

Leaching of chromated copper arsenate (CCA)-treated wood in a simulated monofill and its potential impacts to landfill leachate

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Received 13 June 2005; received in revised form 11 November 2005; accepted 14 November 2005

Available online 6 January 2006

Abstract

The proper end-of-life management of chromated copper arsenate (CCA)-treated wood, which contains arsenic, copper, and chromium, is a concern to the solid waste management community. Landfills are often the final repository of this waste stream, and the impacts of CCA preservative metals on leachate quality are not well understood. Monofills are a type of landfill designed and operated to dispose a single waste type, such as ash, tires, mining waste, or wood. The feasibility of managing CCA-treated wood in monofills was examined using a simulated landfill (a leaching lysimeter) that contained a mix of new and weathered CCA-treated wood. The liquid to solid ratio (LS) reached in the experiment was 0.63:1. Arsenic, chromium, and copper leached from the lysimeter at average concentrations of 42 mg/L for arsenic, 9.4 mg/L for chromium, and 2.4 mg/L for copper. Complementary batch leaching studies using deionized water were performed on similar CCA-treated wood samples at LS of 5:1 and 10:1. When results from the lysimeter were compared to the batch test results, copper and chromium leachability appeared to be reduced in the lysimeter disposal environment. Of the three metals, arsenic leached to the greatest extent and was found to have the best correlation between the batch and the lysimeter experiments.

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Keywords: CCA-treated wood; Disposal; Leaching; Arsenic; Lysimeter

1. Introduction

Once chromated copper arsenate (CCA)-treated wood is removed from service, the risk of direct exposure to humans and the environment is minimized, but management as a solid waste begins. Discarded CCA-treated wood is exempt from characterization as a hazardous waste in the U.S., even though it often leaches arsenic at concentrations greater than the U.S. Environmental Protection Agency (EPA) toxicity characteristic concentration for hazardous wastes [1]. When CCA-treated wood is commingled with untreated wood as part of recycling operations, the mulch product produced often becomes contaminated to such an extent that it cannot be land applied [2,3]. When CCA-treated wood is incinerated, resulting arsenic emissions demand the use of proper air pollution control equipment; in addition, arsenic, copper, and chromium become concen-

trated in the ash, limiting ash management options [4,5]. In some countries (e.g., Germany), discarded CCA-treated wood is banned from landfill disposal, and after all reuse options have been exhausted, the material must be incinerated [6]. In the U.S. (including Florida) and some other countries (e.g., Canada and Australia), CCA-treated wood is typically disposed of in landfills without any processing or pretreatment. A natural concern of landfill disposal of discarded CCA-treated wood is the possibility of preservative elements leaching at levels that result in harm to the environment or that make it difficult for the landfill operator to manage collected landfill leachate.

The leaching of arsenic, copper, and chromium from the in-service use of CCA-treated wood has been examined extensively [7–10], including the development of predictive models [11]. In the past several years, more attention has been placed on the leaching of CCA-treated wood in disposal environments such as landfills. The leaching of arsenic, copper, and chromium from CCA-treated wood using a variety of regulatory batch leaching tests has been completed, along with experiments to investigate the impact of factors such as particle size, pH, contact time, and leaching fluid [1,12]. Batch leaching studies provide

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some indication of which metals are prone to leaching in a disposal scenario, and the research referenced above demonstrated that arsenic, copper, and chromium do leach from CCA-treated wood. The utility of batch tests may be limited, however, since they cannot incorporate all of the factors that impact pollutant leaching and mobility in various landfill environments. The type of landfill can be very important because of differences in oxidation–reduction potential and chemistry resulting from biological reactions in the waste mass.

Several different types of landfills may be used for the disposal of CCA-treated wood. Since CCA-treated wood is a construction material, in some locations it is often managed as part of the construction and demolition (C&D) debris stream. In the U.S., C&D debris is often considered inert; in 27 states, C&D debris landfills are not required to have a liner [13]; in these circumstances, contamination of groundwater is a concern. The disposal of CCA-treated wood as part of C&D debris has been shown to increase leachate concentrations of arsenic and chromium [14,15]. When CCA-treated wood is disposed in lined landfills, where it would normally be disposed with municipal wastes, elevation of preservative elements in leachate becomes a potential issue. An additional disposal scenario, one not currently practiced for CCA-treated wood but practiced for other special wastes, is disposal as a separate material in a lined landfill. In such a monofill, preservative leaching would be concentrated, making it easier to contain and possibly recover the preservative elements.

Research was conducted to study the effects of CCA-treated wood disposal on leachate quality in various landfill scenarios [16]. This paper reports the results of one of these scenarios, one where CCA-treated wood was segregated and separated for management in a monofill. A CCA-treated wood monofill restricts the wood from contaminating other disposal scenarios, thereby more efficiently concentrating and controlling the metals released. The monofill could also be used as a resource if recycling and/or recovery options for CCA-treated wood were developed and became economically feasible. The primary objective of the research was to quantify the release of arsenic, copper, and chromium from a CCA-treated wood monofill by constructing a leaching column (lysimeter) and measuring the concentrations of preservative elements in the leachate over time. An added benefit to the observation of leachate from a lysimeter is that the leaching behavior of CCA-treated wood can be examined and evaluated at very low liquid to solid ratios, those much lower than can be achieved in batch leaching studies. Batch leaching studies were conducted on the same wood used in the monofill simulation in order to compare the results. With the lysimeter representing more realistic conditions, results were compared to the laboratory batch leaching studies conducted on the CCA-treated wood.

2. Experimental

2.1. Leaching column (lysimeter)

A 6.7-m high and 0.3-m (1-ft) diameter leaching column, also called a lysimeter, was constructed at the Alachua County Solid

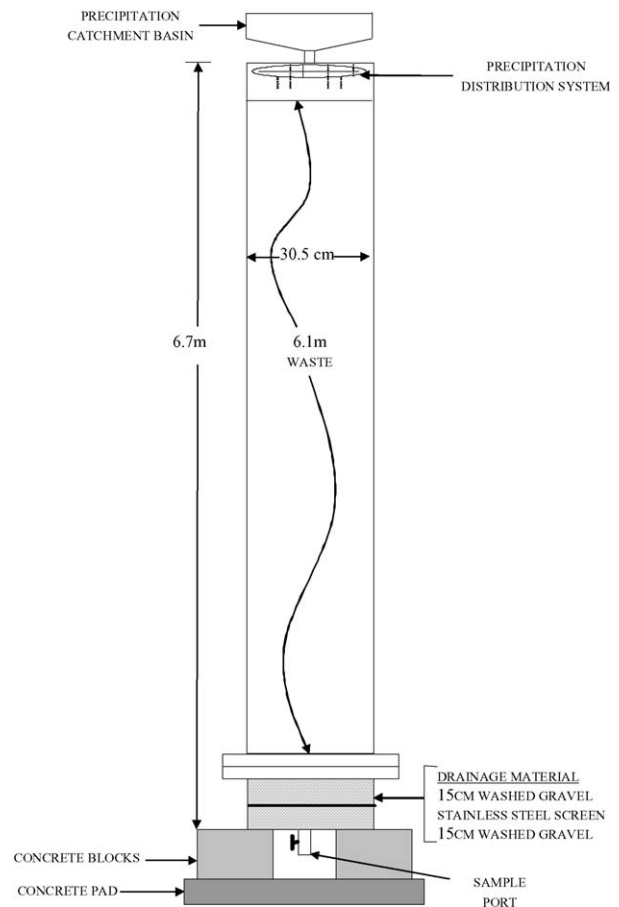


Fig. 1. Diagram of the lysimeter.

Waste Landfill, located in North Central Florida, U.S. Fig. 1 presents a diagram of the lysimeter. The lysimeter was constructed (from the bottom to the top) with: 15.2 cm of washed gravel, a stainless steel screen, 15.2 cm of washed gravel, 6.1 m of simulated waste, a cap with a water distribution system, and a catchment basin for rainwater. Natural precipitation was allowed to infiltrate the lysimeter (1 cm of precipitation applied to the lysimeter is equal to 0.73 L of water addition). Natural precipitation was supplemented by the addition of deionized water during the dry season (September 2002–January 2003) to produce required quantities of leachate for the analysis of general water quality parameters in the field and analysis of other parameters, including arsenic, copper, and chromium in the laboratory. Natural precipitation contributed 207 cm of the total 230 cm of water input throughout the 755 days of the experiment. The lysimeter was located outdoors and exposed to ambient temperature variations. Thermocouple wires (type T) were placed at three separate depths (6.1 m, 4.6 m, and 1.5 m) within the lysimeters to obtain temperature readings.

2.2. Simulated wood waste

The experimental lysimeter contained 100% CCA-treated Southern Yellow Pine (Type C). Southern Yellow Pine is commonly used for treated wood since it contains a large proportion of sapwood (the highly penetrable portion of wood); however,

it also may contain heartwood. The amount of sapwood versus heartwood in the CCA-treated wood utilized in this experiment was not determined, but the relative amounts were assumed to be typical of those products in service as well as those entering the waste stream since they were obtained from conventional use situations. Since the relative contribution of CCA-treated wood from demolition and construction activities varies and has not been well-quantified, 50% of the CCA-treated wood was new and unused (purchased from a home improvement store) and 50% came from the demolition of a playground that had been in service for approximately 10 years.

A miter saw with a 25.4-cm blade was used to size reduce the wood. The sawdust generated from the processing of the wood was kept for analysis. Sawdust samples were also analyzed by X-Ray Fluorescence (XRF) (Asoma, Model 100). The old and new CCA-treated lumber was originally 3.8 cm × 9 cm × 2.4 m (and other various lengths for the demolition CCA-treated wood). These boards were sliced into 5.1-cm sections creating a block with the dimensions of 3.8 cm × 9 cm × 5.1 cm.

The size-reduced wood was weighed and placed in 19-L buckets and the lysimeter was filled with 22 bucket loads. After each load of wood was placed into the lysimeter, a tamping device (7 kg weight was raised 0.6 m and allowed to fall 10 times) was used to compact the wood. The in-place bulk density and porosity (based upon a particle density of 520 kg/m³) of the lysimeter were 324 kg/m³ and 0.37, respectively.

2.3. Sample collection and analysis

Temperature readings (Omega Model HH21 Microprocessor Thermometer) were taken weekly. Leachate samples were collected from the lysimeter one to two times per month in 20-L containers to homogenize the sample before splitting it up into proper containers for preservation and analysis. Samples were analyzed for general water quality parameters and metals through the end of the experiment. Raw data for all analyses completed on the leachate may be found in Jambeck [16]. Quality assurance and quality control (QA/QC) included the collection and analysis of lysimeter leachate field blanks, duplicate analyses, and analysis of matrix spiked blanks and leachate samples with the majority of recoveries between 80% and 120% and all recoveries between 70% and 120%. Specific details on QA/QC procedures and results are contained in Jambeck [16].

General water quality parameters including pH, oxidation–reduction potential (ORP) (Accumet, Model AP62), dissolved oxygen (DO) temperature (YSI Inc., Model 55/12 FT), and conductivity (Hanna Instruments, Model HI 9033) were measured in the field each time leachate was sampled. Samples taken back to the laboratory for analysis were stored at 4 °C. Samples for dissolved anions were filtered through 0.45- μ m membrane filters and analyzed using ion chromatography (Dionex DX 500). Chemical oxygen demand (COD) was analyzed using a spectrometer (Hach, DR/4000) using method 2720 [17]. Analyses for total dissolved solids and alkalinity were performed using standard methods (Methods 2540 C and 2320 B) [18].

For metals analysis (samples preserved below pH of 2 with nitric acid), leachate samples were digested following U.S. EPA Method 3010A [19]. Solid (sawdust) samples were digested following U.S. EPA Method 3050B [19]. All solid and liquid digestates were analysed with an inductively coupled argon plasma (ICP) instrument (Thermo Jarrell Ash, Model 61E). XRF analysis (Asoma, Model 100) was conducted on sawdust obtained from the entire cross-section of the wood.

Arsenic speciation of the leachate from this study was completed on unpreserved samples by high performance liquid chromatography coupled with inductively coupled plasma-mass spectrometry (HPLC ICP-MS). Arsenic species examined in the leachate included arsenate (As(V)), arsenite (As(III)), monomethylarsonic acid (MMAA), and dimethylarsinic acid (DMAA). Unlike other methylated metals (e.g., mercury), the methylated arsenic species are less toxic than the inorganic forms of As(V) and As(III), with As(III) being the most mobile and toxic of the species mentioned [20,21]. Arsenic speciation for the leachate was conducted through day 474 of the experiment. Details and methods can be found in Khan [22].

2.4. Batch leaching tests

Small-scale laboratory leaching tests were performed on the same size blocks of wood used in the lysimeter experiment. Each batch leaching test consisted of the same 50/50 ratio of construction to demolition debris treated wood. The batch tests were conducted in triplicate at two different liquid to solid ratios (LS), 5:1 and 10:1. Each wood sample was weighed and placed in a 2-L container (plastic vessel) with the appropriate amount of liquid (deionized water). The vessels were rotated for 30 days. Previous research has shown that the levels of metals extracted during a batch leaching test on CCA-treated wood reach equilibrium after 14 days [1]. The wood blocks were separated from the leachate by a pressure filtering device fitted with a glass fiber filter (pore size of 0.7 μ m).

Batch leaching tests were conducted to observe the leaching of the CCA-treated wood blocks used in the lysimeter experiment under a higher (but static) LS than would be achieved in the lysimeter experiment. The toxicity characteristic leaching procedure (TCLP), which is prescribed by U.S. federal regulations to determine if a waste is hazardous for the toxicity characteristic, has previously been performed on CCA-treated wood [1,23]. CCA-treated wood subjected to the TCLP often exceeds the toxicity characteristic limits for both arsenic and chromium (both 5 mg/L), which would classify it as a hazardous waste; however, CCA-treated wood waste is exempt from hazardous waste status under federal regulations [24].

In a related study conducted by the authors [1], the results of which are discussed here, other batch leaching tests were performed on CCA-treated wood to examine the variability of leaching in different environments to evaluate disposal options. These tests include the synthetic precipitation leaching procedure (SPLP), toxicity characteristic leaching procedure, variable pH range leaching tests (e.g., pH stat) and time variable leaching tests. The pH stat leaching experiment consisted of a batch study with a 20:1 LS [1]. The time study was consistent with the

parameters of an SPLP test (pH 4.2 and LS of 20:1), but the rotation time was varied from 2 to 40 days [1]. These related studies have shown that factors including particle size, pH, time, liquid to solid ratio, and leaching solution all affect the leachability of metals from CCA-treated wood [1].

3. Results

3.1. Wood waste characterization

Metals concentrations of the CCA-treated wood as determined through acid digestion were 1390 mg/kg arsenic, 1450 mg/kg chromium, and 814 mg/kg copper, for the new CCA-treated wood, and 1960 mg/kg arsenic, 2550 mg/kg chromium, and 1340 mg/kg copper for the weathered demolition CCA-treated wood (Table 1). These results were consistent with those determined through XRF analysis. Conversion of these results to equivalent retention of CCA Type C on an oxide basis indicates that the retention level of the wood as determined through sample digestion was 3.1 kg/m³ for new wood and 5.0 kg/m³ for demolition wood. Of interest is that the “rated” retention level of the new wood as reported by the wood manufacturer was 6.4 kg/m³. This difference may be due to the fact that the rated retention level is based upon measurements of the outer 1.5 cm of wood, whereas the retention level measured in the current study corresponds to the entire cross-section.

3.2. Wood lysimeter leachate characterization

A total of 91.1 L of leachate was collected from the lysimeter on 29 separate occasions. The liquid to solid ratio (proportion of leachate drained to the mass of wood in the lysimeter) is dynamic for a leaching column and this ratio increased to 0.63:1 by the end of the experiment.

3.3. General water quality parameters in the lysimeter leachate

Monitoring of general water quality parameters in the lysimeter leachate can provide an indication of biological activity and assist in characterizing the leachate. Temperatures inside the lysimeter and temperatures of the leachate fluctuated with ambient temperatures; the average leachate temperature was 23 °C. The decreasing pH trend of the lysimeter leachate, with an average of 5.62, is illustrated in Fig. 2a. Leachate produced from

wood has been shown to cause a drop in pH, and an increase in acidity and lignin–tannin content [25]. Similarly, Jang [14] observed an average pH of 4.4 in an untreated Southern Yellow Pine wood lysimeter. Jang attributed the low pH to large organic molecules dissolving from the wood creating organic acids in the leachate; however, it was also acknowledged that the pH might be a function of the initial pH of the leaching solution (4.2). In this experiment, the pH of the rainwater (approximately 6) and deionized water (approximately 6) may have contributed to the somewhat higher pH observed.

Specific conductance in the lysimeter ranged from 500 μS/cm to 1000 μS/cm, with a decreasing trend throughout the experiment (Fig. 2b), which has been observed in other studies [14,26]. The specific conductance observed is greater than that from untreated wood [16], and CCA-treated wood typically contributes more ions to solution than untreated wood. This was also shown to be true for Gifford et al. [27] in lysimeters containing soil with untreated wood and soil with CCA-treated wood.

Dissolved oxygen levels for the lysimeter leachate began in the range of 2–4 mg/L, and then stabilized at approximately 1 mg/L by the end of the experiment (Fig. 2c), although some spikes in DO were observed at various times. The ORP results (Fig. 2d) showed initial oxidizing conditions (approximately 100 mV) for the leachate, then conditions became reducing and remained this way until near the end of the experiment. At the end of the experiment, the leachate became oxidizing (positive ORP) during the last few sample rounds. The low dissolved oxygen levels and reducing conditions could have been indicative of microbial activity within the lysimeters. Jang [14] observed indications of microbial activity such as decreasing DO concentrations (4–1 mg/L), reducing conditions, and an average COD of 648 mg/L in untreated wood lysimeters [14]. COD, as well as alkalinity concentrations, may indicate microbial activity in this experiment as well.

Alkalinity typically results from the concentration of carbonate and bicarbonate ions in solution, but may also be affected by hydroxides, borates, silicates, phosphates, ammonium, sulfides, and organic ligands [28]. The organic compounds released from the wood itself (or from the degradation of components of the wood) likely contributed to the overall alkalinity of the leachate (e.g., the amine group (–NH₂) can act as a weak base and accept an H⁺) (Fig. 2e). Both of these mechanisms have been reported to create an increased buffering capacity in degraded versus undegraded waste material [29]. A decreasing alkalinity has been observed in other trends of waste degradation [14,16,30].

Table 1
Metal content of the CCA-treated wood samples in the lysimeter

	Arsenic (mg/kg)	Copper (mg/kg)	Chromium (mg/kg)
New CCA-treated wood by acid digestion ^a	1390 ± 20.0	814 ± 52.4	1450 ± 68.3
New CCA-treated wood by XRF ^b	1440	960	1602
Demolition CCA-treated wood acid digestion ^a	1960 ± 27.7	1340 ± 54.0	2550 ± 48.0
Demolition CCA-treated wood by XRF ^c	2556	1704	2844

^a Average of five samples.

^b Based on an XRF reading of 3.4 kg/m³ and the density of wood at 530 kg/m³.

^c Based on an XRF reading of 6.2 kg/m³ and the density of wood at 530 kg/m³.

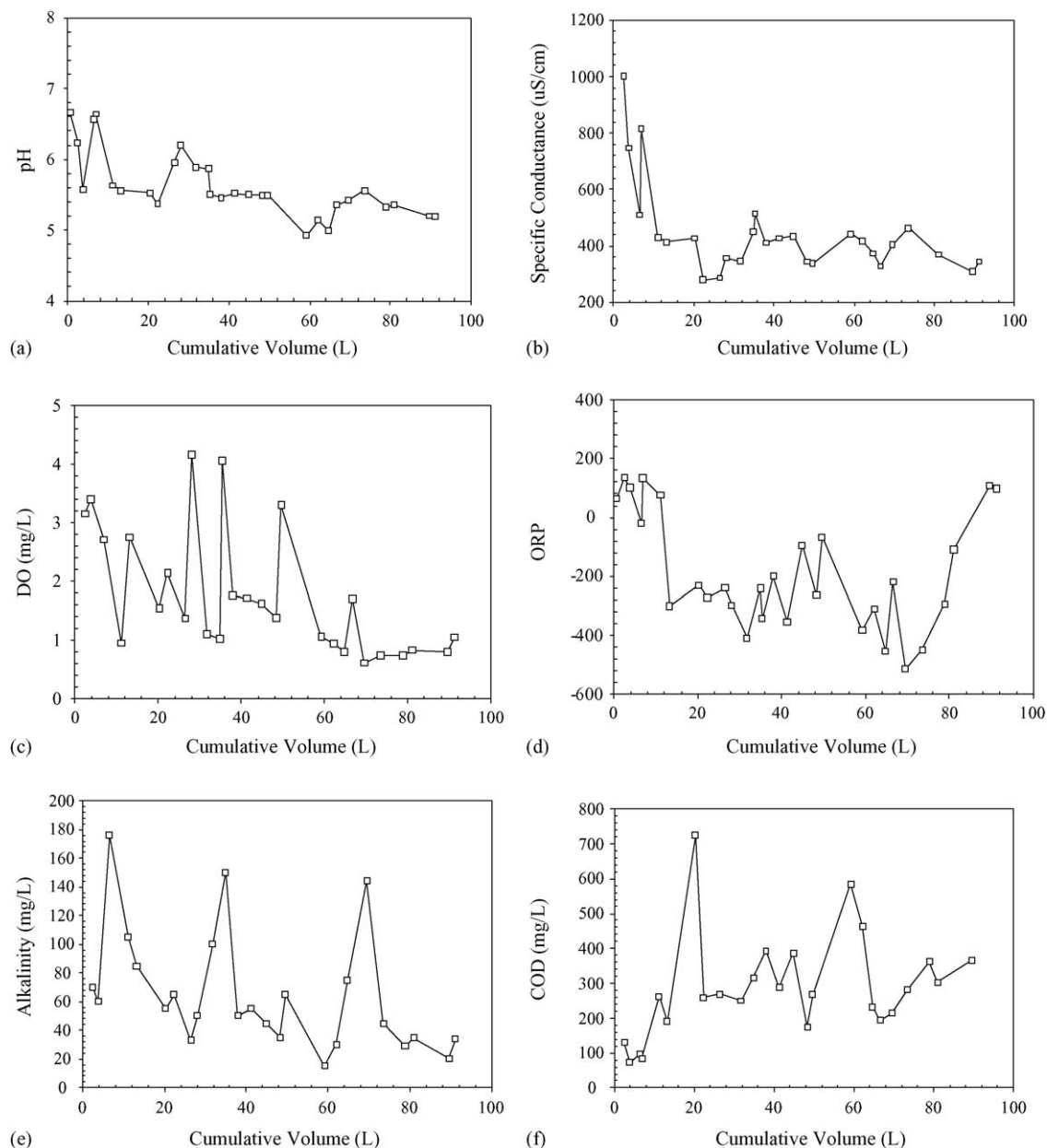


Fig. 2. (a–f) pH, specific conductance, DO, ORP, alkalinity and COD in the CCA-treated wood lysimeter.

Untreated wood leachate has exhibited a higher alkalinity, as well as pH, than the CCA-treated wood leachate observed in this experiment [16]. This would likely occur if the alkalinity is a result of dissolved organic molecules and microbial activity. CCA-treated wood should inhibit some microbial processes and, since it is impregnated, natural resins will not be as soluble. Arsenic speciation by Khan [22] found that the microbes that convert the inorganic forms of arsenic to organic forms were not active in the lysimeter, indicating that if any other microbial activity was occurring it was by microbes with a very high tolerance to the preservative concentrations observed.

Colonization of bacteria and fungi on wood in settings similar to those found in the lysimeters (moisture and darkness) has been observed [31–34]. Some of these bacteria and fungi

are resistant to the metals in CCA-treated wood [31–33] and some of the bacteria naturally consume the fatty acids and resin acids in the natural wood itself [34]. The respiration of these organisms creates carbon dioxide, which can dissolve in solution to influence the carbonate–bicarbonate concentrations of the leachate. Microorganisms such as bacteria and fungi typically require consistent environmental conditions and since the lysimeter process is dynamic (conditions change over time), any potential biological activity occurring would change over time as well. The trend of COD followed that of alkalinity in the lysimeter during the beginning of the experiment (Fig. 2f). The source of the COD potentially included organic acids formed from degradation of wood components (e.g., cellulose), or soluble organic compounds simply dissolved from the wood.

3.4. Arsenic, chromium, and copper concentrations in the lysimeter leachate

Arsenic, chromium, and copper all leached at concentrations that were orders of magnitude higher than those observed from untreated wood [16]. The “overall” average concentration of metals (C_{overall}) from the lysimeters was calculated based upon the total mass of each metal leached during the experiment (mg) divided by the cumulative amount of leachate drained from the lysimeter (L). The C_{overall} for the experimental lysimeter was 42.2 mg/L for arsenic, 9.43 mg/L for chromium, and 2.44 mg/L for copper. The relatively high concentrations of arsenic, chromium, and copper in the experimental lysimeter, as well as the increasing trend (Fig. 3a and b), correspond to a relatively acidic and decreasing pH trend. Correlations between metal concentrations and pH are shown in Fig. 4. Arsenic had the highest correlation ($R^2 = 0.60$) followed by chromium ($R^2 = 0.59$) and then copper ($R^2 = 0.44$). These correlations were also influenced by other factors as will be discussed later. As shown in Fig. 3, the arsenic concentrations in the experimental lysimeter reached a maximum and then remained relatively constant. Research conducted on CCA-treated wood has shown that initial leaching rates were greater than rates observed later in time [7,8,9,35,36]. The initial leachability was likely influenced by the solubility of arsenic based upon pH and redox potential.

Initially, leaching is often influenced primarily by the dissolving of the metals on the surface of particles [37]. However, this is also governed by the solubility of the metals based upon pH and other environmental factors. Once the metals on the surface are removed, a concentration gradient is created and metals move through diffusion to dissolve again into solution [37]. In general, the diffusion process is slower than the dissolution process. As the pH decreased in this experiment, the concentration rose, reaching a maximum. At this point diffusion was the likely mechanism controlling leaching rates. For both copper and chromium, metal concentrations were still increasing at the termination of the experiment. This may mean that surface dissolution of metals was still the prevailing mechanism for leaching at this point. The cumulative amount of each metal that leached from the lysimeter was 3840 mg (1.6%) of the arsenic, 859 mg (0.30%) of the chromium, and 222 mg (0.14%) of the copper (Fig. 3c).

As presented earlier, biological activity affects the overall environment inside the lysimeter and the general quality of the leachate, and as a result affects the release of arsenic, copper, and chromium. Bacteria and fungi with resistance to CCA-treated wood preservative have been shown to extract the metals, as well as change the environment (e.g., lower pH) to cause an accelerated extraction of the arsenic, chromium, and/or copper [31–34]. Some bacteria also consume the fatty acids and resin acids in the natural wood itself, which could also affect the release of preservative compounds [34]. The extraction of metals from CCA-treated wood with bacteria and fungi has been successfully demonstrated; however, it has not yet been performed on a large scale for removal of the metals from the wood prior to disposal. There were no visible indications of fungi or bacterial

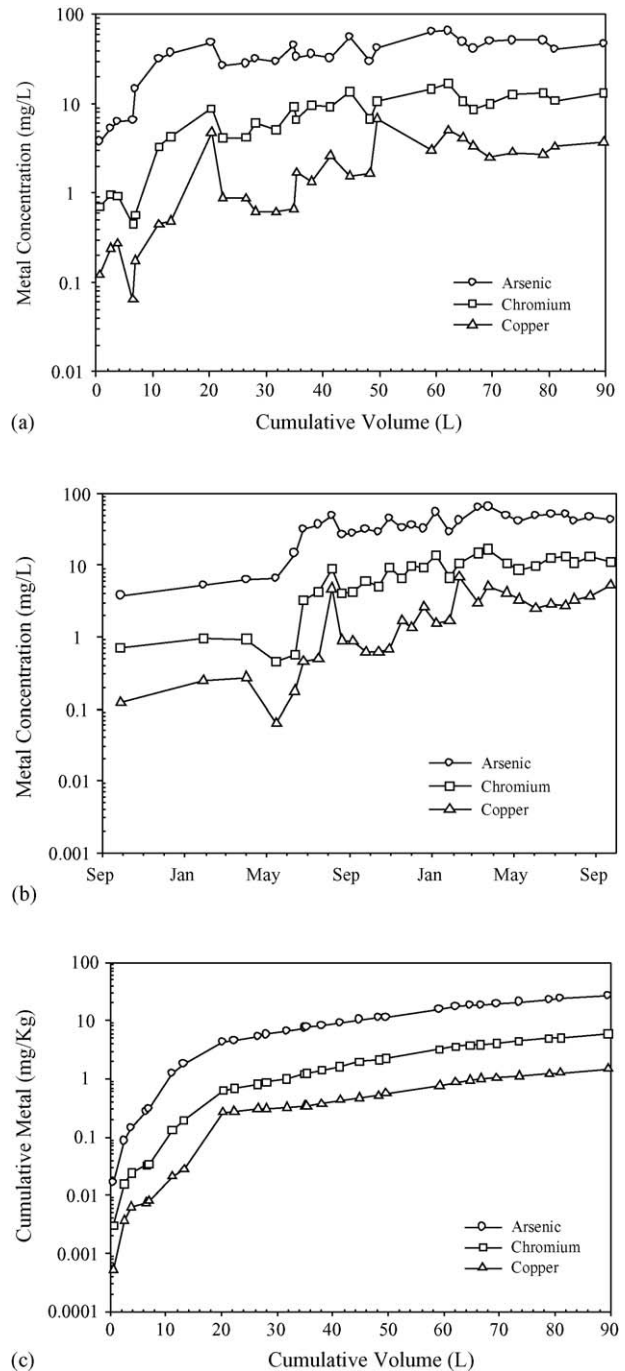


Fig. 3. (a–c) Arsenic, chromium, and copper leaching trends in the CCA-treated wood lysimeter.

growth on the wood after it was removed from the lysimeter and analysis for specific organisms was not completed.

An important aspect of arsenic and chromium toxicity and mobility is the speciation of each element. Cr(VI) is known to be more toxic and mobile than Cr(III) [20,28]. Cr(VI) was not analyzed in this experiment because the pH range and reducing conditions of the lysimeters would tend to promote the reduced Cr(III) species. Also, Cooper [7] did not detect Cr(VI) in leachate generated from fixed CCA-treated wood (detection limit 0.05 mg/L) and Gifford et al. [27] did not detect Cr(VI)

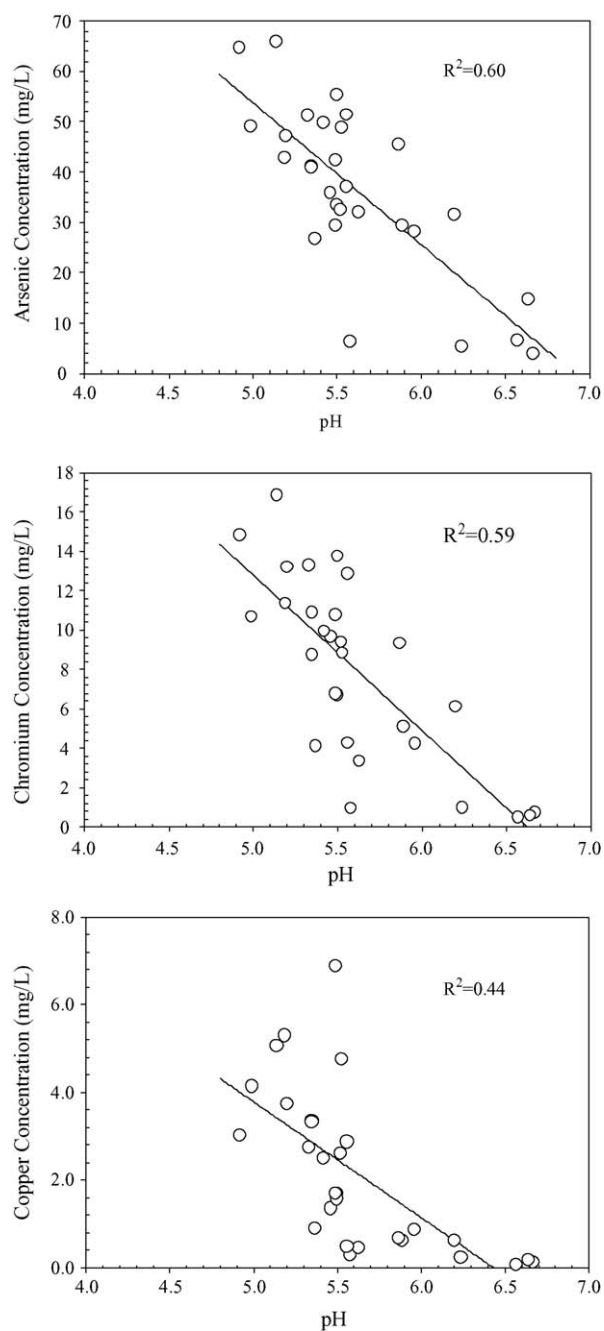


Fig. 4. Arsenic, chromium, and copper concentrations in the CCA-treated wood lysimeter leachate and correlation with pH.

in various lysimeters with CCA-treated wood and CCA-treated wood and soil (detection limit 0.005 mg/L).

The arsenic species that has been shown to leach from untreated wood is dimethylarsinic acid, the less toxic organic species of arsenic [22]. The primary arsenic species found in the lysimeter leachate was arsenic(V) followed by arsenic(III). No organic forms were detected. The arsenic compound in CCA-treated wood is As_2O_5 or As(V) [38], indicating that the arsenic concentrations observed in the experimental lysimeter are from CCA-treated wood [22].

In a solvent extraction test performed on CCA-treated wood samples, only As(V) (no As(III)) was detected in a series of

Table 2

Arsenic, copper, and chromium concentrations in the batch test leachate

LS	Arsenic (mg/L)	Copper (mg/L)	Chromium (mg/L)
5:1 ^a	38.2 ± 7.2	17.7 ± 6.0	14.3 ± 4.0
10:1 ^a	28.1 ± 1.6	12.0 ± 2.0	8.7 ± 1.0

^a Tests conducted in triplicate.

extractions from a pH of 1 to 12.6 for new CCA-treated wood [39]. When weathered wood was extracted over the same pH range, As(III) was detected at pH of 9.5 and below; however, the concentration was still less than the As(V) concentration, which was detected again over the entire pH range. When both weathered and new CCA-treated wood were extracted with rainwater, primarily As(V) was found, with lesser amounts of As(III) [39]. Similar speciation was observed in this experiment in that more As(V) leached, but also some concentrations of As(III) leached as well, likely exacerbated by the reduced conditions of the lysimeter. Of interest is that the concentrations of the less toxic organic species were below detection limits suggesting that the microbes capable of converting arsenic to the less toxic forms were not thriving in the lysimeter environment.

3.5. Batch test leachate results

The arsenic, copper, and chromium leachate concentrations from the batch experiments are shown in Table 2. In related experiments on CCA-treated wood leachability [1], the sawdust from both the new and demolition wood used in this experiment was subjected to the TCLP. The concentrations observed were: new CCA-treated wood leached concentrations of 7.13 mg/L for arsenic, 2.06 mg/L for chromium, and 4.53 mg/L for copper [1]; the demolition CCA-treated wood leached concentrations of 11 mg/L for arsenic, 6.7 mg/L for chromium, and 11 mg/L for copper [23]. The arsenic and chromium concentrations in the TCLP leachate are lower than the $C_{overall}$ observed for the lysimeter; however, the copper concentration in the TCLP leachate was higher than the $C_{overall}$ for the lysimeter.

Comparison between the percent of metals leached from the related batch tests with the deionized water tests conducted for this study (Table 3) shows similar results with the regulatory tests (TCLP and SPLP), even though the LS were different. For example, the percentage of the total available arsenic in the wood leached in the batch tests of the current study was 11.4% and 16.6%, which fell within the range observed for the regulatory tests (1.8–18%). Chromium leached 6.6% and 4.3% and fell into the range for the regulatory tests of 0.8–9.0%. Copper leached 8.3% and 10.9%, which also fell into the regulatory batch test range of 1.0–27%.

CCA-treated wood has been shown to leach primarily arsenic, closely followed by copper, and then smaller amounts of chromium ($As > Cu > Cr$) [10,40]. The batch leaching studies conducted for this experiment exhibited this same characteristic ($As > Cu > Cr$). Another way to express this information is to determine the ratios of arsenic to copper (As/Cu) and copper to chromium (Cu/Cr). As shown in Table 3, the As/Cr ratios determined for the batch tests conducted in this study were at

Table 3
Batch leaching results from this study compared to batch leaching studies in the literature

Test method	Initial pH	Final pH	LS	Time (days)	Particle size	Fraction leached (%)			As/Cr ratio	Cu/Cr ratio
						As	Cr	Cu		
Deionized water	5.88	4.22	5:1	30	100 g blocks	11.4	3.6	8.3	3.2	2.3
Deionized water	5.88	4.31	10:1	30	100 g blocks	16.6	4.3	10.9	3.4	2.5
TCLP ^a (13 samples)	4.93	4.88–5.07	20:1	0.75	Sawdust	4.5–18	1.6–9.0	6.5–27	2–2.8	3–4
SPLP ^a (13 samples)	4.2	4.47–4.86	20:1	0.75	Sawdust	1.8–16	0.8–5.0	1.0–5.3	2.3–3.2	1.1–1.3
pH stat ^a	3	3.17	20:1	0.75	Sawdust	18	5.0	30	3.6	6.0
	7	6.84	20:1	0.75	Sawdust	4.5	1.4	4.9	3.2	3.5
	12	12.05	20:1	0.75	Sawdust	15	9.8	8.9	1.5	0.9
Time ^a	4.2	4.54	20:1	2	Sawdust	14	2.0	6.4	7.0	3.2
	4.2	4.58	20:1	10	Sawdust	19	2.1	7.2	9.0	3.4
	4.2	4.85	20:1	40	Sawdust	21	2.1	6.4	10.0	3.0

^a Results from Townsend et al. [1].

the top end of the range or slightly higher than those observed in the TCLP and SPLP tests (this study observed 3.2 and 3.4, while the TCLP and SPLP ranged from 2 to 3.2). However, the ratios (3.6 and 3.2) were more similar to those found in the pH stat experiment at pH of 3 and 7. The Cu/Cr ratios found in this experiment (2.3 and 2.5) were higher than those shown in the SPLP results (1.1–1.3), but lower than those found in the TCLP results (3–4). The Cu/Cr ratio from this experiment was also lower than those found in the pH stat test and time study, with the exception of the pH stat test at 12 (0.9).

4. Discussion

For comparison purposes, Table 4 presents the LS, the average pH, metal concentrations, total percent of each metal released, and the ORP values observed in both the lysimeter and batch experiments. The batch leaching tests resulted in lower concentrations of arsenic, copper, and chromium in leachate than the lysimeters; however, higher percentages of arsenic, copper, and chromium leached in the batch studies. Also, the proportion of the concentration of metals to each other was different in the lysimeter leachate when compared to the batch experiment. These differences are likely a result of several factors including the leaching environment, pH, and LS.

The final pH of the each batch leaching test was lower than the average pH of the lysimeter experiment. In fact, the batch test

pH was lower than the minimum pH in the lysimeter experiment (5.14). As observed in the lysimeter experiment (Figs. 2 and 4), as pH decreased, both chromium and copper concentrations were continuing to increase at the end of the experiment. Arsenic leachability was affected by pH at the beginning of the lysimeter experiment, but less so at the end. The pH of the lysimeter experiment was still decreasing at the end of the experiment, indicating it had not reached steady state. However, in time, it might eventually reach the same equilibrium pH as the batch experiment (as long as it was not affected by other prevailing factors). As presented in Section 3.3, the alkalinity observed in the lysimeter experiment buffered the lysimeter leachate. Also, organic compounds from wood may dissolve into both the lysimeter and batch study leachate exhibiting COD; however, the batch studies did not exhibit factors of microbiological activity, in contrast to the lysimeters. Jang [14] observed COD concentrations in a DI batch study on untreated wood, attributing the concentrations to dissolved organic compounds and not microbiological activity.

As presented in Table 3, the As/Cr and Cu/Cr ratios of the batch studies were 3.2 and 2.3 for the 5:1 LS and 3.4 and 2.5 for the 10:1 LS, respectively. These ratios were very different than the lysimeter leachate ratios. The As/Cr ratio for the experimental lysimeter was 6.7 while the Cu/Cr ratio was 0.6. This indicates that arsenic leaching may be accelerated in the lysimeter setting or that the copper and chromium leaching was inhibited. These varying ratios are a reflection of the fact that the environment

Table 4
Metal concentrations in the leachate from the lysimeter and batch experiments

	Experimental lysimeter ^a	Batch leaching test ^b
LS at end of test/experiment	0.63	5.00
Leachate pH	5.62 ^c	4.22 ^d
Arsenic (mg/L) (percentage leached)	42.2 (1.6%)	38.2 (11.4%)
Copper (mg/L) (percentage leached)	2.44 (0.14%)	17.7 (8.3%)
Chromium (mg/L) (percentage leached)	9.43 (0.24%)	14.3 (3.6%)
ORP (mV)	–185	124

^a Average concentration of total metal leached over total volume of leachate drained over 755 day experiment.

^b 30-day laboratory vessel leaching test completed in triplicate.

^c Average pH from all values measured during the experiment.

^d Final pH of leachate after batch test completed (average of three samples).

in the lysimeters is different than the environment in the batch leaching tests.

Townsend et al. [41] showed that in batch studies, as the LS increased (more liquid per amount of solid), the concentration of metal in the leachate decreased. Table 4 shows that this is only true for arsenic when examining the lysimeter and batch leaching experiments together. Copper and chromium leachate concentrations increased from the lysimeter to the batch leaching experiments (LS 1 versus 5), indicating again that copper and chromium are inhibited from leaching or are not as soluble in the lysimeter study compared to the batch study. However, both copper and chromium concentrations decreased from the LS of 5 to 10 in the batch experiments, as would be expected.

Another primary difference between the lysimeter experiment and the batch experiment was the reducing conditions. The batch experiment leachate was oxidizing (positive ORP), while the lysimeter experiment had reducing conditions (negative ORP for the most part). Reducing conditions can affect the leachability and solubility of metals [37]. Arsenic leachability correlated with pH and appeared to reach steady-state concentrations in the lysimeter experiment. It also correlated relatively well with the batch experiment, indicating reducing conditions did not appear to affect its leachability as much as chromium and copper. Arsenic is an oxyanion (exists in solution as H_2AsO_4^- or HAsO_4^{2-}) and does not behave like typical metals.

Copper exists as a cation in solution (Cu^{2+}) and so it tends to form compounds with many anions in solution (e.g., S^{2-} , Cl^- , PO_4^{3-} , and CO_3^{2-}), which typically have low to moderate solubility. In reduced conditions, chromium often forms insoluble compounds. However, solubility of both chromium and copper can positively correlate to the presence of dissolved organic carbon (DOC) as indicated by COD [33,42,43]. The overall COD concentrations were relatively low in the lysimeter experiment (when compared to construction and demolition debris and MSW leachate in general). For copper, the positive correlation with DOC is reported to be for low molecular weight (MW), <1000 Da, DOC only [43]. The DOC in the leachate initially was likely high MW DOC from the dissolution of organic compounds from the wood. As the larger organic chain compounds eventually break down, the solubility of copper may increase. The increasing trends of chromium and copper at the end of the experiment are potentially a compounded effect of the reducing pH, increasing ORP and DOC variability.

The percent of each metal released during the lysimeter and batch studies versus the LS was variable (Fig. 5). The LS ratio of the lysimeter was dynamic and increased as more precipitation flowed through the lysimeter (the LS was calculated by dividing the amount of liquid drained by the mass of wood in the lysimeter). The batch study LS was static and remained the same throughout the test. The percent of each metal released as a function of LS can be an indication of lability [29] and the relationship shown in Fig. 5 has been illustrated in the literature as a characteristic contaminant release behavior of percolation tests [44]. The batch leaching results are shown in the figure

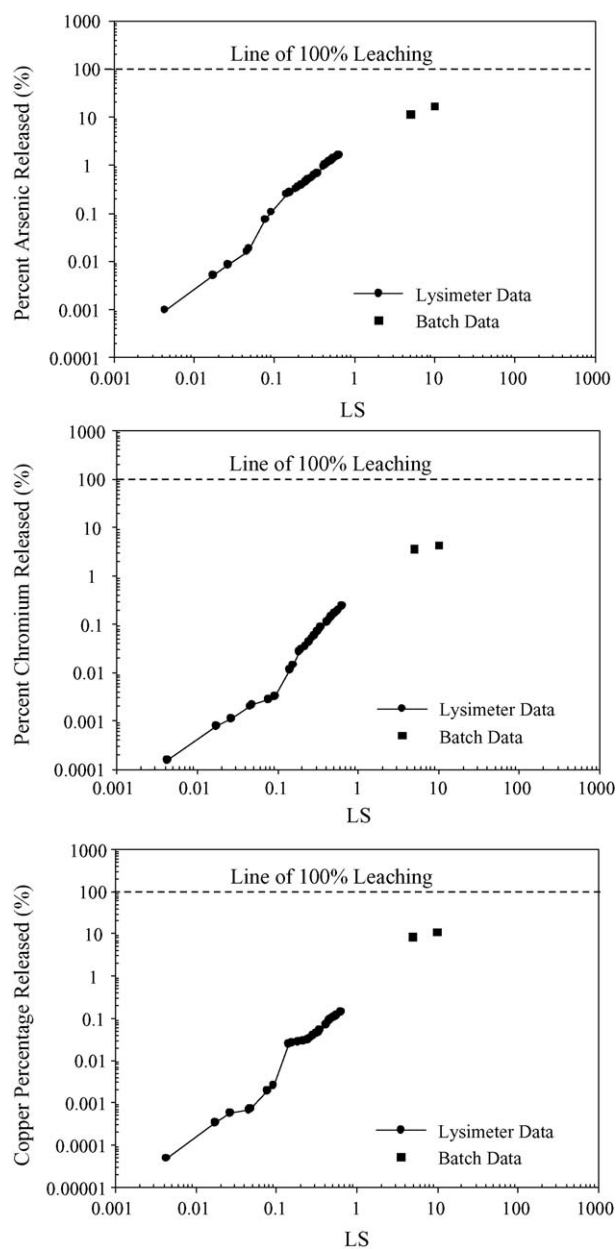


Fig. 5. Cumulative percentage of arsenic, chromium, and copper leached in the lysimeter and batch experiments.

for reference as well, again illustrating arsenic results correlated better than copper with the batch studies (arsenic batch results are closest to the curve generated by the lysimeter data). The percent release plots along a curve in Fig. 5. This curve also provides a potential time frame for the release of each metal based upon LS. If the LS is not allowed to increase, metal leaching could be minimized. Or, if only a small percentage of total metal was available, then the amounts released may be diluted by infiltration. The actual concentration of each metal observed in the leachate is a function of how much liquid exists in relation to the total amount of each metal released [37,41]. Although the cumulative percentage of each metal released increased over time, the concentration varied, eventually decreasing with time as LS increased.

5. End-of-life management of CCA-treated wood

As presented in Section 1, CCA-treated wood is not a good candidate for typical wood recycling (mulch and composting) because of its high metal content. However, if the metals are considered a resource, it may be worthwhile to remove them, leaving wood that may be recycled or combusted without the added metals burden. Removal of metals from CCA-treated wood has been examined, including removal by bacterial and fungal processes as well as electrolytic remediation [31,32,45]. A waste pile or a monofill may be utilized to store CCA-treated wood until metals recovery becomes feasible on a larger scale. However, leachate generation should be minimized. Although the CCA-treated wood itself is not a hazardous waste and may be legally landfilled or stockpiled, this research shows that the leachate generated would likely be a hazardous waste, classifying a storage facility as a hazardous waste generator (depending on the quantity of leachate generated) or even a treatment storage and disposal (TSD) facility under U.S. regulations. With many countries (including the U.S.) moving away from waste management to materials management, the storage of wood for eventual recovery of the metals and use of the biomass for energy may become more likely. Wood is an excellent source of biomass energy and recovery of the metals from the wood before combustion would alleviate concerns about chromium(VI) transformations, partial volatilization of metals, and the increase in metal concentrations within the residues (ash) [4,5,46].

6. Conclusions

Because of the metal content of CCA-treated wood, end-of-life management has been difficult. CCA-treated wood is currently managed in various ways throughout the world including combustion and landfilling. Landfilling is the primary form of management in the U.S. and impacts to various disposal scenarios are not well understood. This research examined the possibility of a monofill to keep CCA-treated wood from increasing metal concentrations in other disposal situations. Disposing of CCA-treated wood in a monofill setting means that the waste is segregated and that the leachate could be controlled separately. The concentrations of arsenic and chromium in the leachate (both above 5 mg/L) would classify it as a hazardous waste under U.S. regulations for toxicity and such generation of leachate should be minimized. However, the metals in CCA-treated wood are a resource and proven recovery technologies may become feasible on a larger scale. This would require storage of the wood in segregated areas, including potentially a monofill. CCA-treated wood with the metals extracted could also be a source of biomass energy without concern for metals concentration, release through air emissions, and residual leaching from ash.

This research provides valuable information on the characteristic leaching behavior of CCA-treated wood and how it may leach in a disposal setting. CCA-treated wood leached differently in lysimeters as compared to batch studies, especially for copper and chromium. The low levels of oxygen and the reducing conditions of simulated disposal appear to inhibit the leaching and/or create less soluble forms of copper and chromium. There-

fore, batch leaching studies appear to conservatively estimate disposal (lysimeter) leachate concentrations for both copper and chromium. Arsenic leachability was comparatively well estimated by batch studies for this disposal scenario.

One advantage of a lysimeter experiment is that metal leachability was observed under more realistic conditions and at a low LS, which is difficult to accomplish in batch leaching studies. The C_{overall} for the experimental lysimeter were 42.2 mg/L for arsenic, 9.43 mg/L for chromium, and 2.44 mg/L for copper. The long-term trend of metal concentrations in the leachate from CCA-treated wood is not known, but may potentially be predicted by the data from this research as well as models developed by others. Furthermore, disposal of other components with CCA-treated wood may affect the leachability of arsenic, copper, and chromium and this issue should be explored further.

Acknowledgements

Funding and support for this project was received from the Florida Center for Solid and Hazardous Waste, Gainesville, FL, and from the Alachua County Department of Public Works, Solid Waste Division.

References

- [1] T. Townsend, T. Tolaymat, H. Solo-Gabriele, B. Dubey, K. Stook, L. Wadanambi, Leaching of CCA treated wood: implications for waste disposal, *J. Hazard. Mater.* 114 (3) (2004) 75–91.
- [2] T. Townsend, H. Solo-Gabriele, T. Tolaymat, K. Stook, Impact of chromated copper arsenate (CCA) in wood mulch, *Sci. Total Environ.* 309 (2003) 173–185.
- [3] H. Solo-Gabriele, T. Townsend, D. Hahn, T. Moskal, N. Hosein, J. Jambeck, G. Jacobi, Evaluation of XRF and LIBS technologies for on-line sorting of CCA-treated wood waste, *Waste Manage.* 24 (2004) 413–424.
- [4] H. Solo-Gabriele, T. Townsend, B. Messick, V. Calitu, Characteristics of chromated copper arsenate-treated wood ash, *J. Hazard. Mater.* 89 (2002) 213–232.
- [5] K. Iida, J. Pierman, T. Tolaymat, T. Townsend, C. Wu, Control of heavy metal emissions and leaching from incineration of CCA-treated wood using mineral sorbents, *J. Environ. Eng. ASCE* 1302 (2) (2004) 184–192.
- [6] R.-D. Peek, EU Directives and National Regulations for the Recycling and Disposal of Waste Wood, in: *Proceedings of the Environmental Impacts of Preservative Treated Wood Conference*, Orlando, FL, February 8–11, 2004.
- [7] P.A. Cooper, Leaching of CCA: is it a problem? in: *Environmental Considerations in the Manufacture, Use and Disposal of Preservative-Treated Wood*, Forest Prod. Soc., 1994, pp. 45–57.
- [8] S.T. Lebow, D.O. Foster, P.K. Lebow, Release of copper, chromium, and arsenic from treated southern pine exposed in seawater and freshwater, solid wood products *Forest Prod. J.* 49 (7/8) (1999) 80–89.
- [9] S.T. Lebow, S.A. Halverson, J.J. Morrell, J. Simonsen, Role of construction debris in release of copper, chromium, and arsenic from treated wood structures, Research Paper FPL-RP-584, Forest Prod. Lab., 2000.
- [10] J.A. Hingston, C.D. Collins, R.J. Murphy, J.N. Lester, Leaching of chromated copper arsenate wood preservatives: a review, *Environ. Pollut.* 111 (2001) 53–66.
- [11] L. Waldron, P. Cooper, T. Ung, Modeling of wood preservative leaching in service, in: *Proceedings of the Environmental Impacts of Preservative Treated Wood Conference*, Orlando, FL, February 8–11, 2004.
- [12] B. Dubey, T. Townsend, H. Solo-Gabriele, Metal leaching from pressure treated wood in sanitary landfill leachate, in: *Proceedings of the IRG 35th Annual Meeting*, Ljubljana, Slovenia, June 6–10, 2004.

- [13] C. Clark, J. Jambeck, T. Townsend, A review of construction and demolition debris regulations in the U.S., *Crit. Rev. Environ. Sci. Technol.*, in press.
- [14] Y.C. Jang, A study of construction and demolition waste leachate from laboratory landfill-simulators, Ph.D. Dissertation, University of Florida, 2000.
- [15] W.J. Weber, Y.C. Jang, T.G. Townsend, S. Laux, Leachate from land disposed residential construction waste, *J. Environ. Eng. ASCE* 128 (3) (2002) 237–245.
- [16] J.R. Jambeck, The disposal of CCA-treated wood in simulated landfills: potential impacts, Ph.D. Dissertation, University of Florida, 2004.
- [17] Hach Company, Hach DR/4000 Procedure, Chemical Oxygen Demand, Reactor Digestion Method, 2003.
- [18] L. Clescerl, A. Greenberg, A. Eaton (Eds.), *Standard Methods for Examining Water and Wastewater*, American Public Health Association (APHA)/the American Water Works Association (AWWA)/the Water Environment Federation (WEF), Washington, DC, 1999.
- [19] United States Environmental Protection Agency (U.S. EPA), *Test Methods for Evaluating Solid Waste, Physical/Chemical Methods*, SW-846, third ed., Office of Solid Waste, 2003.
- [20] D.C. Adriano, *Trace Elements in Terrestrial Environments, Biochemistry, Bioavailability and Risks of Metals*, Springer Press, New York, 2001.
- [21] K.A. Francesconi, D. Kuehnelt, Arsenic compounds in the environment, in: W.T. Frankenberger Jr. (Ed.), *Environmental Chemistry of Arsenic*, Marcel Dekker, Inc., New York, 2002.
- [22] B.I. Khan, Quantification, speciation, and impact of arsenic leaching from in-service and disposed CCA-treated wood on the environment, Ph.D. Dissertation, University of Miami, Coral Gables, FL, 2004.
- [23] T. Townsend, B. Dubey, T. Tolaymat, H. Solo-Gabriele, Preservative leaching from weathered CCA-treated wood, *J. Environ. Manage.* 75 (2005) 105–113.
- [24] Code of Federal Regulations (CFR), Title 40—Protection of the Environment, Chapter 1—Environmental Protection Agency, Part 261—Identification and Listing of Hazardous Waste, 2003.
- [25] H.R. Sweet, R.H. Fetrow, Ground-water pollution by wood waste disposal, *Groundwater* 13 (2) (1975) 227–231.
- [26] T. Townsend, Y. Jang, L. Thurn, Simulation of construction and demolition waste leachate, *J. Environ. Eng. ASCE* 125 (11) (1999) 1071–1081.
- [27] J.S. Gifford, N.A. Marvin, P.H. Dare, Composition of leachate from field lysimeters containing CCA treated wood, New Zealand Forest Research Institute, in: *Proceedings of the 93rd Annual Meeting, American Wood Preservers' Association (AWPA)*, 1997.
- [28] W.J. Deutsch, Groundwater geochemistry, in: *Fundamentals and Applications to Contamination*, CRC Press, Boca Raton, FL, 1997.
- [29] H.A. van der Sloot, R.P.J.J. Rietra, R.C. Vroon, H. Scharff, J.A. Woelders, Similarities in the long term leaching behavior of predominantly inorganic waste, MSWI bottom ash, degraded MSW and bioreactor residues, in: *Proceedings of the 8th International Waste Management and Landfill Symposium, Sardinia, Italy, October 1–5, 2001*.
- [30] F.G. Pohland, S.R. Harper, *Critical Review and Summary of Leachate and Gas Production from Landfills*, EPA Doc. SCEGIT-84-104, U.S. EPA Office of Research and Development, 1985.
- [31] B.L. Illman, T.L. Highley, Fungal Degradation of Wood Treated with Metal-Based Preservatives: 1. Fungal Tolerance, Prepared for the IRG 27th Annual Meeting, Guadeloupe, French West Indies, 1996.
- [32] F.A. Cole, C.A. Clausen, Bacterial biodegradation of CCA-treated waste wood, in: *Forest Prod. Soc. Conf. Proceedings, Madison, WI, September 1996*.
- [33] R.-D. Peek, Recycling of treated poles in Germany, in: *Workshop on Utility Poles: Environmental Issues, Gainesville, FL, Forest Prod. Soc., 1999*.
- [34] T.A. Burnes, R.A. Blanchette, R.L. Farrell, Bacterial biodegradation of extratives and patterns of bordered pit membrane attack in pine wood, *Appl. Environ. Microb.* 66 (12) (2000) 5201–5205.
- [35] P.B. Merkle, D.L. Gallagher, T.N. Solberg, Leaching rates, metals distribution, and chemistry of CCA treated lumber: implications for water quality modeling, in: *Environmental Considerations in the Manufacture, Use and Disposal of Preservative-Treated Wood, Forest Prod. Soc., 1994*, pp. 69–78.
- [36] M. Kennedy, P. Collins, Leaching of preservative components from pine decking treated with CCA and copper azole, and Interactions with soils, in: *Proceedings of the IRG 32, Nara, Japan, May 20–25, 2001*.
- [37] H.A. van der Sloot, L. Heaseman, Ph. Quevauviller, Harmonization of Leaching/Extraction Tests, Elsevier Science Limited, Amsterdam, 1997.
- [38] American Wood Preservers' Association (AWPA), *Standard for Waterborne Preservatives*, American Wood Preservers' Association, Granbury, TX, 1998.
- [39] B. Khan, H. Solo-Gabriele, B. Dubey, T. Townsend, Y. Cai, Arsenic speciation of solvent-extracted leachate from new and weathered CCA-treated wood, *Environ. Sci. Technol.* 38 (17) (2004) 4527–4534.
- [40] P.A. Cooper, Leaching of CCA from treated wood: pH effects, *Forest Prod. J.* 41 (1) (1991) 30–32.
- [41] T. Townsend, B. Dubey, T. Tolaymat, Interpretation of SPLP results for assessing risk to groundwater from land-applied granular waste, *J. Environ. Eng. Sci. Contam. Leaching Cemented Particulate Media*, in press.
- [42] D.T. Long, G. Icopini, R. Ellis, T. Marsh, C. Merlin, H. Thacker, L. Forney, Chromium mobility, DOC, and microbiological populations, in: *11th Annual V.M. Goldschmidt Conference, 2001*.
- [43] R. Vulkin, U. Mingelgrin, J. Ben-Asher, H. Frenkel, Copper and zinc speciation in the solution of a soil–sludge mixture, *J. Environ. Qual.* 31 (2002) 193–203 (Technical Report: Heavy Metals in the Environment).
- [44] H.A. van der Sloot, European activities on harmonization of leaching/extraction tests and standardization in relation to the use of alternative materials in construction, in: *Proceedings of the International Conference on Materials for Advanced Technologies (ICMAT), Singapore, July 1–6, 2001*.
- [45] I.V. Christensen, A.J. Pedersen, L.M. Ottosen, A. Ribeiro, Electrodialytic remediation of CCA-treated wood in larger scale, in: *Proceedings of the Environmental Impacts of Preservative Treated Wood Conference, Orlando, FL, February 8–11, 2004*.
- [46] J. Song, B. Dubey, Y. Jang, T. Townsend, H. Solo-Gabriele, Implication of chromium speciation on disposal of discarded CCA-treated wood, *J. Hazard. Mater.* 128 (2006) 280–288.