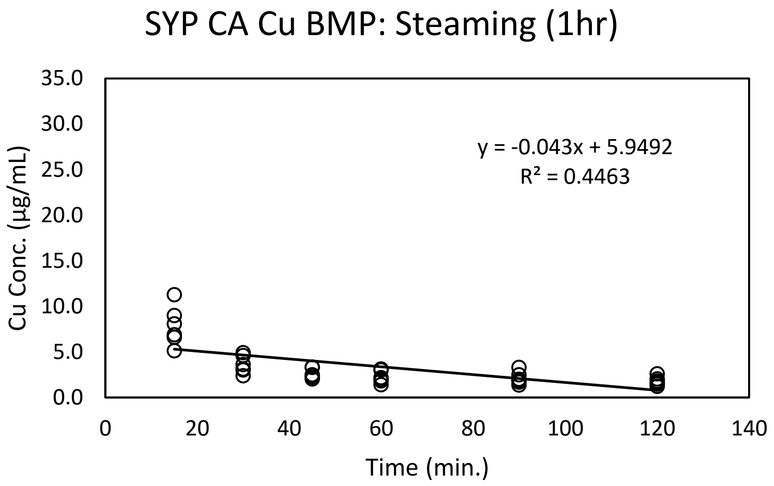
Copper levels in runoff from the first 15 minutes of rainfall on non-BMP treated SPF were the highest of any treatment in the test and then declined by almost 50% in the second 15 minutes of rainfall and by 75% at the end of the rainfall exposure (Figure 8, 13, 15). Copper levels in runoff from BMP treated samples were all lower than from non-BMP treated samples except for the one hour ammonia bath, which had similar copper levels. Copper levels in runoff after 15 minutes of rainfall on air and kiln dried samples were 20 to 30 times lower than those found in runoff from non-BMP treated samples. Copper levels in runoff from samples receiving the remaining BMP's were somewhat lower than those from the non-BMP samples, but to a much lesser extent. Runoff from samples receiving the one hour ammonia bath contained copper levels that were similar to those for the non-BMP treated samples suggesting that ammonia treatment was not suitable for limiting copper losses.

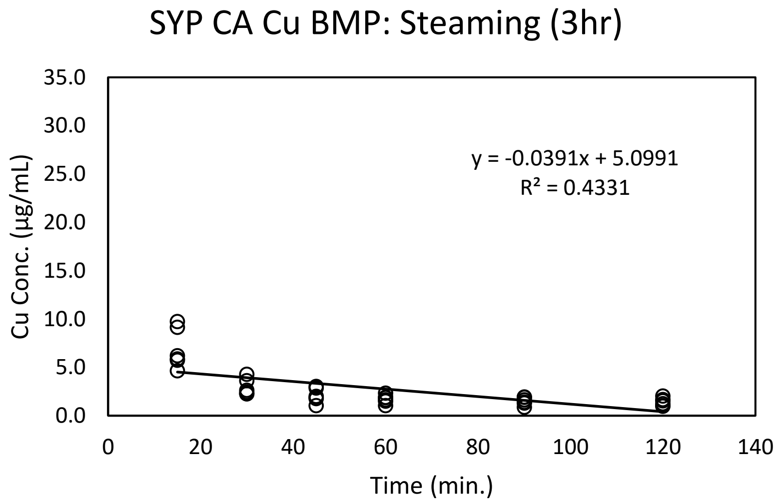
Copper levels in runoff from air or kiln dried Douglas-fir samples were also lower than those from samples receiving other BMP processes. Once again, ammonia soaking had little positive effect on reducing copper losses. Hot water bathes also had little positive effect on initial copper losses. Copper levels in steamed material were lower than those from the ammonia or hot water soaked materials, but much higher than those from air or kiln dried materials. The results suggest that drying represents one of the best approaches for minimize copper losses form ACZA treated Douglas-fir, while steaming reduces copper losses, but not to the same extent as drying (Figure 11).

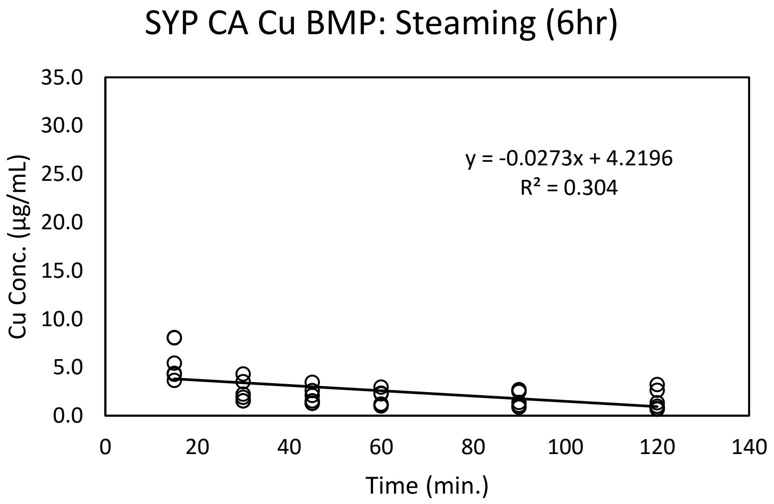
Figure 3. Effect of various BMP processes on copper losses from copper azole (CA) treated southern pine lumber exposed to simulated rainfall.




SYP CA Cu BMP: Hot Water Bath (3hr)
y = -0.0235x + 3.5372
R² = 0.3093
Cu Conc. (µg/mL)
35.0
30.0
25.0
20.0
15.0
10.0
5.0
0.0
0
20
40
60
80
100
120
140
Time (min.)


SYP CA Cu BMP: Steaming (1hr)
y = -0.043x + 5.9492
R² = 0.4463
Cu Conc. (µg/mL)
35.0
30.0
25.0
20.0
15.0
10.0
5.0
0.0
0
20
40
60
80
100
120
140
Time (min.)


SYP CA Cu BMP: Steaming (3hr)
y = -0.0391x + 5.0991
R² = 0.4331
Cu Conc. (µg/mL)
35.0
30.0
25.0
20.0
15.0
10.0
5.0
0.0
0
20
40
60
80
100
120
140
Time (min.)


SYP CA Cu BMP: Steaming (6hr)
y = -0.0273x + 4.2196
R² = 0.304
Cu Conc. (µg/mL)
35.0
30.0
25.0
20.0
15.0
10.0
5.0
0.0
0
20
40
60
80
100
120
140
Time (min.)

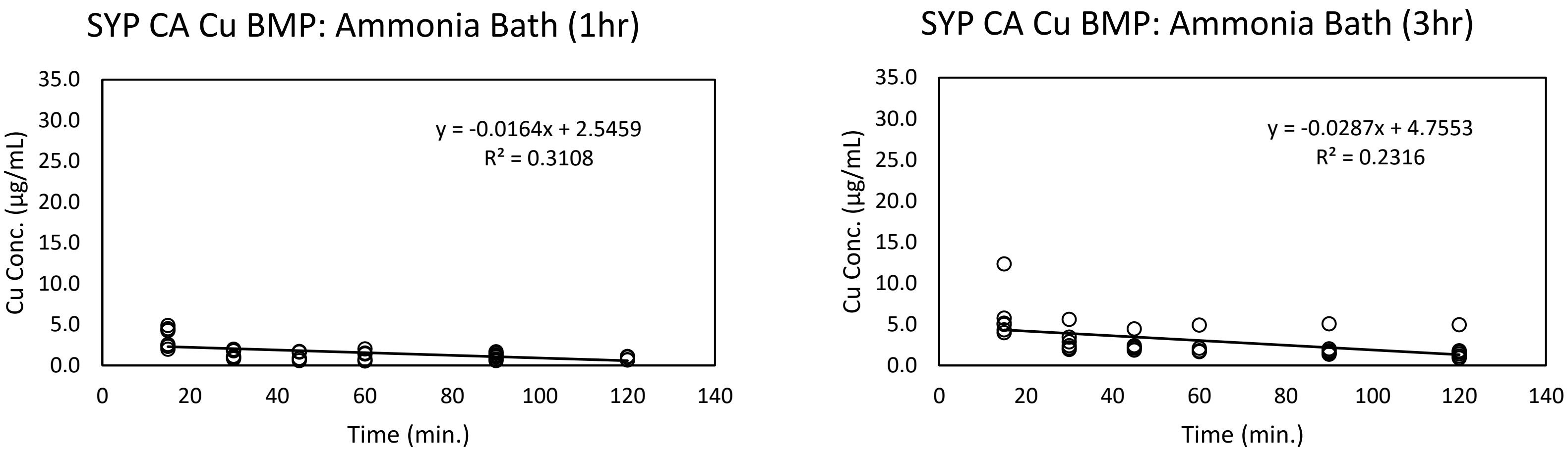
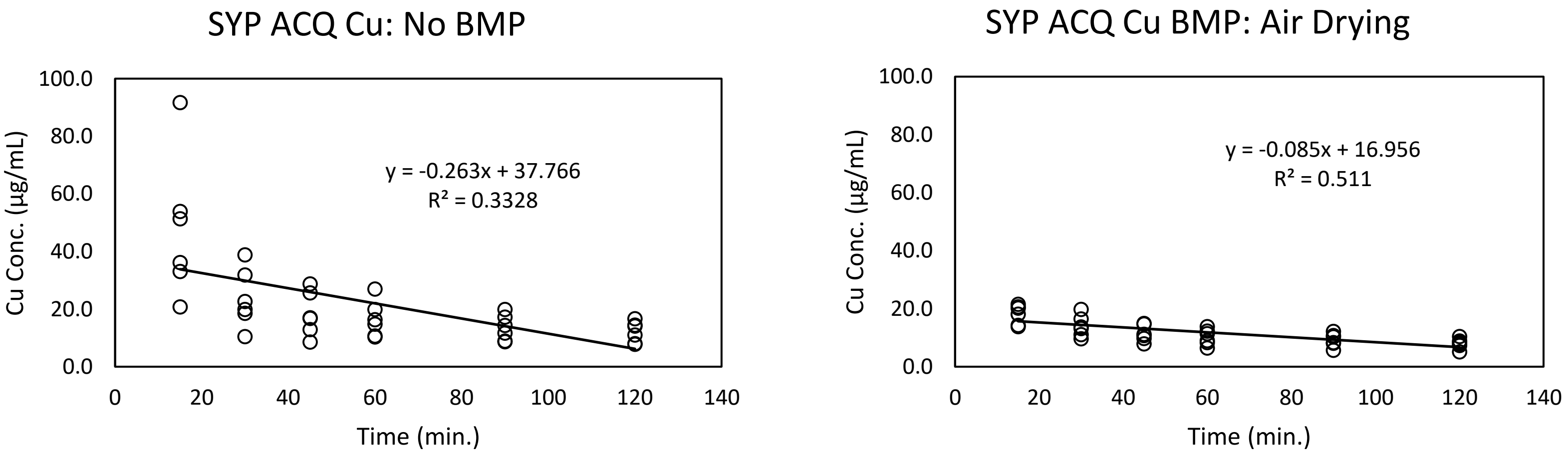
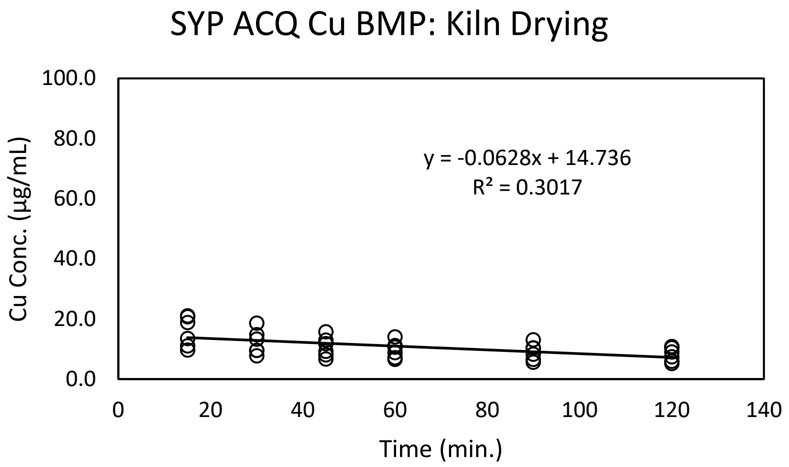
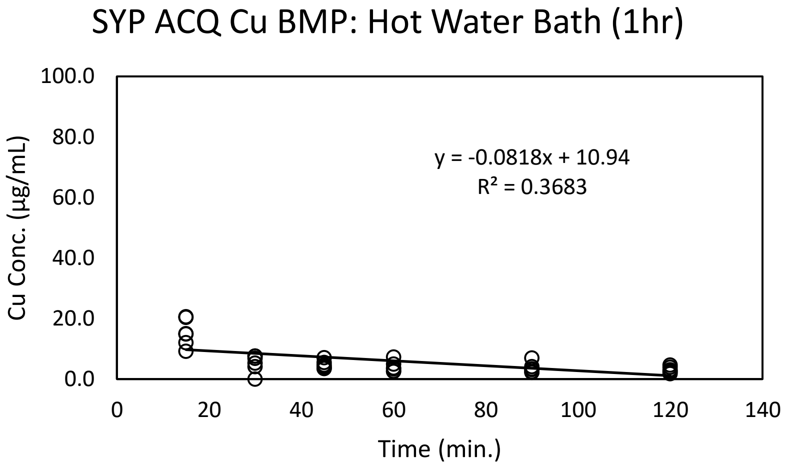
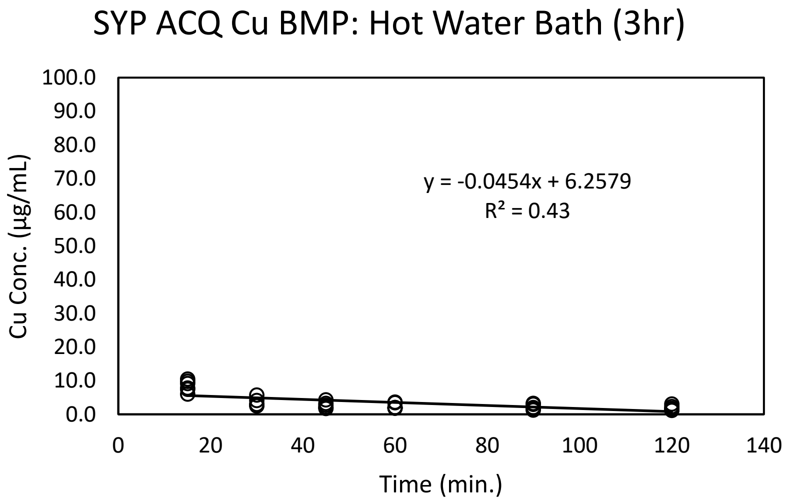


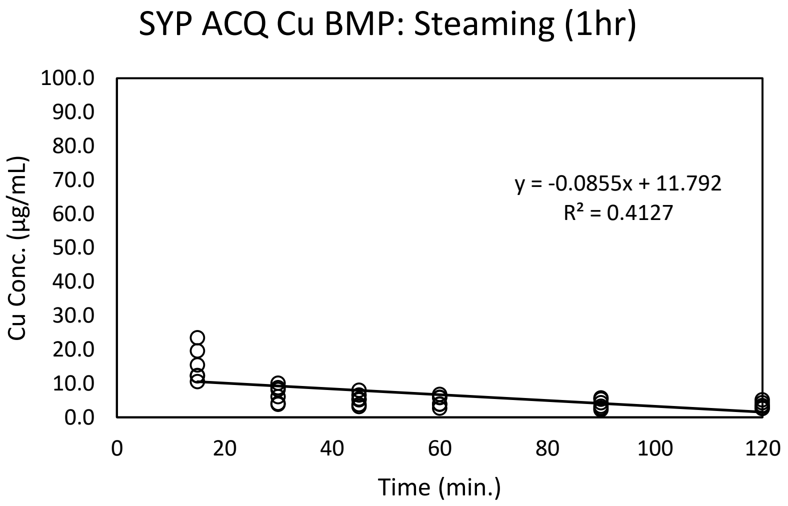
Figure 4. Effect of various BMP processes on copper losses from alkaline copper quaternary (ACQ) treated southern pine lumber exposed to simulated rainfall.

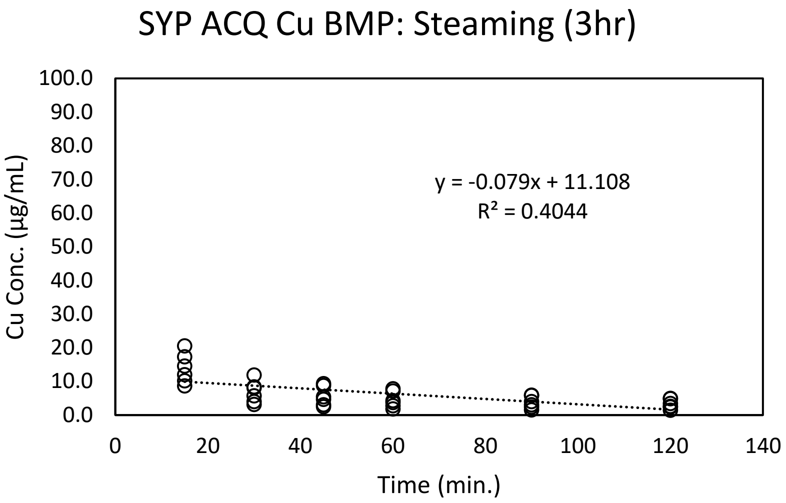


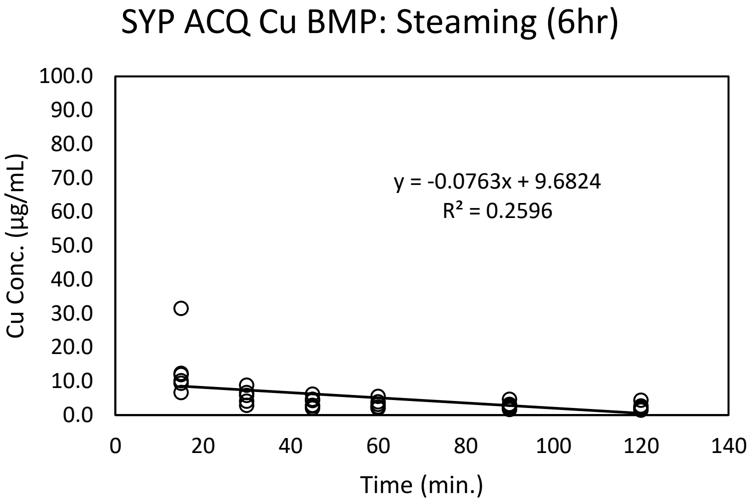

SYP ACQ Cu BMP: Kiln Drying
Cu Conc. (µg/mL)
100.0
80.0
60.0
40.0
20.0
0.0
y = -0.0628x + 14.736
R² = 0.3017
0
20
40
60
80
100
120
140
Time (min.)

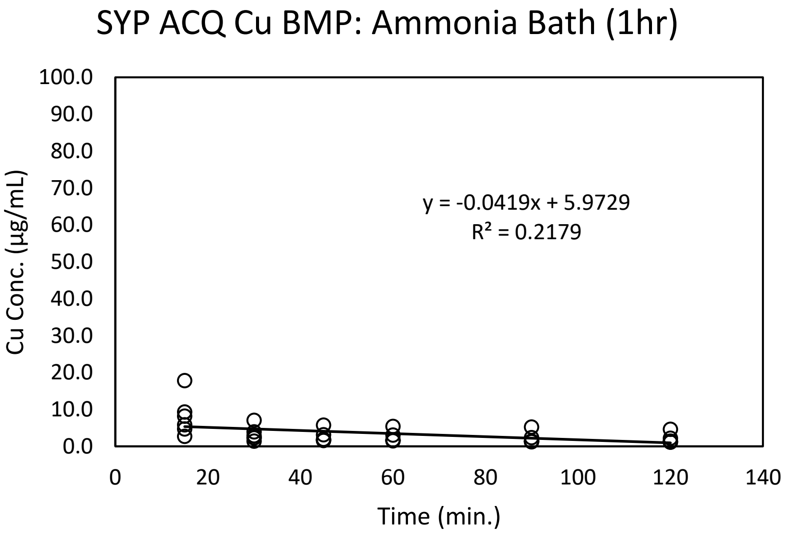

SYP ACQ Cu BMP: Hot Water Bath (1hr)
Cu Conc. (µg/mL)
100.0
80.0
60.0
40.0
20.0
0.0
y = -0.0818x + 10.94
R² = 0.3683
0
20
40
60
80
100
120
140
Time (min.)


SYP ACQ Cu BMP: Hot Water Bath (3hr)
Cu Conc. (µg/mL)
100.0
90.0
80.0
70.0
60.0
50.0
40.0
30.0
20.0
10.0
0.0
y = -0.0454x + 6.2579
R² = 0.43
0
20
40
60
80
100
120
140
Time (min.)


SYP ACQ Cu BMP: Steaming (1hr)
Cu Conc. (µg/mL)
100.0
90.0
80.0
70.0
60.0
50.0
40.0
30.0
20.0
10.0
0.0
y = -0.0855x + 11.792
R² = 0.4127
0
20
40
60
80
100
120
Time (min.)


SYP ACQ Cu BMP: Steaming (3hr)


SYP ACQ Cu BMP: Steaming (6hr)


SYP ACQ Cu BMP: Ammonia Bath (1hr)

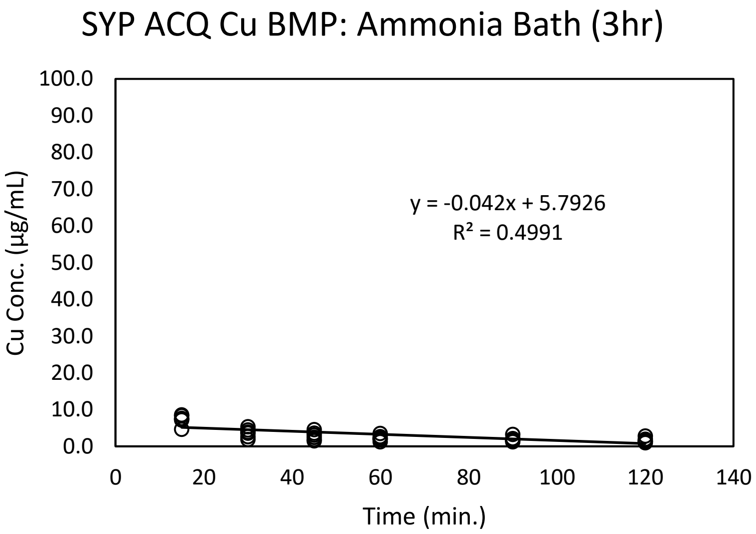
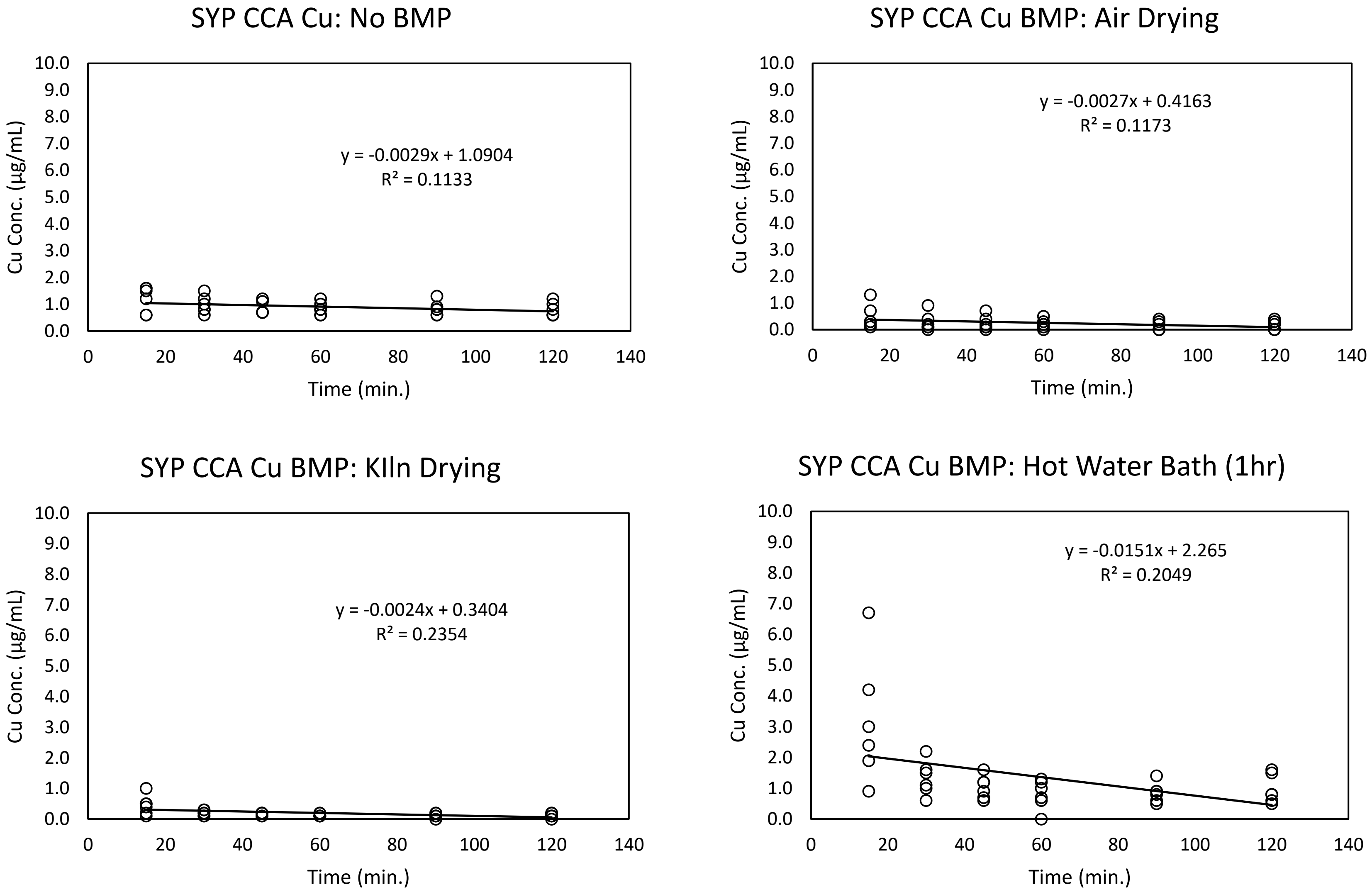
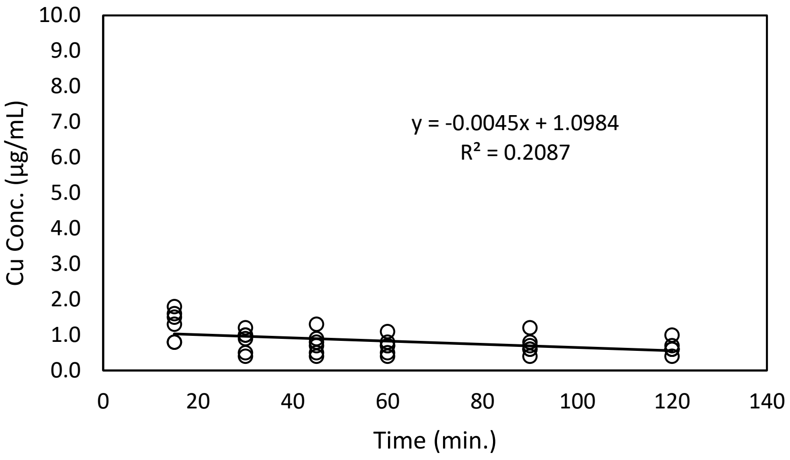
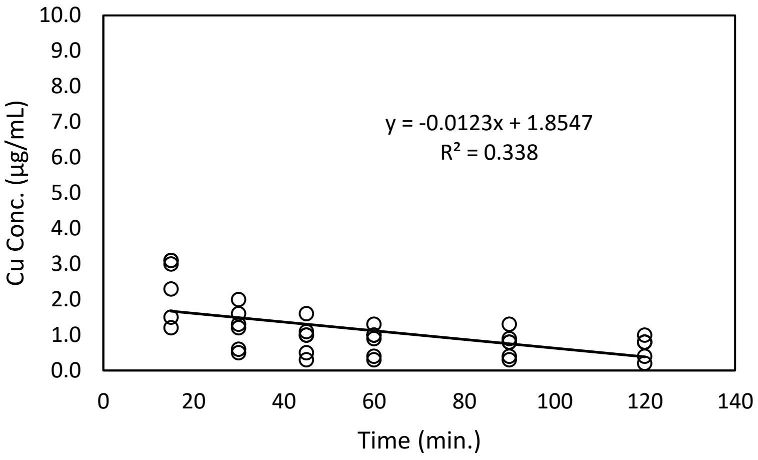

SYP ACQ Cu BMP: Ammonia Bath (3hr)

Figure 5. Effect of various BMP processes on copper losses from chromated copper arsenate (CCA) treated southern pine lumber exposed to simulated rainfall.

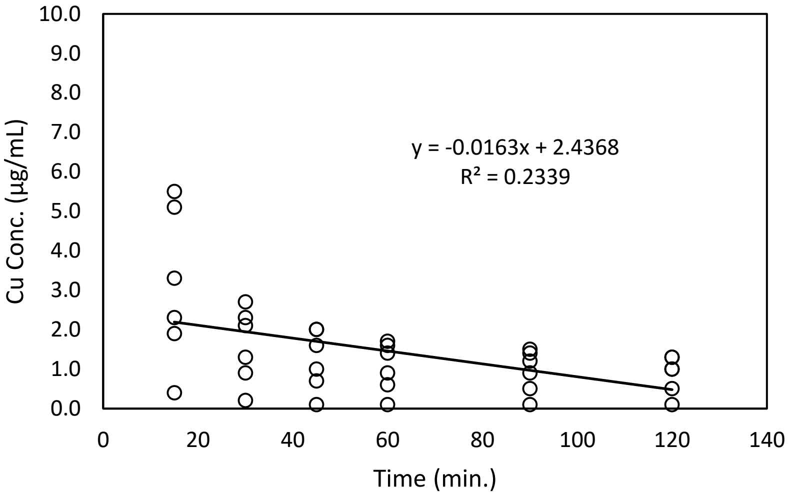




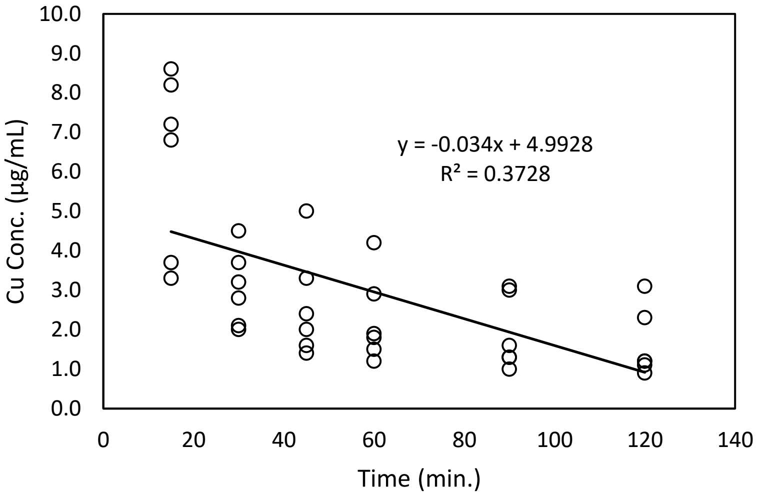
SYP CCA Cu BMP: Hot Water Bath (3hr)



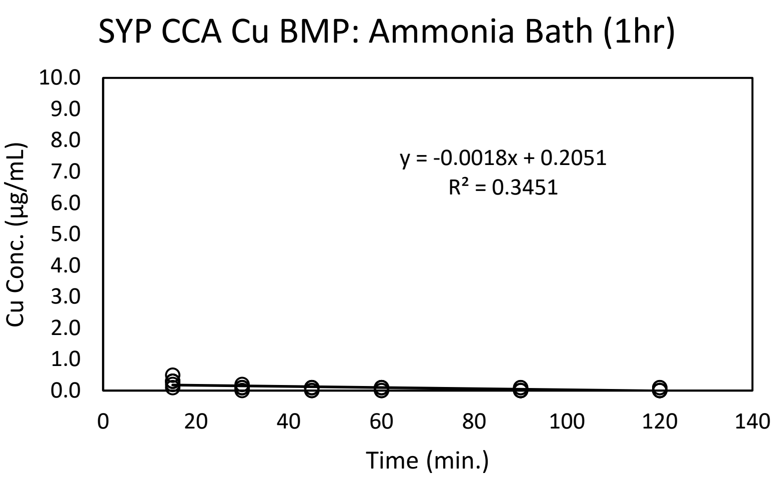
SYP CCA Cu BMP: Steaming (1hr)



SYP CCA Cu BMP: Steaming (3hr)



SYP CCA Cu BMP: Steaming (6hr)



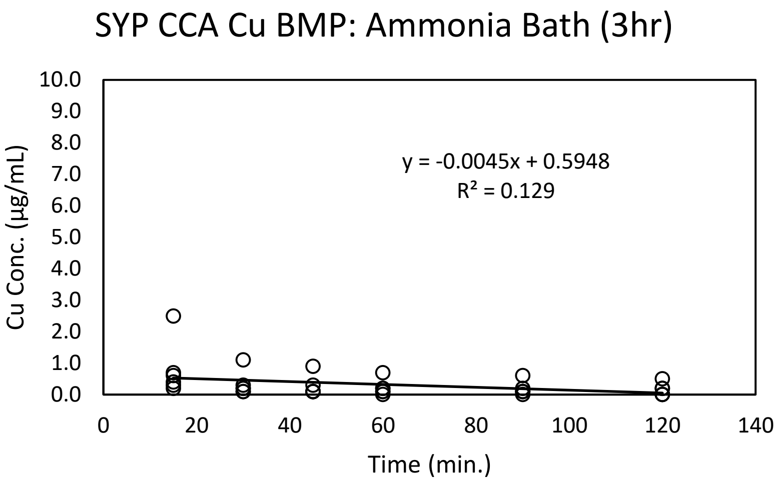
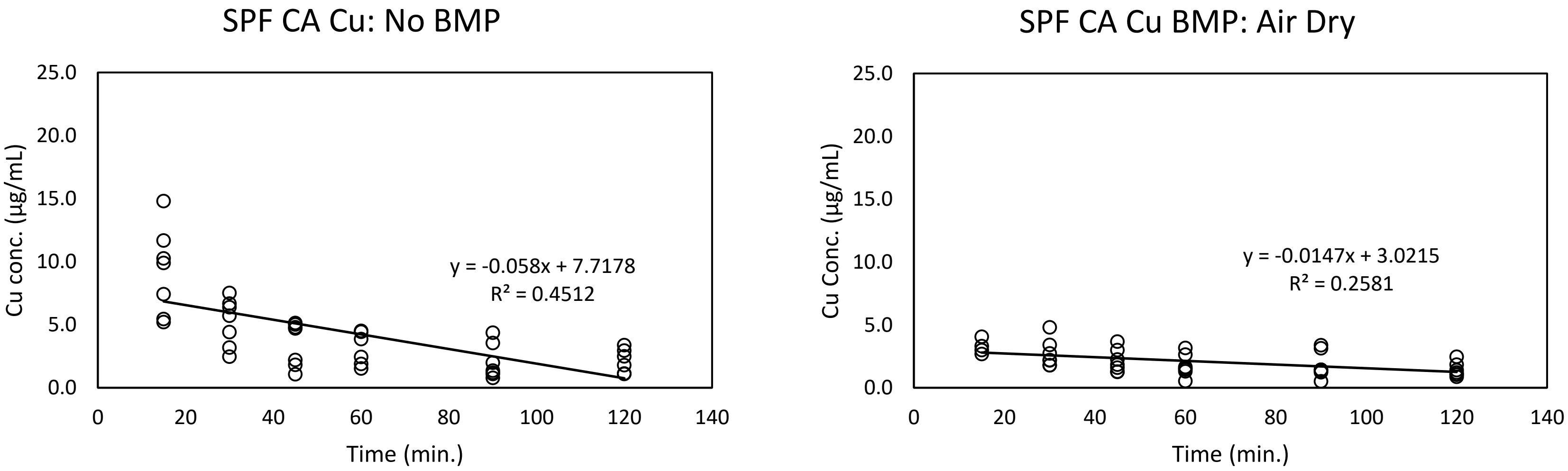
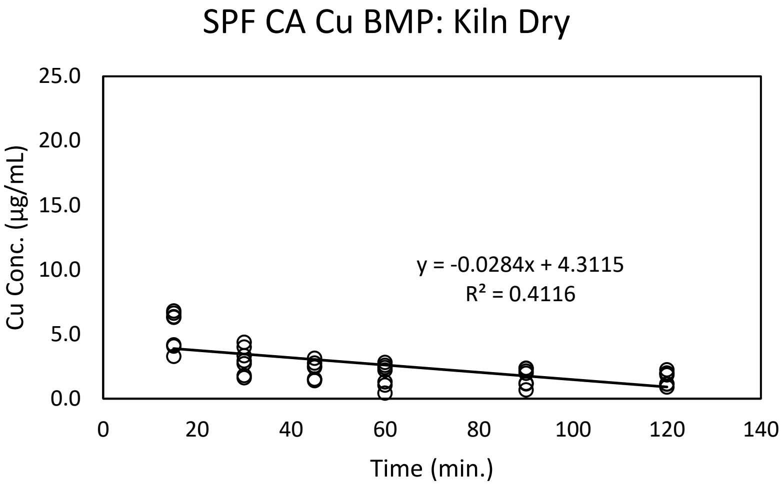
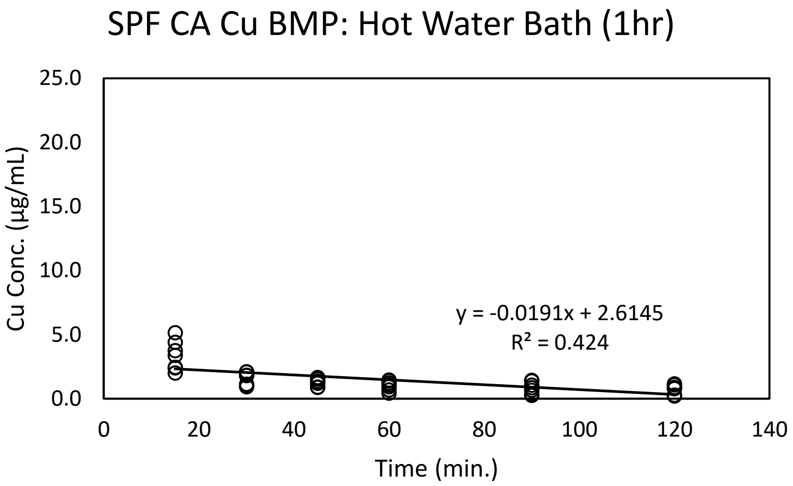
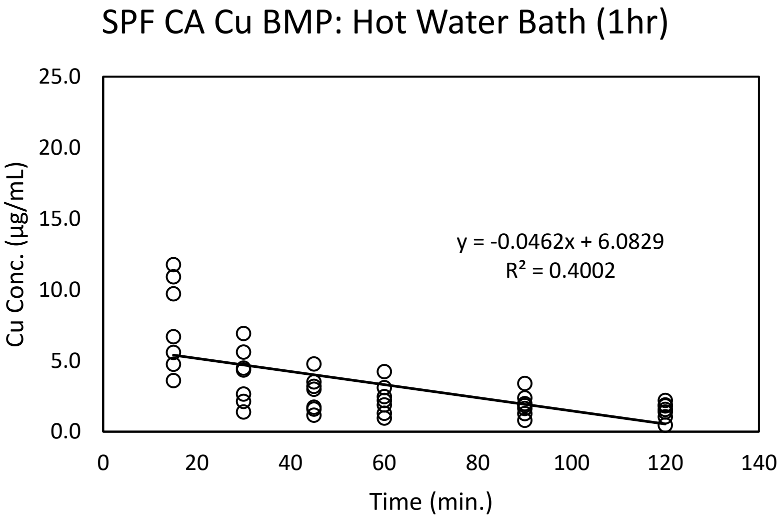


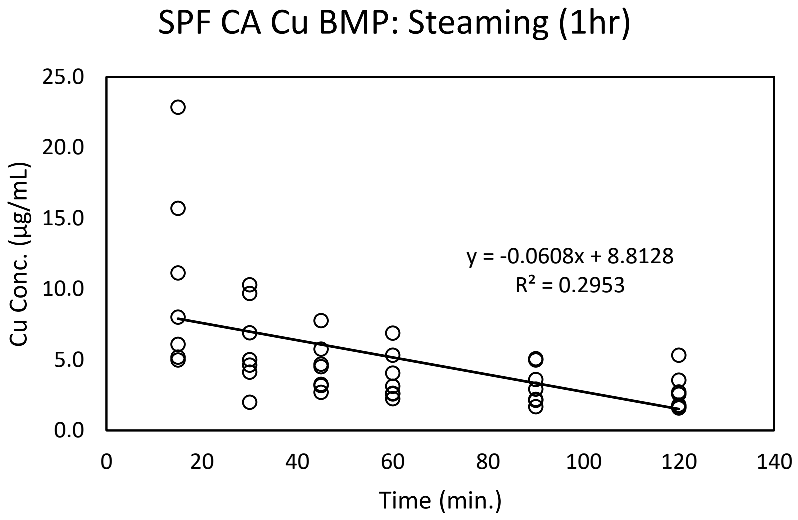
Figure 6. Effect of various BMP processes on copper losses from copper azole (CA) treated spruce pine fir lumber exposed to simulated rainfall

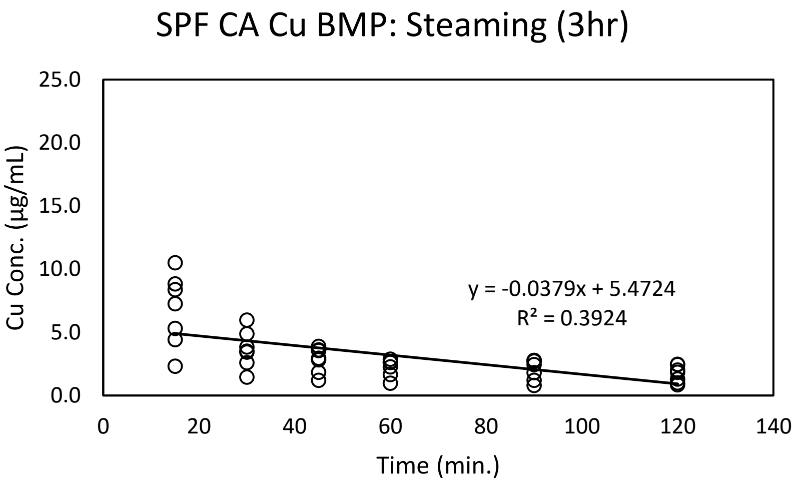


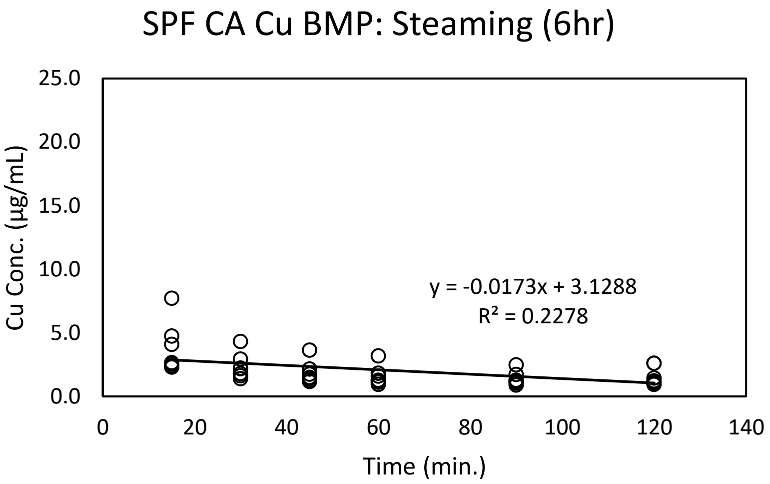

SPF CA Cu BMP: Kiln Dry

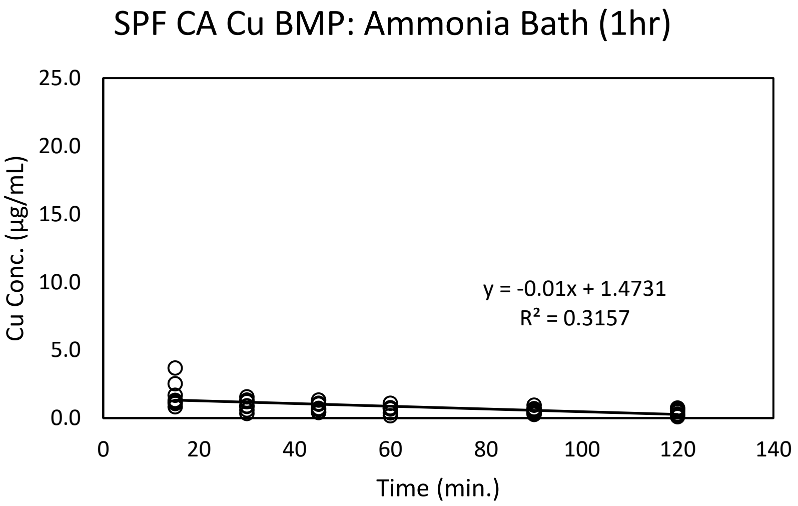

SPF CA Cu BMP: Hot Water Bath (1hr)


SPF CA Cu BMP: Hot Water Bath (1hr)


SPF CA Cu BMP: Steaming (1hr)


SPF CA Cu BMP: Steaming (3hr)
Cu Conc. (µg/mL)
25.0
20.0
15.0
10.0
5.0
0.0
0
20
40
60
80
100
120
140
Time (min.)
y = -0.0379x + 5.4724
R² = 0.3924


SPF CA Cu BMP: Steaming (6hr)
Cu Conc. (µg/mL)
25.0
20.0
15.0
10.0
5.0
0.0
0
20
40
60
80
100
120
140
Time (min.)
y = -0.0173x + 3.1288
R² = 0.2278


SPF CA Cu BMP: Ammonia Bath (1hr)
Cu Conc. (µg/mL)
25.0
20.0
15.0
10.0
5.0
0.0
0
20
40
60
80
100
120
140
Time (min.)
y = -0.01x + 1.4731
R² = 0.3157

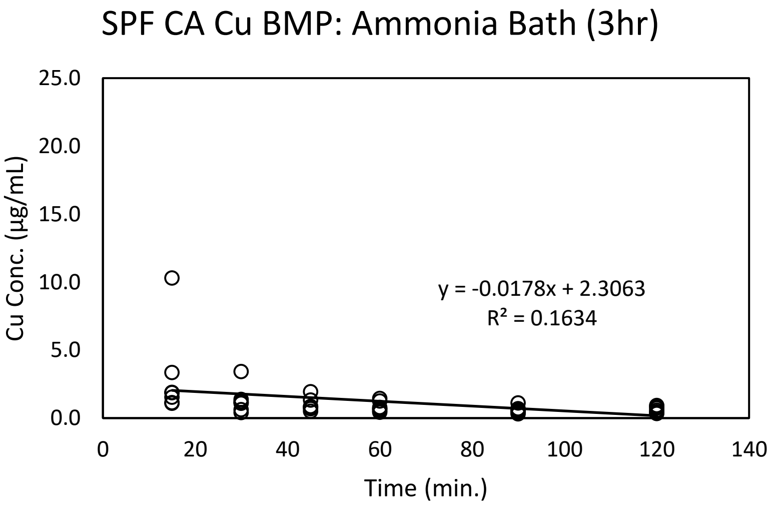
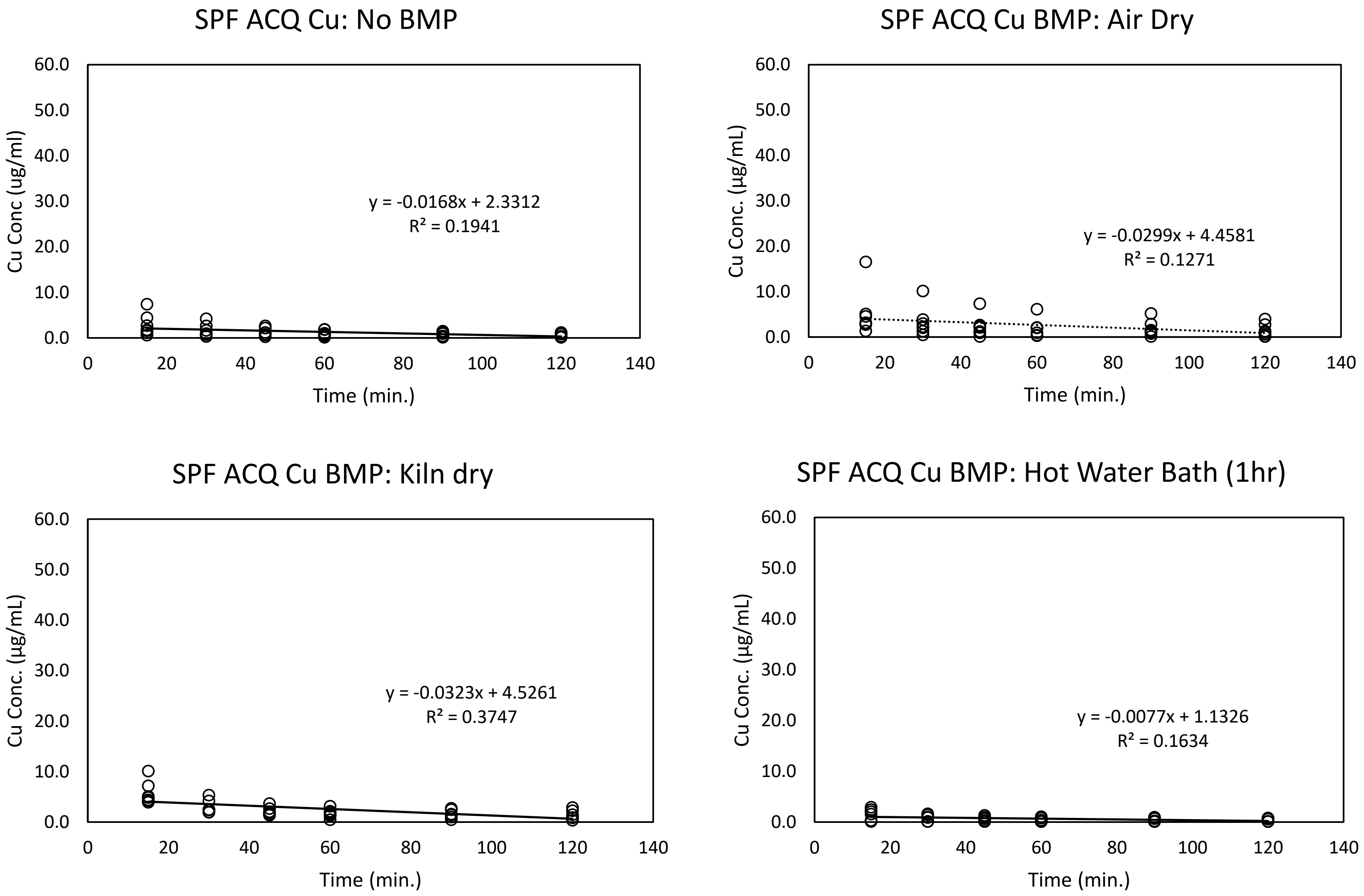
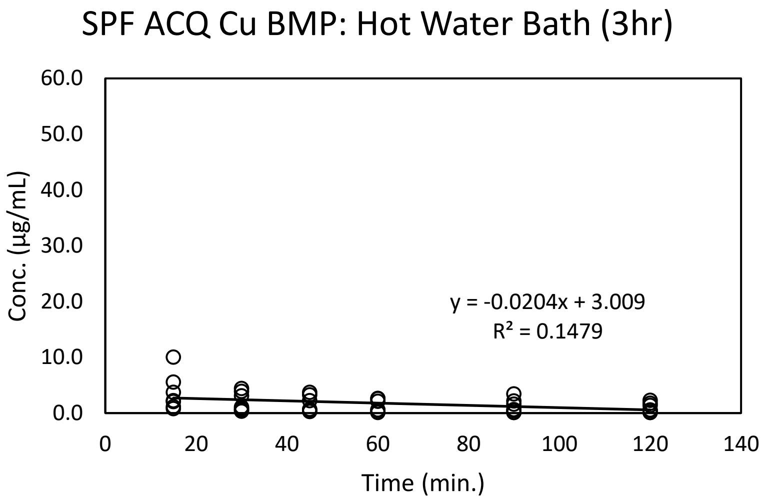
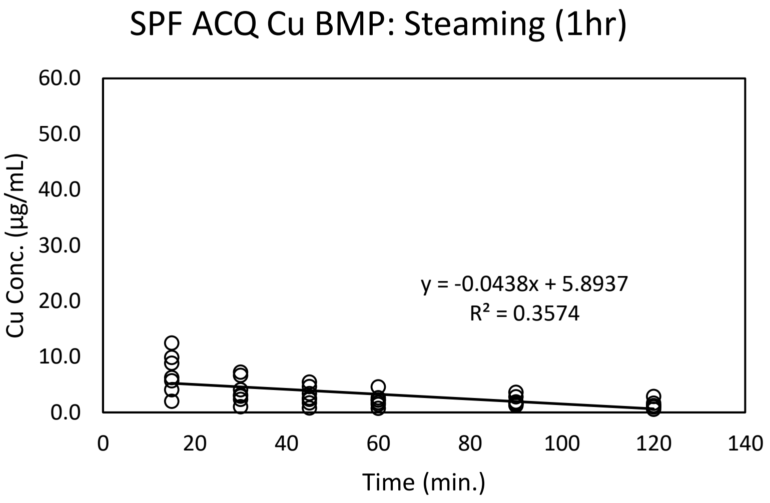
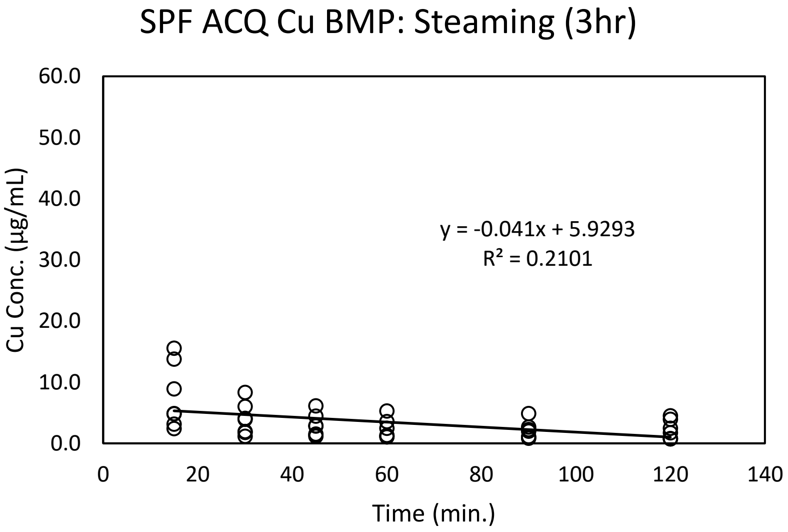

SPF CA Cu BMP: Ammonia Bath (3hr)
Cu Conc. (µg/mL)
25.0
20.0
15.0
10.0
5.0
0.0
0
20
40
60
80
100
120
140
Time (min.)
y = -0.0178x + 2.3063
R² = 0.1634

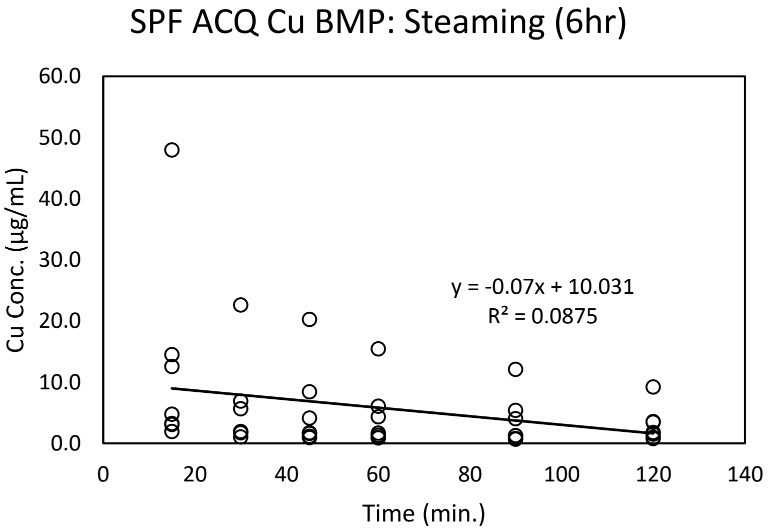
Figure 7. Effect of various BMP processes on copper losses from ammoniacal copper quaternary (ACQ) treated spruce pine fir lumber exposed to simulated rainfall

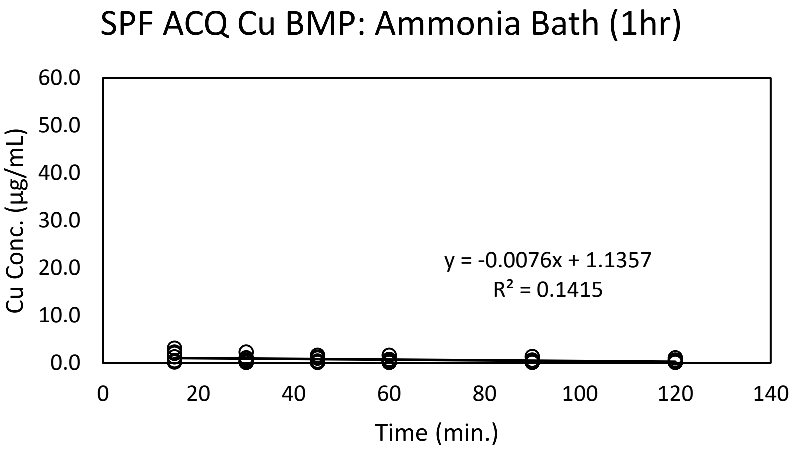



SPF ACQ Cu BMP: Hot Water Bath (3hr)


SPF ACQ Cu BMP: Steaming (1hr)


SPF ACQ Cu BMP: Steaming (3hr)


SPF ACQ Cu BMP: Steaming (6hr)



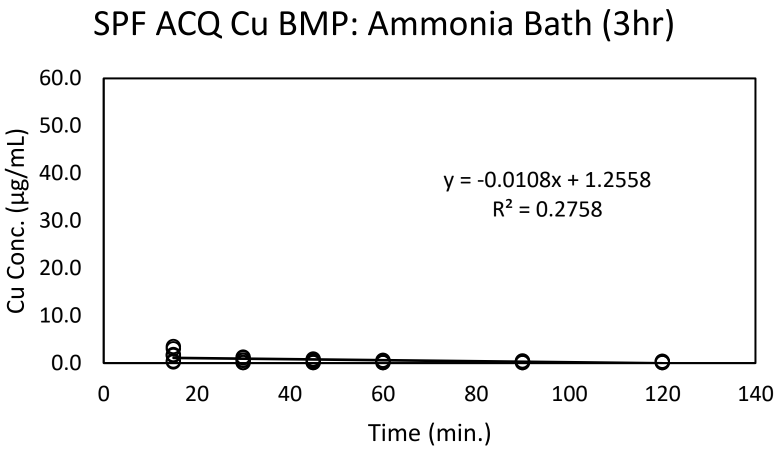
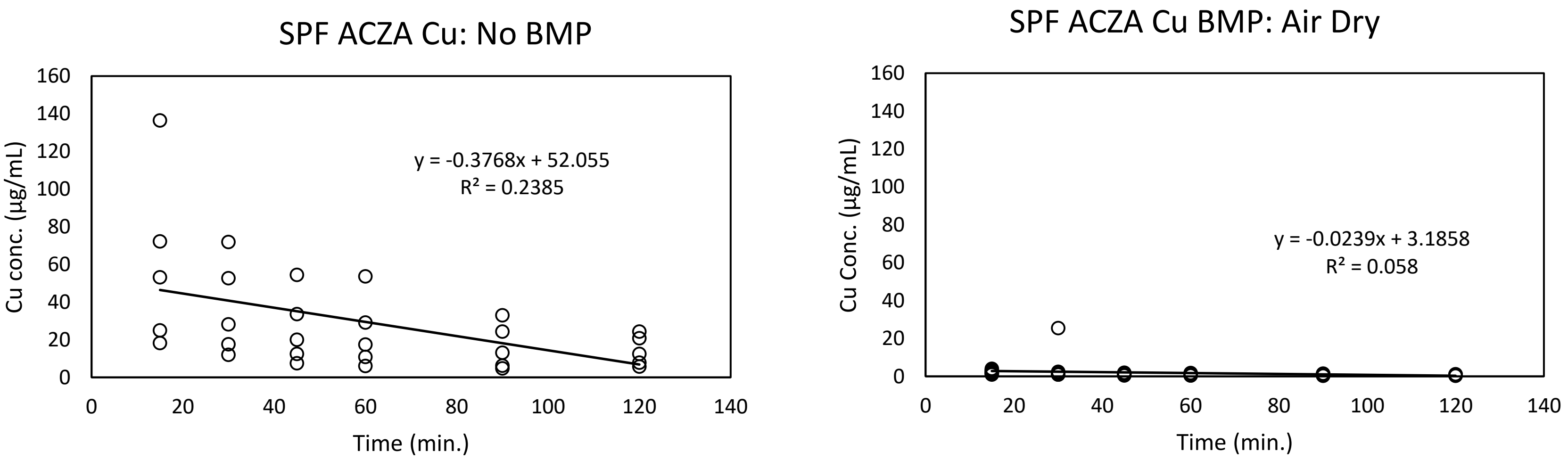
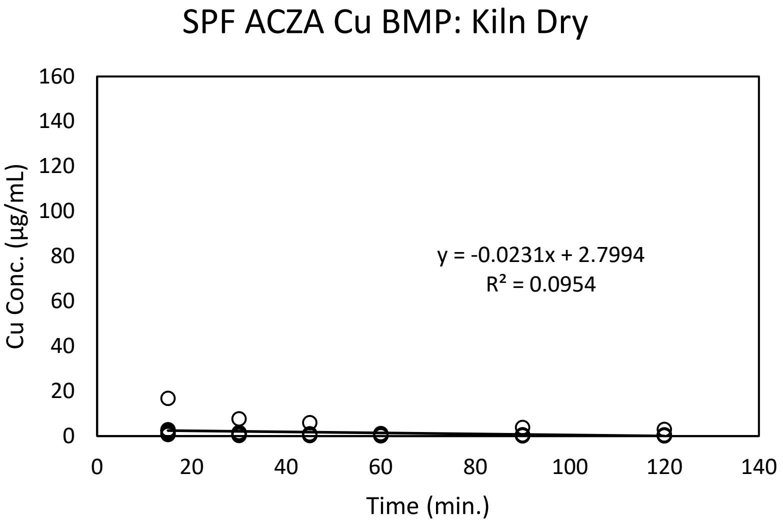
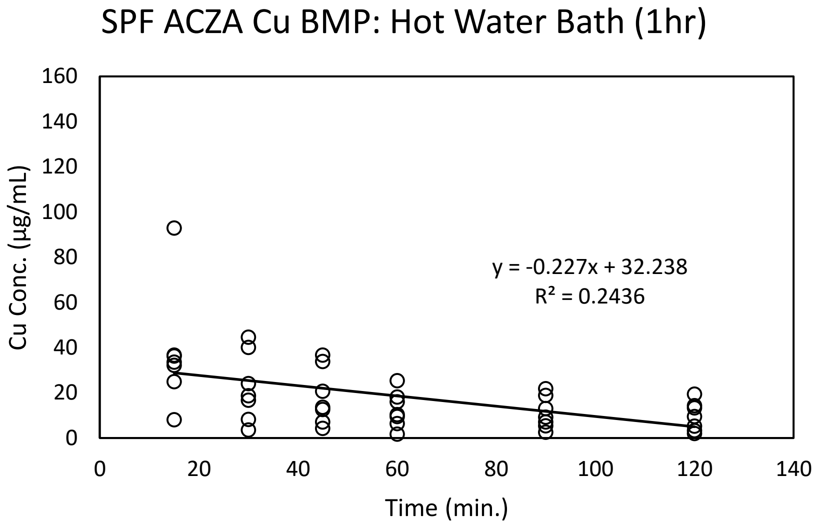
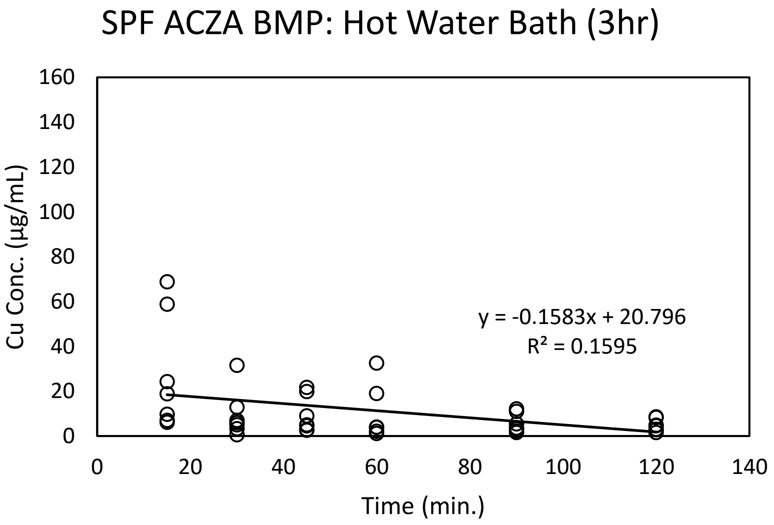


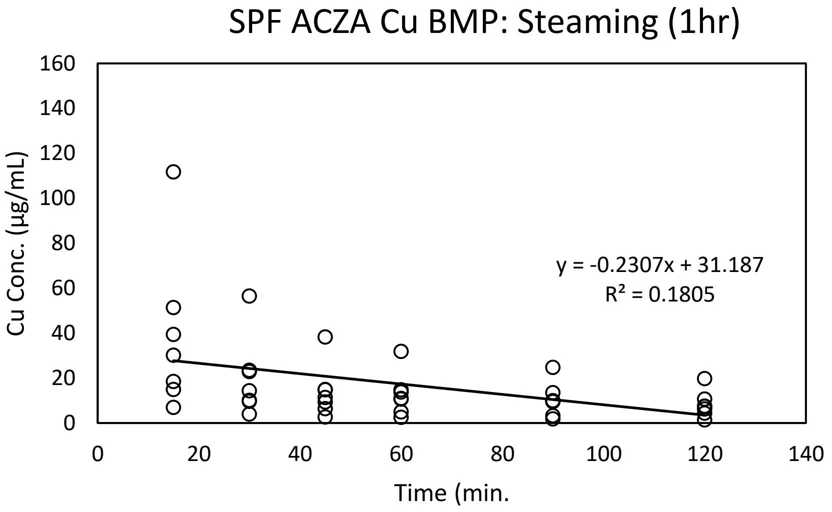
Figure 8. Effect of various BMP processes on copper losses from ammoniacal copper zinc arsenate (ACZA) treated spruce pine fir lumber exposed to simulated rainfall

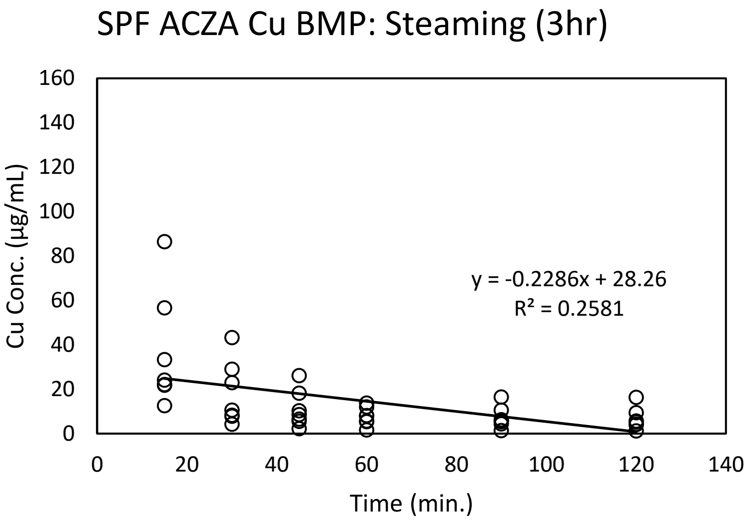



SPF ACZA Cu BMP: Kiln Dry

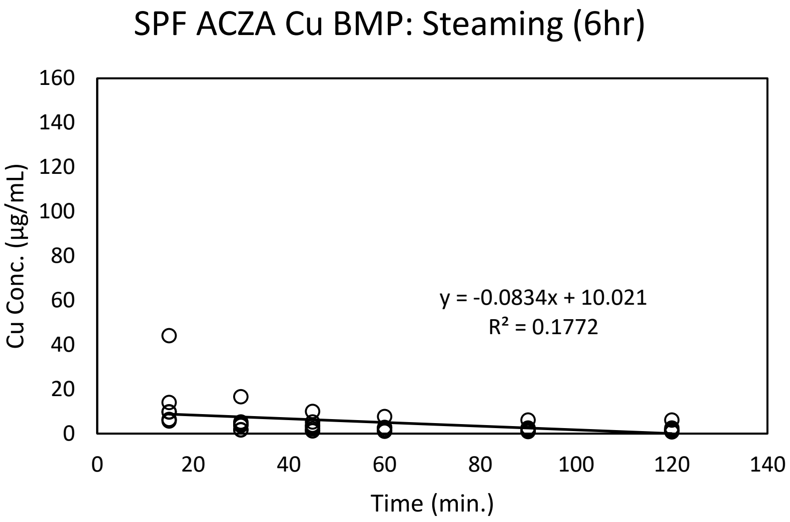

SPF ACZA Cu BMP: Hot Water Bath (1hr)


SPF ACZA BMP: Hot Water Bath (3hr)

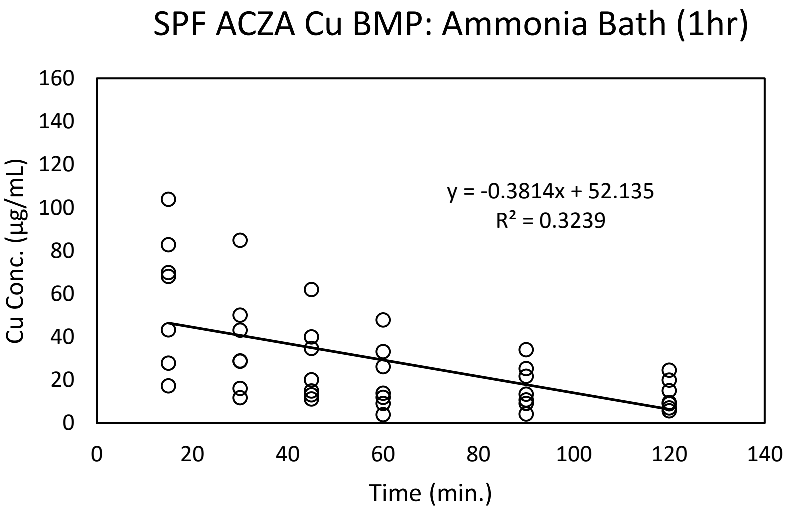

SPF ACZA Cu BMP: Steaming (1hr)



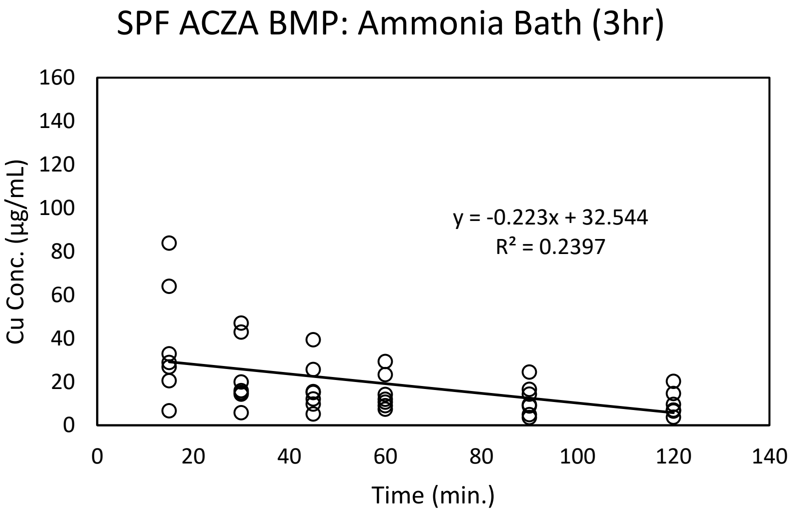
SPF ACZA Cu BMP: Steaming (3hr)



SPF ACZA Cu BMP: Steaming (6hr)

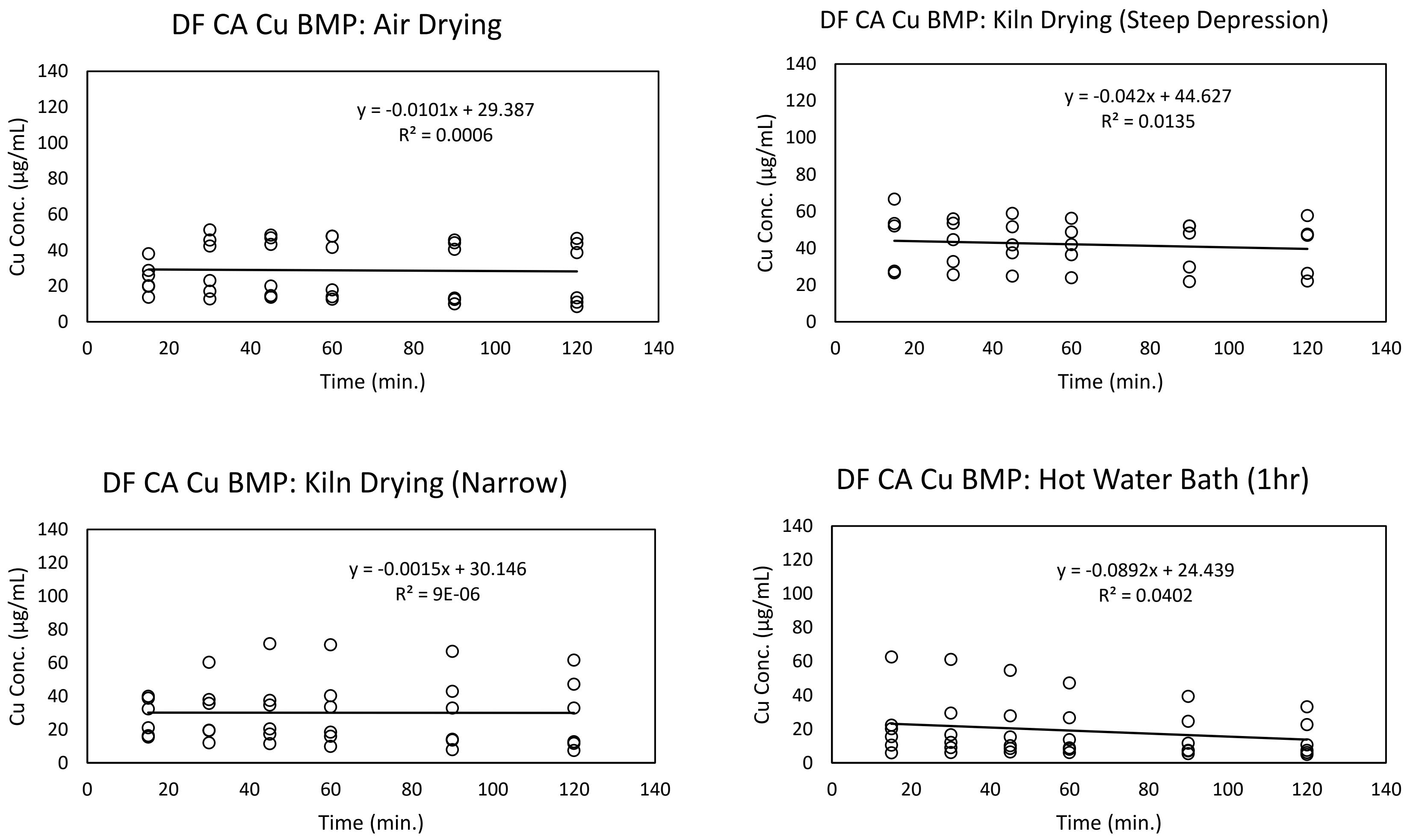


SPF ACZA Cu BMP: Ammonia Bath (1hr)



SPF ACZA BMP: Ammonia Bath (3hr)

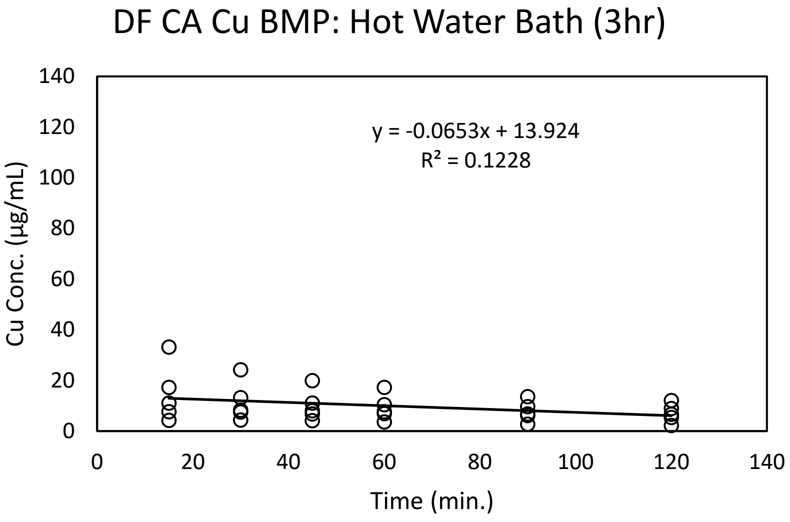
Figure 9. Effect of various BMP processes on copper losses from copper azole (CA) treated douglas fir lumber exposed to simulated rainfall

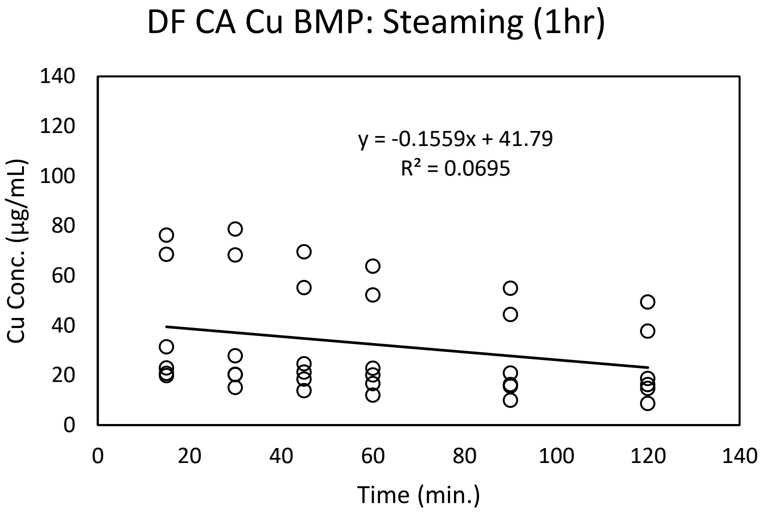

DF CA Cu BMP: Air Drying

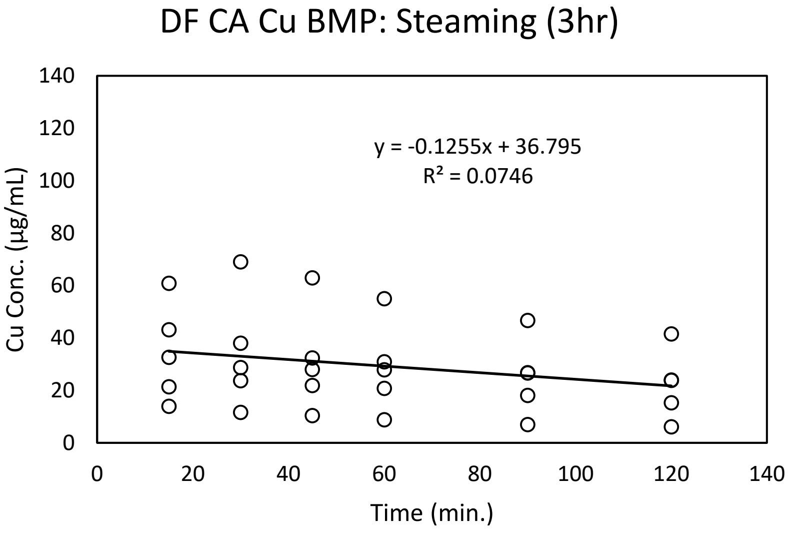
DF CA Cu BMP: Kiln Drying (Steep Depression)

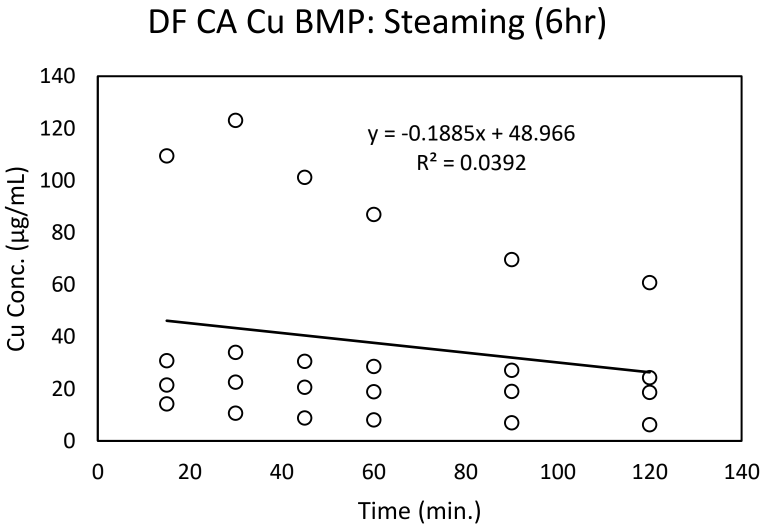
DF CA Cu BMP: Kiln Drying (Narrow)

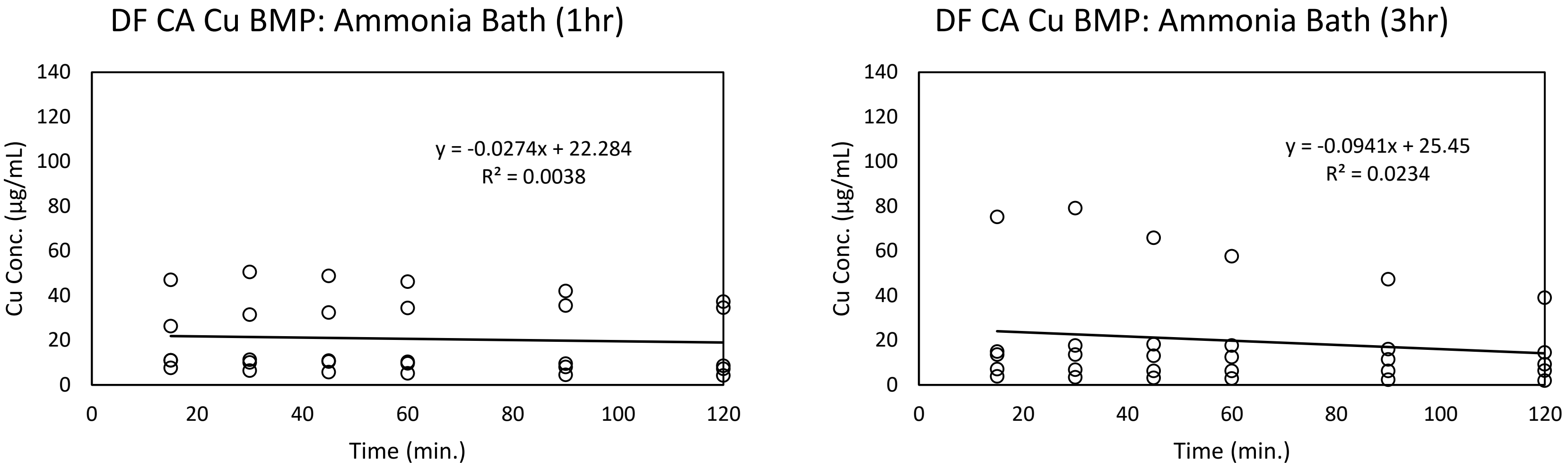
DF CA Cu BMP: Hot Water Bath (1hr)


DF CA Cu BMP: Hot Water Bath (3hr)
y = -0.0653x + 13.924
R² = 0.1228
Cu Conc. (µg/mL)
Time (min.)
0
20
40
60
80
100
120
140


DF CA Cu BMP: Steaming (1hr)
y = -0.1559x + 41.79
R² = 0.0695
Cu Conc. (µg/mL)
Time (min.)
0
20
40
60
80
100
120
140


DF CA Cu BMP: Steaming (3hr)
y = -0.1255x + 36.795
R² = 0.0746
Cu Conc. (µg/mL)
Time (min.)
0
20
40
60
80
100
120
140

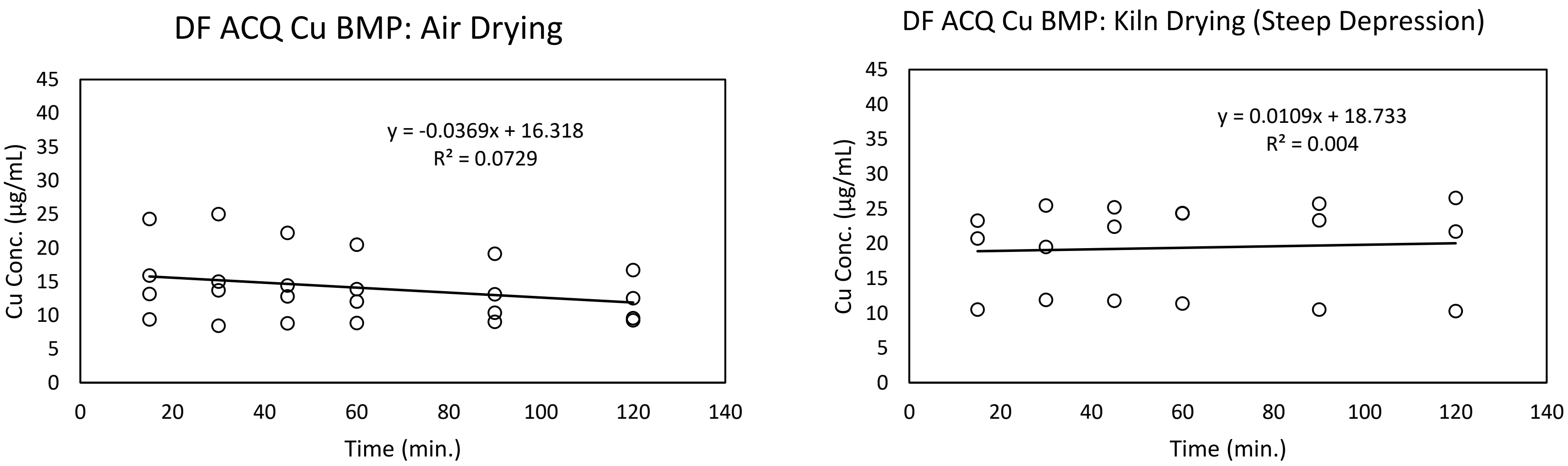

DF CA Cu BMP: Steaming (6hr)
y = -0.1885x + 48.966
R² = 0.0392
Cu Conc. (µg/mL)
Time (min.)
0
20
40
60
80
100
120
140



DF CA Cu BMP: Ammonia Bath (1hr)

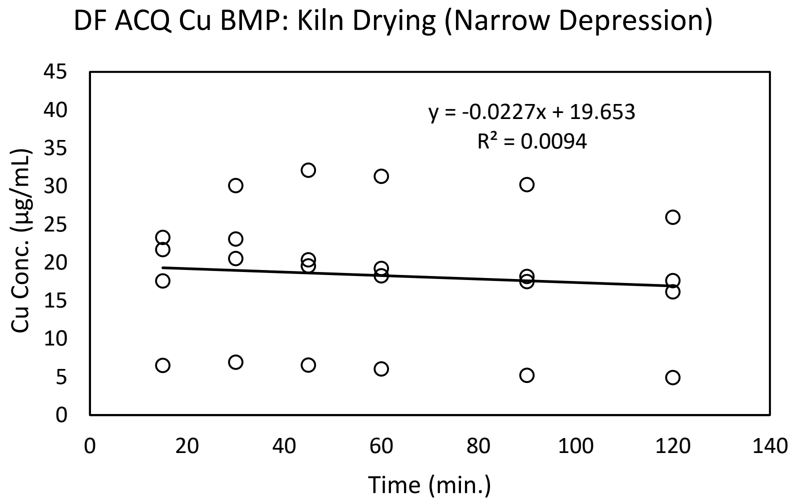
DF CA Cu BMP: Ammonia Bath (3hr)

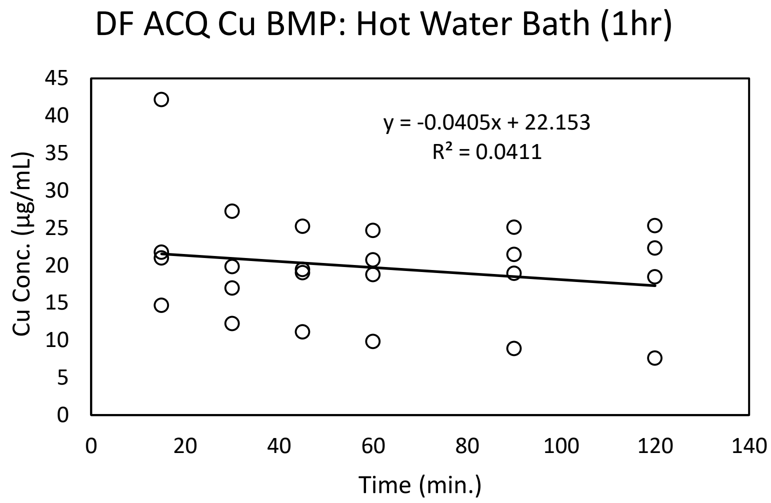
Figure 10. Effect of various BMP processes on copper losses from ammoniacal copper quaternary (ACQ) treated douglas fir lumber exposed to simulated rainfall

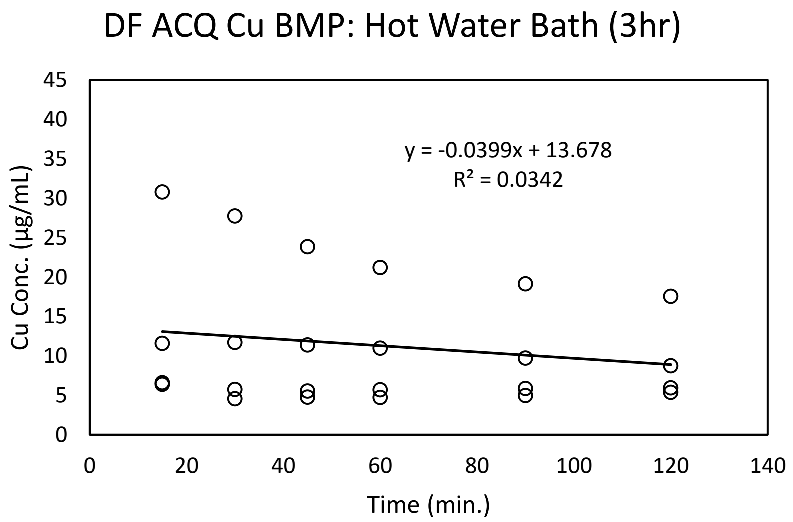


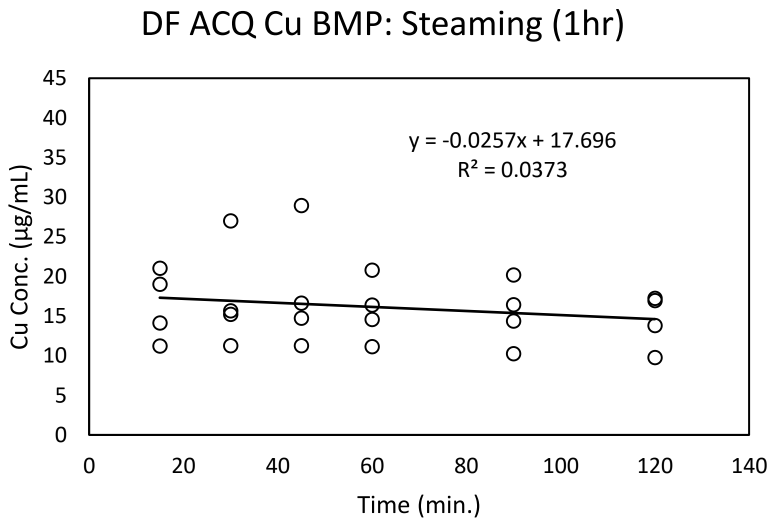
DF ACQ Cu BMP: Air Drying

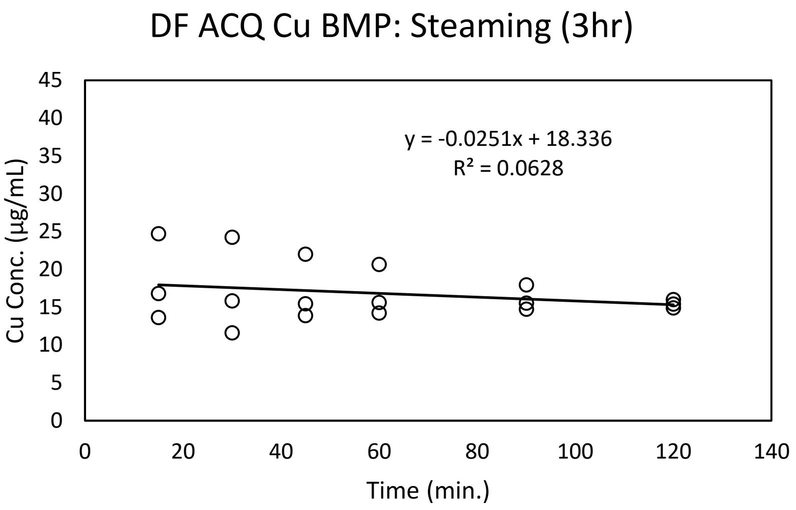
DF ACQ Cu BMP: Kiln Drying (Steep Depression)

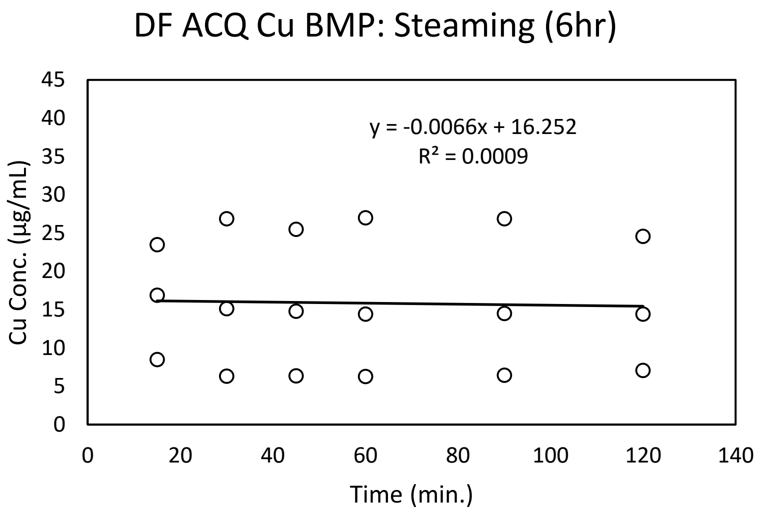

DF ACQ Cu BMP: Kiln Drying (Narrow Depression)

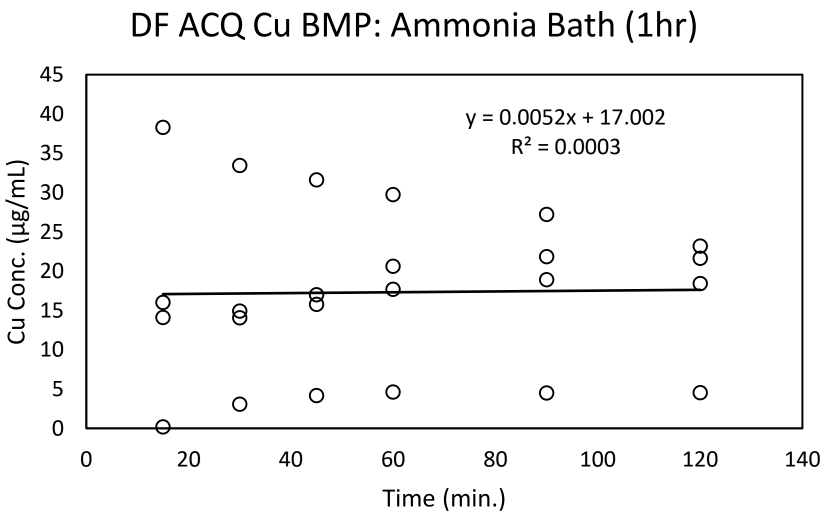

DF ACQ Cu BMP: Hot Water Bath (1hr)


DF ACQ Cu BMP: Hot Water Bath (3hr)


DF ACQ Cu BMP: Steaming (1hr)


DF ACQ Cu BMP: Steaming (3hr)
y = -0.0251x + 18.336
R² = 0.0628
Cu Conc. (µg/mL)
0
5
10
15
20
25
30
35
40
45
0
20
40
60
80
100
120
140
Time (min.)


DF ACQ Cu BMP: Steaming (6hr)
y = -0.0066x + 16.252
R² = 0.0009
Cu Conc. (µg/mL)
0
5
10
15
20
25
30
35
40
45
0
20
40
60
80
100
120
140
Time (min.)


DF ACQ Cu BMP: Ammonia Bath (1hr)
y = 0.0052x + 17.002
R² = 0.0003
Cu Conc. (µg/mL)
0
5
10
15
20
25
30
35
40
45
0
20
40
60
80
100
120
140
Time (min.)

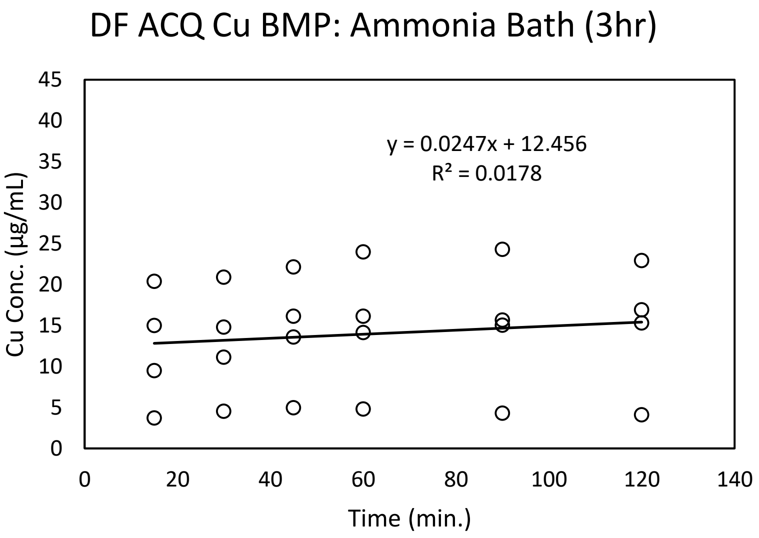
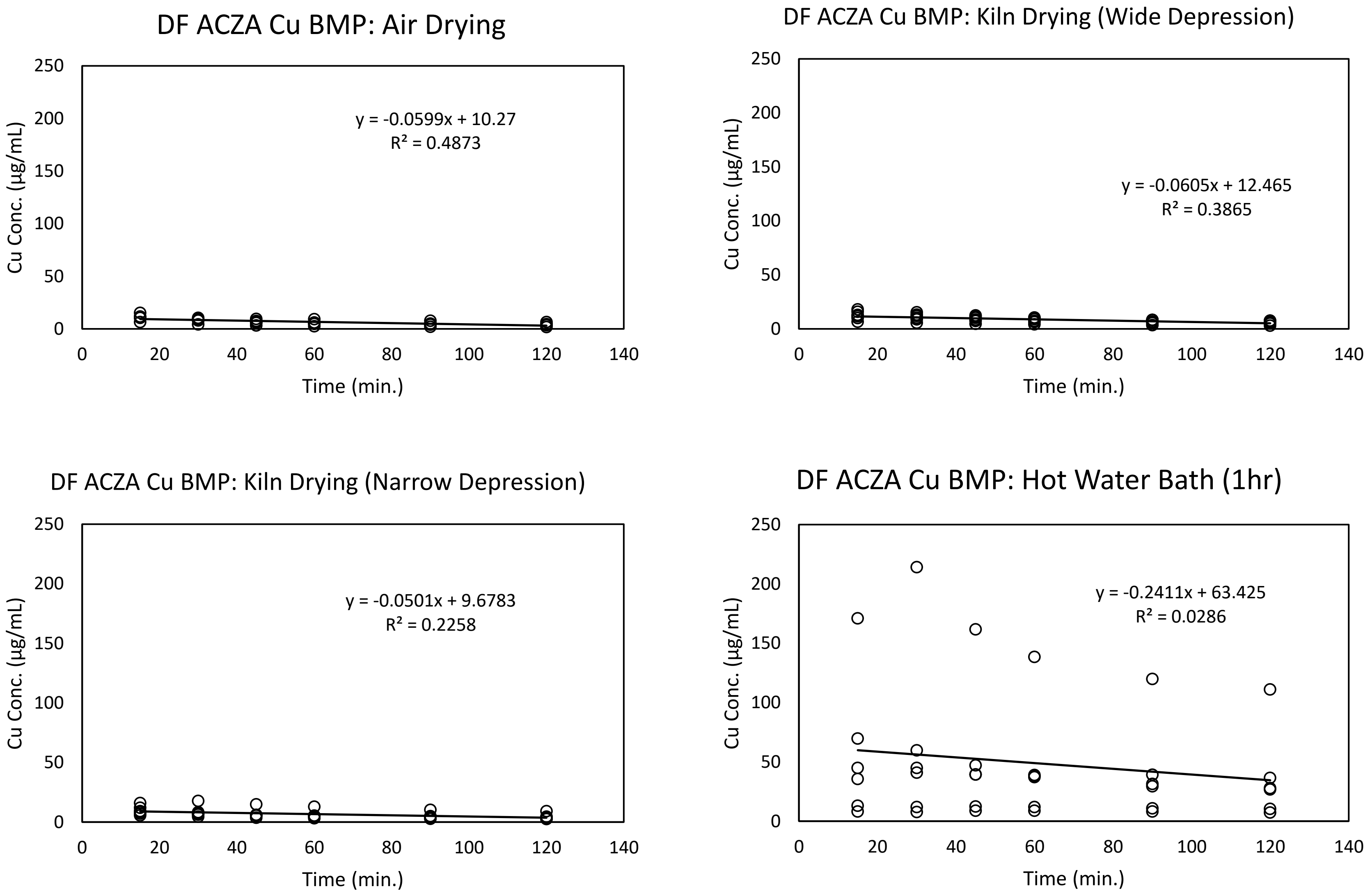
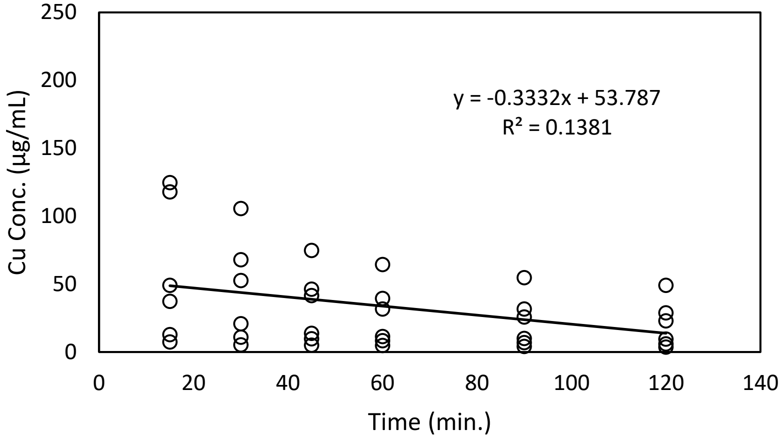

DF ACQ Cu BMP: Ammonia Bath (3hr)
y = 0.0247x + 12.456
R² = 0.0178
Cu Conc. (µg/mL)
0
5
10
15
20
25
30
35
40
45
0
20
40
60
80
100
120
140
Time (min.)

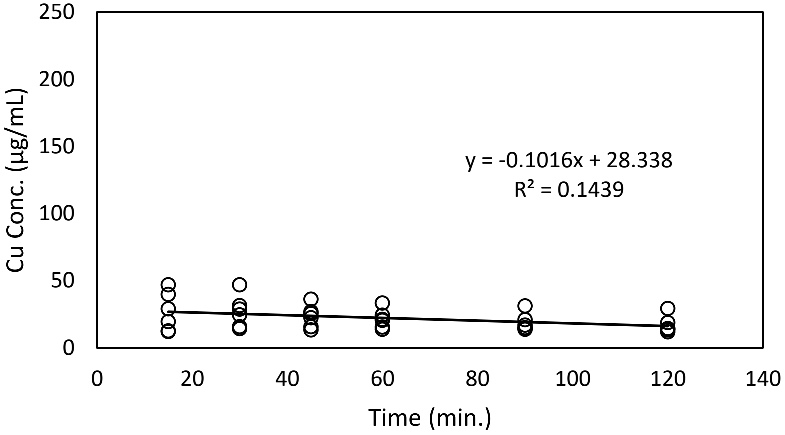
Figure 11. Effect of various BMP processes on copper losses from ammoniacal copper zinc arsenate (ACZA) treated douglas fir lumber exposed to simulated rainfall



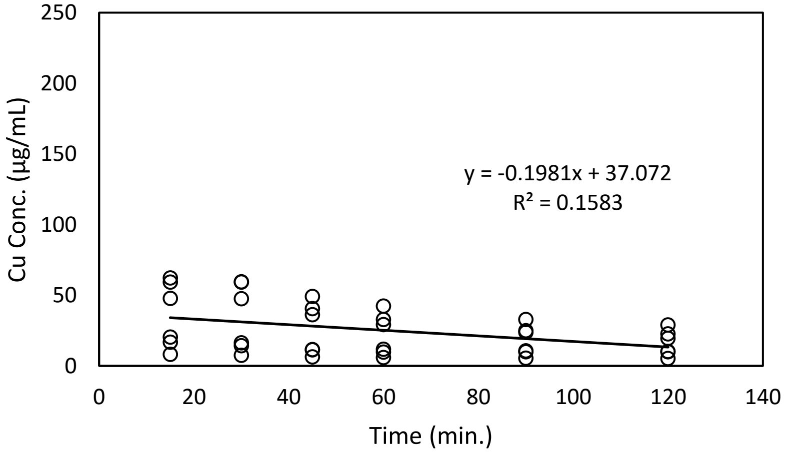
DF ACZA Cu BMP: Hot Water Bath (3hr)



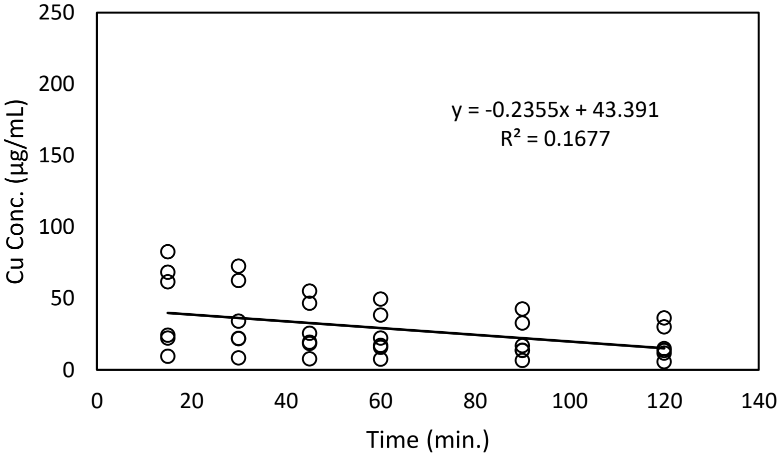
DF ACZA Cu BMP: Steaming (1hr)



DF ACZA Cu BMP: Steaming (3hr)



DF ACZA Cu BMP: Steaming (6hr)



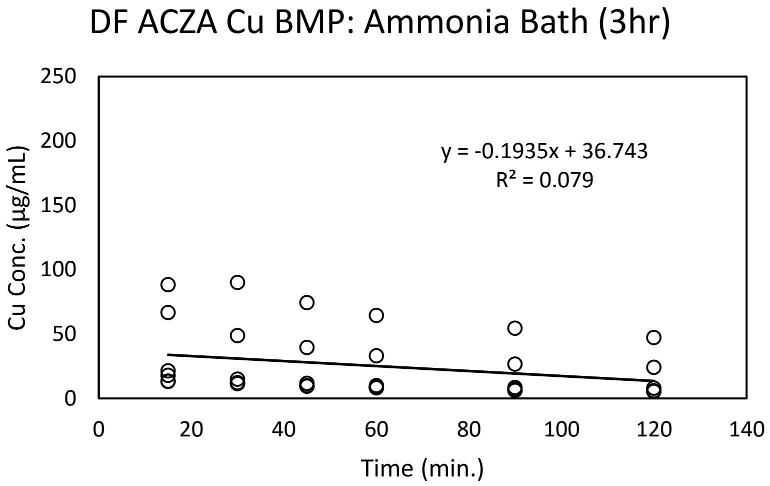
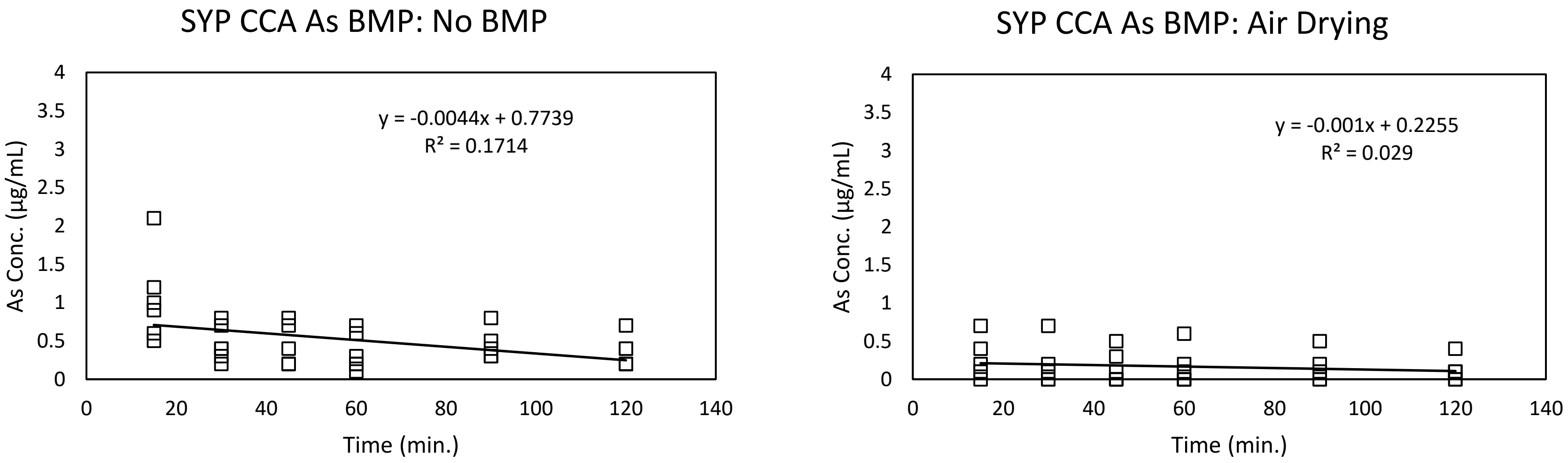
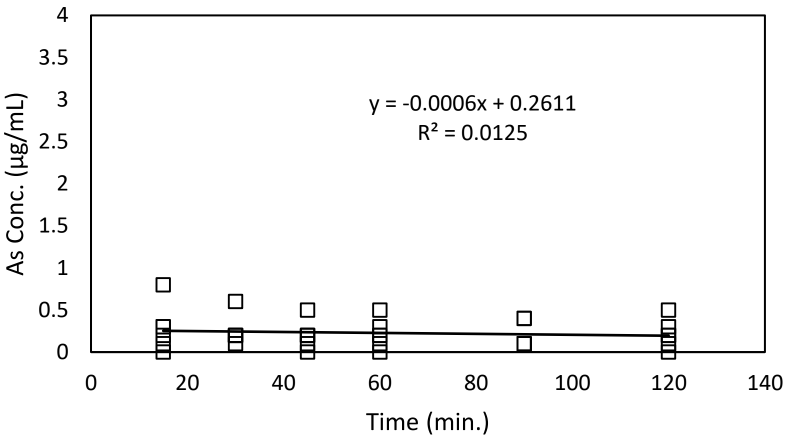
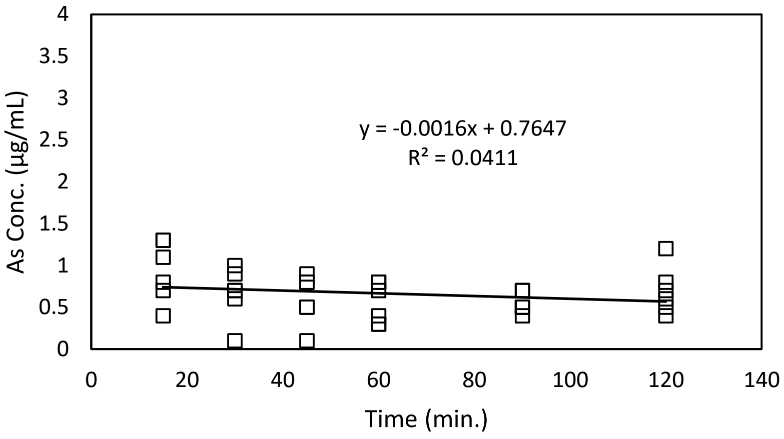
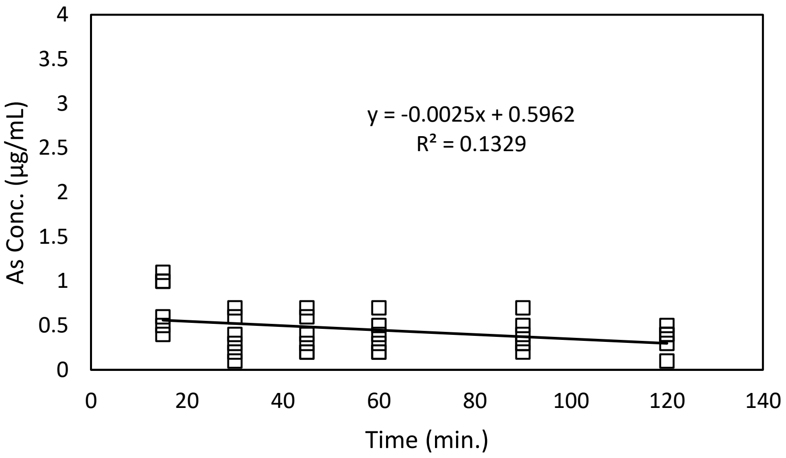


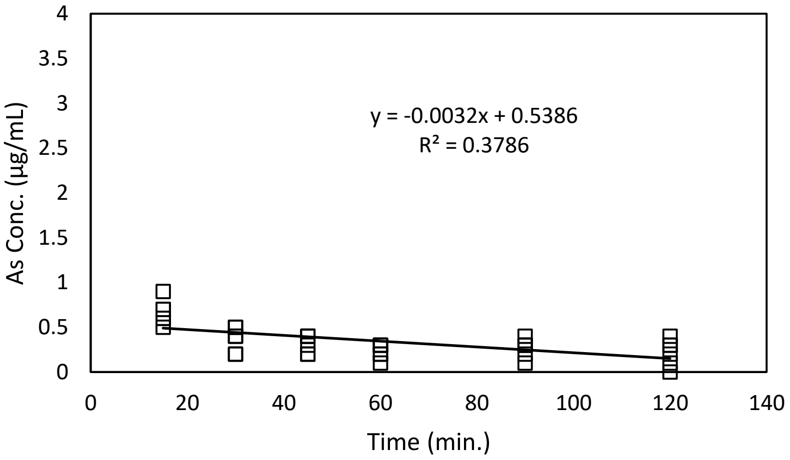
Figure 12. Effect of various BMP processes on arsenic losses from chromated copper arsenate (CCA) treated southern pine lumber exposed to simulated rainfall




SYP CCA As BMP: Kiln Drying


SYP CCA As BMP: Hot Water Bath (1hr)


SYP CCA As BMP: Hot Water Bath (3hr)


SYP CCA As BMP: Steaming (1hr)

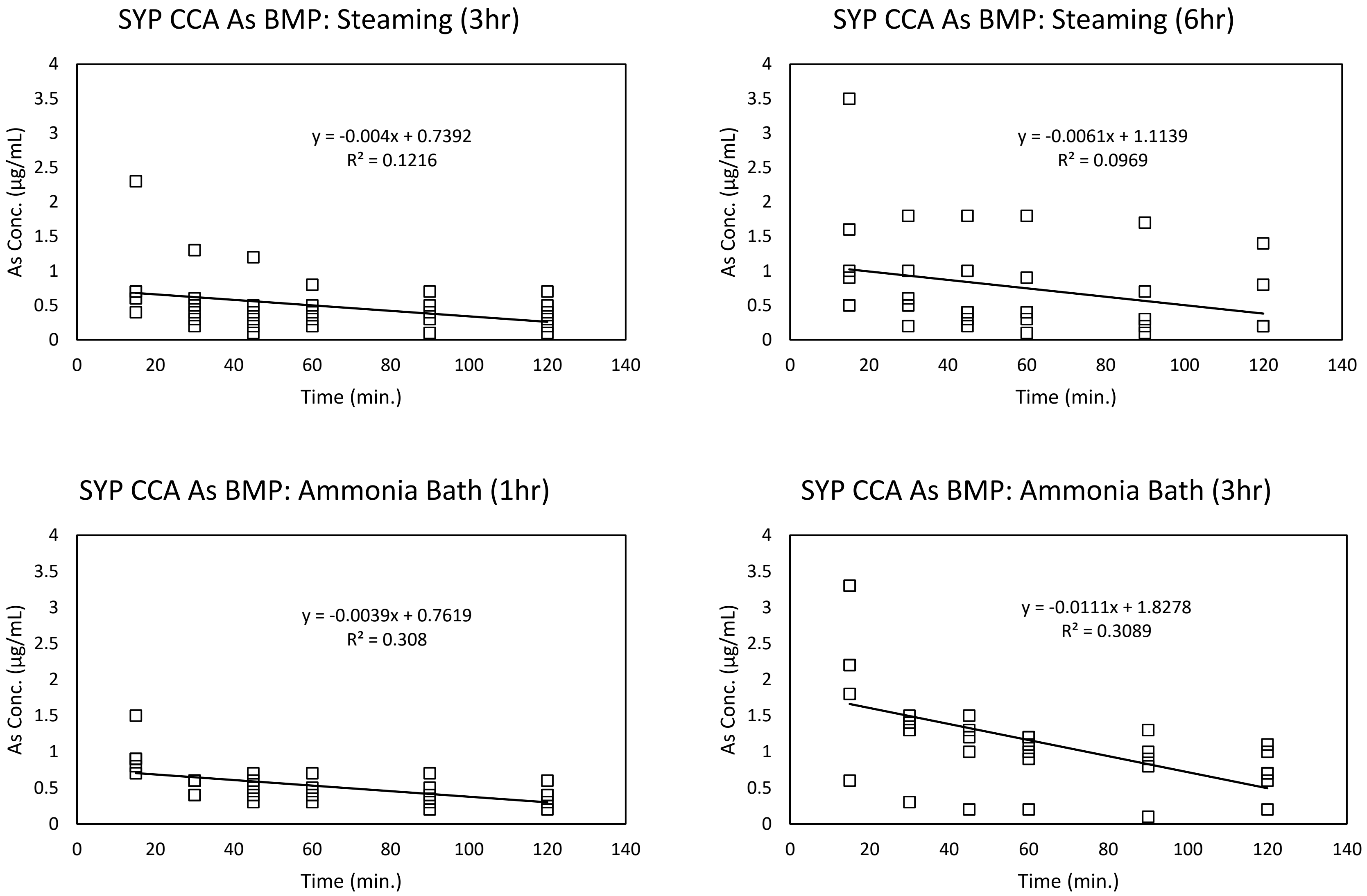
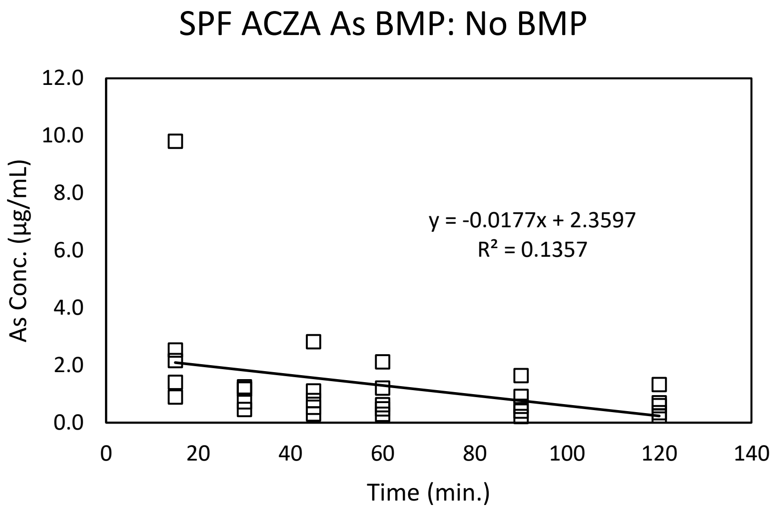
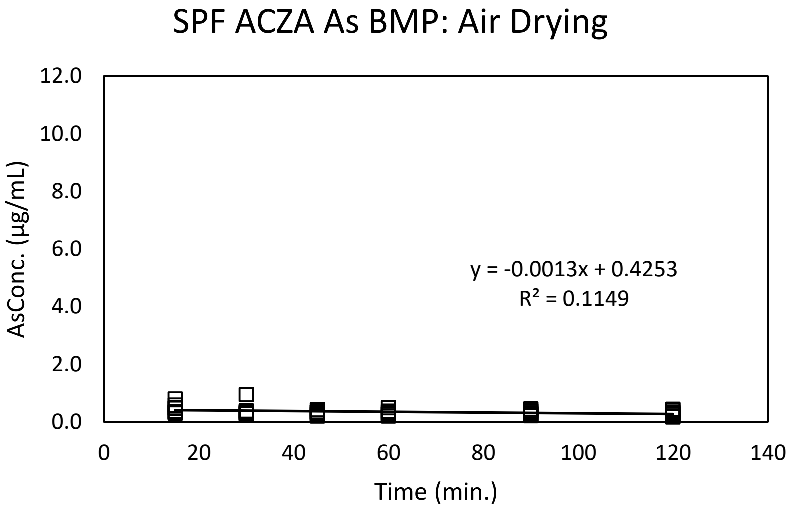
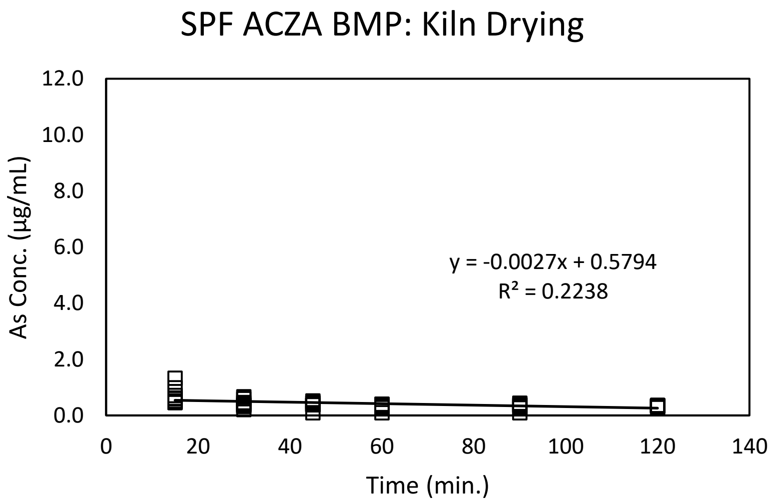
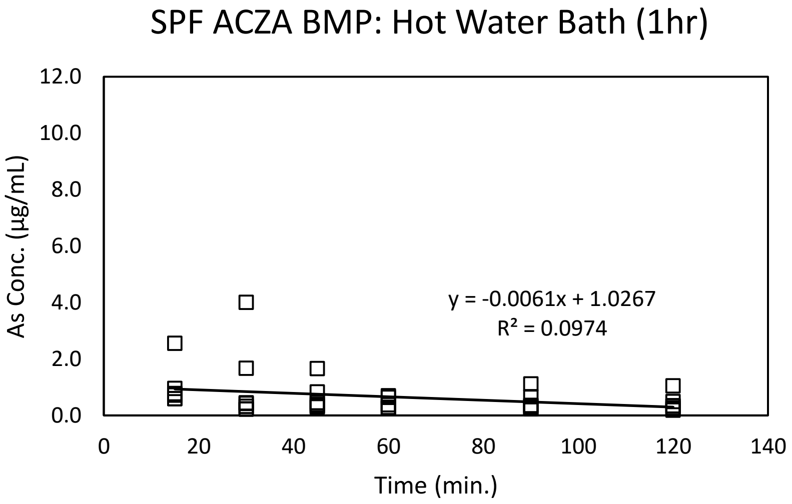


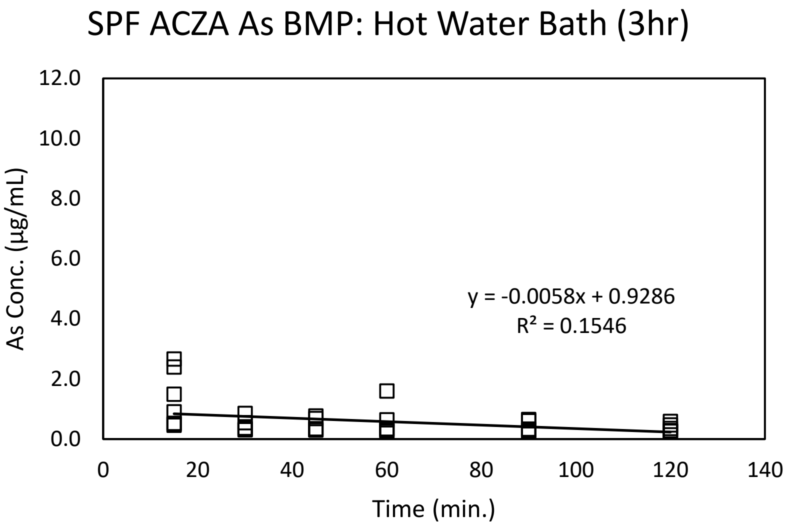
Figure 13. Effect of various BMP processes on arsenic losses from ammoniacal copper zinc arsenate (ACZA) treated spruce pine fir lumber exposed to simulated rainfall


SPF ACZA As BMP: No BMP

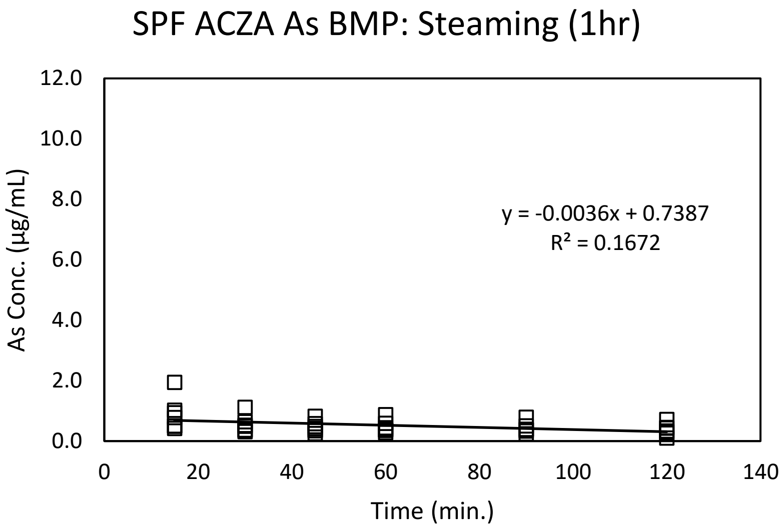

SPF ACZA As BMP: Air Drying


SPF ACZA BMP: Kiln Drying

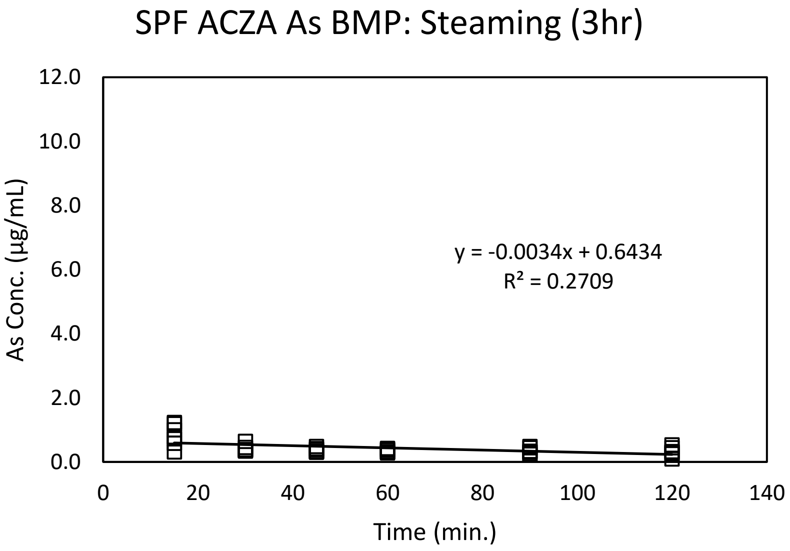

SPF ACZA BMP: Hot Water Bath (1hr)



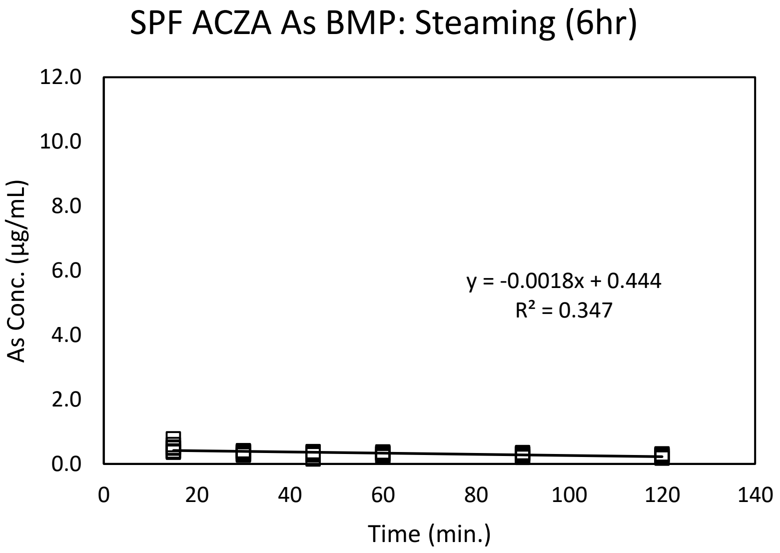
SPF ACZA As BMP: Hot Water Bath (3hr)



SPF ACZA As BMP: Steaming (1hr)



SPF ACZA As BMP: Steaming (3hr)



SPF ACZA As BMP: Steaming (6hr)

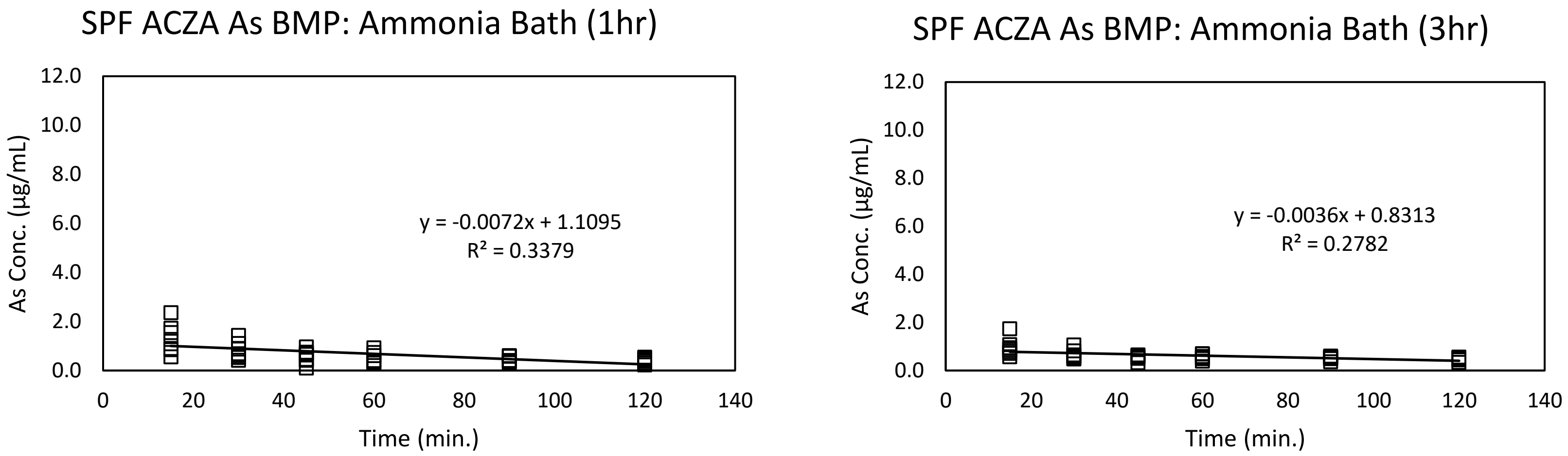
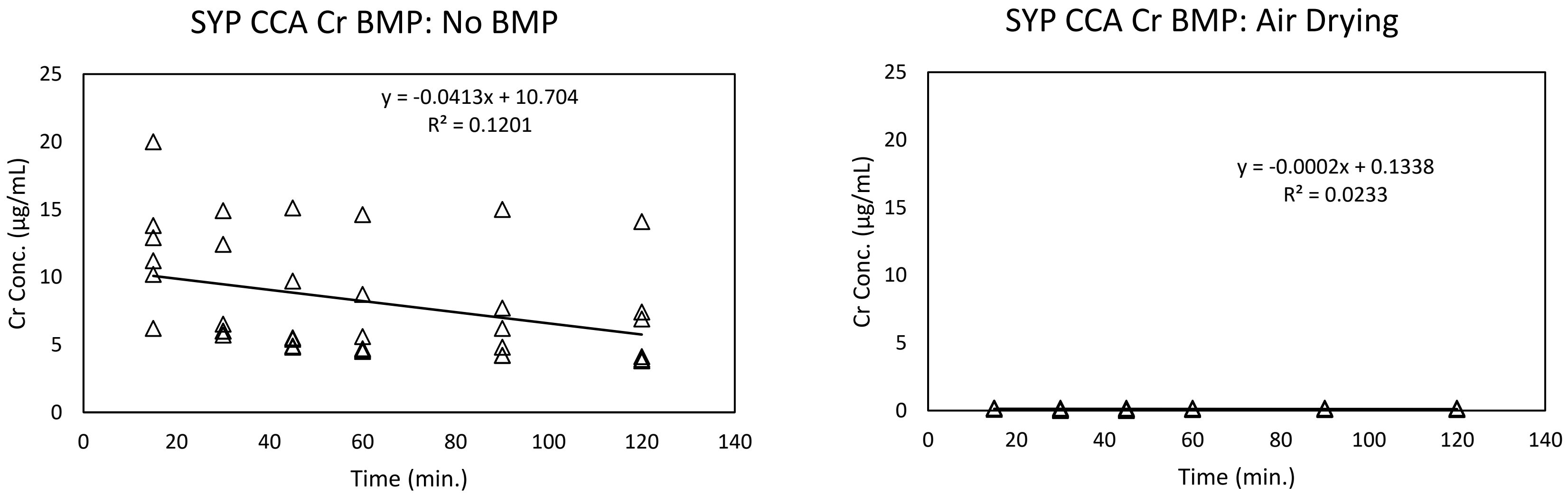
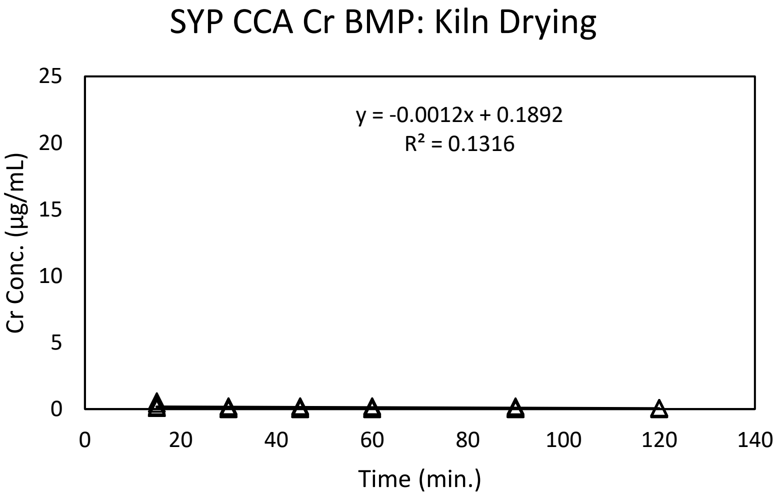
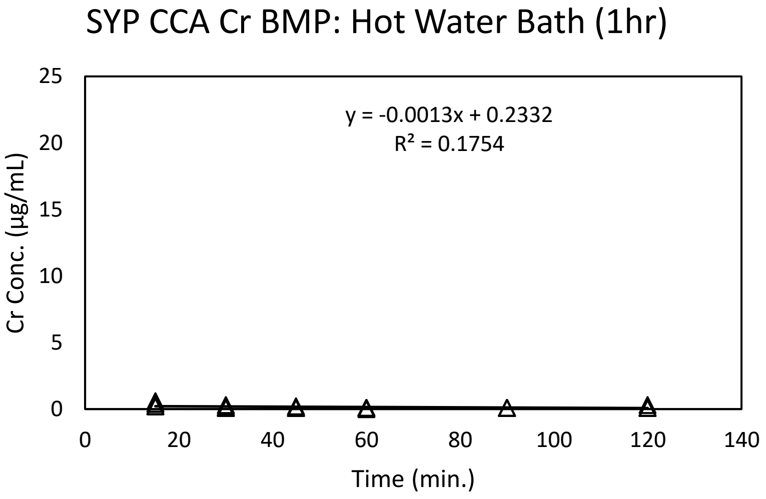
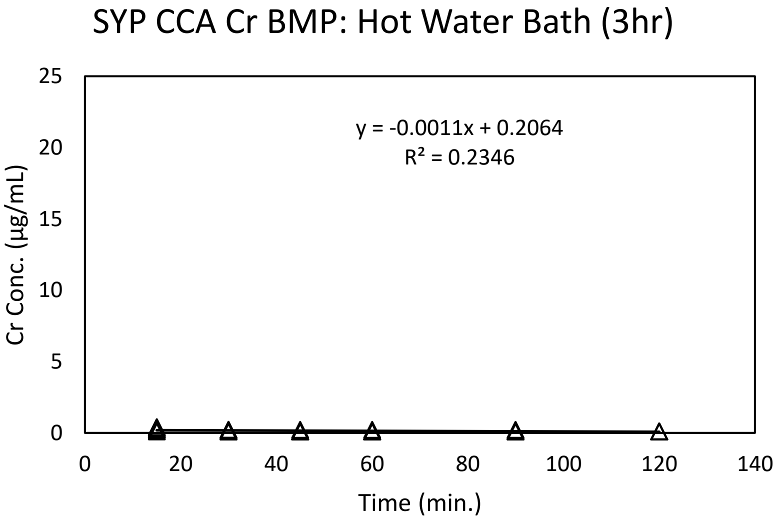


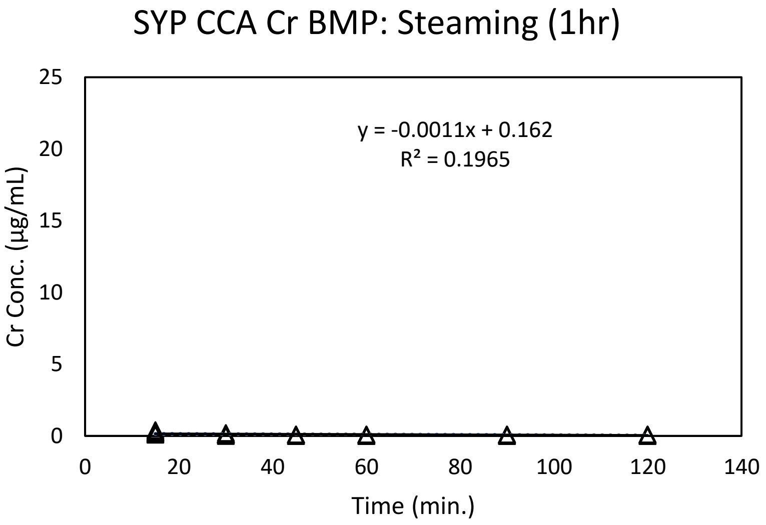
Figure 14. Effect of various BMP processes on chromium losses from chromated copper arsenate (CCA) treated southern pine lumber exposed to simulated rainfall

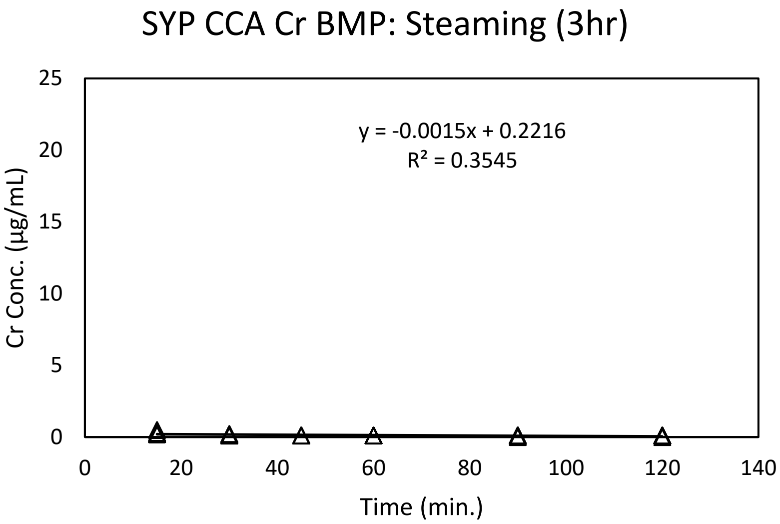


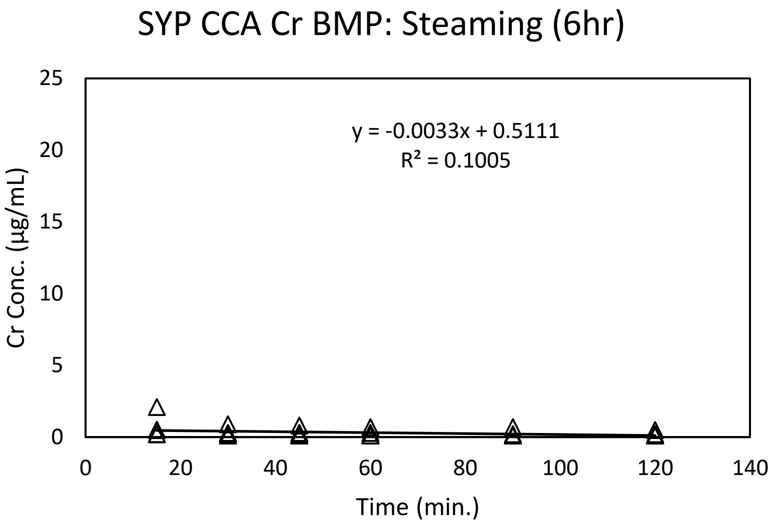

SYP CCA Cr BMP: Kiln Drying

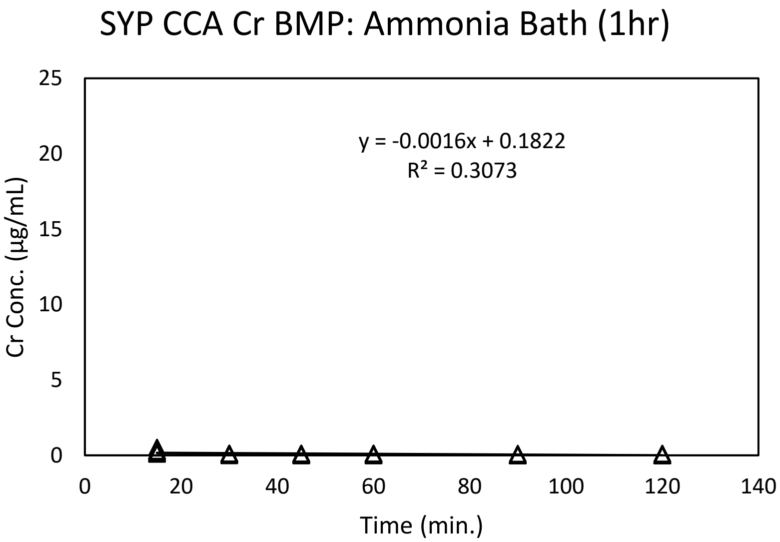

SYP CCA Cr BMP: Hot Water Bath (1hr)


SYP CCA Cr BMP: Hot Water Bath (3hr)


SYP CCA Cr BMP: Steaming (1hr)


SYP CCA Cr BMP: Steaming (3hr)


SYP CCA Cr BMP: Steaming (6hr)


SYP CCA Cr BMP: Ammonia Bath (1hr)

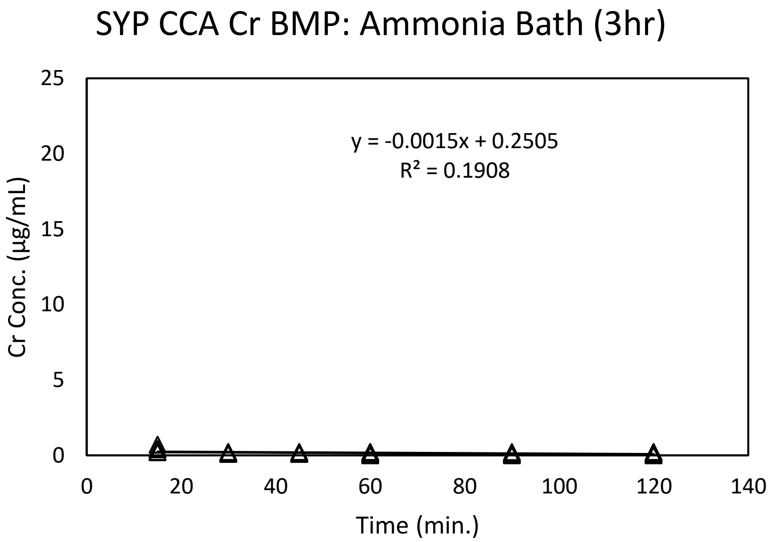
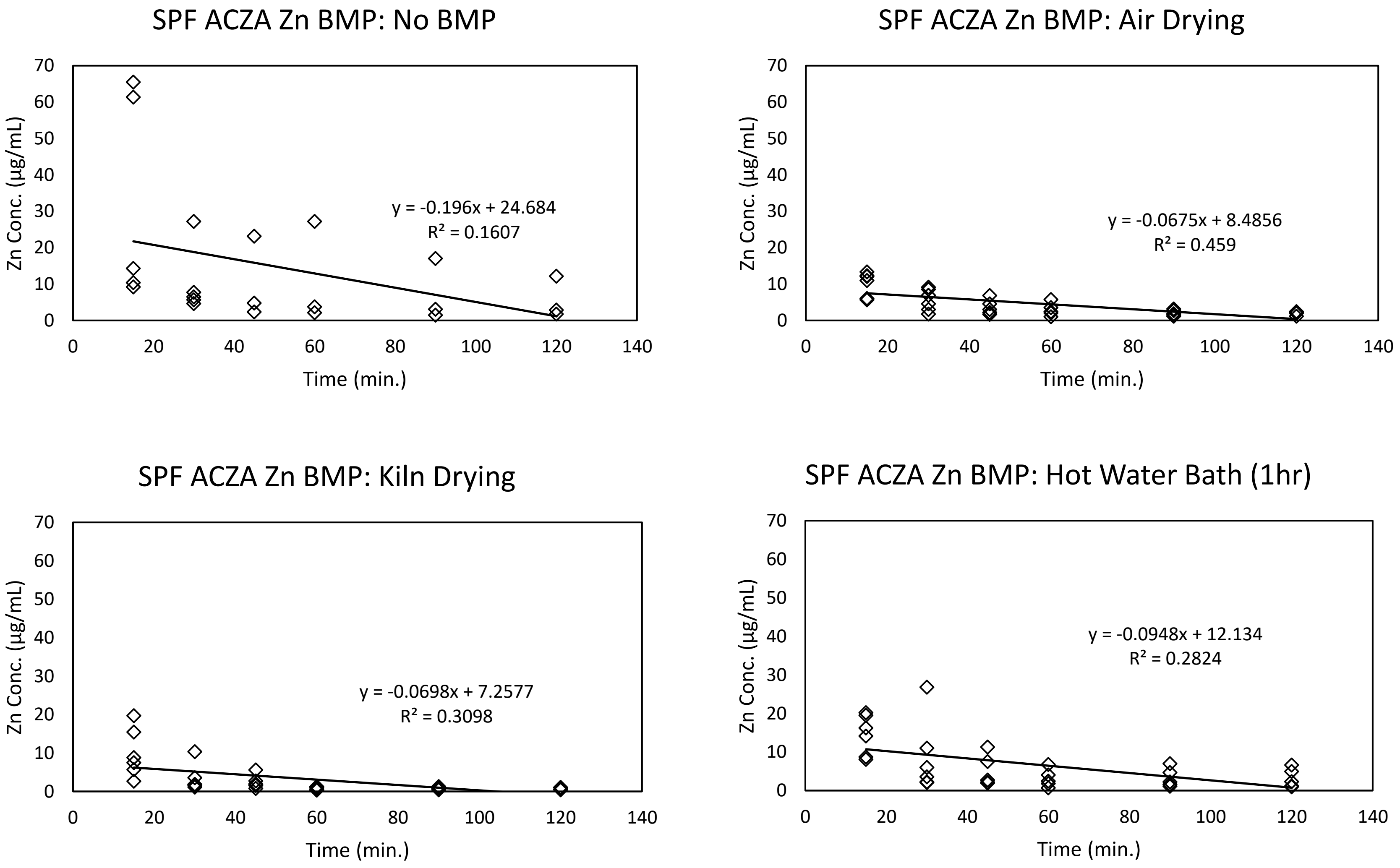
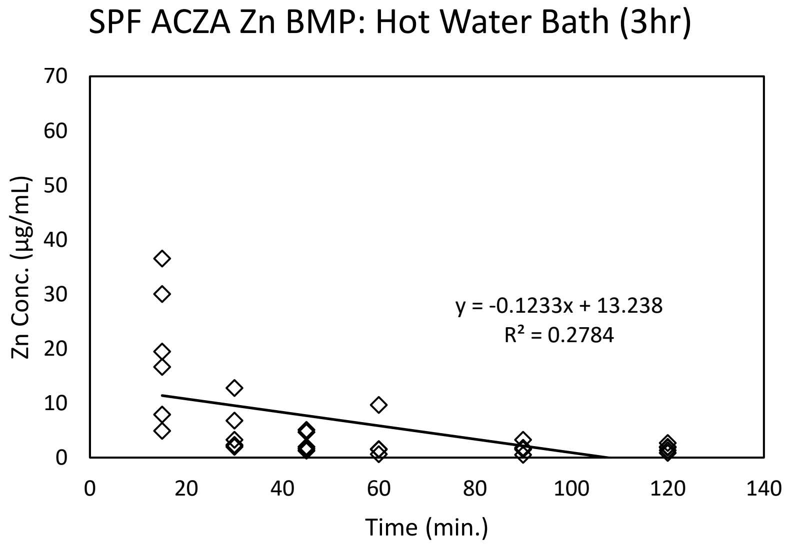
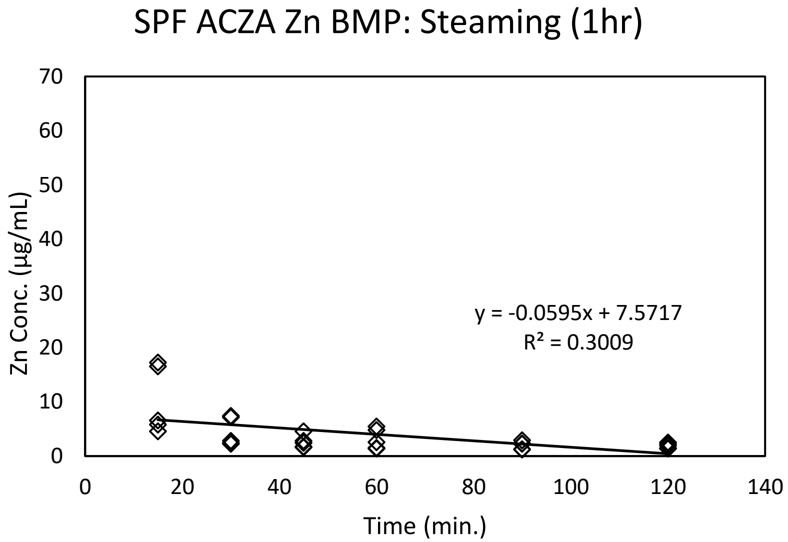
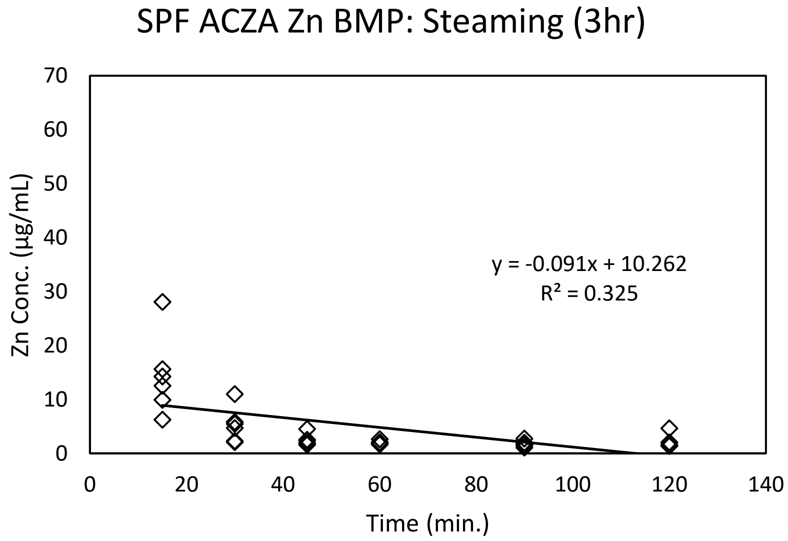

SYP CCA Cr BMP: Ammonia Bath (3hr)

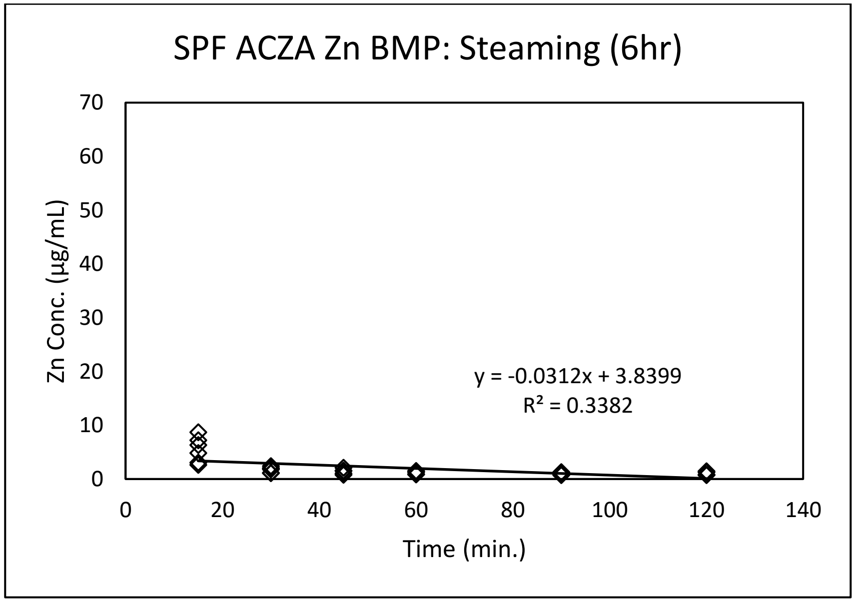
Figure 15. Effect of various BMP processes on zinc losses from ammoniacal copper zinc arsenate (ACZA) treated spruce pine fir lumber exposed to simulated rainfall

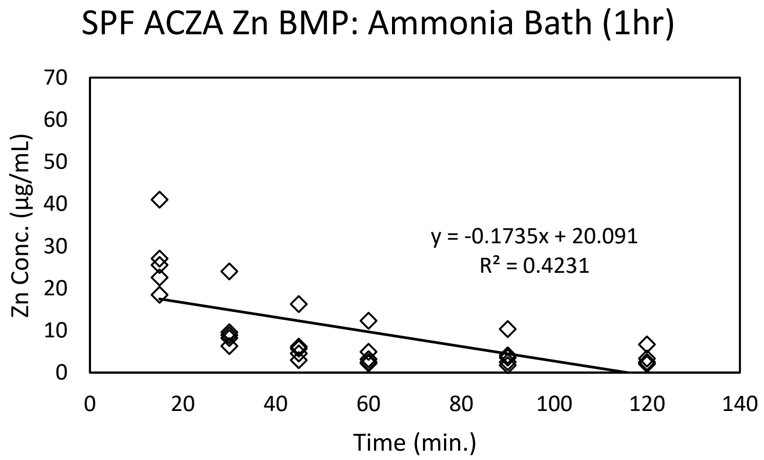



SPF ACZA Zn BMP: Hot Water Bath (3hr)


SPF ACZA Zn BMP: Steaming (1hr)


SPF ACZA Zn BMP: Steaming (3hr)


SPF ACZA Zn BMP: Steaming (6hr)


SPF ACZA Zn BMP: Ammonia Bath (1hr)

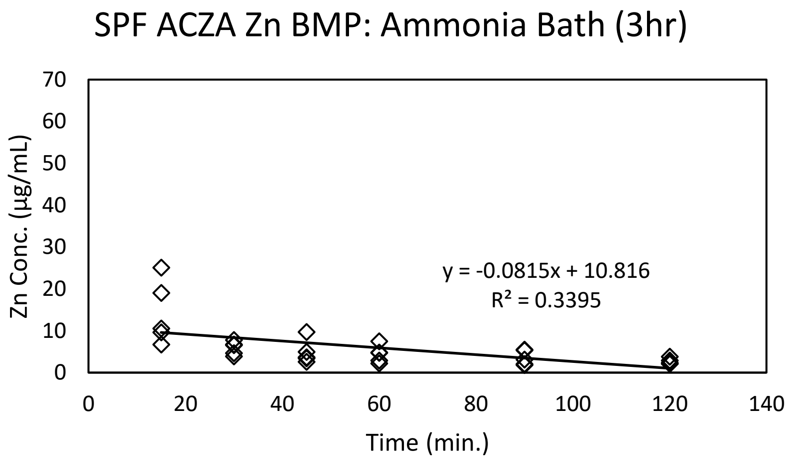

SPF ACZA Zn BMP: Ammonia Bath (3hr)

Table 3. Copper levels in runoff from southern pine and spruce-pine-fir decking materials treated with selected copper based preservatives and subjected to 15, 30, and 120 minutes of simulated rainfall.

System	Wood Species	Rainfall Time (Min)	Copper Levels in Runoff (µg/mL)[a]									
			None	Air Dry	Kiln dry	Hot water		Steam			Ammonia Bath	
						1 hr	3 hr	1 hr	3 hr	6 hr	1 hr	3 hr
Copper azole	SPF	15	9.26 (3.47)	4.08 (1.48)	5.38 (1.47)	3.36 (1.16)	7.57 (3.21)	10.56 (6.64)	6.70 (2.84)	3.78 (1.98)	1.77 (1.01)	3.04 (3.29)
		30	5.21 (1.89)	2.70 (1.09)	2.97 (1.04)	1.56 (0.51)	3.92 (1.98)	6.09 (3.30)	3.65 (1.47)	2.35 (1.00)	2.97 (1.04)	1.34 (0.98)
		120	2.01 (0.95)	1.42 (0.56)	1.60 (0.53)	0.75 (0.37)	1.48 (0.58)	2.74 (1.34)	1.69 (0.66)	1.57 (0.73)	0.45 (0.24)	0.62 (0.23)
	SYP	15	18.15 (9.00)	18.11 (9.05)	17.23 (8.13)	6.10 (2.89)	4.53 (2.03)	7.83 (2.15)	6.89 (2.05)	5.65 (1.96)	3.44 (1.27)	6.09 (3.12)
		30	9.54 (6.44)	11.98 (6.67)	14.64 (9.95)	3.10 (1.70)	2.22 (1.13)	3.62 (0.98)	2.91 (0.84)	2.51 (1.16)	1.45 (0.52)	3.07 (1.36)
		120	4.48 (3.55)	8.02 (3.98)	10.93 (4.23)	1.71 (1.34)	1.28 (0.62)	1.79 (0.48)	1.41 (0.40)	1.59 (1.06)	0.95 (0.21)	1.97 (1.49)
	DF	15	-	24.42 (8.47)	45.17 (17.59)	22.88 (20.37)	14.62 (11.39)	39.93 (25.56)	34.38 (18.49)	44.05 (44.16)	20.62 (16.48)	22.96 (29.62)
		30	-	32.07 (16.35)	42.41 (13.08)	22.47 (20.66)	11.52 (7.77)	38.38 (27.68)	34.24 (21.66)	47.62 (51.25)	21.98 (18.76)	24.15 (31.29)
		120	-	26.99 (17.78)	40.08 (15.20)	14.18 (11.27)	7.01 (3.68)	24.22 (15.76)	22.16 (13.08)	27.53 (23.40)	18.41 (16.16)	14.27 (14.62)
ACQ	SPF	15	2.79 (2.38)	5.17 (5.17)	5.71 (2.22)	1.38 (1.16)	3.66 (3.26)	7.03 (3.60)	7.61 (5.24)	12.56 (16.37)	1.37 (1.13)	1.76 (1.20)
		30	1.60 (1.36)	3.28 (3.22)	2.99 (1.28)	0.75 (0.66)	2.03 (1.72)	3.92 (2.27)	3.87 (2.58)	5.95 (7.67)	0.76 (0.77)	0.63 (0.45)
		120	0.65 (0.46)	1.39 (1.44)	1.39 (0.88)	0.37 (0.34)	0.96 (0.87)	1.38 (0.73)	2.11 (1.57)	3.02 (2.93)	0.39 (0.36)	0.23 (0.13)
	SYP	15	47.84 (24.72)	18.09 (3.33)	15.83 (5.00)	15.34 (4.53)	8.48 (1.65)	15.57 (5.02)	13.92 (4.49)	13.68 (8.95)	8.11 (5.32)	7.28 (1.40)
		30	23.72 (10.12)	14.00 (3.68)	12.27 (4.06)	5.26 (2.92)	3.48 (1.25)	6.82 (2.55)	6.89 (3.23)	4.70 (3.12)	3.34 (2.00)	3.64 (1.26)
		120	12.04 (3.66)	8.00 (1.76)	8.16 (2.35)	3.04 (1.03)	1.89 (0.69)	3.56 (0.99)	3.33 (1.41)	2.46 (1.06)	1.97 (1.34)	1.66 (0.63)
	DF	15	-	15.70(6.32)	17.28 (7.57)	24.93 (11.95)	13.85 (11.55)	16.33 (4.48)	18.37 (5.71)	16.30 (7.52)	17.15 (15.76)	12.15 (7.18)
		30	-	15.55 (6.93)	20.17 (9.70)	19.09 (6.28)	12.46 (10.67)	17.27 (6.77)	17.22 (6.42)	16.10 (10.32)	16.38 (12.59)	12.85 (6.84)
		120	-	12.03 (3.45)	16.17 (8.65)	18.44 (7.75)	9.42 (5.64)	14.42 (3.49)	15.43 (0.55)	15.34 (8.79)	16.95 (8.52)	14.82 (7.87)
CCA	SPF	15	1.31 (0.49)	0.23 (0.11)	0.14 (0.05)	0.67 (0.23)	1.69 (0.28)	1.60 (087)	3.47 (0.46)	3.71 (2.06)	0.22 (0.12)	0.31 (0.16)
		30	0.73 (0.26)	0.12 (0.04)	0.10 (0.00)	0.36 (0.10)	0.92 (0.21)	0.84 (0.57)	2.09 (0.36)	1.95 (0.98)	0.10 (0.00)	0.16 (0.06)
		120	0.44 (0.12)	0.10 (0.01)	0.10 (0.00)	0.17 (0.05)	0.44 (0.09)	0.37 (0.14)	0.93 (0.33)	1.16 (0.79)	0.10 (0.00)	0.11 (0.02)
	SYP	15	1.18 (0.48)	0.48 (0.45)	0.45 (0.31)	3.18 (2.04)	1.30 (0.42)	2.37 (0.85)	3.08 (1.96)	6.30 (2.27)	0.28 (0.13)	0.78 (0.86)
		30	0.98 (0.33)	0.28 (0.33)	0.20 (0.09)	1.33 (0.56)	0.83 (0.31)	1.20 (0.58)	1.58 (0.95)	3.05 (0.96)	0.10 (0.06)	0.33 (0.38)
		120	0.80 (0.25)	0.15 (0.18)	0.12 (0.08)	0.97 (0.47)	0.65 (0.20)	0.67 (0.30)	0.87 (0.48)	1.63 (0.87)	0.03 (0.05)	0.15 (0.20)
ACZA	SPF	15	60.95 (47.44)	2.33 (1.03)	3.70 (5.35)	37.80 (26.23)	27.69 (25.72)	38.94 (35.50)	36.70 (26.01)	13.73 (13.72)	58.99 (30.92)	37.67 (26.76)
		30	36.43 (25.23)	4.46 (8.51)	1.69 (2.43)	22.28 (15.31)	9.54 (10.45)	20.03 (17.54)	18.00 (14.29)	5.33 (5.14)	37.66 (24.82)	23.03 (15.65)
		120	14.16 (8.12)	0.77 (0.26)	0.61 (0.93)	9.61 (6.43)	4.90 (2.69)	8.14 (5.84)	6.58 (4.93)	2.19 (1.78)	12.99 (7.12)	9.83 (5.74)
	DF	15	-	10.97 (2.85)	12.47 (4.07)	57.07 (60.08)	58.20 (51.25)	26.57 (14.53)	35.65 (23.50)	44.83 (29.79)	66.18 (71.42)	36.85 (32.37)
		30	-	8.29 (2.11)	10.82 (3.42)	63.22 (76.54)	43.87 (38.94)	26.82(11.97)	33.97 (23.97)	36.94 (25.34)	56.90 (64.38)	31.58 (32.10)
		120	-	4.04 (1.57)	6.00 (1.80)	36.65 (38.09)	19.97 (17.36)	16.87 (6.45)	15.97 (9.05)	18.77 (11.83)	34.18 (35.74)	16.09 (16.90)

[a]Values represent means of 8 replicates per treatment while figures in parentheses represent one standard deviation.

Effects of BMP's on Pentachlorophenol (PCP) Migration: Unlike the copper-based systems, PCP does not directly interact or fix with the wood. As a result, migration becomes more dependent on the characteristics of the solvent employed, presence of surface deposits that might lead to whole oil migration, and the characteristics of the wood. BMP tests on PCP treated wood have only been completed for steaming on southern pine and spruce-pine-fir (SPF); further tests are planned using combinations of steam, vacuum and expansion baths to evaluate the benefits of these procedures.

PCP was analyzed by adding 2.5 mL 1N NaOH to each flask containing runoff water. 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. The extraction was repeated with another 2.5 mL of 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 N H_2SO_4. The flask was stirred for 1 min and allowed to stand for 30 min. Then 2.5 mL iso-octane was added to the flask which was stirred for 1 min to extract the PCP. The iso-octane layer was transferred to a 20 mL glass vial and the extraction repeated with an additional 2.5 mL iso-octane. This second extract was added to the first.

High resolution gas chromatography – low resolution mass spectrometry (HRGC-LRMS) analysis was carried out by injecting 1 µL of sample into a Shimadzu QP2010S GS-MS equipped with an RXI-5ms column (0.25 mm inner diameter by 30m long) at a flow rate of 1 mL/min. The carrier gas was helium (grade 5) and the system was operated in 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 standards containing 5, 10, 25, 50, 100, 200, 300, 400, 500 µg of PCP/mL. A nine-point calibration was employed, i.e., for each single batch a minimum of 9 consecutive standards were selected depending on the range of concentration of the samples.

PCP treatments of southern pine and SPF produced very different results. Assayed retentions for the southern pine boards were 7.87 kg/m^3, which was close to the target of 8.00 kg/m^3, while SPF retentions were only 4.37 kg/m^3. The difference reflects the lower permeability of the SPF.

PCP was detected in every water sample from the simulated overhead runoff system at levels ranging from 1 to 60 µg/mL for southern pine treated boards and 0.5 to 23 µg/mL for the SPF (Table 4). This was expected since PCP has limited water solubility and any rainfall striking the wood will solubilize PCP from the surface.

For comparison purposes, the data were plotted over time and then compared on the basis of PCP concentration in runoff for the first 15 and 30 minutes of rainfall as well as the concentration at the end of the 2 hour rainfall period. The current aquatic risk models are based upon what is perceived to be the maximum risk of preservative entering a body of water. This is typically the first rainfall event immediately after installation of treated wood. Thus, the first two rainfall collections represent the greatest risk of migration. The 120 minute collection was examined to determine if PCP levels declined with continued rainfall.

In general, PCP levels in runoff from SPF boards tended to be lower than those from southern pine boards regardless of whether a BMP was applied (Table 4, Figure 16-17). The differences may reflect the initial preservative retentions since southern pine was more heavily treated. PCP levels in runoff declined slightly over the 120 minute rainfall period for all treatments, but concentrations in runoff tended to be fairly steady after 60 to 120 minutes of rainfall. These results reflect the differences in how PCP is retained in the wood. Waterborne copper-based systems are solubilized for delivery into the wood. Once the co-solvents used for this purpose evolve from the wood, the copper undergoes either precipitation or limited reactions with the wood. These characteristics produce a different pattern of migration when the wood is subjected to rainfall. Any residual copper near the surface will be solubilized by the first rainfall and migrates from the wood. This is a short term effect, but it results in elevated metal levels in runoff water. Once that surface copper is released, the remaining copper tends to be more tightly retained and copper levels in rainfall runoff decline sharply. This characteristic spike in chemical levels followed by a sharp decline is considered in the aquatic model. As noted, oil-solubilized PCP has low water solubility and limited interactions in the wood, but its release characteristics can be similar. In this case, PCP in residual debris or oil deposits on the surface are removed through the initial rainfall, creating a concentration spike. Once these deposits are removed, PCP concentrations in the runoff are a function of water solubility as well as water contact time with the wood. Previous studies suggest that contact time, total rainfall amount, and even temperature have relatively little effect on the resulting PCP concentration in the runoff. BMP’s for this system are therefore primarily designed to reduce the presence of surface deposits that can contribute to the initial concentration spike.

PCP levels in runoff from non-BMP treated southern pine and SPF lumber followed different trends with rainfall time (Figures 16,17). PCP levels in SPF samples averaged 11.15 µg/mL in the first 15 minutes and then declined slightly over the next 105 minutes of exposure (Table 4). PCP levels in runoff from southern pine samples were almost two times higher than those from the SPF boards after 15 minutes, but then continued to increase over time. The initial differences could reflect the higher retentions in the southern pine boards, but the reasons for the increases are unclear.

The application of post-treatment steaming to both SPF and southern pine boards was associated with a reduction in PCP concentrations in runoff and this effect was improved with prolonged steaming (Table 4). One hour of steaming was associated with a nearly 50% reduction in PCP concentrations in the first 15 minutes of runoff from SPF treated boards. Six hours of steaming reduced concentrations a further 50% and also tended to produce a much lower steady state loss level at 120 minutes.

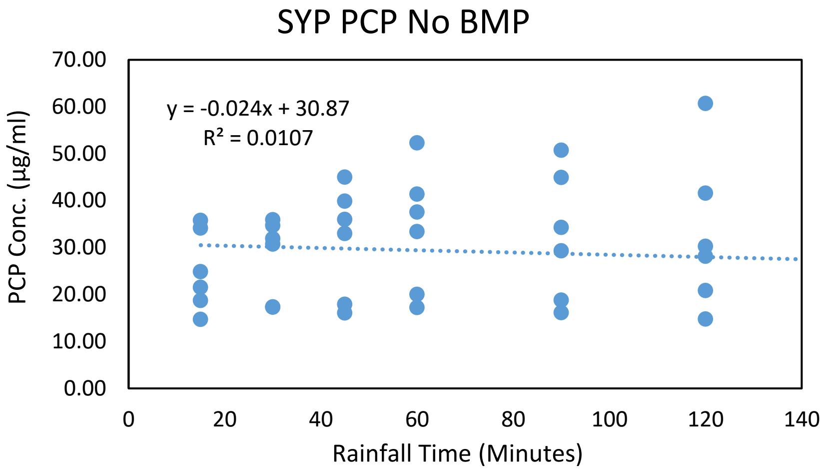
PCP levels in runoff from southern pine boards were also reduced by steaming, but the effect appeared to require more steaming (Figure 16). PCP levels in runoff were little changed by 1 hour of steaming, but levels then declined by approximately 50% with an additional 3 hours of steaming. Steaming for an additional 3 hours (6 hours of total steam) had little further effect (Table 4). However, steaming was associated with a steady decline in PCP levels in runoff with continued rainfall rather than the increases noted with non-BMP treated materials.

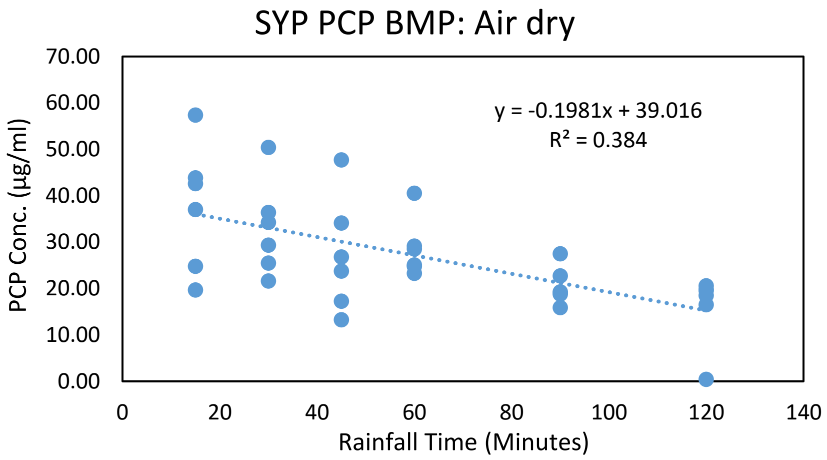
In general, the results indicate that steaming of southern pine markedly reduced the level of PCP in runoff and illustrate the benefits of using the BMP processes.

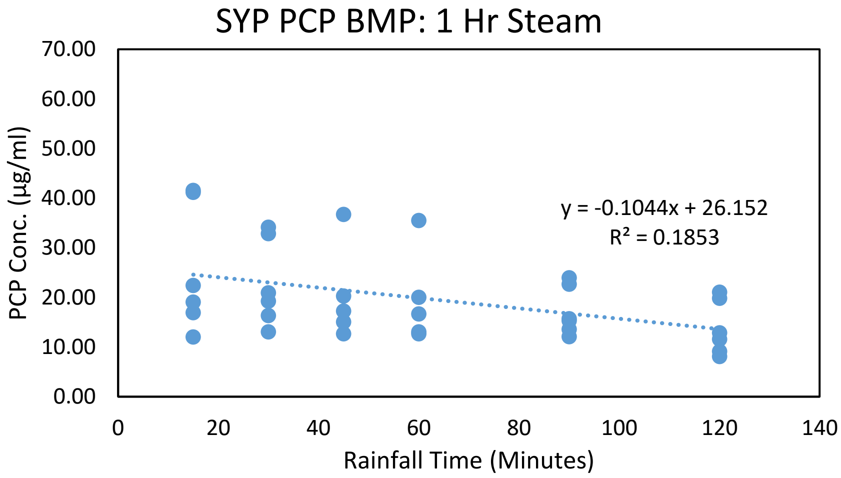
In addition to steaming, the potential for using one or three hours of hot water immersion to reduce PCP losses was also explored on southern pine (Table 4). The effects of either immersion period on PCP levels in runoff was difficult to detect in the first 15 minutes of runoff, however, there was a steady decline in PCP levels in runoff with continued rainfall. This effect was not noted in the materials that received no BMP treatment. PCP levels in runoff collected after 120 minutes of rainfall were similar to those observed with the 1 hour steam treatment on the same materials, suggesting that hot water immersion was less effective than prolonged steaming (3 to 6 hours), but still had a positive effect compared to using no BMP (Table 4).

The final assessment on the effects of BMP processes on PCP treated lumber was to determine if the BMP's had an effect on long-term exposures to repeated wetting. In this case, SPF samples from the first exposure were dried and then exposed to an additional 120 minutes of simulated rainfall.

Interestingly, PCP levels in the second runoff test closely followed trends observed in the first test. Water from non-BMP treated material again had the highest PCP concentrations and the levels were similar to those observed in the first wetting period (Table 5). Steamed samples followed similar trends, with lower PCP levels in the initial 15 and 30 minute wetting periods followed by a steady decline over the next 90 minutes of rainfall (Figure 18). The results illustrate the initial effects of steaming on PCP losses, but also indicate that the benefits of using this BMP process continue into at least a second wetting period.


SYP PCP No BMP
PCP Conc. (µg/ml)
70.00
60.00
50.00
40.00
30.00
20.00
10.00
0.00
y = -0.024x + 30.87
R² = 0.0107
0
20
40
60
80
100
120
140
Rainfall Time (Minutes)


SYP PCP BMP: Air dry
PCP Conc. (µg/ml)
70.00
60.00
50.00
40.00
30.00
20.00
10.00
0.00
y = -0.1981x + 39.016
R² = 0.384
0
20
40
60
80
100
120
140
Rainfall Time (Minutes)


SYP PCP BMP: 1 Hr Steam
PCP Conc. (µg/ml)
70.00
60.00
50.00
40.00
30.00
20.00
10.00
0.00
y = -0.1044x + 26.152
R² = 0.1853
0
20
40
60
80
100
120
140
Rainfall Time (Minutes)

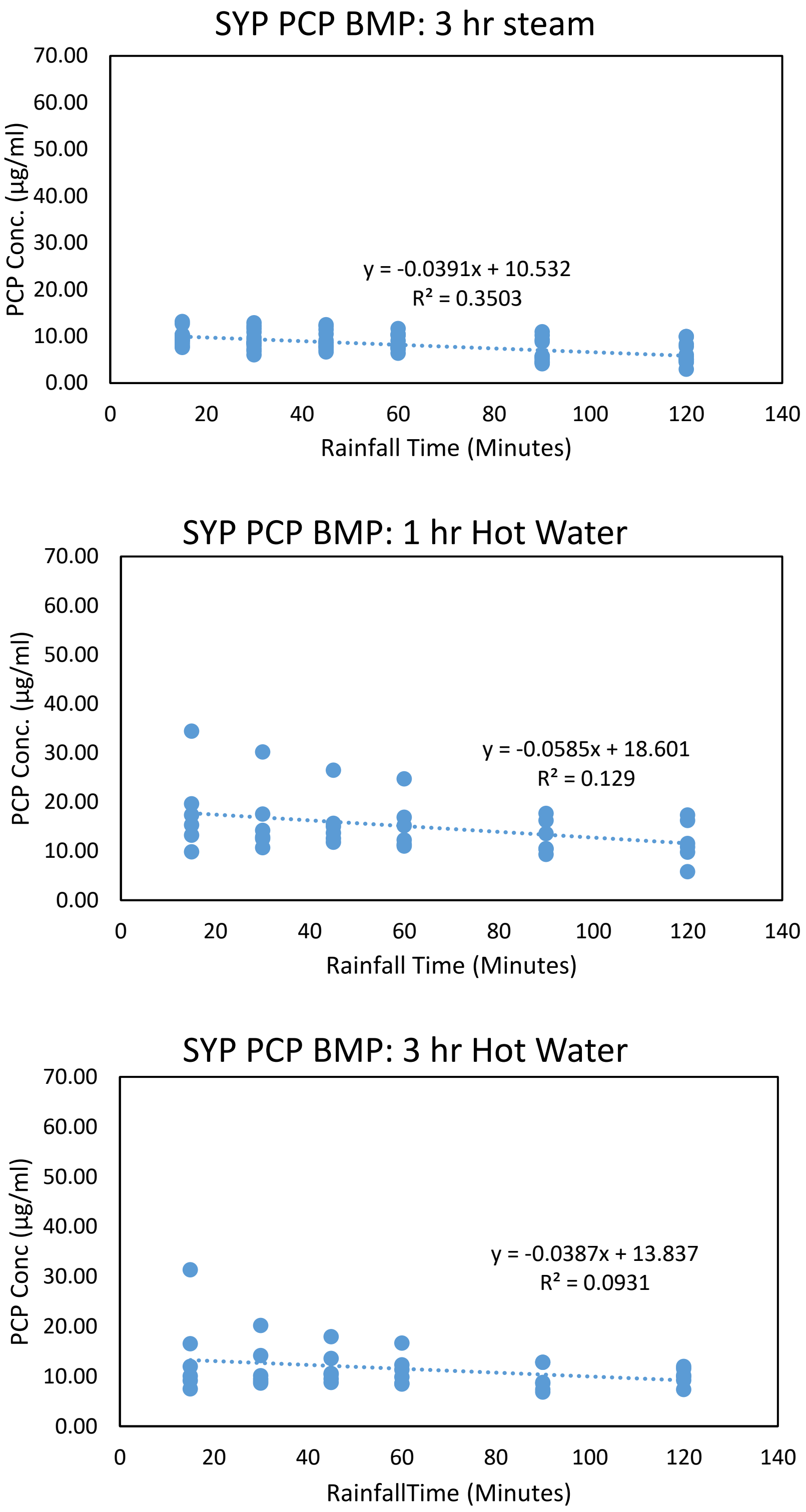
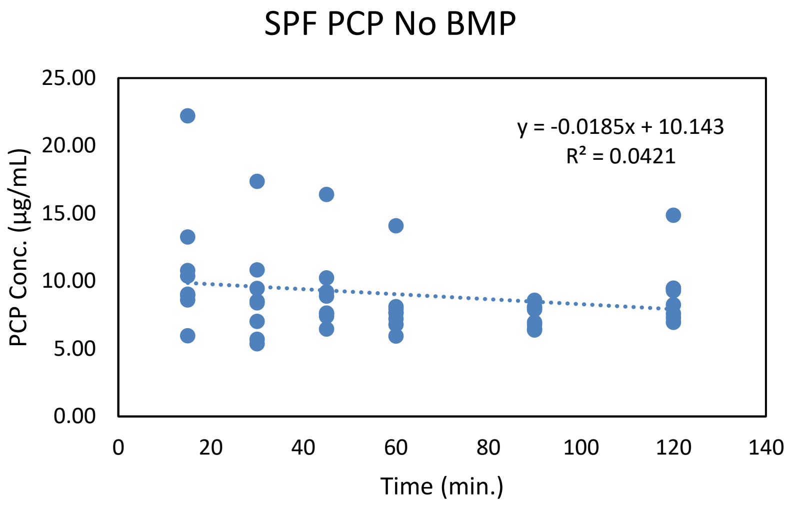
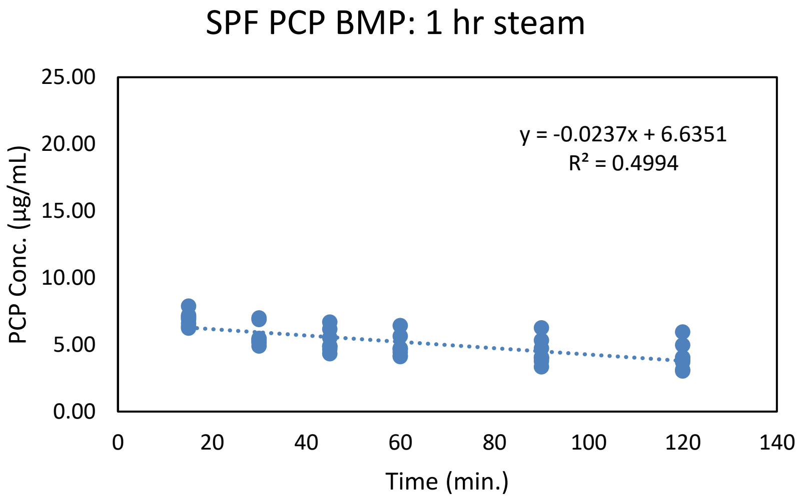
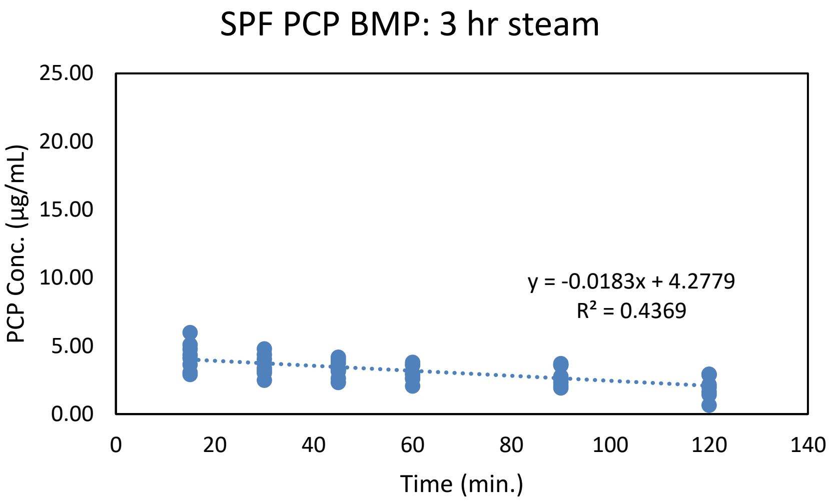


Figure 16. PCP Concentrations in simulated rainwater runoff from pentachlorophenol (PCP) treated southern pine (SYP) decking materials exposed directly after treatment or after being subjected to various post-treatment Best Management Practices (BMP).


SPF PCP No BMP
y = -0.0185x + 10.143
R² = 0.0421
PCP Conc. (µg/mL)
25.00
20.00
15.00
10.00
5.00
0.00
0
20
40
60
80
100
120
140
Time (min.)


SPF PCP BMP: 1 hr steam
y = -0.0237x + 6.6351
R² = 0.4994
PCP Conc. (µg/mL)
25.00
20.00
15.00
10.00
5.00
0.00
0
20
40
60
80
100
120
140
Time (min.)



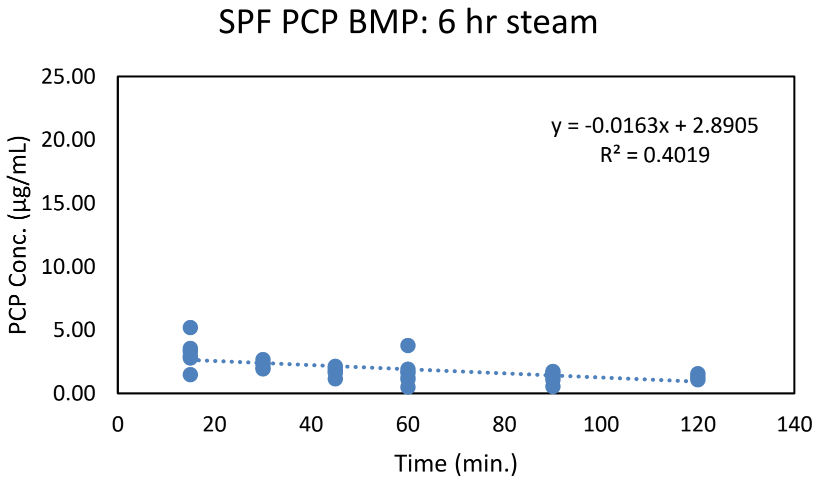
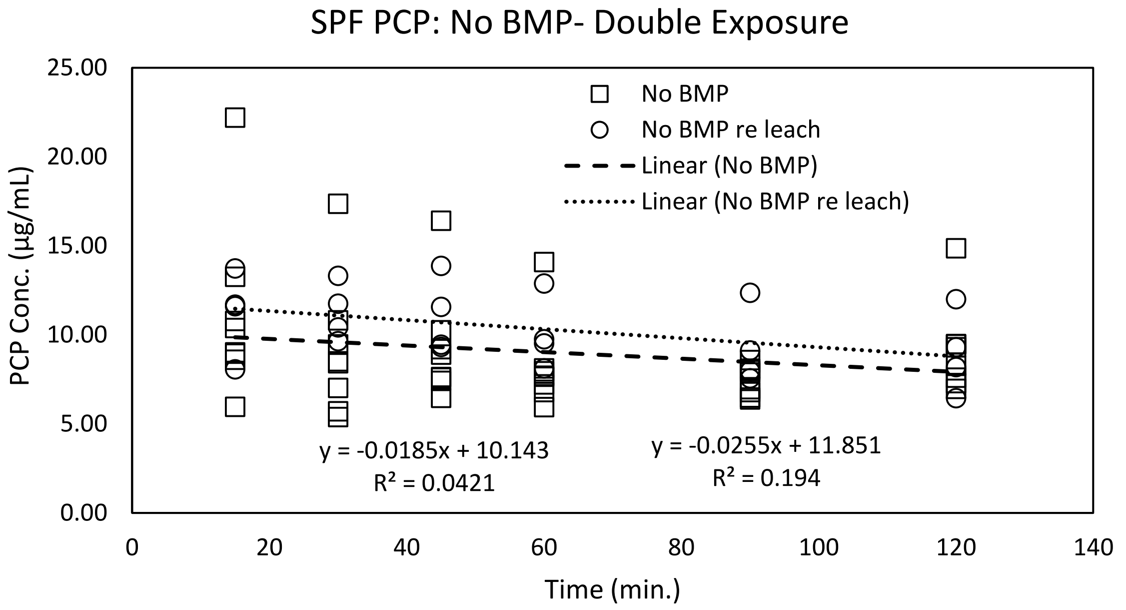
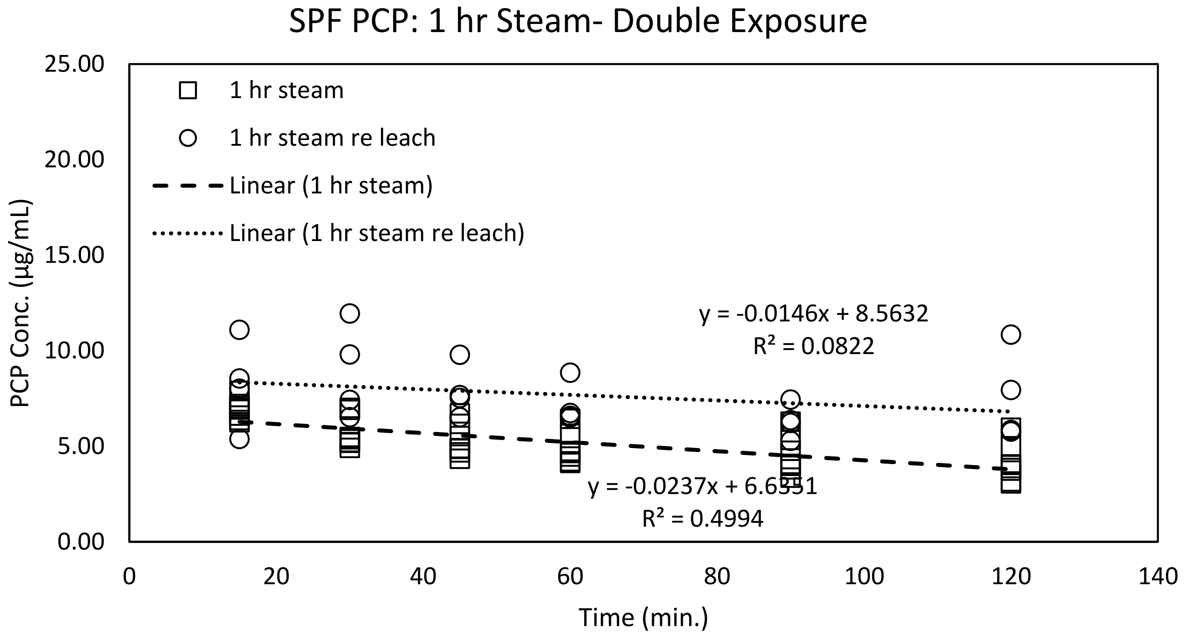
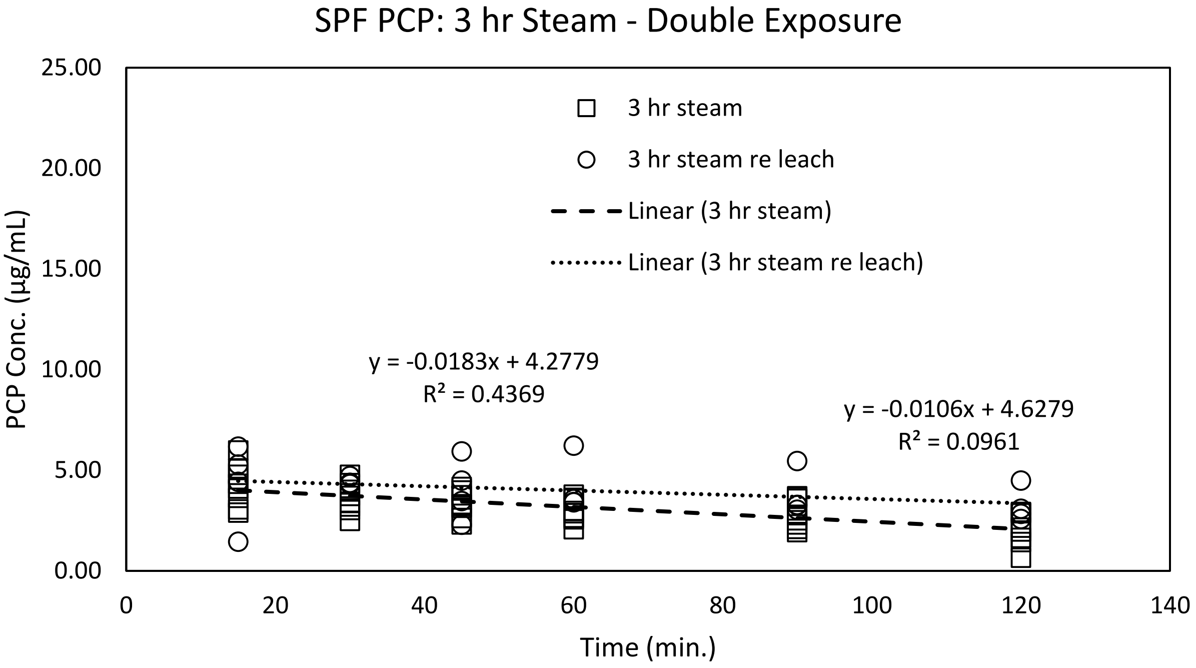


Figure 17. PCP Concentrations in simulated rainwater runoff from pentachlorophenol (PCP) treated Spruce-Pine-Fir (SPF) decking materials exposed directly after treatment or after being subjected to various post-treatment Best Management Practices (BMP).


SPF PCP: No BMP- Double Exposure
No BMP
No BMP re leach
Linear (No BMP)
Linear (No BMP re leach)
y = -0.0185x + 10.143
R² = 0.0421
y = -0.0255x + 11.851
R² = 0.194
PCP Conc. (µg/mL)
25.00
20.00
15.00
10.00
5.00
0.00
0
20
40
60
80
100
120
140
Time (min.)


SPF PCP: 1 hr Steam- Double Exposure
1 hr steam
1 hr steam re leach
Linear (1 hr steam)
Linear (1 hr steam re leach)
y = -0.0146x + 8.5632
R² = 0.0822
y = -0.0237x + 6.6351
R² = 0.4994
PCP Conc. (µg/mL)
25.00
20.00
15.00
10.00
5.00
0.00
0
20
40
60
80
100
120
140
Time (min.)



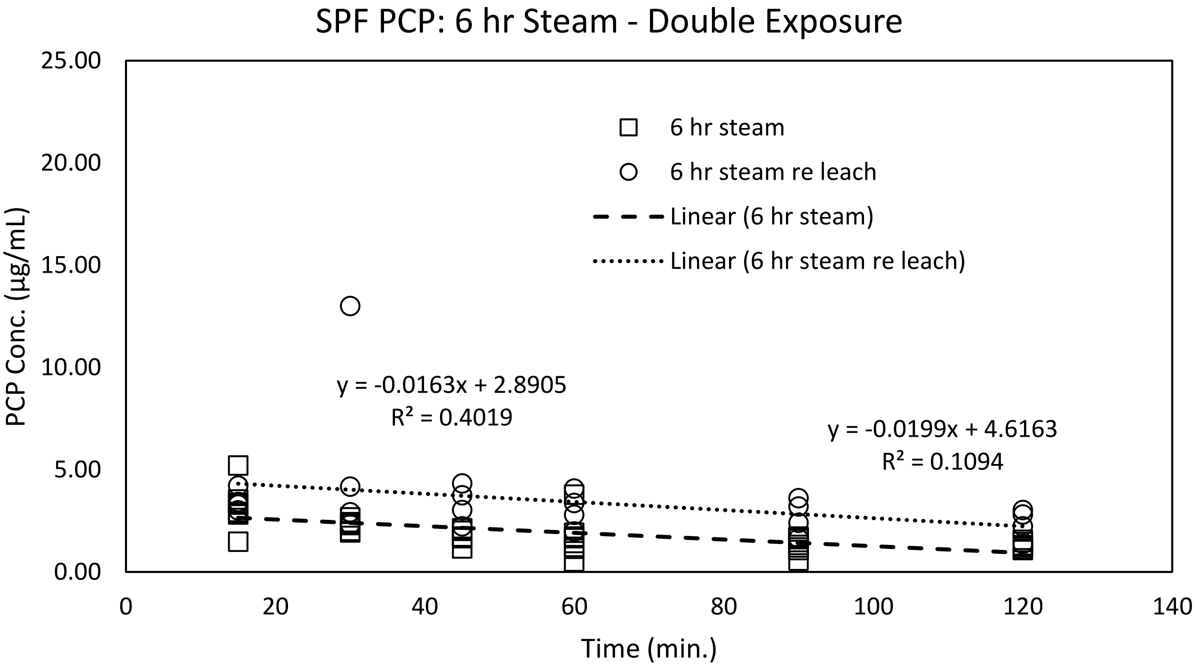


Figure 18. Effect of sequential overhead rainfall exposures on PCP concentrations in rainwater runoff from PCP treated SPF boards subjected to no BMP or 1 to 6 hours of steaming.

Table 14. PCP levels in rainwater runoff from southern pine and spruce pine fir lumber treated with pentachlorophenol in an HS-A solvent and subjected to 15 to 120 minutes of simulated rainfall.

Wood Species	Rainfall Time (min)	PCP Concentration in Runoff (µg/mL[a])						
		None	Air-dry	Hot Water Bath		Steam		
				1 hr	3 hr	1 hour	3 hours	6 hours
Spruce-Pine Fir	15	11.15 (4.93)	-	-	-	6.92 (0.53)	4.23 (1.04)	3.19 (1.03)
	30	9.09 (3.82)	-	-	-	5.68 (0.80)	3.62 (0.75)	2.26 (0.26)
	45	9.23 (3.14)	-	-	-	5.26 (0.81)	3.32 (0.64)	1.76 (0.31)
	60	8.18 (2.49)	-	-	-	4.87 (0.79)	3.02 (0.60)	1.70 (0.95)
	90	7.40 (0.84)	-	-	-	4.45 (0.96)	2.81 (0.72)	1.36 (0.41)
	120	9.15 (2.52)	-	-	-	4.10 (0.96)	2.07 (0.82)	1.30 (0.19)
Southern pine	15	20.40 (5.17)	37.59 (13.72)	18.30 (8.58)	14.46 (8.84)	25.51 (12.72)	9.79 (1.60)	9.42 (1.35)
	30	27.99 (9.61)	32.95 (10.15)	16.32 (7.17)	11.96 (4.52)	22.74 (8.74)	9.22 (2.03)	8.70 (1.17)
	45	32.99 (13.81)	27.18 (12.44)	15.85 (5.39)	11.81 (3.43)	20.38 (9.53)	9.13 (1.84)	7.73 (1.64)
	60	37.92 (16.39)	28.59 (6.29)	15.22 (5.18)	11.23 (3.09)	19.55 (9.40)	8.55 (1.52)	7.33 (1.36)
	90	38.18 (17.01)	20.55 (4.03)	12.94 (3.44)	9.56 (2.65)	17.18 (4.91)	6.36 (2.38)	6.11 (1.58)
	120	41.07 (19.95)	15.93 (7.70)	11.92 (4.28)	10.07 (1.67)	13.73 (5.46)	6.06 (2.12)	5.67 (1.48)

[a]Values represent means of 8 replicates per treatment, while figures in parentheses represent one standard deviation.

Table 5. PCP levels in runoff from SPF lumber treated with pentachlorophenol in an HS-A solvent and subjected to two periods of 15 to 120 minutes of simulated rainfall with prolonged drying in between rainfall events.

Rainfall Time (min)	PCP Concentration in Runoff (µg/mL)[a]							
	No BMP		1 Hr Steam		3 hr Steam		6 hr Steam	
	Initial	Second	Initial	Second	Initial	Second	Initial	Second
15	11.15 (4.93)	11.28 (2.35)	6.92 (0.53)	8.25 (2.34)	4.23 (1.04)	4.33 (2.05)	3.19 (1.03)	3.48 (0.52)
30	9.09 (3.82)	11.29 (1.61)	5.68 (0.80)	8.92 (2.44)	3.62 (0.75)	4.43 (0.19)	2.26 (0.26)	5.60 (4.99)
45	9.23 (3.14)	11.06 (2.15)	5.26 (0.81)	7.88 (1.37)	3.32 (0.64)	4.04 (1.54)	1.76 (0.31)	3.33 (0.91)
60	8.18 (2.49)	10.07 (2.02)	4.87 (0.79)	7.16 (1.12)	3.02 (0.60)	4.15 (1.38)	1.70 (0.95)	3.05 (0.88)
90	7.40 (0.84)	9.26 (2.17)	4.45 (0.96)	6.32 (0.89)	2.81 (0.72)	3.76 (1.14)	1.36 (0.41)	2.71 (0.87)
120	9.15 (2.52)	8.99 (2.33)	4.10 (0.96)	7.60 (2.39)	2.07 (0.82)	3.25 (0.85)	1.30 (0.19)	2.36 (0.74)

[a]Values represent means of 8 replicates per treatment, while figures in parentheses represent one standard deviation.

Effect of BMP's on Migration of Creosote from Southern Pine Decking: The ability of BMP's to reduce migration of creosote components from treated wood has only been assessed on southern pine, although we also have SPF sample treated and ready to test. Creosote contains a range of polycyclic aromatic hydrocarbons (PAH's), making analysis much more difficult and time consuming. It would be virtually impossible to analyze all possible creosote components migrating from wood on a large scale. Instead, we have elected to examine the migration of the 16 EPA priority pollutants. This has several advantages. First, these are the components that the EPA has judged to be most important from a toxicity perspective. Second, these compounds are commercially available in mixtures that greatly simplify quantification. The one difficulty in assessing migration of creosote components in overhead rainfall exposures is the generally low water solubility of a given PAH component, necessitating the use of more water to capture a given PAH.

The test configuration for the creosote treated boards was the same as that used for the other treatments. The BMP processes examined so far for creosote are Air-drying, 1 hour of steaming and 3 hours of steaming. Air-drying was considered to be the non-BMP control. Each BMP treatment was evaluated on samples cut from six parent boards. Water collected from the overhead leaching device was analyzed as follows.

PAHs from the creosote treated posts were extracted and analyzed as follows:

The total amount of water collected at each time point was weighed, then 5 ml of methanol and 5 ml of 10 % nitric acid were added before the water was drawn through a solid-phase micro-extraction cartridge (SPME) under vacuum. The filter captured the organic material in the water. The cartridge was initially conditioned by applying a vacuum and adding 5 ml of ethyl acetate, followed by 5 ml of dichloromethane (DCM). The DCM was allowed to evaporate then the resin was activated by adding 10 ml of methanol. Ten ml of HPLC grade water was then added before the rainwater sample was applied to capture the organic matter.

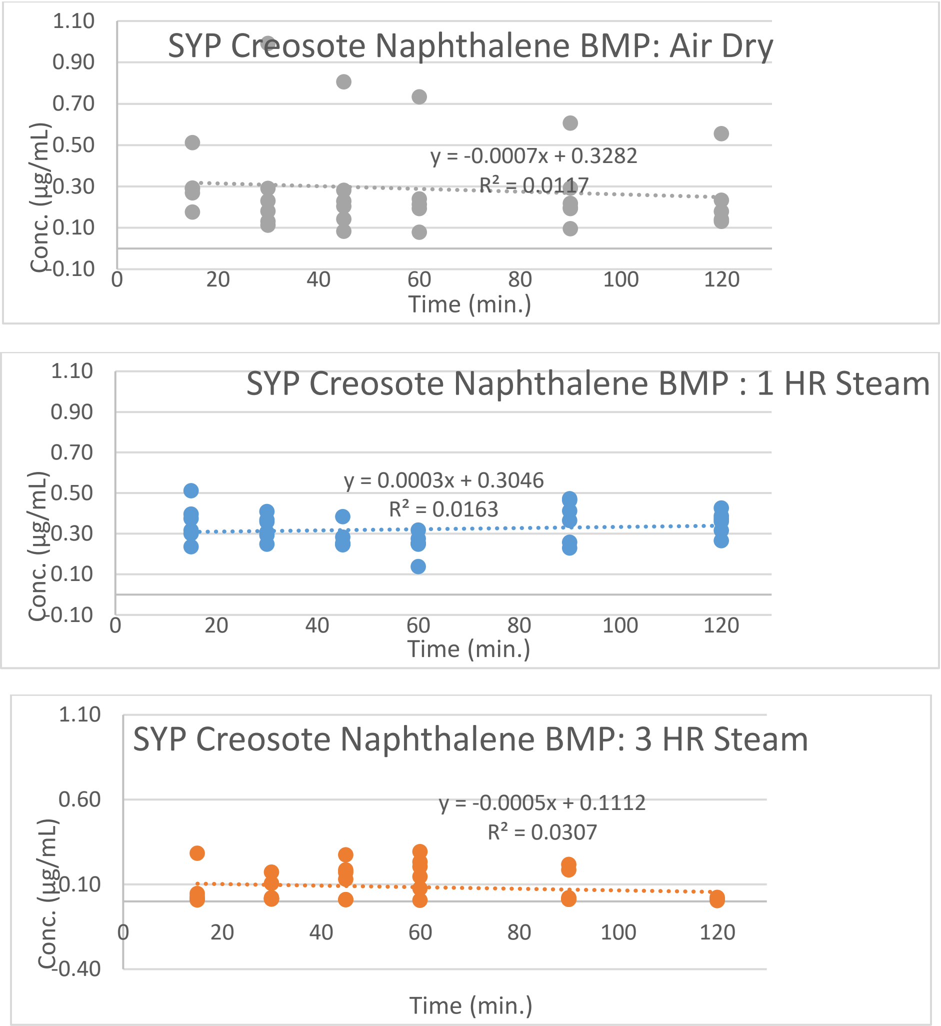
The materials captured on the SPME cartridge were eluted by adding 3.5 ml of ethyl acetate followed by 3.5 ml of DCM. Approximately 1 g of sodium sulfate was added to each sample and then the mixture was frozen until it could be analyzed

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

Twelve of the 16 EPA priority pollutants were detected at some point in runoff from the decks. For the purposes of discussion, we have evaluated water concentrations of a given PAH after 15, 30 and 120 minutes of simulated rainfall. In general, PAH levels declined slightly between 15 and 30 minutes of rainfall and then more markedly with an additional 90 minutes of rainfall. These results are consistent with an initial loss of materials present on the wood surface after treatment followed by losses that more closely aligned with the water solubility of a given PAH.

Naphthalene, acenaphthene, phenanthrene, and fluoranthrene were present at the highest levels in runoff from air-dried boards (Figures 19-21). Naphthalene tends to be present at high levels in creosote, is among the most volatile components and is most water soluble. Thus, its presence in runoff is not surprising. The remaining compounds were present at varying rates and 4 were below the detection limits of our methods.

Napththalene levels tended to decrease slightly with increasing rainfall, but the trend was weak. Air-drying samples prior to exposure was associated with the highest naphthalene levels in the runoff suggesting that the additional drying and evaporation had brought materials to the surface that were then available for solubilization as water struck the samples. Steaming for one hour was also associated with higher naphthalene levels in the runoff, while steaming for 3 hours was associated with decreased levels These trends also occurred with the other PAH's, especially the trend to increases in PAH levels in runoff from samples that were steamed for one hour followed by a decrease with longer steaming. Post-treatment steaming is widely used with creosote treatments because it reduces residual pressure and decreases the risk of bleeding in service. It also cleans the wood surface, helping to remove deposits that might be more susceptible to migration when the wood is placed into service. Short steaming periods have the potential to exacerbate creosote migration because the creosote migrates to the surface, but has not been steamed for a sufficient period to remove it from the wood surface. Longer steaming periods appear to reduce this risk. The results illustrate the benefits of post-treatment steaming as a BMP and longer steaming period tests are planned with the remaining materials. In addition, we plan to perform similar tests on the SPF.


SYP Creosote Naphthalene BMP: Air Dry

SYP Creosote Naphthalene BMP : 1 HR Steam

SYP Creosote Naphthalene BMP: 3 HR Steam

Figure 19. Levels of naphthalene in rainwater runoff from creosote treated southern pine boards receiving various BMP treatments.

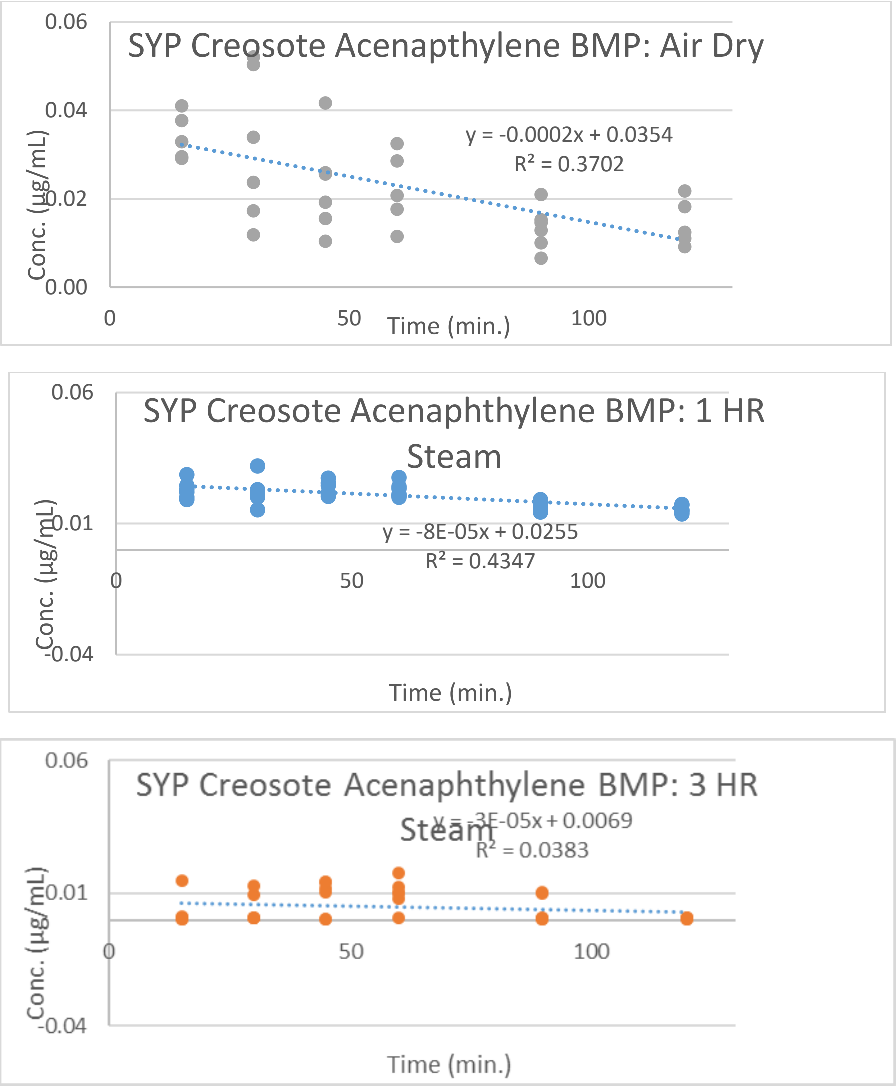


Figure 20. Levels of acenathylene in rainwater runoff from creosote treated southern pine boards receiving various BMP treatments.

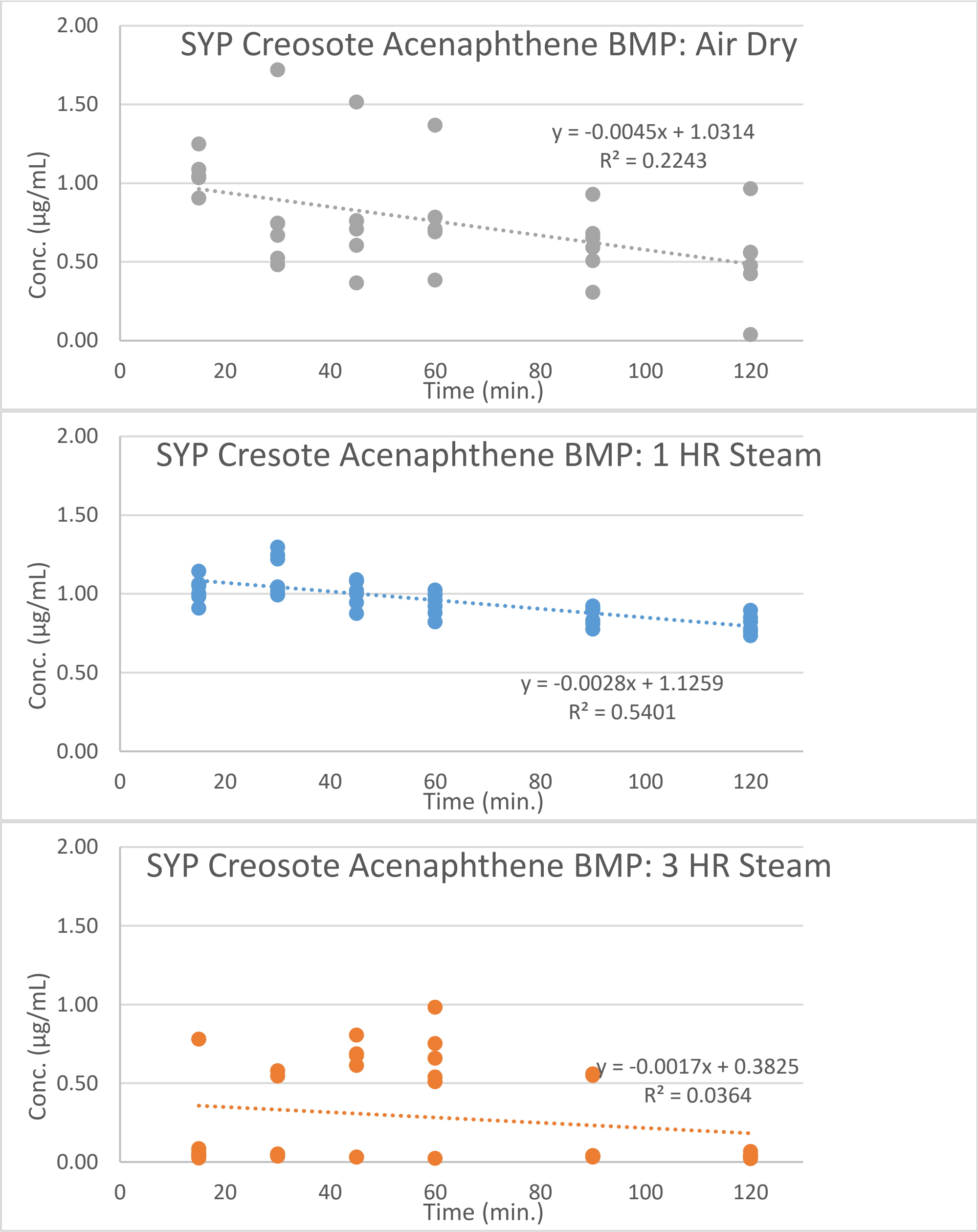


Figure 21. Levels of acenaphthene in rainwater runoff from creosote treated southern pine boards receiving various BMP treatments.

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

A second component of the BMP verification process was to assess the potential migration of preservatives from round-timbers with and without BMP treatments. Doulgas-fir posts (125 to 150 mm in diameter by 1.8 m long) were treated with either

ACZA or creosote to the northern retentions for each system (24 kg/m for ACZA or 384 kg/m for creosote). One half of the posts were subjected to a BMP treatment while the others were provided without this process

The posts were set in a freshwater pond located approximately 20 km southwest of Corvallis, OR. In our initial trials, we found that the sediment at this pond was far too inconsistent to allow for regular sampling. Instead, we created sediment packets that could be placed in the actual sediment at selected distances away from each post. The packets (200 mm long by 25 mm in diameter) or sachets contain a known soil that is heat sealed into an inert plastic mesh. The mesh allows water to move through the sediment, but contains the material for later analysis. Preliminary tests indicated that the mesh material did accumulate PAH's and, to a lesser extent metals, but the sachets provided a uniform sediment media that could be easily removed for sampling.

We have established ACZA and creosote treated Douglas-fir piling in two separate tests, 9 or 48 months ago. The former test was installed because we felt our PAH recovery ability has improved and we wanted to confirm that premise. In the initial test, two creosote treated posts were installed, while 4 posts have been installed in the more recent test. The initial ACZA test consisted of 2 posts installed approximately 31 months ago. We also installed 5 more ACZA posts at the same time as the new creosote study.

Sachets removed at selected time intervals have been used to assess polycyclic aromatic hydrocarbons (PAHs) or metals, depending on the posts involved. The metals were analyzed in the same manner as described for the water samples, with the exception that the sediment and sachets were acid digested prior to analysis. PAHs from the creosote treated posts were extracted and analyzed as follows: collected sachets were frozen until analysis. Upon analysis the sachets were thawed and the sediment was separated from the sachet. Three 10 g subsamples were taken from the homogenized sediment and placed into 40 mL amber glass scintillation vials. The sachet material was split into two sections and analyzed separately from the sediment but in the same manner. Twenty mL of a 2:2:1 acetone:ethyl acetate:iso-octane mixture was added to the scintillation vials. The vials were vigorously agitated for 5 minutes to ensure that the sediment was in intimate contact with the solvent. The samples were then treated with a salt mixture containing 6 g of magnesium sulfate and 1.5 g of sodium acetate. The mixture was again agitated for 5 minutes and then centrifuged for 5 minutes. A 1.5 mL aliquot of the supernatant was removed and added to a solid phase extraction (SPE) microcentrifuge tube, and agitated further for 5 minutes. These dual procedures were used to precipitate polar compounds, lipids, fatty acid, sterols and other compounds that would interfere with the PAH analysis. The tube was then centrifuged one last time for 5 minutes and a 1 mL aliquot of the supernatant was removed for analysis by GC-MS.

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

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

Copper levels in sachets removed 1 and 3 months after post installation were generally at background levels 300 and 900 mm away from the post; however, levels were elevated immediately adjacent to wood 3 months after installation (Table 6). Arsenic was generally below the detection limit (0.1 ppm) except immediately adjacent to the posts at 3 months and even this level was below 1 ppm. The presence of elevated metal levels immediately adjacent to the treated wood is consistent with previous reports as is the sharp drop-off in levels with increasing distance from the wood.Sediment around these posts will continue to be sampled over time to establish long term release data.

Zinc and copper levels were elevated immediately adjacent to the posts 31 months after installation. Metal levels declined 300 mm away, but were still slightly above the background levels. Levels declined to near background levels 900 mm from the post. This drop off is consistent with previous reports showing that metal migration is largely confined to a narrow zone around a treated wood sample and does not change appreciably over time. Zinc levels have continued to decline after 47 months, suggesting that the rates of metal loss from the piling have declined. Arsenic remains at very low levels except immediately adjacent to the posts where it had increased sharply over the 28 month interval between sampling. As with copper and zinc, arsenic levels were much lower 47 months after installation. The results indicate that all three metals migrate away from the posts into the surrounding sediment, but the extent of migration is limited and declines sharply with distance away from the treated wood source.

The more recently installed ACZA test has followed trends similar to those found with the older test. Copper, zinc and arsenic levels were elevated immediately adjacent to the piling 3 and 9 months after installation. Metal levels declined sharply 0.3 m away 3 months after installation and were similar to those found in the control sediment. Zinc levels were slightly elevated 0.9 m away from the wood 3 months after installation.

Table 6. Copper, zinc and arsenic levels in sediments exposed immediately, 300 and 900 mm away away from an ACZA treated Douglas-fir piling 1 to 47 months after installation.

Time (months)	Distance from pile (m)	Metal level in soil (ppm)[a]		
		Cu	Zn	As
1	0.3	3.05	4.00	BDL
	0.9	3.35	4.55	BDL
3	0	117.95	57.60	0.35
	0.3	4.65	5.55	BDL
	0.9	3.85	5.00	BDL
31	0	496.25	564.31	34.10
	0.3	30.85	67.58	BDL
	0.9	6.50	3.98	BDL
41	0	244.5	618.00	57.85
	0.3	39.09	84.28	2.05
	0.9	34.22	81.73	1.96
47	0	182.50	363.50	12.05
	0.3	11.27	11.51	0.05
	0.9	7.47	10.43	0.05

[a] Values represent means of two samples per time per location. BDL= below the detection limit (<0.1 ppm)for that anlaysis. Assay sensitivity improved in subsequent years.

Table 7. Metal levels in soil samples removed from various distances around ACZA treated Douglas-fir poles 3 to 9 months after immersion.

Distance from Pile (m)	Time in Test (Months)	Metal Levels in Sediment (mg/kg)		
		Cu	Zn	As
0	3	427.23 (114.06)	521.68 (154.32)	88.21 (32.99)
	9	256.28 (115.23)	306.67 (71.26)	11.29 (2.70)
0.3	3	39.10 (2.49)	78.50 (6.48)	2.20 (0.21)
	9	39.25 (73.41)	38.35 (64.95)	1.45 (3.15)
0.9	3	33.07 (2.61)	77.60 (4.15)	1.99 (0.06)
	9	15.51 (16.46)	19.92 (19.1)	0.40 (0.53)
Control	3	28.81	105.34	2.32
	9	2.95	6.68	0.05

Values represent the means of analysis of samples around 5 poles. Figures in parentheses represent one standard deviation. Control samples were exposed up-current from the test piling.

Fifteen of the 16 PAH’s we evaluated were detected in one or more sachets sampled in the test installed in 2013, while only 12 were detected in the more recent test installed in October, 2016 (Tables 8, 9). Two PAH’s were combined with other PAH’s because they eluted so closely from one another that they were dificult to accurately separate.

Naphthalene and several other PAH’s were detected at very low levels (<1 ppm) in sachets exposed at the inlet of the pond (Table 8). We are unsure whether this background contamination originated from other anthropogenic sources. The site is in a forested area that is near areas where fire is periodically used as part of the silvicultural regime. No PAH’s were detected in control sachets at the 39 month sampling point.

Naphthalene was present at elevated levels immediately adjacent to the post, but declined sharply 300 mm away. Slightly elevated levels were detected 900 mm away at 32 months after installation, but these levels had declined to background levels at 42 months. Naphthalene can represent a high percentage of creosote, but it is also one of the more easily biodegradable components. As a result, it should be rapidly degraded as it moves out of the wood. This PAH is also difficult to quantify because of its high volatility. The results at 39 months support that premise.

The other components present at elevated levels (>5 ppm) immediately adjacent to the posts included acenaphthene, fluorine, fluoranthrene, and pyrene which were all well above background levels at all three sampling times (Table 8). PAH levels immediately adjacent to the posts tended to remain elevated over the 39 month exposure period for all of the PAH’s, but did not appear to be increasing. Benzo(α)anthracene/chrysene and Benzo(j,k) fluoranthrene levels were also elevated immediately adjacent to the post at the 18 month sampling point, but then declined to near or below the 5 ppm level. These levels were still well above the background levels for either compound. Levels of all of the same PAH’s 300 and 900 mm away were sharply lower than those found adjacent to the post and tended to be similar to those found in the background sediment. Levels of benzo(j,k)fluoranthrene and benzo(α)pyrene were also elevated immediately adjacent to the posts, but not at all sampling times. Levels of these compounds also declined sharply 300 and 900 mm from the posts, indicating that either migration was limited or that microbial decomposition was occurring at a rate similar to any migration. All PAH’s were below our detection limits 0.9 m from the post 39 months after installation, indicating hat nay PAH’s that were migrating were being degraded farther from the wood sample.

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

Only 10 PAH’s were detected around posts exposed for only 3 months (Table 9). The three PAH’s detected in the older test, but not in this one were present at the lowest levels in the older test and at levels similar to the background levels. As in the earlier test, naphthalene, acenapthylene, acenahthalene, fluorene, phenanthrene/anthracene, fluoranthrene and pyrene were present at elevated levels (>5 ppm) immediately adjacent to the posts. Bezno(α)anthracene/chrysene was present immediately adjacent to the posts at a concentration of 3.06 ppm, but then declined sharply away from the post. The remaining PAH’s were present at very low levels approaching background.

PAH levels have either remained the same or continued to increase immediately adjacent to the wood with an additional 9 months of exposure.

PAH levels 300 mm from the posts were sharply lower than those immediately adjacent to the wood, reflecting both dilution and biological degradation. PAH levels continued to decline 900 mm away for the posts, suggesting that, as with the older test, any migration was either limited or the PAH's were degrading at rates that were similar to the rate of migration. Either way, the results show that PAH migration from the posts into the surrounding sediment is extremely limited.

Table 8. Concentrations of 13 PAH's in sediment at selected distances from creosote treated Douglas-fir posts exposed in freshwater for 39 months.

PAH's	0 m					0.3 m				0.9 m			
	5 mo	19 mo	29 mo	34 mo	39 mo	5 mo	19 mo	29 mo	34 mo	5 mo	19 mo	29 mo	34 mo
Napthalene	34.47 (18.48)	29.44 (21.01)	56.24 (12.21)	21.17	43.75 (28.37)	2.04 (2.36)	0.54 (0.16)	0.61 (0.32)	1.82 (1.31)	0.37	0.20 (0.11)	0.57 (0.29)	0.62 (0.36)
Acenaphthylene	2.29 (2.26)	0.78 (0.60)	1.66 (1.05)	2.57 (2.07)	0.85 (0.95)	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL
Acenaphthene	56.47 (22.69)	23.20 (6.76)	43.01 (5.92)	52.86 (16.95)	27.64 (9.65)	BDL	BDL	BDL	0.27	BDL	BDL	BDL	BDL
Fluorene	33.80 (15.95)	14.55 (3.16)	27.16 (2.28)	34.87 (7.14)	19.70 (4.04)	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL
Phenanthrene & Anthracene	10.23 (4.77)	6.84 (0.34)	51.91 (36.44)	43.28 (8.38)	71.85 (0.81)	BDL	BDL	0.22 (0.11)	0.74	BDL	BDL	0.21 (0.09)	BDL
Fluoranthrene	39.42 (27.31)	17.32 (5.08)	29.56 (8.31)	25.48 (9.52)	34.23 (2.32)	BDL	BDL	BDL	0.16	BDL	BDL	BDL	BDL
Pyrene	26.30 (17.42)	11.81 (3.91)	19.33 (6.41)	27.20 (26.34)	23.36 (1.92)	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL
Benz(α)anthracene &Chrysene	7.15 (2.16)	4.97 (1.85)	4.70 (0.91)	5.70 (3.96)	8.15 (1.44)	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL
Benzo (j,k) fluoranthrene	3.21 (0.41)	1.55 (1.26)	1.33 (0.93)	3.07 (1.74)	2.63 (1.24)	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL
Benzo (α) pyrene	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL

[a] Values represent triplicate analyses of sediment from two piling at each time point. Figures in parenthesis represent one standard deviation.

Table 9. Concentrations of 10 PAH's in sediment at selected distances from Douglas-fir posts treated to the northern marine retention and exposed in freshwater for 2 to 12 months.

PAH's	0 m			0.3 m			0.9 m		
	2 mo	7 mo	12 mo	2 mo	7 mo	12 mo	2 mo	7 mo	12 mo
Napthalene	11.50 (3.25)	16.33 (6.92)	13.00 (8.33)	0.42 (0.05)	1.27 (0.69)	BDL	0.23 (0.11)	0.29 (0.21)	BDL
Acenaphthylene	0.20 (0.08)	0.44 (0.06)	0.40 (0.21)	BDL	BDL	BDL	BDL	BDL	BDL
Acenaphthene	10.41 (3.32)	12.47 (3.25)	12.47 (4.51)	2.38	4.30	1.04	2.06	1.37	BDL
Fluorene	7.98 (2.77)	9.39 (2.16)	10.97 (2.44)	0.97	3.15	0.83	0.69	0.41	0.14
Phenanthrene & Anthracene	24.17 (9.99)	35.49 (7.75)	54.02	0.86 (1.07)	2.70	3.81 (5.24)	0.38 (0.19)	0.47	0.39
Fluoranthrene	15.46 (2.93)	15.47 (6.50)	32.43	0.88 (0.82)	0.65 (0.43)	1.76 (2.28)	1.52	1.51	1.14 (0.95)
Pyrene	9.74 (2.30)	10.18 (4.52)	22.27 (9.31)	1.28	2.60 (2.84)	2.37	0.93	1.01	1.63
Benz(α)anthracene &Chrysene	3.06 (1.24)	3.15 (1.54)	9.32 (5.92)	BDL	BDL	BDL	BDL	BDL	BDL
Benzo (j,k) fluoranthrene	1.17 (0.34)	1.86 (0.64)	4.38 (3.37)	BDL	BDL	BDL	BDL	BDL	BDL
Benzo (α)pyrene	0.68 (0.19)	0.93 (0.26)	1.80 (1.22)	BDL	BDL	BDL	BDL	BDL	BDL

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

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

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

C. *Concentrations of Pentachlorophenol and Copper Naphthenate in Rainwater Runoff from a bridge in Western Oregon*

We have worked to establish field trials evaluating preservative migration from various treated wood commodities. Two years ago, we identified a bridge located near Sweet Home, Oregon that had been constructed with decking treated with pentachlorophenol in oil and laminated beams treated with copper naphthenate for supporting the structure (Figure 22). The House Rock Bridge spans the South Santiam River in the Willamette National Forest. Unfortunately, we did not learn about the bridge until it had been in service for several weeks and had been subjected to several rainfall events; however, we have been able to monitor the bridge since that time.

Figure 22. Photograph of the House Rock Bridge showing copper naphthenate treated laminated beams and pentachlorophenol treated decking.

The preservatives present in the runoff from the bridge were examined by constructing a rainfall runoff collection system beneath a section of the bridge that funneled water from the surface into a large container (Figure 23). Water in the container was weighed after each rainfall event, then 3 300 mL sub-samples were taken for later analysis. The total area of treated wood from which the runoff was collected was measured so that we could later determine preservative loss per square cm of wood surface area.

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

Figure 23. System used to collect water from the House Rock Bridge located near Upper Soda, Oregon.

Wood is one of the most important renewable structural materials and is used in a variety of applications. One negative wood attribute is a propensity to deteriorate when used in exterior exposures. While the heartwoods of some species have exceptional resistance to deterioration, most woods are susceptible to biodegradation (Zabel and Morrell,1992). Deterioration can be arrested through impregnation with preservatives; combinations of vacuum and pressure force chemical into wood to create a barrier of protection. Effective wood preservatives have been available since the mid 1800’s and there are thousands of facilities globally that treat wood to extend its useful life; reducing pressure to harvest additional trees.

At the same time, all wood preservatives are inherently toxic and virtually all have some degree of water solubility (Lebow, 1996). Water solubility is essential; chemical must be available in water within wood cells for it to be absorbed and kill or inhibit growth of degrading organisms. Solubility also results in migration of preservative into the surrounding environment. For decades preservative migration from wood was viewed positively because it provided an added area of protection in surrounding soil. Growing concerns about uncontrolled chemical releases into the environment and the risks these chemicals might pose to non-target organisms have fostered a shift in attitudes.

Increased regulations and restrictions on treated wood use, especially in aquatic applications in the U.S. Pacific Northwest (PNW); home to many threatened and endangered salmon species, encouraged the development of models to predict the risk of chemical migration combined with Best Management Practices (BMP's) to reduce the potential for chemical migration (WWPI). These tools allow users and regulators of treated wood to make more informed decisions concerning the use of these materials (Lebow and Tipple, 2001; WWPI, 2012, 2014). While the models draw from results of previous studies, there are relatively few field assessments of chemical migration from preservative treated wood in service and even fewer studies investigating the ability of the BMP's to reduce preservative migration. These data could be used to assess the validity of the models and to more carefully define loss rates for various treatments.

The purpose of this research was to investigate preservative migration from a Douglas-fir bridge in the foothills of the Cascade Mountains in Oregon and to use these data in combination with reported stream flow data to predict the levels of preservative migration into a receiving stream.

The House Rock Bridge is located on the South Santiam River east of Sweet Home Oregon in the Willamette National Forest. The nearest town (Sweet Home, Oregon) receives an average of 1.375 m of rainfall per year, mostly falling between October and May. The climate is Mediterranean, with mild winters and warm, dry summers. The bridge was constructed with Douglas-fir (*Pseudotsuga menziesii*) decking treated with pentachlorophenol (PCP) to a retention of 9.6 kg/m^3 in a petroleum solvent and supported by laminated beams pressure treated with copper naphthenate (CuNaph) in diesel oil to a retention of 1.2 kg/m^3 (as Cu). While PCP is not widely used elsewhere in the world, it remains an important industrial preservative in the United States. CuNaph is less commonly used, but has been proposed as a PCP replacement. The materials were treated following the standards of the American Wood Protection Association following recommendations for Best Management Practices (AWPA, 2016; WWPI, 2011). The bridge had already been in place for several months prior to the start of the test, preventing any initial background surveys. However, the construction took place during the drier summer months and the wood was only subjected to a few light rainfalls before monitoring began.

The bridge was too big to sample completely. Instead, a temporary collection system was built below a section of the bridge representing 7.1 % of the total surface area. Plastic tarps were attached below the bridge super-structure so that they could capture all rainwater runoff from the desired portion of the bridge. Runoff was funneled into a tared collection container and the total amount was determined by weight gain. This system was easily assembled each time a collection was made. The collected runoff was agitated, then three 300 mL sub-samples were removed for analysis.

Samples for PCP analysis were processed immediately to minimize the risk of sample degradation (Simonsen et al., 2008). Two hundred mL of each sub-sample were transferred to a tared 250 mL glass volumetric flask and weighed to the nearest 0.01 g.

Samples were causticized by adding 2.5 mL of 1N NaOH to each flask. A Teflon™ stir bar was added and the flasks were stirred for 1 min and allowed to stand for 30 min. This procedure converted PCP to sodium pentachlorophenate. Next 2.5 mL of iso-octane was added and the flasks were stirred for 1 min. The solvent layer was removed from the top and discarded. This step was repeated with another 2.5 mL of iso-octane. The process removed residual oils and other organics from the sample.

Sodium pentachlorophenate was converted back to PCP by adding 3.0 mL 1N H_2SO_4, stirring for 1 min and allowing the mixture to stand for 30 min. 2.5 mL of iso-octane was added to the flask and stirred for 1 min. The iso-octane layer was removed and transferred to a 20 mL glass vial. The extraction was repeated with an additional 2.5 mL of iso-octane and the two extracts were combined.

PCP was quantified with high resolution gas chromatography – low resolution mass spectrometry (HRGC-LRMS). Analysis was carried out by injecting 1 µL of sample into a Shimadzu HRGC-LRMS system class 5000 equipped with an RXI-5ms column (0.25 mm inner diameter by 30-mm long) at a flow rate of 1.0 mL/min. The carrier gas was helium (grade 5) and the system was operated in 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.

PCP was scanned and identified using the National Institute of Science and Technology (NIST) Mass Spectral Library #107 software. The retention time was 9.70 min and the selected ion for quantitation was m/z = 266, with reference ions of 264 and 268. HRGC-LRMS auto tuning was performed with perfluorotributylamine (PTFB). An 8 point calibration curve was employed for PCP quantitation. Standard concentrations were 5, 10, 25, 50,100, 150, 200, and 250 µg/mL. The limit of detection (LOD) of this method was estimated to be 0.025 ng/mL as defined in the Federal Register Part 136, Appendix B, procedure (b), as three times the standard deviation of replicate analyses of the analyte.

Ten mL of the remaining runoff sub-samples were acidified with 0.5 mL of 1N nitric acid and analyzed for copper (Cu) by ion coupled plasma spectroscopy. These results were used to determine the amount of CuNaph (as Cu) leached.

Migration was assessed 15 times over a 3 year period. Total amounts of PCP and Cu migrating from the bridge to the stream were estimated by measuring the surface area of all bridge components and the surface area from which runoff was collected. Results were extrapolated for the entire structure. The area surrounding the bridge was extremely rocky and this, in combination with the fast water flow, precluded sediment collection beneath or downstream from the structure.

Potential impacts of PCP and/or Cu runoff from the bridge on the receiving river were determined by comparing total runoff from a given precipitation event with nearby stream flow gauges for the same time period. In addition, stream flow data were examined to identify typical low and high flow conditions. Low stream flow conditions were of more interest since they had the greatest potential to result in elevated downstream chemical concentrations. Gauge data were obtained from the closest USGS gauge located about 10 miles downstream (https://waterwatch.usgs.gov/?m=real&r=or, accessed 3/27/2017). These data were used to determine the concentration of PCP and/or Cu that could develop downstream and these levels were compared with either regulatory limits or minimum effects levels.

Amounts of water collected varied widely over the 15 collections from a low of 970 mL to over 44,840 mL (Table 10). The bridge is located in the foothills of the Cascade Mountain Range and rainfall is normally steady, but light. Typical total daily precipitation might be 25 mm even though it rained all day. This precipitation pattern might be expected to result in near continuous wetting of exposed surfaces during the wet winter, which should facilitate solubilization and eventual loss of preservatives near the wood surface. However, streams in this region are characterized by relatively low buffering capacity that should reduce the potential for preservative migration.

PCP levels in runoff: PCP was detected in water collected from all 14 rainfall events (Table 10). The initial PCP concentrations averaged 6 ug/mL, then declined to less than 2 ug/mL after 3 rainfall events. Concentrations declined even further to less than 1 ug/mL in the 6th and 7th collections, but then rose sharply to 8.7 ug/mL in the 8th collection. Concentrations declined slightly to 5.7 ug/mL in the 9th collection which was made only 13 days later. PCP concentrations since that time have all been below 1 ug/mL. It is unclear why concentrations rose so sharply in two of the collections, but the more recent analyses are consistent with previous results (Simonsen et al., 2008). 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 numerous rainfall events between individual water collections. However, previous studies of PCP runoff from stored utility poles have shown that PCP levels in runoff are more a function of solubility than time or rainfall intensity once any surface deposits of chemical have been removed (Love and Morrell, 2014; Morrell and Chen, 2008).

The relatively small range of PCP concentrations found in repeated rainwater runoff collections reflects the high concentrations of PCP available near the wood surface coupled with the low water solubility of this biocide. PCP solution concentrations used in most wood treatments range from 5 – 9 % solubilized in some type of hydrocarbon solvent. Assuming minimal loss of solvent following treatment, this translates to a concentration of 50,000 ng of PCP/kg in a 5 % treatment solution. In addition, there is a tendency for preservative concentrations in wood to follow a gradient of high to low concentration with distance inward from the wood surface. This leaves an abundant amount of PCP available near the wood surface for potential interaction with precipitation. PCP has a water solubility of 10 – 20 mg per kg of water at 20 °C (Dean, 1973). However, solubility can vary greatly due to PCPs complex aqueous speciation. PCP is a weak acid that partially dissociates in water and its dissolution is dependent upon the equilibrium between two chemical forms: the slightly soluble undissociated PCP0 and the highly soluble PCP- (Arcand et al, 1995). The temperature of the

Table 10. Concentrations of Cu and pentachlorophenol (PCP) in rain water runoff collected at various times from the House Rock Bridge near Upper Soda, Oregon.

Date Collected	Total Runoff (L)	Runoff Concentration (µg/mL)[a]	
		PCP	Cu
1/9/2014	40.07	6.183 (3.494)	4.27 (0.32)
1/10/2014	20.35	3.264 (0.206)	4.90 (0.26)
3/26/2014	40.6	1.165 (0.004)	3.03 (0.81)
3/27/2014	30.48	1.506 (0.051)	2.00 (0.00)
3/28/2014	36.49	1.362 (0.025)	2.03 (0.06)
11/20/2014	21.62	0.506 (0.009)	2.67 (0.58)
11/21/2014	0.97	0.608 (0.020)	7.80 (0.35)
12/10/2015	40.2	_[b]	1.40 (0.00)
12/11/2015	40.66	8.728 (0.143)	1.40 (0.00)
12/23/2015	12.09	5.717 (0.036)	0.73 (0.02)
12/8/2016	39.68	0.432 (0.026)	0.37 (0.06)
2/16/2017	44.84	0.296 (0.022)	0.83 (0.06)
3/22/2017	12.58	0.669 (0.001)	0.91 (0.09)
3/23/2017	10.42	0.672 (0.004)	0.97 (0.04)
3/24/2017	39.58	0.681 (0.100)	0.53 (0.03)

[a] = Values represent means of 3 replicates per time point. Figures in parentheses represent one standard deviation.
[b] = Samples lost.

rainwater in our collections would range from 5 – 8 °C, further reducing the amount of PCP that can be solubilized as precipitation strikes the wood. Low PCP concentrations, < 2 ug/mL, found in runoff from all but 4 collections suggest that other factors limited dissolution. One possibility is pH since the ratio of PCP^0 and PCP$^-$ changes with pH which affects total PCP solubility (Arcand et al, 1995). PCP is more soluble in alkaline waters and, generally, rivers in the PNW are slightly acidic which would affect PCP solubility found in our runoff collections. Leaf litter on the bridge deck surface sorbing PCP could account for the low PCP levels observed; but this material would intersect the water prior to contact with the treated wood. PCP levels were also poorly correlated with total runoff collected (Figure 24). These results are consistent with previous tests on runoff from stored utility poles (Morrell and Chen, 2008). The results suggest that

PCP migration from the wood in this structure is lower than that found in previous tests on other PCP treated materials.

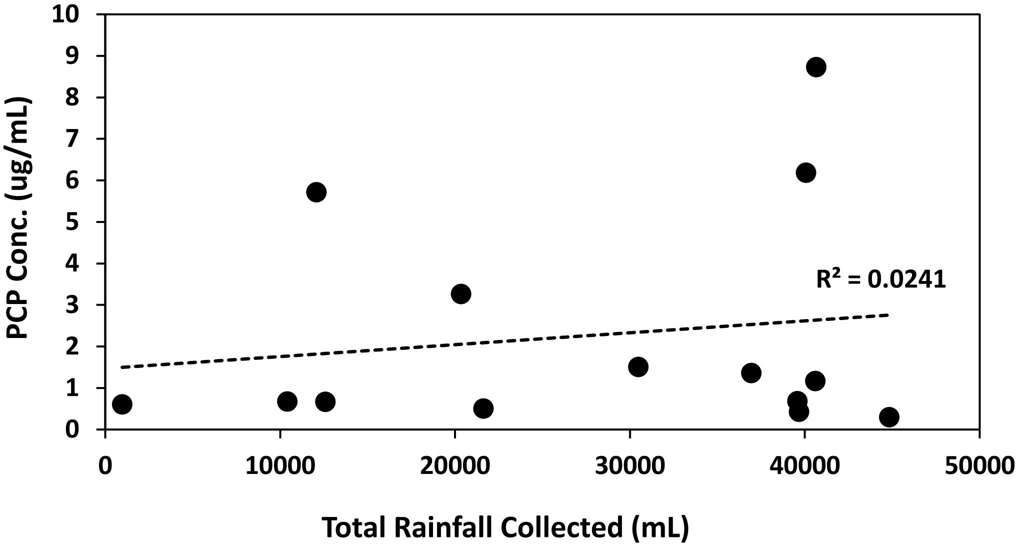


Figure 24. Association between concentration of PCP in runoff and total runoff collected at each of 14 sampling times from House Rock Bridge.

Copper Levels in Runoff: CuNaph levels in runoff ranged from 0.53 to 7.80 ug/mL (Table 10). Cu concentrations were highest when the lowest levels of runoff were collected. With the exception of one especially high value, Cu concentrations gradually declined over time. There was a slight trend for lower Cu levels with increased runoff, but this trend was heavily influenced by the high Cu value in the sample from the lowest runoff collection (Figure 25; R^2= 0.15). The results indicate that Cu concentrations in runoff were also not closely related to total rainfall collected.

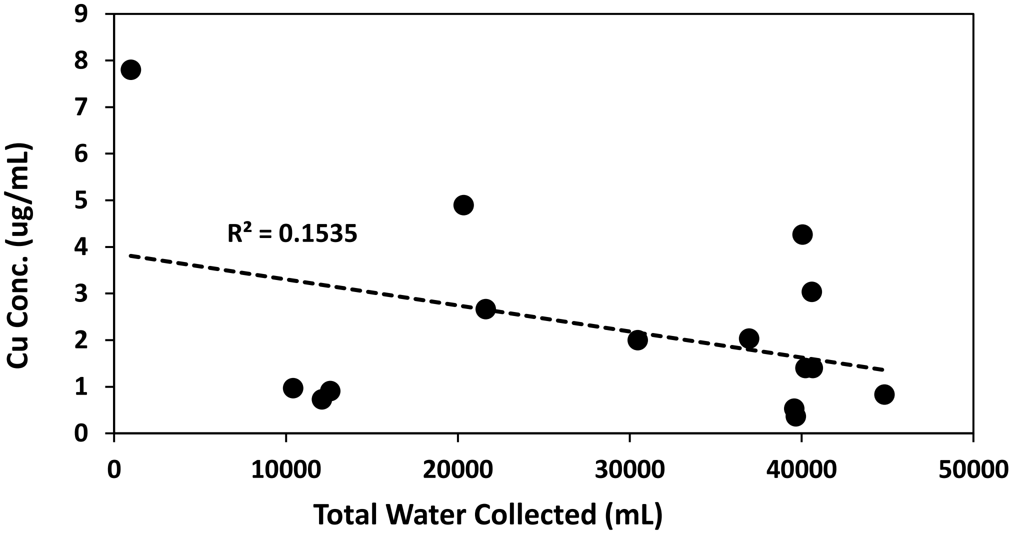


Figure 25. Association between concentration of Cu in runoff and total runoff collected at each of 15 sampling times from House Rock Bridge.

Although Cu is only part of CuNaph, it was selected as the analyte of interest because it has known toxicity to aquatic organisms and has been reported to affect the ability of salmon to locate their native stream (McIntyre et al. 2008; Wendt et al., 1996). While naphthenic acid may also be present in the runoff, it was not investigated in this study.

Implications of Migration: Developing data on the absolute amounts of chemical migrating from a structure is useful, but must be placed in context with the potential impacts of the chemical on the receiving body of water. In order to investigate possible effects on the receiving stream, stream flow was obtained from the closest stream gauge. We recognize the possibility of additional water entering the stream below our bridge site. Data for stream flow were taken as the high and low flow in megaliters per day for each collection period (Table 11). The bridge area from which the water was collected represented 7.1 % of the total bridge surface area and all runoff was assumed to leave the bridge and enter the stream. Total PCP and/or Cu collected from our sampled portion of the bridge was multiplied by 14 to estimate migration from the entire bridge. All faces of treated wood were considered to be capable of contributing to preservative migration. This was an over-estimate because there were areas of the bridge that would not be wetted and short banks next to the bridge abutments that might intercept some runoff before it entered the stream. The resulting value was used to calculate the total PCP and/or Cu entering the stream from the bridge using either high or low water flow values.

Potential PCP levels in the river ranged from 0.02 – 1.31 ng/L (parts per trillion) over the 14 collection periods when low flow at each sampling time was considered (Table 11). These values decreased to 0.01 – 0.91 ng/L when the high flow for that collection point was used. Cu levels in the river downstream from the bridge for the 15 collection periods would be 0.02 – 5.51 ng/L using the low flow rate and 0.02 – 1.74 ng/L for the high flow condition.

No Cu concentration data were available for this river, but the WWPI Risk Assessment Model uses an assumed 1.5 µg Cu/L of water as a baseline Cu level (1500 ng/L; Brooks, 2011; WWPI, 2012). While it would be difficult to completely assess the toxicity of added Cu in this river, it is possible to look at the proportional increase in Cu levels in the receiving water with varying precipitation levels. The highest Cu concentration in runoff was 5.50 ng/L which would represent a 0.033% increase in background Cu levels. In most other cases, the changes were less than 0.005% under the low stream flow condition and less than that at the higher flow rates. While any change in Cu concentrations could influence behavior, the levels noted herein would generally fall within the range of error for most analytical methods given the variability in flow conditions and collection methods. They were also well below those examined for their potential effects on salmon migration (McIntyre et al., 2008; Wendt et al., 1996).

Clearly, there should be no background PCP in the river above the bridge. Thus, any PCP introduced from the bridge would need to be examined alone. The highest level of PCP estimated to be in the stream below the bridge was 1.31 ng/L when the collection was made during a period of low stream flow. The Risk Assessment Model uses a value of 9.8 µg/L (9.8 ppb) as a minimum effects threshold (Brooks, 2011) or approximately 0.01 % of that level. Values were still well below minimum effects levels when the lowest flow and highest PCP and Cu value recorded during our study were used. Maximum PCP and Cu concentrations would be 23.67 ng/L and 5.50 ng/L, respectively. These estimates also ignore the potential for photodegradation and settlement into the sediment where PCP is microbially degraded over time (Brooks, 2011). It is also important to note that high chemical migration levels coupled with low stream flow are less likely to occur at this site because rainfall is very limited during the dry summer months when stream flow is low.

There are several aspects of this study that merit further discussion. First, this bridge contained two different preservatives and it would be difficult to determine if there might be interactions between the two systems in terms of toxicity. Cu has broad spectrum physiological effects on organisms, while PCP is acutely toxic to target organs and/or systems within an organism (Brooks, 2011). However, our results likely over-estimate possible levels in the receiving body because we used the entire bridge surface area even though a portion was over land and other potions would not be wetted. We also used low stream flows as the primary guide to possible chemical concentrations.

A more important aspect of this test was the fact that, to our knowledge, the South Santiam River has little or no treated wood over water above or below this bridge. Thus, any possible inputs should be confined to this bridge. The use of treated wood in additional projects should require, at the least, using the predictive models to determine potential effects. It would also be prudent to consider the combined effects of projects were they to be located within close proximity to one another.

PCP and Cu were both detected in runoff from a bridge containing wood treated with both PCP and CuNaph at every collection point. While the levels detected varied, there was a general trend towards lower levels with increasing exposure time. Estimates of total preservative entering the receiving stream showed that PCP and Cu concentrations were well below minimum effects levels at all sampling points.

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

Port Authorities in many locations are returning to the use of preservative treated pilings in place of concrete, but still have some concerns about the potential for preservative migration from these products. This is particularly true in ports where prior activities, notably the presence of ships with copper-based anti-fouling coatings, have resulted in an excess of copper in water column and sediment. One possible solution for limiting additional copper input would be to coat pilings with impermeable barriers to limit preservative migration. Barriers have long been used for protection against marine borer attack, but they are increasingly used to limit preservative loss into the surrounding environment. Salt water presents an especially rigorous environment for coatings; the risk of debris or ships damaging the wood surface further limits their application. However, a number of coatings systems have been developed for this application including fiberglass and polyurea coatings. The latter systems are currently required in several California ports while the former are used on the East coast of the U.S. These barriers have been reported to be effective, but there are relatively few data demonstrating their ability to restrict preservative loss. In this report, we describe preliminary evaluations of polyurea-coated pilings treated to the marine retention (2.5 pcf or 40 kg/m^3) with ammoniacal copper zinc arsenate (ACZA).

Table 11. Average PCP and Cu concentrations below House Rock Bridge as determined by the total amount of chemical migrating from the bridge during low/high stream flows.[a]

Collection Date	Total Chemical Released (mg)		Discharge ML/Day		Low Flow Conc. (ng/L)		HighFlow Conc. (ng/L)	
	PCP	Cu	Low	High	PCP	Cu	PCP	Cu
1/9/2014	3468.1	2393.2	2642.3	3792.2	1.31	0.91	0.91	0.63
1/10/2014	929.9	1396.0	3327.3	4452.8	0.28	0.42	0.21	0.31
3/26/2014	662.3	1723.9	1585.4	2221.5	0.42	1.09	0.30	0.78
3/27/2014	642.7	853.4	2201.9	3987.9	0.29	0.39	0.16	0.21
3/28/2014	704.6	1051.7	3987.9	12697.7	0.18	0.26	0.06	0.08
10/20/2014	153.1	807.1	146.5	464.8	1.04	5.51	0.33	1.74
10/21/2014	8.3	105.9	479.5	660.6	0.02	0.22	0.01	0.16
12/10/2015	_[b]	788.6	8293.9	9125.7	_[b]	0.10	_[b]	0.09
12/11/2015	4967.5	796.8	5945.2	8293.9	0.84	0.13	0.60	0.10
12/23/2015	967.2	122.9	5480.3	7364.2	0.18	0.02	0.13	0.02
12/8/2016	240.0	203.7	2099.2	3400.7	0.11	0.10	0.07	0.06
2/16/2017	185.8	523.1	3669.9	8098.2	0.05	0.14	0.02	0.06
3/22/2017	117.7	159.7	4281.5	4526.2	0.03	0.04	0.03	0.04
3/23/2017	98.0	140.9	3596.5	4306	0.03	0.04	0.02	0.03
3/24/2017	377.1	294.8	3669.9	7168.5	0.10	0.08	0.05	0.04

[a] = Values represent triplicate analysis at each collection point.
ML = megaliters and ng = nanograms.
[b] = Samples lost.

Materials and Methods: ACZA treated Douglas-fir pilings with and without a ~125 or 250 mil thick polyurea coating from the butt to the tip were received from Thunderbolt Wood Treating (Riverbank, CA) as 1.4 m long by 153mm diameter sections (Figure 26). The coating was only on the vertical surfaces, not the cross sections. Four sections were coated and three were left uncoated. Pilings were buried to a depth of 400 mm in soil in 208 L Nalgene tanks and the tanks were filled with artificial seawater (1.5% salt) to a depth of 600 mm so that the base of the pile was in sediment, but the remaining 400 mm of the section was not immersed. Tanks were covered to limit evaporation and stored at room temperature. Sediment and water were periodically sampled for copper, zinc and arsenic levels. Coated pilings were installed November 20, 2015, while the non-coated pilings were installed January 27, 2016, but both sets of materials were exposed to the same conditions after installation.

Sediment samples were removed immediately adjacent to pilings, oven dried and ground to a fine powder for acid extraction. Resulting extracts were analyzed for total copper, zinc and arsenic by Ion Coupled Plasma Spectroscopy (ICP). Water was gently agitated to more evenly distribute any metal. Care was taken not to disturb the sediment and a 20 mL sample of water was removed, acidified with 1N nitric acid, and analyzed for metal content by ICP. Initial sampling was frequent (daily, then weekly), but then decreased as trends became evident. Detection limits for copper, zinc, and arsenic via this method were <0.05 mg/kg for all three metals.

<u>Water column</u>: Metal levels in the water column in tanks containing coated ACZA were below detection limits (0.05 mg/kg for each element) over the entire 384 day exposure period. Results illustrate the ability of these coatings to contain metallic elements in salt water.

Metal levels in water containing non-coated piling exposed in the same manner steadily increased over the exposure (Figure 27), although there has been some variation in levels with prolonged exposure as a result of less frequent sampling. The overall concentration trend, however, was steadily upwards with the possible exception of the 2 final collections that suggested that a plateau had been reached. Interestingly, there did not appear to be a large surge in metal concentrations in the water immediately after installation; copper, zinc and arsenic levels steadily increased over the exposure period. Previous reports have shown that metal levels in water surrounding a sample of treated wood increase sharply shortly after immersion as residual metals on the wood surface are solubilized (as reviewed in Morrell et al., 2011). These pilings were subjected to post-treatment Best Management Practices according to procedures described in the Western Wood Preservers Institute (WWPI) Guidelines (WWPI, 2012). While these processes reduce the presence of surface deposits and help ensure immobilization of metals, the lack of any noticeable surge is interesting, although not pertinent to the current test (Ye and Morrell, 2015).

<u>Sediment Metal Levels:</u> Sediment analysis after 309 and 340 days of exposure show that metal levels remained exceedingly low in the sediment around the coated samples (Table 12). These results agree closely with the water column analysis and indicate that the coating is restricting potential metal movement.

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

Table 12. Residual copper, zinc and arsenic in sediment surrounding non-coated and polyurea coated ACZA treated Douglas-fir.[a]

Treatment	Exposure Time (Days)	Metal Concentration (uμg/kg of sediment)		
		Copper	Zinc	Arsenic
Coated	309	2.38 (1.90)	3.48 (0.90)	1.18 (1.33)
	340	3.40 (0.54)	4.00 (1.70)	0.75 (0.85)
Non-Coated	241	81.37 (106.97)	46.57 (39.49)	15.07 (10.43)
	272	188.50 (200.34)	70.33 (38.47)	11.73 (8.03)

[a] Values represent means of 3 or 4 samples per time point. Figures in parentheses represent one standard deviation.

Figure 26. Example of polyurea coated piling in exposure tanks.

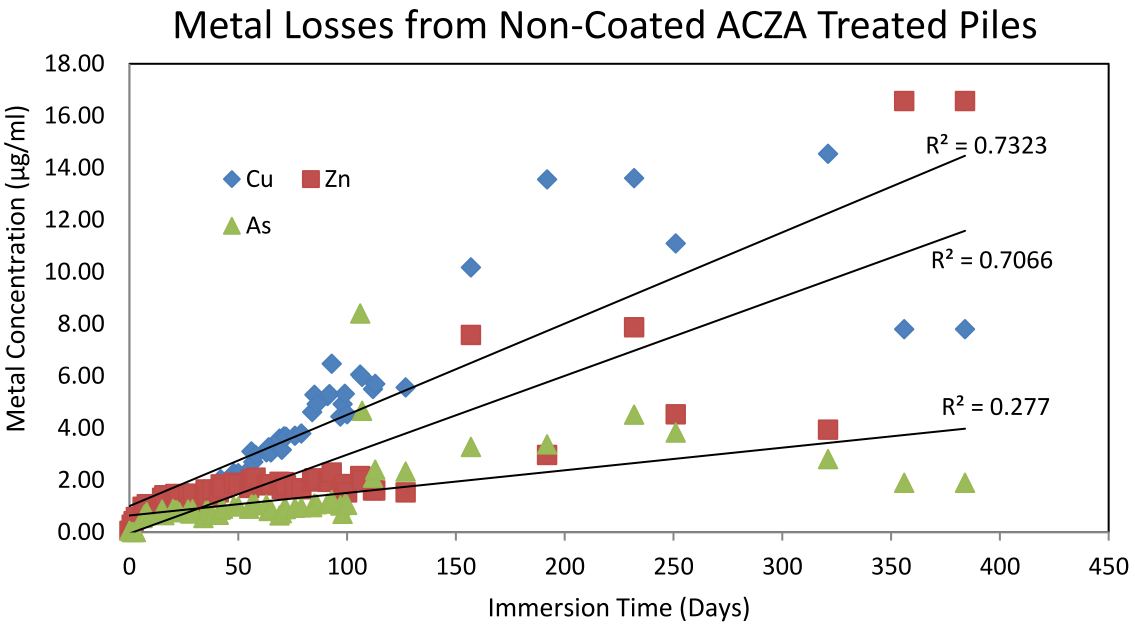


Figure 27. Copper, zinc and arsenic levels in salt water samples removed over a 384 day period from tanks containing ACZA treated Douglas-fir piling with no polyurea coating.

The polyurea coating completely inhibited copper zinc and arsenic migration from ACZA treated piling in synthetic salt water in a non-circulating environment where metal build-up would be especially critical. The results illustrate the benefits of these types of coatings.

As a follow-up to the initial assessment, the piling were intentionally damaged by removing a band approximately 50 mm wide completely around each pile . This represented removal of approximately 8.33 % of the total wrap area exposed to seawater. The intent was to simulate field damage to an in-service piling. The test was designed to help regulators understand how much damage could occur on a coated piling before repairs were required to limit preservative migration from becoming a concern. This is important since coated piling have been allowed in a number of ports and regulatory authorities have now created guidelines stipulating that these piling be regularly inspected and repaired if damage occurs. The lack of data makes it difficult to determine how much damage triggers a repair.

The piling were damaged to completely remove the polyurea coating in the affected area and then immersed in fresh (1.5%) synthetic seawater as previously described. Seawater samples were removed at regular intervals and analyzed for copper, zinc and arsenic as previously described. These tests have only been underway for a month.

Background metal levels in the seawater were 0.034, 0113, and 0.063 µg/mL of seawater for the Cu, Zn and As, respectively, at the start of the test. Copper levels in the seawater rose to approximately 0.80 µg/mL over the first 23 days of immersion, while zinc reached a maximum of 0.41 µg/mL after 21 days, and arsenic was detected at 0.18 µg/mL after 23 days (Figure 28). By comparison, copper, zinc and arsenic levels in fully immersed non-coated piling in the first test were 1.38, 1.36 and 0.77 µg/mL, respectively, after 23 days. These results illustrate the obvious fact that damage to the coating can negate its value, although the metals levels that develop in the surrounding water are much lower than with no coating. We will monitor these piling for another 50 days to determine if losses stabilize or continue to occur. We will then increase the amount of damaged surface area and monitor losses. Ultimately, our goal is to establish a threshold for the amount of coating area that can be damaged before repairs are advisable.

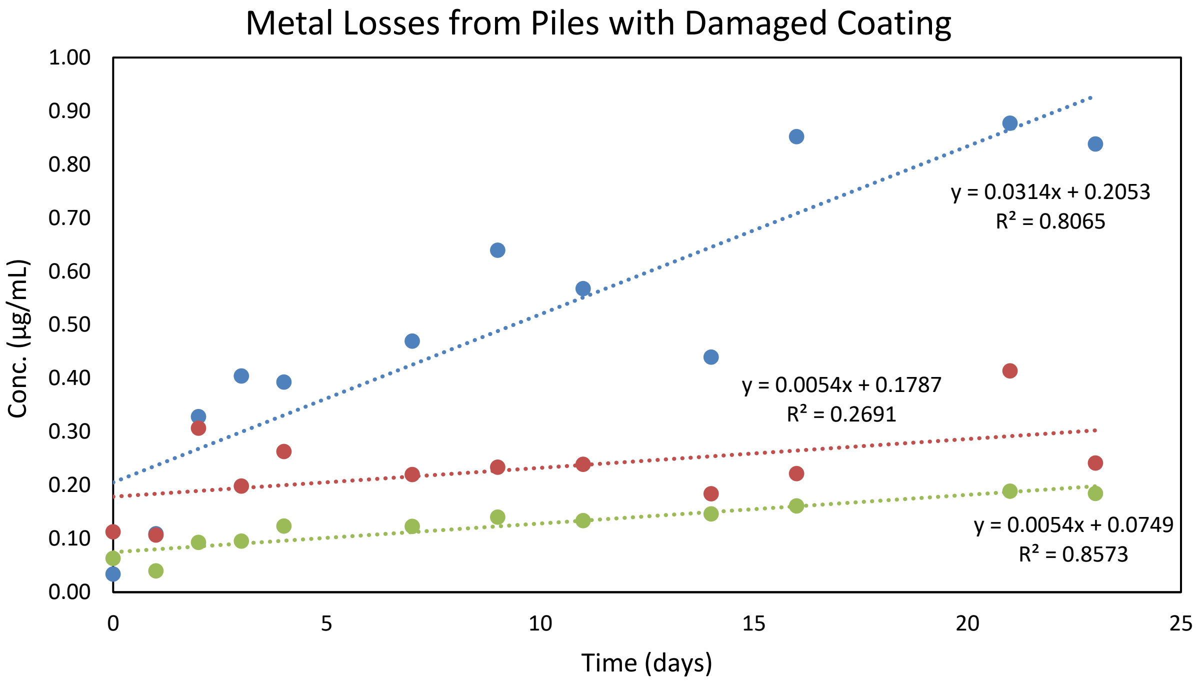


Figure 28. Copper zinc and arsenic levels in seawater surrounding polyurea coated ACZA treated piling with 8.33 % of the coating area removed.

2. Develop standardized accelerated methodologies for assessing treated wood risks

We are working to develop a number of standardized methodologies that can be used to assess preservative mobility under varying regimes. These include the small scale BMP verification procedures, the sachets used to detect preservative migration in aquatic environments, and our efforts to quantify the levels of PAH's in the water column that have been described earlier. Our intent is to publish the results of these tests in peer-reviewed journals and, once they are accepted in that venue, to move to make these methods standards under the appropriate organizations.

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

The BMP veriifcation studies, coupled with our field trials provide us with a wealth of data that can be used to assess the accuracy of the models. We are still sorting through these data, but the intent will be to use these results to examine the efficacy of various BMP’s and to make recommendaiotns to the BMP Coalition concerning the most appropriate BMP’s for a given system.

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 treated Douglas-fir, SPF, and southern pine lumber have provided valuable information on the effects of the BMP’s on metal migration from wood treated with the various preservative systems. We intend to use these data to explore improved methods for reducing metal losses

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

We have continued to examine treated wood entering the recycling stream. The Recycling Center where we have performed these studies has changed their operation, making it difficult to regularly access the site. We are working with the facility to identify a system that meets their safety concerns, while allowing us access to the materials in a timely fashion.

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

We held one meeting in Oakland,CA in cooperation with WWPI on the use of treated wood, the model premise and to provide hands-on experience with the new model. The new model is vast improvement in terms of user friendliness and received very favourable comments from the participants

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