

Journal of Hazardous Materials B114 (2004) 75-91

Materials

*Journal of* Hazardous

www.elsevier.com/locate/jhazmat

# Leaching of CCA-treated wood: implications for waste disposal

Timothy Townsend<sup>a,\*</sup>, Thabet Tolaymat<sup>a,1</sup>, Helena Solo-Gabriele<sup>b</sup>, Brajesh Dubey<sup>a</sup>, Kristin Stook<sup>a</sup>, Lakmini Wadanambi<sup>a</sup>

<sup>a</sup> Department of Environmental Engineering Sciences, University of Florida, Gainesville, FL 32611-6450, USA <sup>b</sup> Department of Civil Architectural and Environmental Engineering, University of Miami, Coral Gables, FL 33124-0630, USA

> Received 30 September 2003; received in revised form 25 June 2004; accepted 28 June 2004 Available online 20 August 2004

#### Abstract

Leaching of arsenic, chromium, and copper from chromated copper arsenate (CCA)-treated wood poses possible environmental risk when disposed. Samples of un-weathered CCA-treated wood were tested using a variety of the US regulatory leaching procedures, including the toxicity characteristic leaching procedure (TCLP), synthetic precipitation leaching procedure (SPLP), extraction procedure toxicity method (EPTOX), waste extraction test (WET), multiple extraction procedure (MEP), and modifications of these procedures which utilized actual MSW landfill leachates, a construction and demolition (C&D) debris leachate, and a concrete enhanced leachate. Additional experiments were conducted to assess factors affecting leaching, such as particle size, pH, and leaching contact time. Results from the regulatory leaching tests provided similar results with the exception of the WET, which extracted greater quantities of metals. Experiments conducted using actual MSW leachate, C&D debris leachate, and concrete enhanced leachate provided results that were within the same order of magnitude as results obtained from TCLP, SPLP, and EPTOX. Eleven of 13 samples of CCA-treated dimensional lumber exceeded the US EPA's toxicity characteristic (TC) threshold for arsenic (5 mg/L). If un-weathered arsenic-treated wood were not otherwise excluded from the definition of hazardous waste, it frequently would require management as such. When extracted with simulated rainwater (SPLP), 9 of the 13 samples leached arsenic at concentrations above 5 mg/L. Metal leachability tended to increase with decreasing particle size and at pH extremes. All three metals leached above the drinking water standards thus possibly posing a potential risk to groundwater. Arsenic is a major concern from a disposal point of view with respect to ground water quality.

© 2004 Elsevier B.V. All rights reserved.

Keywords: CCA-treated wood; Metal leaching; pH; TCLP; WET

### 1. Introduction

### 1.1. CCA-treated wood

Chromated copper arsenate (CCA) is a water-borne wood preservative applied to wood products to deter environmental decay. CCA has been the most commonly used wood preservative in North America in recent decades [1]. In the CCA treatment process, wood products such as dimensional lumber, plywood, and poles, are preserved by impregnating the wood with an aqueous solution containing CrO<sub>3</sub>, CuO, and As<sub>2</sub>O<sub>5</sub> in a pressurized treating cylinder [2]. After preservative addition, the wood is removed from the cylinder and allowed to dry. Arsenic and copper act as biocides, and chromium acts as a "fixing" agent to bind the metals to the wood. The CCA fixation process refers to the chemical reactions that take place when hexavalent chromium is reduced to trivalent chromium in the wood [3]. The chemical species occurring in the wood after fixation include CuCrO<sub>4</sub>, CrAsO<sub>4</sub>, Cu(OH)CrAsO<sub>4</sub>, and a variety of metal complexes with lignin and cellulose [4]. The AWPA has standardized three separate CCA formulations, types A, B, and C. CCA type C (CCA-C) is the formulation in current use in the US and contains

<sup>\*</sup> Corresponding author. Tel.: +1 352 392 0846; fax: +1 352 392 7735. *E-mail address:* ttown@ufl.edu (T. Townsend).

<sup>&</sup>lt;sup>1</sup> US Environmental Protection Agency, Office of Research and Development, Cincinnati, OH 45211, USA.

<sup>0304-3894/\$ –</sup> see front matter © 2004 Elsevier B.V. All rights reserved. doi:10.1016/j.jhazmat.2004.06.025

47.5% (44.5–50.5%) CrO<sub>3</sub>, 18.5% (17.0–21.0%) CuO, and 34.0% (30.0–38.0%) As<sub>2</sub>O<sub>5</sub> [5].

Arsenic, chromium, and copper all present potential risks to human health and the environment when exposures occur at sufficiently high concentrations. Exposure routes of concern include direct human contact with the treated wood, human exposure to media impacted by preservatives migrating from the treated wood, and exposure of organisms to preservative compounds in the environment. Pathways of concern resulting from direct human contact with wood products include those resulting from touching the wood (e.g., dermal sorption, ingestion of dislodged chemicals from hand-to-mouth contact) and inhalation of wood particles during construction and maintenance activities [6–8]. Concerns over possible human health impacts from contact with CCA-treated wood have prompted the wood treating industry to phase out the manufacture of CCA-treated wood for most residential uses in the US by the end of 2003 [9]. When environmental media such as groundwater, surface water or soil become contaminated by preservatives migrating from CCA-treated wood, human exposure may also result [10]. While the arsenic, chromium, and copper in CCA-treated wood are "fixed" such that the majority of preservative remains in the wood for several decades, small amounts of the metals nonetheless do leach over time [11–16]. Preservative leaching from CCA-treated wood in the environment is an issue of concern with respect to both the wood product performance and possible impacts on human health and the environment [10,17–19].

#### 1.2. Leaching tests for pressure treated wood

The wood treatment industry and the scientific community utilize a variety of methods to evaluate preservative loss from treated wood products. One objective of such testing is to measure preservative depletion from the wood products so that the effective service life of the product can be assessed [20]. A second objective is to measure the amount and rate of preservative leaching when the wood is exposed to water. This provides an assessment of potential contamination of water, soil, and sediment and the resulting impacts to human health and the environment [12-14,21-24]. Investigators have employed several different testing protocols to evaluate preservative leaching from treated wood products, including: (1) tests in which the wood is exposed to the soil environment and preservative loss is measured over time [25-28]; (2) tests in which small pieces of wood are leached with aqueous solutions and the preservative concentrations in the leachate are measured [5,11,12]; and (3) tests in which structures are leached with actual or simulated rainfall and the resulting runoff is captured and analyzed [16].

Lebow [29] reviewed the pertinent literature associated with leaching of wood preservatives from treated wood, including CCA-treated wood. More recently, Hingston et al. [15] conducted a review specific to CCA-treated wood leaching, including a discussion of those parameters impacting leaching. Results of leaching studies are reported in several different ways, including the concentration of preservative component in the leachate (mg/L), the fraction of the original preservative leached (%), and in terms of a leaching flux ( $\mu$ g/cm<sup>2</sup> day). Since many different factors (e.g., wood type and preservation method, solution pH and ionic strength, leaching test liquid-to-solid ratio, specimen size, time of contact) impact the amount of arsenic, chromium, and copper that leach from CCA-treated wood and because of the different reporting formats, care must be taken when comparing results from different studies. In the following paragraphs, a few selected leaching studies are reviewed to provide the reader with a broad overview of typical results encountered.

Prior to the 1990s, most studies on preservative depletion or leaching from CCA-treated wood were conducted to assess and predict treated wood performance [20,30,31]. Much of this work was conducted by the wood preservation industry as part of the standardization process for treated wood products. In the 1990s, more of the leaching work began to focus on potential environmental impacts associated with preservative leaching. Warner and Solomon [11] published results of experiments in which CCA-treated wood was leached in a variety of different pH solutions. Six 5-cm<sup>3</sup> blocks were submerged in 5 L of leaching solution for 40 days. One experiment used a citric acid/sodium hydroxide solution to buffer the pH to 3.5, 4.5, 5.5, 7.0, and 8.5. A second experiment used diluted sulfuric acid to control pH (3.5, 4.5, 5.5); the pH was adjusted daily. Results are summarized in Table 1 as percentage of preservative compound leached. Even at pH values of 5.5, the relatively large fraction of preservative that leached prompted the authors to conclude that leaching of CCA-treated wood in acid waters may present an unacceptable environmental risk. This research received some media attention, especially as related to the possible impact of acid rain on CCA-treated structures used in residential settings. This spurred additional research into the leaching of CCAtreated wood with respect to environmental impacts.

Cooper [12] reported results from leaching of  $10 \,\mathrm{mm} \times$  $10 \,\mathrm{mm} \times 40 \,\mathrm{mm}$  blocks in different pH solutions. Cooper utilized American Wood Preservers' Association (AWPA) leaching protocols that existed at the time. The blocks were leached in 50 mL of leaching solution for 14 days, and the unabsorbed leaching solution (the leachate) was replaced at specified time intervals. The leachate was analyzed, and the total mass of preservative leached was calculated. The following leaching solutions were tested: pH values of 3.5, 4.5, and 5.5 using deionized water diluted with equal molar mixtures of nitric and sulfuric acid, and a citric acid/sodium hydroxide solution buffered to a pH of 5.5. Cooper's results are also summarized in Table 1. Fewer metals leached in Cooper's experiment than Warner and Solomon's, which might be a result of differences in the testing procedures (e.g., leaching time, liquid-to-solid ratio, pH control). Cooper concluded that the high leaching losses reported by Warner were the result of the citric acid buffer and not just pH.

Over the next decade, other CCA-treated wood leaching studies with a specific focus on examining preservative

 Table 1

 Historical research of metal leachability from CCA-treated wood

Source	Test type	Variable	Fraction leached (%)			
			As	Cr	Cu	
Warner and Solomon <sup>a</sup> [11]	Buffered citric acid	pH = 3.5	68.2	52.9	111	
		pH = 4.5	51.6	27.9	105	
		pH = 5.5	31.7	12.1	91.6	
		pH = 7.0	17.3	0.95	5.22	
		pH = 8.5	8.99	1.14	0.87	
	Dilute H <sub>2</sub> SO <sub>4</sub>	pH = 2.5	39.7	28.9	145	
		pH = 3.5	22.9	6.32	74.6	
		pH = 4.5	17.3	2.80	21.0	
Cooper <sup>b</sup> [12]	Buffered citric acid	pH = 5.5	27.4-46.7	3.6-10.9	52.7-80.5	
·	Dilute H <sub>2</sub> SO <sub>4</sub> /HNO <sub>3</sub>	pH = 3.5	3.4-6.9	0.24-1.4	3.1-9.6	
		pH = 4.5	2.9-6.3	0.19-1.05	2.4-5.0	
		pH = 5.5	3.1-6.0	0.24-1.10	2.1-6.4	
Kennedy and Collins <sup>c</sup> [16]	E-11	t = 14 days	18.9–19.1	2.5-4.1	4.9-6.5	
		t = 50  days	27.0	2.9-4.9	5.0-7.1	
	Deck Study	t = 300  days	4.0-4.4	0.9-1.2	1.2-1.3	

<sup>a</sup> Some depletion of CCA was over 100%.

<sup>b</sup> The range presented is based on different wood species.

<sup>c</sup> Only the range was given and two different leaching methods were used.

leaching rates and the resulting potential environmental impacts were conducted. The majority of these studies focused on the impact of metal leaching from CCA-treated wood on aquatic systems [13,14,21]. In 1997, the AWPA published a new leaching protocol, E-11, that involved leaching 19mm blocks in 300 mL of deionized water for 14 days [5]. The water is replaced at specified intervals, and the collected leachate is analyzed. In an analysis of preservative leaching from treated decks, Kennedy and Collins [16] performed E-11 on CCA-treated wood but collected additional data beyond 14 days. They also subjected a series of deck-boards to rainfall for 300 days and measured the preservative leached by the rain (Table 1).

The data presented in Table 1 represent only a fraction of the leaching test results reported in the literature. They do, however, represent the range of typical preservative depletion measured in these types of tests. In general, arsenic and copper leach more than chromium, and leaching rates increase with a decrease in pH. The use of weak acids with a strong ability to complex or chelate metals (e.g., citric acid) increases the mass of metals leached above that expected to result from pH alone. As would be anticipated, the small wood specimens tested at the laboratory scale leach a greater amount of preservative relative to the larger wood products in actual use.

## 1.3. CCA-treated wood in the waste stream

The focus of the aforementioned studies has been on leaching during in-service application, i.e., leaching under environmental conditions where CCA-treated wood products are used (e.g., water bodies, terrestrial settings). Another scenario where the leaching of metals from CCA-treated wood poses potential environmental concern is disposal. CCA-treated wood enters the waste stream in several locations. New construction activities result in discarded scrap wood, sawdust and other debris. Demolition and renovation activities result in a larger quantity of wood, which often occurs in sizes and shapes the same as the original wood products. While CCAtreated wood products have a predicted in-service life of 20 [32] to 25 [26] years for lower retention treated wood (lumber, timber, and fences), more recent surveys show the "actual" in-service life to be 9 years [33], 10-12 years [34], and about 13 years [35], and that this early retirement of the wood is attributed to aesthetics due to the effects of natural weathering. For higher retention treated wood (utility poles and crossties), the "actual" in-service life is approximately 40 years [1] and greater in some cases [26]. Disposal of CCA-treated wood is an issue to the solid waste profession because of the magnitude of the waste stream and the lack of viable recycling markets. For example, in Florida, USA, Solo-Gabriele and Townsend [36] estimated that roughly  $140,000 \,\mathrm{m}^3$ of discarded CCA-treated wood were disposed during 2000, and that this amount would increase to  $900,000 \text{ m}^3$ by 2015.

In the US, the majority of discarded CCA-treated wood products are managed in landfills. In some US states, construction and demolition (C&D) debris landfills that accept CCA-treated wood are not required to have liner systems. Leaching of preservatives from landfilled CCA-treated wood poses a concern because of possible impact on leachate at lined landfills and groundwater at unlined facilities. Some CCA-treated wood is commingled with untreated wood and becomes part of the recovered wood mixture at C&D debris recycling facilities [37,38]. One market for recovered C&D debris wood is landscape mulch; leaching of CCA preservatives from this mulch has been identified as a possible concern [39].

Table 2

The waste management profession has historically used leaching tests to evaluate the risk of disposal of solid waste to the environment. Leaching tests are often a required component of solid and hazardous waste regulations. For example, in the US, the toxicity characteristic leaching procedure (TCLP) is performed to determine whether a solid waste is a toxicity characteristic (TC) hazardous waste. Unlike leaching tests designed to examine preservative leaching in aquatic and terrestrial environments, data from the US solid waste regulatory leaching tests on CCA-treated wood have not been reported. This paper adds to the body of literature regarding the leaching of arsenic, chromium, and copper from CCA-treated wood, but from a waste-management perspective rather than an in-service perspective. Even though CCA-treated wood is no longer used for most the US residential applications starting in 2004, the majority of CCA-treated wood ever sold remains in service. Disposal of this stock will be an issue for the coming decades.

# 2. Objectives

The objectives of the research presented in this paper were:

- 1. To determine typical leaching behavior of CCA-treated wood using standardized regulatory leaching tests for solid wastes required in the US;
- To conduct a preliminary evaluation of CCA preservative leaching using leachates designed to simulate specific disposal scenarios;
- 3. To examine several sample and test method characteristics impacting leaching test results (i.e., pH, particle size, leaching time) to aid in the interpretation of regulatory leaching test results;
- To compare leaching test results for CCA-treated wood to existing regulations and policies so that current and future regulatory status can be examined; and
- 5. To identify remaining unknowns regarding how the disposal of CCA-treated wood might impact the environment as a result of preservative leaching.

The wood tested in this research was un-weathered wood as might be encountered as scrap at construction sites or manufacturing facilities, or as sawdust. Much of the wood encountered in disposal situations will be weathered (i.e., demolition debris) and may contain less preservative than newly treated wood. Limitations of the results with regard to this, and additional research needs, are discussed.

## 3. Methods

## 3.1. Sample processing and collection

A total of thirteen CCA-treated dimensional lumber samples (designated as A–M in Table 2) were collected. Eleven of the samples (A through J and M) were purchased from

Sample description								
Name	Dimens	ion (cm)	Retention value (kg/m <sup>3</sup> )					
	Width	Length	Nominal	Outer 1.5 cm	Composite			
A <sup>a</sup>	3.8	8.9	4.0	5.9	3.7			
B <sup>a</sup>	3.8	14	4.0	1.8	3.8			
C <sup>a</sup>	3.8	19	4.0	3.7	2.6			
D <sup>a</sup>	8.9	8.9	6.4	9.2	4.1			
E <sup>a</sup>	8.9	8.9	6.4	2.2	3.4			
F <sup>a</sup>	3.8	8.9	6.4	12	6.6			
G <sup>a</sup>	3.8	14	6.4	6.6	3.8			
H <sup>a</sup>	3.8	8.9	6.4	5.0	4.9			
Ia	3.8	14	6.4	2.2	4.7			
Ja	3.8	8.9	6.4	8.2	3.0			
K <sup>b</sup>	3.8	8.9	4.0	4.0	3.5			
Lb	3.8	8.9	4.0	4.0	4.1			
M <sup>c</sup>	3.8	19	4.0	5.1	3.4			

<sup>a</sup> Size reduced to 100 g and 20 g blocks, chips, and sawdust.

<sup>b</sup> Cut and ground to satisfy TCLP requirement.

<sup>c</sup> Sliced into 5-cm (2-in.) sections, sawdust was collected, outer 1.5 cm measurement for this sample were conducted by total metal analysis.

lumberyards located in Gainesville, Florida. These pieces of dimensional lumber were selected off the shelf and represented the variety of dimensions, wood treaters, and retention values available to the average homeowner in the area. Samples K and L (originally purchased as untreated southern yellow pine dimensional lumber) were obtained from a lumberyard in Miami, Florida. These two samples were treated at two different commercial wood treating facilities. This process was conducted as part of a related study examining the leachability and toxicity of wood products treated with different types of waterborne preservatives [40]. In all cases, the wood preservation facilities identified the CCA treatment solution used as type C.

## 3.2. Preservative content

The wood preservation industry rates the degree of chemical treatment that a wood product receives in terms of its retention value, which is the mass of preservative per unit volume of wood. For example, the AWPA's minimum retention value for above-ground use of CCA-treated wood is  $4.0 \text{ kg/m}^3$  (0.25 lb/ft<sup>3</sup>). The minimum retention value for ground-contact wood is  $6.4 \text{ kg/m}^3$  (0.4 lb/ft<sup>3</sup>), while marine applications frequently require  $40 \text{ kg/m}^3$  (2.5 lb/ft<sup>3</sup>). The information end tags accompanying treated wood products list the nominal retention value based on the outer 1.5 cm (0.6 in.)of wood. Retention values can be quite variable, even in the same piece of lumber [15]. The reported retention values on the end tags for samples A–J and M were 4.0 or  $6.4 \text{ kg/m}^3$ . The target retention value for samples K and L was  $4.0 \text{ kg/m}^3$ . The standard industry method for measuring retention value, X-ray fluorescence (XRF), was used to measure retention values in samples from the outer 1.5 cm of the wood and samples that represented the entire wood specimen tested (Table 2). The content of arsenic, chromium and copper in the sawdust of sample M was further analyzed by acid digestion of the wood followed by analysis using inductively coupled plasma atomic emission spectroscopy (ICP-AES). The retention value results were variable. While one would expect the retention values from the outer 1.5 cm to be greater than the bulk retention values, no such observation was made. This was attributed to sample variability such as treatment gradient across the specimen, grain orientation, presence of heartwood, or specimen imperfections such as tension wood or knots etc. [41]. Retention values ranged from a minimum of  $1.8 \text{ kg/m}^3$  (sample B outer 1.5 cm) to a maximum of  $12 \text{ kg/m}^3$ (sample F outer 1.5 cm).

#### 3.3. Sample preparation

Since the results presented in this paper represent a compilation of several different experiments, the methods of sample preparation differ slightly. Samples A through J were evaluated as part of one experiment to look at metal leaching from CCA-treated wood using different regulatory batch tests and to evaluate the impact of particle size [42]. Samples K and L were used for TCLP and SPLP tests only. Sample M was subjected to a large battery of tests including the regulatory batch tests, experiments to examine the impacts of leaching time and pH, and tests using actual or simulated landfill leachates for the purpose of examining leaching under specific disposal scenarios.

Dimensional CCA-treated lumber for samples A through J was cut into 100-g and 20-g pieces using an electric saw. The sawdust from this operation was saved for testing. Some of the wood blocks were further processed using a chipper–shredder to obtain a particle size distribution similar to landscape mulch. Samples K and L were prepared by cutting lumber into  $3.8 \text{ cm} \times 8.9 \text{ cm} \times 2.5 \text{ cm} (2 \text{ in.} \times 4 \text{ in.} \times 1 \text{ in.})$  blocks and then processing them through a Fritsch Pulverisette<sup>®</sup> 19 mill to a particle size less than 3.0 mm [40]. Sample M consisted of sawdust generated during the processing of wood for a different experiment [43].

# 3.4. Leaching and analytical procedures

Two types of leaching procedures were performed: (1) batch leaching tests standardized by regulatory agencies and (2) modifications of standardized leaching experiments conducted to evaluate how several test variables impact leaching procedure results. The regulatory leaching tests included TCLP, the synthetic precipitation leaching procedure (SPLP), the extraction procedure toxicity test (EPTOX), California's waste extraction test (WET), and the multiple extraction procedure (MEP). The variables examined using modified tests included pH, contact time, and particle size. In addition, several experiments were conducted in a similar fashion as TCLP but using actual or simulated landfill leachates as the leaching fluid. A list of samples and leaching tests conducted in this experiment is presented in Table 3.

## 3.4.1. Regulatory leaching tests

Five regulatory-based leaching tests were performed. The TCLP, SPLP, EPTOX, and MEP were developed by the US Environmental Protection Agency (EPA). The WET was developed by the state of California.

The TCLP utilizes a buffered organic acid solution as an extraction fluid. This test was designed to simulate contaminant leaching in a municipal solid waste (MSW) landfill environment [44,45]. The acid used is acetic acid, one of the organic acids formed during the anaerobic decomposition of organic matter in MSW. The TCLP extraction fluid was prepared by adding 11.4-mL of glacial acetic acid (CH<sub>3</sub>COOH) to 1 L of deionized water in a 2-L volumetric flask. Then 128.6 mL of 1N sodium hydroxide (NaOH) was added to the flask, and the solution was brought to volume (2 L) with deionized water. The resulting solution pH was  $4.93 \pm 0.05$ . The TCLP requires that samples first be size-reduced to less than 0.95 cm. One hundred grams of the size-reduced samples were placed in a 2.2-L polyethylene extraction vessel, and 2 L of the extraction solution were added. The slurry was mixed on a rotary extractor for  $18 \pm 2h$  and then filtered through a 0.7-µm glass fiber filter. The filtrate was collected

Table 3
Leaching procedure performance

Sample name TCLP SPLP WET EPTOX	SPLP	WET EPTOX MEP		Leachate Extractions			Particle Size	Time		pH static		
		MSW LF	C&D	Concrete		Exp. #1	Exp. #2					
A	<b>~</b>	<b>v</b>							✓			
В	$\checkmark$	$\checkmark$							$\checkmark$			
С	$\checkmark$	$\checkmark$							$\checkmark$			
D	$\checkmark$	$\checkmark$							$\checkmark$			
Е	$\checkmark$	$\checkmark$							$\checkmark$			
F	$\checkmark$	$\checkmark$							$\checkmark$			
G	$\checkmark$	$\checkmark$							$\checkmark$			
Н	$\checkmark$	$\checkmark$							$\checkmark$			
I	$\checkmark$	$\checkmark$							✓			
J	$\checkmark$	$\checkmark$			$\checkmark$				$\checkmark$			
K	$\checkmark$	✓										
L	$\checkmark$	$\checkmark$										
М	$\checkmark$	$\checkmark$	$\checkmark$	$\checkmark$	$\checkmark$	$\checkmark$	$\checkmark$	✓		$\checkmark$	<b>~</b>	$\checkmark$

in 1-L plastic bottles and preserved to a pH of less than 2 using nitric acid [46].

The EPTOX was the predecessor of the TCLP. This test requires the continual addition of acid to maintain a constant extraction pH [46]. For the EPTOX, 100 g of sample were placed in 1.6 L of deionized water and agitated. The method requires that the pH of the mixture be maintained at 5 by adding 0.5N acetic acid. The CCA-treated wood samples in this study did not require any further acid addition. After 24 h of extraction, deionized water was added to bring the total volume of the extraction fluid to 2 L. The leachate was filtered and acidified in the same fashion as TCLP [46].

The SPLP was conducted in a similar fashion as the TCLP with the exception of the leaching fluid. The SPLP leaching fluid is a simulated acid rain which was prepared by adding a dilute sulfuric acid and nitric acid solution (60/40 mix) to a 19-L container and diluting to volume with reagent water. The extraction solution pH was  $4.20 \pm 0.05$  [46].

The WET is used in California, US, in a similar manner as the TCLP (determination of whether a solid waste is a hazardous waste). The WET leaching fluid is a buffered citric acid solution and was prepared by titrating a 0.2 M citric acid ( $C_6H_8O_7$ ) solution with 4.0N NaOH to a pH of  $5.0 \pm 0.1$ . One liter of this fluid was added to a 100-g sample and rotated for a period of 48 h. The procedure performed here deviated slightly from the method as defined by California in that deoxygenation of the extraction solution by bubbling nitrogen was not carried out. With the exception of the liquid-to-solid ratio (10:1) and the leaching time, the remainder of the test was the same as the TCLP [47].

The US EPA developed the MEP as a method to estimate the potential long-term leachability of contaminants from solid wastes. This test utilizes an initial acetic acid extraction followed by sequential extractions with simulated acid rain. The initial extraction fluid is the same as the EPTOX. The simulated rainfall extraction solution is similar to the SPLP leaching fluid but with a pH of  $3.0 \pm 0.2$ . An initial sample size of 60 g was used. Each extraction step was performed for 24 h. After each filtration, both the filter and the sample were added to the next extraction vessel. A 20:1 liquid-to-solid ratio was used throughout [46].

## 3.4.2. Additional leaching experiments

Although the TCLP was designed to simulate leaching conditions in MSW landfills, the amount of acid contained and the resulting pH (4.93) may not always represent what is encountered under typical conditions at actual landfills. A method that has been suggested to examine more realistic conditions for waste leaching from a landfill is to conduct a batch leaching test using actual landfill leachate. Hooper et al. [48] performed leaching tests with leachate collected from California landfills on a number of solid wastes (not treated wood) and compared the results to standardized regulatory leaching tests. A similar approach was applied to sample M using a limited number of leachates representative of different waste disposal conditions.

Sample M was leached using leachate from a lined MSW landfill, a simulated C&D debris landfill and a simulated concrete monofill. The extraction tests were carried out in a similar fashion as TCLP; the acetic acid leaching solution was replaced, however, with leachate. The MSW leachate (pH =8.0) was collected from a lined landfill in Florida that has been closed since 1998. C&D debris landfill leachate (pH = 6.9) was collected from a set of simulated C&D debris landfill columns [43]. The simulated concrete monofill leachate (pH = 10.0) was used to assess potential leaching that might occur in a disposal fill dominated by concrete. The simulated concrete monofill leachate was generated by placing 100 g of crushed concrete collected from a local concrete recycling facility in 2L of deionized water and rotating for 18h. The mixture was filtered and the leachate produced was used as the extraction fluid.

Particle size, pH and leaching contact time can have a major impact on the leachability of metals from waste [12,49,50]. To examine particle size effect, the TCLP and the SPLP were performed on samples A–J using a 100-g block, five 20-g blocks, 100 g of chipped wood, and 100 g of sawdust for each sample. The MEP was performed on 100-g blocks and chipped wood from sample J. A 20:1 liquid-to-solid ratio was maintained in each case. The impact of the leaching solution pH was examined by leaching sawdust from sample M over a broad pH range using a method similar to the TCLP; the leaching fluid was changed. The leaching fluid for the pH test consisted of various proportions of nitric acid (HNO<sub>3</sub>) and sodium hydroxide (NaOH) in deionized water. The pH was monitored continuously and adjusted as necessary to obtain the desired pH value (pH 1 through pH 13). Duplicate samples were leached for 18 h at a 20:1 liquid-to-solid ratio (10 g of wood plus 0.2 L of leaching solution).

Two separate leaching experiments were used to evaluate the impact of leaching contact time. Both of the tests were conducted on sample M. In each case, a modified SPLP was followed. In one experiment, the samples (originally 100 g of wood) were filtered every 24 h. The solids retained on the filter, along with the filter itself, were then leached again using new SPLP solution (a 20:1 liquid-to-solid ratio was maintained). This experiment was conducted for 14 days. In a second experiment, replicate samples were leached starting at the same time. At various times throughout the experiment (1 h, 2 h, 3 h, 8 h, 18 h, 2 days, 5 days, 10 days, 20 days, and 40 days), replicates were removed from the rotary extractor, filtered and preserved. Because of the large number of samples, the tests were performed on 10 g samples; the 20:1 liquid-to-solid ratio was maintained by adding 0.2 L of SPLP solution in 250-mL plastic container. Triplicate samples were filtered and analyzed for each time period.

### 3.5. Leachate digestion and analysis

Prior to analysis, the leachate samples were digested according to the US EPA method 3010 [46]. This open-vessel method requires the addition of concentrated nitric acid to a representative 100-mL sample. The analysis of arsenic, copper, and chromium was conducted following US EPA method 6010B [46] using a Thermo Jarrel Ash inductively coupled plasma atomic emission spectrometer (model Environ 60) with 0.03, 0.017, and 0.014 mg/L detection limits for arsenic, chromium, and copper, respectively. Laboratory blanks, spikes, and duplicate samples were analyzed for quality control purposes.

## 4. Results and discussion

## 4.1. Regulatory batch tests

# 4.1.1. TCLP

The TCLP was performed on sawdust from all 13 samples. As discussed previously, when used for the purpose of hazardous waste characterization, the TCLP requires that samples be size reduced to less than 0.95 cm. The results are presented in Table 4. In general, copper leached at higher concentrations than arsenic (9 of the 13 samples), which leached at higher concentrations than chromium. The mean copper concentration of all 13 samples was 9.9 mg/L (4.0-16.6 mg/L). The mean concentrations of arsenic and chromium were 7.0 mg/L (3.7-12.5 mg/L) and 2.6 mg/L (1.1-4.1 mg/L), respectively. While previous studies have found chromium to leach the least of all three metals, results differ as to which metal (copper or arsenic) leaches the most. In the case of TCLP, copper leaches more because of the affinity for acetate ions to complex with copper (more so than arsenic). This falls in line with observations from leaching studies where citric acid was used [11,12]. Citrate also complexes with copper more readily than arsenic.

The TCLP was designed to provide a relatively quick test that could be performed on a solid waste to determine whether that waste should be characterized as hazardous and thus be managed in a more controlled fashion. As discussed previ-

Table 4 Metal concentrations leached from CCA-treated wood sawdust using the TCLP and the SPLP

Sample name	TCLP concentr	rations (mg/L)		SPLP concentration (mg/L)			
	As	Cr	Cu	As	Cr	Cu	
A	4.55	2.10	9.63	3.53	1.12	2.01	
В	6.66	4.06	14.2	5.32	2.16	3.45	
С	7.76	3.28	16.2	6.85	1.69	3.23	
D	12.5	3.02	10.4	8.35	1.90	2.46	
Е	7.25	2.62	7.78	6.21	1.71	2.15	
F	5.11	2.79	16.6	3.08	1.09	2.97	
G	5.35	2.66	5.81	4.46	1.54	1.81	
Н	3.70	1.09	14.2	1.46	0.52	1.20	
I	7.68	1.83	7.12	6.66	1.23	1.83	
J	8.13	2.36	4.72	7.82	1.34	1.53	
К	7.88	3.33	8.71	8.90	2.47	4.13	
L	7.87	3.36	8.67	6.44	2.08	3.97	
М	6.27	1.76	4.01	7.32	1.40	1.40	
Average	6.98	2.64	9.85	5.63	1.56	2.47	

ously, the acetic acid used in the test simulates the organic acids produced from decomposing waste in anaerobic environments such as a landfill. The regulations require the concentrations of specific compounds in the TCLP leachate to be compared to TC concentrations in the regulations [51]. Both arsenic and chromium have TC concentration limits of 5 mg/L, while copper is not a TC metal (i.e., a waste can not be a TC hazardous waste because of copper). Eleven of the 13 samples exceeded 5 mg/L for arsenic. None of the samples exceeded 5 mg/L for chromium.

Although the majority of the CCA-treated wood samples tested exceeded the regulatory TC limit for arsenic, the regulations exclude CCA-treated wood from the definition of hazardous waste. Specifically, Title 40 of the US Code of Federal Regulations (CFR) part 261.4 b (9) excludes the following from the definition of hazardous waste:

"Solid waste which consists of discarded arsenical-treated wood or wood products which fails the test for the Toxicity Characteristic for Hazardous Waste Codes D004 through D017 and which is not a hazardous waste for any other reason if the waste is generated by persons who utilize the arsenical-treated wood and wood product for these materials' intended end use" [52].

In the absence of this exclusion, CCA-treated wood similar to the types tested here would require management as a TC hazardous waste. This would include scraps and sawdust from construction sites and manufacturing facilities that use CCA-treated wood in their products. The question of whether CCA-treated wood removed from service (i.e., weathered wood) exceeds the TC for arsenic remains uncertain. Additional research should be conducted to examine this. It is noted that the US EPA was petitioned during July 2002 to remove the hazardous waste exclusion for CCA-treated wood [53]. Clearly, removal of the exclusion would have a major impact on those discarding CCA-treated wood.

## 4.1.2. SPLP

The SPLP was also performed on sawdust from all 13 samples (see Table 4). Unlike TCLP, arsenic leached at greater concentrations than copper (in all cases). Copper leached more than chromium. The mean arsenic concentration of all 13 samples was 5.6 mg/L (1.5–8.9 mg/L). The mean concentrations of copper and chromium were 2.5 mg/L (1.2–4.1 mg/L) and 1.6 mg/L (0.5–2.5 mg/L), respectively. As summarized previously, arsenic has often been observed to leach more than copper in leaching tests at more neutral pH conditions where water is used as the leaching medium [12,16]. As a whole, the TCLP leached greater concentrations of all three metals than the SPLP, with the difference being more pronounced for copper.

Differences in metal leachability between TCLP and SPLP result from several factors. As has been discussed previously and as will be demonstrated in greater detail later, solution pH plays a major role in metal leachability. The initial pH of the SPLP solution (4.2) is less than the initial pH of the TCLP solution (4.9). The SPLP solution, however, is not buffered like the TCLP. Depending on the alkalinity of the waste tested, changes in the solution pH that occur during the 18 h of leaching may differ between SPLP and TCLP, and thus result in different amounts of metal leaching. Another factor is the complexation ability of the acid used in the leaching fluid. The anions resulting from organic acids such as citric or acetic acid can complex metals causing them to leach in greater concentrations. The degree of complexation differs depending on the metal. In the case of CCA-treated wood, the pH difference between the two tests was not very pronounced. The complexation ability of acetate in the TCLP solution did increase the concentration of metals leached somewhat, most notably for copper. The difference in metal concentrations between SPLP and TCLP for CCA-treated wood are relatively small, however, compared to other waste streams (lead-based paint, printed wire boards) where differences are often several orders of magnitude [54,55].

The SPLP does not play a specific role in the US regulatory hazardous waste characterization. It is frequently used to assess the risk to groundwater posed by contaminated soils [56]. The SPLP is sometimes used to assess the potential for a waste to leach in landfill environments where large amounts of organic acids are not expected. For example, when assessing the potential risks posed by the disposal of lead-based paint debris in MSW landfills and C&D debris landfills, the US EPA equated TCLP to MSW landfills and SPLP to C&D debris landfills [54]. The SPLP is also commonly used in the risk assessment process for determining beneficial use of solid wastes [57,58]. One way that SPLP results are commonly applied is to compare the SPLP leachate concentrations to applicable groundwater quality standards or goals. Most US states set groundwater quality standards to the drinking water standards, which are 0.05, 0.1, and 1.0 mg/L for arsenic, chromium, and copper, respectively [59]. The SPLP results for all three metals exceeded the respective drinking water standards, most notably for arsenic. It is interesting to note that even when the SPLP results are compared to the TC hazardous waste limit, 9 of the 13 samples exceeded 5 mg/L. It is also worth noting that the US drinking water standard for arsenic will be lowered to 0.01 mg/L in 2006 [60].

Utilizing the SPLP results presented above, one could argue that CCA-treated wood does leach metals, particularly arsenic, at concentrations such that it should not be disposed in unlined landfills. The average SPLP arsenic concentration was 5.6 mg/L, 100 times greater than the existing drinking water standard and 500 times greater than the future drinking water standard. While a direct comparison of batch leaching test results to groundwater standards seems an over-simplified approach (neglecting factors such as dilution, attenuation, and immobilization), the comparison certainly justifies examining the issue in much greater detail. In Florida, USA, for example, groundwater monitoring well data for unlined C&D debris landfills will be closely tracked in the coming years.

From a land application standpoint, the SPLP results indicate that size-reduced CCA-treated wood should not be land applied. While it is unlikely that size-reduced CCA-treated wood would be proposed as a soil amendment, it is very likely CCA-treated wood is contained in landscape mulch derived from C&D debris. A previous study found chipped wood from C&D debris recycling facilities in Florida, US, to contain an average of 6% CCA-treated wood [37]. Separation of CCA-treated wood from un-treated wood can be difficult, especially if the wood is weathered, painted, or dirty. In many areas, a large fraction of the recovered C&D debris wood is used as landscape mulch, especially after dyeing. Assuming a SPLP arsenic leaching concentration of 5.0 mg/L from chipped CCA-treated wood and neglecting the impact of other materials in the mulch, greater than 1% CCA-treated wood in a wood mulch mixture would likely exceed the existing drinking water standard (greater than 0.2% would exceed the future drinking water standard). While one would expect the amount of preservative leaching from landscape mulch to be less than that leaching from sawdust (due to the difference in particle size), results in the next section will show that substantial concentrations leach from chipped wood as well. Townsend et al. [39] performed SPLP on chipped wood collected from C&D debris recycling facilities in Florida and found that the majority of samples tested exceeded the current drinking water standard for arsenic.

## 4.1.3. EPTOX, WET, and MEP

Fig. 1 compares the average leachate concentrations for sample M (sawdust) using SPLP, TCLP, WET and EP-TOX for arsenic, chromium and copper. The error bars refer to the standard deviation of triplicate leaching runs. The most notable observation is the obvious difference in the concentrations extracted by the WET relative to the other procedures. WET extracted more than 5 times as much arsenic as TCLP and more than 10 times as much copper and chromium as TCLP. This results from the much greater chelating ability of citrate. Hooper et al. [48] observed

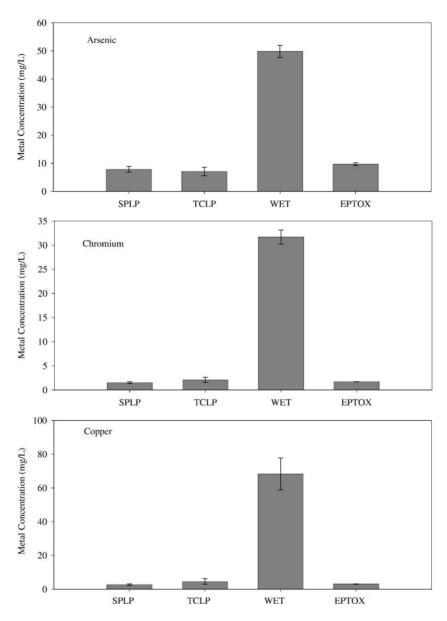


Fig. 1. CCA leaching from treated wood using four regulatory batch tests.

concentrations of many metals at much higher levels in WET relative to TCLP. EPTOX leached similar amounts as TCLP. This is not surprising considering both tests use acetic acid.

The WET is a California-specific leaching procedure used to determine whether a solid waste is a TC hazardous waste. It is used in addition to TCLP. The concentrations in the WET leachate are compared to the appropriate regulatory criteria. In addition to arsenic and chromium (5 mg/L), if the concentration of copper in either the WET or the TCLP exceeds 25 mg/L, the waste is a TC hazardous waste under California regulations. The results indicate that CCA-treated wood of the type tested here is a California TC hazardous waste for arsenic, chromium and copper. This raises the interesting possibility that the arsenic- and chromium-free wood preservatives in line to replace CCA may also be TC hazardous waste in California due to their additional criteria for copper. This merits further investigation.

Fig. 2 presents the results of MEP conducted on sample M. As a reminder, the first extraction of the MEP is performed using EPTOX extraction fluid (at a pH of 5.0). The subsequent extractions are performed using a pH 3 synthetic rainwater. The arsenic and chromium results are typical of most sequential leaching tests, with the concentrations decreasing with consecutive extractions. The behavior of copper, however, is different. While the copper concentration decreased from the first extraction to the second, it then increased until the fourth extraction. This increase likely results from the decrease in pH that occurs with the synthetic rainwater (pH 3.0). As will be shown later, copper leaching increases greatly at a lower pH (more so than arsenic and chromium). After the fourth extraction, copper concentrations decreased in a similar fashion

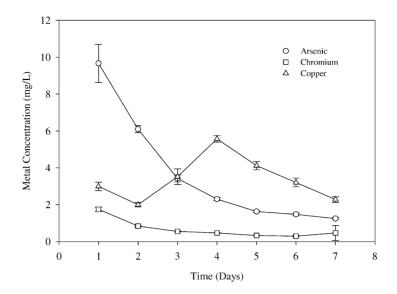


Fig. 2. Multiple extraction procedure (MEP) test results.

as arsenic and chromium. The MEP was designed to assess long-term contaminant leachability from solid wastes. The designers of the MEP proposed that it would simulate 70 years of leaching (after seven extractions) [61]. The results show relatively high residual concentrations of all three metals at the end of the test, with both arsenic and copper above 1 mg/L.

## 4.2. Additional leaching testing

#### 4.2.1. Landfill leachate as extraction solutions

Table 5 presents the results of the leaching tests where actual or simulated landfill leachates were used as the extraction fluids. TCLP, SPLP, and WET results are included for comparison. Because of the limited number of leachates evaluated, only general and preliminary observations may be made. As a whole, the concentrations of arsenic, copper and chromium extracted by the leachates were similar to the concentrations extracted by the SPLP and the TCLP (within the same order of magnitude). The WET clearly extracted more than any other leaching solution. The concentration of arsenic extracted by the MSW landfill leachate was somewhat smaller than that extracted by the TCLP and SPLP. The concentration of copper on the other hand was somewhat greater

Table 5 Metal concentrations leached from CCA-treated wood sawdust using different extraction solutions

Extraction	Extract	ion pH	As (mg/L)	Cr (mg/L)	Cu (mg/L)
solution	Initial	Final	_		
SPLP	4.2	4.2	7.89	1.51	2.67
TCLP	4.9	4.9	7.13	2.06	4.53
WET	5.0	4.1	49.8	31.7	68.2
MSW	8.0	7.4	4.48	1.76	8.21
Concrete	10	8.7	5.98	1.32	2.72
C&D Leachate	6.9	6.5	2.57	0.766	0.891

in the MSW landfill leachate. The fact that arsenic leaches less in the MSW landfill leachate relative to TCLP and SPLP is likely a result of the higher pH (pH impacts are discussed in greater detail later). In a like fashion, copper would also be expected to leach less in the MSW landfill leachate. The fact that copper leaches more indicates that this particular leachate complexed more copper. The leachate was collected from an older landfill. Large concentrations of humic and fulvic acids are typical of such leachates, and these chemicals are known to strongly complex copper [62,63].

The C&D debris leachate was collected from a simulated C&D debris landfill. In Florida, C&D debris is disposed in unlined landfills and thus actual leachate samples are not available. In some cases, large amounts of concrete are disposed as clean fill material. While the pH of typical C&D debris landfill leachate is near neutral [64,65], large amounts of concrete (either in a clean fill scenario or in a C&D debris landfill) can result in alkaline pH conditions [64]. Thus a concrete monofill leachate was simulated as well. For the most part, metal concentrations resulting from the C&D debris and concrete leachates were less than the TCLP and SPLP concentrations. The differences in concentration between the two can be attributed to the different pH conditions. This will be discussed in greater detail later.

#### 4.2.2. Particle size impact

The impact of particle size was examined on samples A–J by conducting the TCLP and the SPLP on four different sample sizes (a single 100-g block, five 20-g blocks, 100 g of chipped wood, and a 100 g of sawdust). The only sample that truly met the size requirements required in the methodology was the sawdust. As expected, the leachable metal concentrations inversely correlated with the sample size (smaller samples leached more). An example of these results is presented in Fig. 3 for arsenic TCLP measurements. For results of the other metals and SPLP, see Townsend et al. [42]. Variability

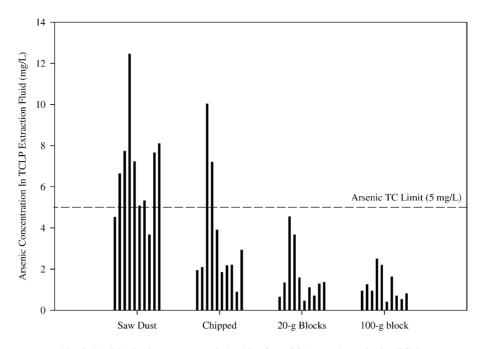


Fig. 3. Particle size impact on arsenic leaching from CCA-treated wood using TCLP.

exists among the different samples at a given size, but a definite trend can be observed. Greater concentrations of arsenic leach from the sawdust relative to the larger size samples. A line corresponding to the TC limit (5 mg/L) is superimposed on the results. While 8 of 10 sawdust samples leach greater than 5 mg/L arsenic, only 2 of the 10 chipped wood samples and none of the block samples leach greater than 5 mg/L. From a hazardous waste characterization standpoint, the fact that larger sizes (those more representative of what might be disposed) leach less metals has no bearing since the TCLP requires samples to be size reduced. From a practical standpoint, however, the results clearly indicate that less metals will leach from larger pieces of CCA-treated wood such as dimensional lumber. The impact of particle size is also illustrated in Fig. 4. The MEP was performed on 100-g blocks and chipped wood from sample J and on sawdust from sample M. Fig. 4 presents the arsenic concentrations for all three sizes as a function of leaching time (up to 7 days). The leaching patterns are similar in each case, with the concentrations differing as expected by particle size. It is of interest to note that

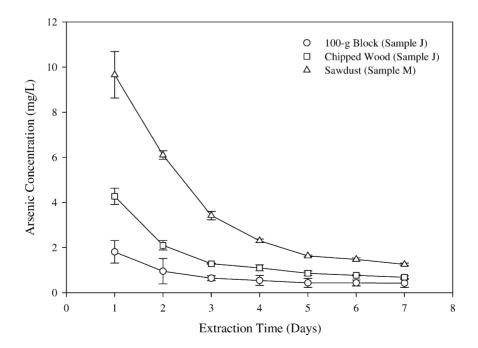


Fig. 4. Impact of particle size on arsenic leaching from CCA-treated wood using MEP.

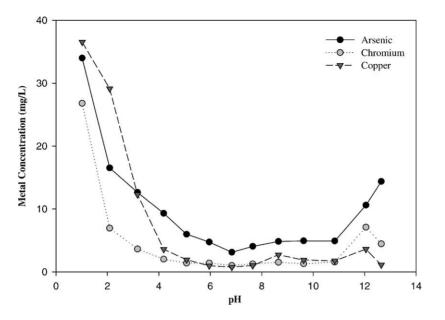


Fig. 5. CCA leachability from CCA-treated wood sawdust (final leaching solution pH values are presented).

even for the 100-g blocks, after 7 days leaching, the arsenic concentration (0.42 mg/L) still remains eight times greater than the current drinking water standard.

#### 4.2.3. pH impact

The impact of pH on metal leaching was examined from pH 1 to pH 13. Fig. 5 plots the concentrations of arsenic, copper and chromium as a function of pH for sample M. All three metals show similar leaching patterns; leached metal concentrations were the highest at low pH values (four and less) and high pH values (greater than 11). The metals in CCA-treated wood leached the least at pH values near neutral. This observation is in line with the results from most previous studies [11,12]. Copper had the greatest difference between the minimum and maximum concentrations measured. Both copper and chromium exhibited a decrease in leachability at the highest pH tested (pH = 12.7).

The relationship between pH and leachate concentrations helps explain some of the previous observations. For example, arsenic leached more than twice as much in the concrete leachate (final pH = 8.7) compared to the C&D debris leachate (final pH = 6.5). This matches what is observed in Fig. 5. The SPLP (pH = 4.2) leaches more than both of these, which again follows the relationship shown in Fig. 5. As another example, copper leaches approximately the same concentration in the SPLP and concrete leachates (2.7 mg/L). This is again confirmed by the relationship described in Fig. 5. As previously discussed, other factors besides pH alone impact leaching. This is illustrated by comparing the WET results for all metals and the TCLP and MSW landfill leachate results for copper to the results from Fig. 5; metals are leached above the concentrations expected to result from the pH alone. Thus while a pH relationship such as that shown in Fig. 5 can be helpful for assessing potential leachability, other factors impacting leachability (e.g., complexation) should not be neglected.

# 4.2.4. Impact of contact time

Two separate experiments were conducted to evaluate the impact of contact time. In the first experiment, the extraction solution (SPLP) was kept in contact with the sawdust for the duration of the experiment. Arsenic leached the most and achieved a maximum concentration of approximately 14 mg/L after the 40-day extraction period (Fig. 6). Copper and chromium approached their respective equilibrium concentrations within one day of extraction. Arsenic, on the other hand, did not approach equilibrium concentrations until approximately the 10th day. In general, batch tests such as the TCLP are designed so that equilibrium concentrations are reached by the end of the test (size reduction, agitation). The results presented in Fig. 6 show that equilibrium concentrations were not reached for arsenic within the period of the TCLP and SPLP (18h). Equilibrium concentrations are approached during this period for copper and chromium. This could be important when interpreting batch leaching test results.

In the second test, the leachate was filtered from the wood sample every 24 h and replaced with SPLP solution. The concentrations measured on each day were multiplied by the volume of leachate produced on the respective days to determine the total mass of metal leached. The cumulative masses of metals leached were divided by the total concentration of the metals in the wood (as determined from the composite sawdust sample: 1390 mg/kg of As, 1450 mg/kg of Cr, 814 mg/kg of Cu). Fig. 7 presents the cumulative percentage leached as a function of time for all three metals. Similar to the results in Fig. 6, arsenic leached the most (41% at 14 days). This compares to 6.5% for chromium and 8.2% for copper. The results

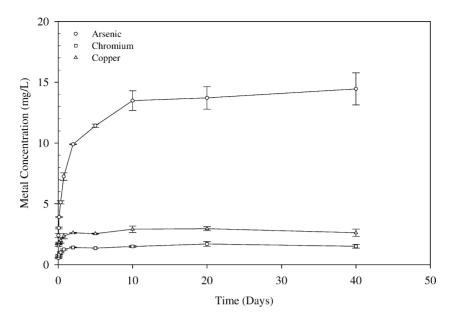


Fig. 6. Time effect on CCA leachability from CCA-treated wood sawdust. SPLP extraction solution not replaced.

of both experiments indicate that arsenic has the potential to continue to leach for extended periods of time.

#### 4.3. Comparison to other studies

The leaching concentrations were converted from mg/L to the fraction of metal that leached from the wood (%). These results are summarized for many of the experiments in Table 6. The fraction of metals leached were compared to the results from other leaching experiments summarized in Table 1. Considering the differences in leaching that might be expected to occur as a result of different testing protocols and wood conditions (degree of agitation, liquid-to-solid ra-

tio, wood species), the results presented in this paper compare relatively well and fall within the range of other experiments. For example, the WET results in Table 6 are similar to the results presented by Warner and Solomon [11]. The WET (initial pH = 5) extracted 36% of the arsenic compared to 32–52% extracted in Warner and Solomon's citric acid buffered leaching experiment (pH = 4.5-5.5). The SPLP (initial pH = 4.2) extracted an average of 10% arsenic and 2.8% copper. Cooper's [12] dilute nitric and sulfuric acid solution (initial pH = 4.5) leached 2.9–6.3% arsenic and 2.4–5.0%copper. Warner and Solomon's [11] leaching experiment performed using a dilute sulfuric acid solution at a constant pH of 4.5 leached 17.3% arsenic and 21% copper. The AWPA's

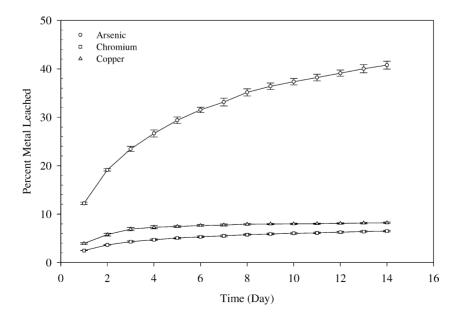


Fig. 7. Time effect on CCA leachability from CCA-treated wood sawdust. SPLP extraction solution replaced every 24 h.

Table 6 Fraction of As, Cr, and Cu leached from CCA-treated wood under various leaching conditions

Method		Fraction leached (%)					
		As	Cr	Cu			
TCLP <sup>a</sup>		4.5–18	1.6–9.0	6.5–27			
SPLP <sup>a</sup>		1.8-16	0.8 - 5.0	1.0-5.3			
WET		36	22	84			
pН	3.0	18	5.0	30			
1	7.0	4.5	1.4	4.9			
	12	15	9.8	8.9			
Time <sup>b</sup> (days)	2	14	2.0	6.4			
	10	19	2.1	7.2			
	40	21	2.1	6.4			
Time <sup>c</sup> (days)	2	19	3.5	5.8			
	10	37	5.8	14			
	14	41	6.2	14			

<sup>a</sup> Number of samples = 13.

<sup>b</sup> Solution not replaced.

c Solution replaced.

E-11 test results (as reported by Kennedy and Collins [16]) leached somewhat greater amounts of arsenic (19%) and similar amounts of copper (5.7%) and chromium (3.3%) when compared to SPLP. Thus, while methods such as the SPLP and TCLP are often criticized for over-predicting leaching because of the size reduction involved, they predict similar or lower concentrations relative to the wood preservation industry standard testing protocol.

#### 4.4. Evaluating potential impacts on landfills

The recommended disposal management technique for CCA-treated wood has traditionally been landfilling [66]. The potential environmental impact will differ according to the type of landfill in which the wood is disposed. In the US, CCA-treated wood is disposed in both lined and unlined landfills. The US federal regulations require landfills used for MSW disposal to be constructed with liners and leachate collection systems. C&D debris landfills, on the other hand, do not require liner systems at the federal level; some states require liner systems while others do not. In locations where unlined landfills are permitted, C&D debris materials including CCA-treated wood are typically disposed in unlined facilities. Some states have specific disposal requirements for CCA-treated wood. California, for example, requires the disposal of used CCA-treated electrical and telephone utility poles in lined landfills [67].

The results of leaching tests reported here found CCAtreated wood to leach arsenic, chromium and copper above the drinking water standards (many times greater in some cases). Arsenic often leached above the TC hazardous waste limit. These results suggest that in the case of unlined landfills, the potential impact of metals leaching from the disposed CCA-treated wood on groundwater quality is the greatest concern. They also suggest that CCA-treated wood might have an impact on lined landfill leachate quality if disposed in sufficient quantities. It is important to note, however, that batch leaching tests concentrations may be greater than is expected to occur in actual landfill leachate under normal landfill conditions. In a landfill, disposed CCA-treated wood will be found in some loads of waste but not others. Leachate from areas where CCA-treated wood is disposed will be diluted with leachate from locations without CCA-treated wood. While some sawdust and size-reduced treated wood may be disposed in landfills, most of the material will be of a greater particle size than that required in TCLP and SPLP testing. Lower metal concentrations leach at larger particle sizes. These results suggest that metal concentrations encountered in landfill leachate may be lower than those predicted by batch leaching tests because of the relatively small particle size required by these tests.

Landfill leaching environments may differ depending on the type of landfill. For example, while leachate from C&D debris landfills is dominated by large concentrations of inorganic ions, and may be heavily influenced by sulfate-reducing bacteria when gypsum drywall is present [65], MSW landfill leachate chemistry is determined by the biological reactions occurring as a result of the anaerobic waste decomposition [68,69]. Although leaching environments in landfills may be different that those encountered in batch leaching tests, results presented earlier show similar CCA-treated wood leaching behavior in these environments. Leaching results presented in this research indicate that arsenic and chromium concentrations extracted by the TCLP and SPLP from CCAtreated wood were relatively close to one another, and to those measured when leached in landfill leachate. Two primary factors control metal leachability: the presence of organic acids and extraction solution pH. While one would expect metals to be complexed by the organic acids present in landfill leachate as well as the TCLP, that was not necessarily the case with arsenic and chromium. The similar concentrations of arsenic and chromium measured in the TCLP relative to the SPLP indicate that acetic acid did not form complexes with either arsenic or chromium. Hooper et al. [48] reported that acetic acid in TCLP tended not to complex with oxyanions like arsenic and chromium. This indicates that the presence of acetic acid in the TCLP as well as the MSW landfill leachate examined was not a large factor in controlling arsenic and chromium leachability from CCA-treated wood. The second factor effecting metal leachability is extraction pH. As apparent in Fig. 5 at extreme pH values, a unit change in pH was accompanied by a large change in arsenic and chromium concentrations. For example, when pH increased from 2 to 3, the arsenic concentration decreased from 18 to 8 mg/L. That trend was not observed at neutral to alkaline pH values (pH values 5 through 9). Since most of the leachate examined in this study had a pH value within this range (see Table 5), the difference in extraction pH also was not a major factor in controlling the leachability of arsenic and chromium from CCA-treated wood.

Subsequent interaction of the leached metals with the surrounding landfill environment may also impact metal concentrations in landfill leachates. Landfills are biologically active and often very reducing. Metals can be removed from solution by entrainment, sorption and precipitation. Previous research indicates the three metals in CCA-treated wood will behave differently in a landfill environment relative to that predicted in a leaching test. In simulated C&D debris landfill columns containing 0.5% by mass CCA-treated wood, both arsenic and chromium were found to leach at measurable concentrations, but copper was below detection limit for most of the duration of the experiment [65]. Weber et al. [70] in a study of leachate from land disposed construction debris containing CCA-treated wood observed arsenic and chromium in the leachate, but little copper.

It is important to note that the tests results presented herein were performed on un-weathered CCA-treated wood. While the results are directly applicable to scrap from construction sites and sawdust, discarded wood removed from service after exposure to weathering conditions might display different characteristics. Some copper, chromium, and arsenic will leach from CCA-treated wood when exposed to water and soil in the environment. The amount that leaches will be a function of the ambient conditions (i.e., above ground, in soil, submerged) and is estimated to be up to 20%. Additional research is needed to characterize leaching behavior of weathered CCA-treated wood, both from a regulatory perspective and to evaluate the impact on landfill disposal.

The information presented above indicates that arsenic, chromium and copper contamination of leachate at lined landfills and groundwater at unlined landfills might be a concern when CCA-treated wood is disposed in sufficient quantities. The fact that more CCA-treated wood is expected to enter the waste stream in the future [36] compounds this problem. Arsenic appears to be the most troublesome element of the three. The complexities and differences between laboratory batch tests and actual landfill environments, however, leave some uncertainty as to the magnitude of the impact. Additional research needed to address these questions would be a rigorous evaluation of landfill leachate and groundwater concentrations at landfills that have accepted this material, and more realistic simulations of CCA-treated wood leaching in landfill environments.

## 5. Conclusions

CCA-treated wood leaches arsenic, chromium, and copper when exposed to water, and therefore may impact the environment where the wood is disposed. The leaching of metals from CCA-treated wood has been well-studied in recent years, but primarily from the standpoint of in-service use (terrestrial and aquatic uses). Leaching is also a concern, however, when the wood is removed from service and enters the waste stream. Leaching tests not only help assess the potential impact of CCA-treated wood on the disposal stream, but also must often be performed to meet regulatory requirements. Regulatory leaching tests were performed on new CCA-treated wood. Eleven of thirteen CCA-treated wood samples exceeded the RCRA TC limits for arsenic (5 mg/L). If CCA-treated wood were not otherwise excluded from the definition of hazardous waste, it would need to be managed as a hazardous waste in the US. Arsenic appears to present the greatest potential risk from a waste management perspective. Arsenic concentrations exceeded 5 mg/L in 9 of 13 samples using a simulated rainwater test (the SPLP) and therefore also exceeded the drinking water standards (DWS). When compared to the literature, the SPLP leached similar or lower concentrations metals compared to the AWPA's E-11 test procedure for examining leaching from treated wood products.

Of the regulatory batch leaching tests, the WET extracted more metals than any other batch leaching tests. This is caused by the use of citric acid which chelates heavy metals relatively more than the acids used in other tests. The other three tests (SPLP, TCLP and EPTOX) extracted similar metal concentrations. Actual leachate extractions resulted in lower metal concentrations than the regulatory batch leaching tests, except for copper. Leaching of arsenic and chromium was controlled by solution pH. Copper leaching was influenced by interaction with chemicals in the leachate. Metal leachability from CCA-treated wood is the highest at extreme pH values and lowest around pH 7. As particle size decreases metal leachability increases. Metal leachability increases with increasing contact time. Although the copper and chromium concentrations reached equilibrium concentrations within 7 days, the arsenic concentrations continued to increase throughout the test.

The results indicate that there is certainly a potential for concern with respect to leachate quality from lined landfills, groundwater quality at unlined landfills, and processed wood mulch from C&D debris. More research is needed to assess the exact magnitude of the problem at actual disposal sites.

### References

- H. Solo-Gabriele, et al., Generation, Use, Disposal, and Management Options for CCA-Treated Wood, Florida Center for Solid and Hazardous Waste Management, Gainesville, FL, 1998.
- [2] F. Milton, The Preservation of Wood. A Self Study Manual for Wood Treaters, College of Natural Resources, University of Minnesota, 1995, p. 102.
- [3] P.A. Cooper, Y.T. Ung, C. Timusk, Comparison of empty-cell and full-cell treatment of red-pine and lodgepole-pine pole sections with CCA-peg, Forest Prod. J. 44 (4) (1994) 13–18.
- [4] A. Pizzi, The chemistry and kinetic behavior of Cu–Cr–As/B wood preservatives. IV. Fixation of CCA to wood, J. Polym. Sci. 20 (1982) 739–764.
- [5] AWPA, American Wood Preservers' Association Book of Standards, American Wood Preservers' Association, Grandbury, TX, 1999.
- [6] S. Fields, Environmental Health Perspectives, 2001 (p. A262).
- [7] T. Gordon, et al., In vitro bioavailability of heavy metals in pressuretreated wood dust, J. Toxicol. Sci. 67 (1) (2002) 32–37.
- [8] P. Decker, et al., Exposure to wood dust and heavy metals in workers using CCA pressure-treated wood, The Science of Occupational

and Environmental Health and Safety 63 (2) (2002) 166–171.

- [9] FR, Federal Register Petition H 01-3 Requesting a Ban on Use of Chromated-Copper-Arsenate (CCA) Treated Wood in Playground Equipment, vol. 66, 2001, pp. 36756–36757.
- [10] D. Stilwell, K. Gorny, Contamination of soil with copper, chromium, and arsenic under decks built from pressure treated wood, Bull. Environ. Contam. Toxicol. 58 (1997) 22–29.
- [11] J.E. Warner, K.R. Solomon, Acidity as a factor in leaching of copper, chromium and arsenic from CCA-treated dimension lumber, J. Environ. Toxicol. Chem. 9 (11) (1990) 1331–1337.
- [12] P.A. Cooper, Leaching of CCA from treated wood—pH effects, Forest Prod. J. 41 (1) (1991) 30–32.
- [13] V.T. Breslin, L. Adler-Ivanbrook, Release of copper, chromium and arsenic from CCA-C treated lumber in estuaries, Estuarine Coastal Shelf Sci. 46 (1) (1998) 111–125.
- [14] S.T. Lebow, D.O. Foster, P.K. Lebow, Release of copper, chromium, and arsenic from treated southern pine exposed in seawater and freshwater, Forest Prod. J. 49 (7-8) (1999) 80–89.
- [15] J.A. Hingston, et al., Leaching of chromated copper arsenate wood preservatives: a review, J. Environ. Pollut. 111 (1) (2001) 53–66.
- [16] M. Kennedy, D. Collins, Leaching of Preservative Components from Pine Decking Treated with CCA and Copper Azole, and Interactions with Soils, in: 32nd Annual Meeting of the International Research Group on Wood Preservation, 2001, Naru, Japan.
- [17] P. Weis, et al., Pathological and genotoxicological observations in oysters (*Crassostrea virginica*) living on chromated copper arsenate (CCA)-treated wood, Marine Environ. Res. 39 (1–4) (1995) 275–278.
- [18] P. Weis, J.S. Weis, Accumulation of metals in consumers associated with chromated copper arsenate-treated wood panels, Marine Environ. Res. 48 (1) (1999) 73–81.
- [19] L. Adler-Ivanbrook, V.T. Breslin, Accumulation of copper, chromium, and arsenic in blue mussels (*Mytilus edulis*) from laboratory and field exposures to wood treated with chromated copper arsenate type C, Environ. Toxicol. Chem. 18 (2) (1999) 213–221.
- [20] C.A. Green, G.M. Smith, B. King, The effects of aqueous leaching on the moisture uptake and decay of CCA-treated wood exposed to soil burial, Mater. Und Organismen 24 (3) (1989) 193–205.
- [21] P. Merkle, D. Gallagher, T. Solberg, Leaching rates metal distribution and chemistry of cca treated lumber: implications for water quality monitoring, in: Environmental Considerations in the Use of Pressure Treated Wood, Forest Products Society, Madison, WI, 1993.
- [22] G. Van Eetvelde, et al., Effect of Leaching Teperature and Water Acidity on the Loss of Metal Elements from CCA-Treated Timber in Aquatic Conditions. Part 1: Laboratory Scale Investigation, The International Research Group on Wood Preservation, Stockholm, 1995.
- [23] G. Van Eetvelde, et al., Effect of Leaching Teperature and Water Acidity on the Loss of Metal Elements from CCA-Treated Timber in Aquatic Conditions. Part 2: Semi-Industrial Investigation, The International Research Group on Wood Preservation, Stockholm, 1995.
- [24] J.A. Hingston, et al., The importance of the short-term leaching dynamics of wood preservatives, Chemosphere 47 (2002) 517–523.
- [25] C. Hickson, Copper Azole Wood Preservative (CBA-Type A) Proposal to the General Preservatives Committee and Sub-Committee P-4 for Ground Contact Listing, Hickson Corporation, Conley, GA, 1999.
- [26] P. Cooper, D. Stokes, Leaching characteristics and fixation of copper dimethyldithiocarbamate treated wood, in: Proceedings of the 89th Annual Meeting of the American Wood Preservers' Association, American Wood Preservers' Association, Granbury, TX, 1993.
- [27] K. Archer, et al., Technical Information on the Performance of the Ammoniacal Copper Quat Wood Preservative ACQ 2100, Chemical Specialties Inc., Charlotte, NC, 1992.
- [28] T. Anderson, et al., Proposal for the Standardization of Ammoniacal Copper Citrate Submitted to AWPA Committee P-4 and The General Preservatives Committee, Osmose Wood Preserving Inc., Buffalo, NY, 1993.

- [29] S.T. Lebow, Leaching Of Wood Preservative Components And Their Mobility In The Environment, US Department of Agriculture, Forest Service, Forest Products Laboratory, Madison, WI, 1996.
- [30] G. Fahlstrom, P. Gunning, J. Carlson, A study of the influence of composition on leachability, Forest Prod. J. 17 (7) (1967) 17–22.
- [31] B. Hager, Leaching tests on copper-chromium-arsenic preservatives, Forest Prod. J. 19 (10) (1969) 21–26.
- [32] I.N. Stalker, in: Paper Presented to the Canadian Wood Preservation Association, Michigan Universal Forest Production, Grand Rapids, 1993.
- [33] J. McQueen, J. Stevens, Disposal of CCA treated wood, Forest Prod. Soc. J. 48 (11–12) (1998) 86–90.
- [34] J. Truini, Complete guide to decks, Creat. Publ. Int. 92 (1996) 12.
- [35] D. Alderman, R. Smith, P. Araman, A profile of CCA-treated lumber removed from service in the southeastern United States decking market, Forest Prod. J. 53 (1) (2003) 38–45.
- [36] H.M. Solo-Gabriele, T. Townsend, Disposal practices and management alternatives for CCA-treated wood waste, Waste Manag. Res. 17 (1999) 378–389.
- [37] T. Tolaymat, T. Townsend, H. Solo-Gabriele, Chromated copper arsenate-treated wood in recovered wood, J. Environ. Eng. Sci. 17 (1) (2000) 19–28.
- [38] H. Solo-Gabriele, et al., Characteristics of chromated copper arsenate-treated wood ash, J. Hazard. Mater. 89 (2-3) (2002) 213–232.
- [39] T. Townsend, et al., Impact of chromated copper arsenate (CCA) in wood mulch, J. Sci. Total Environ. (2003) 309.
- [40] T. Townsend, et al., Leaching and Toxicity of CCA-Treated Wood and Alternative-Treated Wood Products, Florida Center for Solid and Hazardous Waste Management, Gainesville, 2003.
- [41] S. Lebow, P. Cooper, P. Lebow, Variability in Evaluating Environmental Impacts of Treated Wood, Environmental Impacts of Preservative-Treated Wood Conference, Orlando, FL, 8–11 Feburary 2004.
- [42] T. Townsend et al., New Lines of CCA-Treated Wood Research: In-Service and Disposal Issues, Florida Center For Solid and Hazardous Waste Management, Gainesville.
- [43] J. Jambeck, T. Townsend, H. Solo-Gabriele, The Disposal of CCA-Treated Wood in Simulated Landfills: Potential Impacts, in: The 34th Annual Meeting of the International Research Group on Wood Preservation, Brisbane, Australia, 2003.
- [44] C.W. Francis, M.P. Maskarinec, J.C. Goyert, Mobility of Toxic Compounds from Hazardous Wastes, US DOE, Oak Ridge, Tennessee, 1984.
- [45] C.W. Francis, M.P. Maskarinec, Field and Laboratory Studies in Support of a Hazardous Waste Extraction Test, US Environmental Protection Agency, Oak Ridge, TN, 1986, p. 198.
- [46] US EPA, Test Methods For Evaluating Solid Waste, SW846, vol. 3, Office of Solid Waste and Emergency Response, Washington, DC, 1996.
- [47] CCR, California Code of Regulations, Title 22, Chapter 11, Article 5, Appendix II, 1998.
- [48] K. Hopper, et al., Toxicity characteristic leaching procedure fails to extract oxoanion-forming elements that are extracted by municipal solid waste leachates, Environ. Sci. Technol. 32 (1998) 3825–3830.
- [49] B.A. Buchholz, S. Landsberger, Leaching dynamics studies of municipal solid waste incinerator ash, J. Air Waste Manag. Assoc. 45 (1995) 579–590.
- [50] D.S. Kosson, et al., An integrated framework for evaluating leaching in waste management and utilization of secondary materials, J. Environ. Eng. Sci. 19 (3) (2002) 195–204.
- [51] CFR, Code of Federal Regulations, Title 40, Part 261.4 (b) (1), 2003.
- [52] CFR, Title 40, Part 261.4 (B) (9), Code of Federal Regulation, 2002.
- [53] B. Pesticides, Beyond Pesticides, Daily News Archive, Washington, DC. 2002.
- [54] FR, Lead; Management and Disposal of Lead-Based Paint Debris, Federal Register 63 (243) (1998) 70190–70233.

91

- [55] Y. Jang, T. Townsend, Leaching of lead from computer printed wire boards and cathode ray tubes by municipal solid waste landfill leachates, Environ. Sci. Technol. 37 (2003) 4718–4784.
- [56] EPA, U.S., Supplemental Guidance for Developing Soil Screening Levels for Superfund Sites, Office of Emergency and Remedial Response, Washington, DC, 2001.
- [57] DEP, Florida, Guidelines for The Management of Recovered Screen Material from C&D Debris Recycling Facilities in Florida, Department of Environmental Protection: Tallahassee, FL, 1998, p. 92.
- [58] DEP, Florida, Guidelines for Preparing Municipal Waste-to-Energy Ash Beneficial Use Demonstrations, Department of Environmental Protection, Tallahassee, FL, 2001, p. 81.
- [59] CFR, Code of Federal Regulations, Title 40, Part 141, 2003.
- [60] FR, National Primary Drinking Water Regulations; Arsenic and Clarifications to Compliance and New Source Contaminants Monitoring, Federal Register 66 (194) (2001) 50961–50963.
- [61] T. Kimmell, D. Friedman, Model Assumptions and Rationale behind the Development of EP-III, in: Hazardous and Industrial Solid Waste Testing, ASTM, Arlington, VA, 1984.
- [62] P. Cooper, D. Jeremic, J. Taylor, Y. Ung, F. Kazi, Effect of humic acid on leaching of CCA from treated wood, Forest Prod. J. 51 (9) (2001) 73–77.

- [63] C. Flemming, J. Trevors, Copper toxicity and chemistry in the environment: a review, Water Air Soil Pollut. 44 (1989) 143– 158.
- [64] T. Townsend, Y. Jang, L. Thurn, Simulation of construction and demolition waste leachate, J. Environ. Eng. Sci. 125 (11) (1999) 1071–1081.
- [65] Y. Jang, T. Townsend, Effect of waste depth on leachate quality from laboratory construction and demolition debris landfills, J. Environ. Eng. Sci. 20 (3) (2003) 183–196.
- [66] AWPI, Answers to Often-Asked Questions about Treated Wood, second ed., American Wood Preservers' Institute Vienna, VA, 1995.
- [67] CCR, California Code of Regulation, Title 22, Section 66261.24 (a) (2), 2003.
- [68] G. Tchobanglous, H. Theisen, S. Vigil, Integrated Solid Waste Management, McGraw-Hill Inc., New York, 1993 (p. 978).
- [69] P. Kjeldsen, et al., Present and long-term composition of MSW landfill leachate: a review, Crit. Rev. Environ. Sci. Technol. 32 (4) (2002) 297–336.
- [70] W. Weber, et al., Leachate from land disposed residential construction waste, J. Environ. Eng. Sci. 128 (3) (2002) 237– 245.