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Arsenic Speciation of Solvent-Extracted Leachate from New and Weathered CCA-Treated Wood

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Abstract

For the past 60 yr, chromate-copper-arsenate (CCA) has been used to pressure-treat millions of cubic meters of wood in the United States for the construction of many outdoor structures. Leaching of arsenic from these structures is a possible health concern as there exists the potential for soil and groundwater contamination. While previous studies have focused on total arsenic concentrations leaching from CCA-treated wood, information pertaining to the speciation of arsenic leached is limited. Since arsenic toxicity is dependent upon speciation, the objective of this study was to identify and quantify arsenic species leaching from new and weathered CCA-treated wood and CCA-treated wood ash. Solvent-extraction experiments were carried out by subjecting the treated wood and the ash to solvents of varying pH values, solvents defined in the EPA's Synthetic Precipitation Leaching Procedure (SPLP) and Toxicity Characteristic Leaching Procedure (TCLP), rainwater, deionized water, and seawater. The generated leachates were analyzed for inorganic As(III) and As(V) and the organoarsenic species, monomethylarsonic acid (MMAA) and dimethylarsinic acid (DMAA), using high-performance liquid chromatography followed by hydride generation and atomic fluorescence spectrometry (HPLC–HG–AFS). Only the inorganic species were detected in any of the wood leachates; no organoarsenic species were found. Inorganic As(V) was the major detectable species leaching from both new and weathered wood. The weathered wood leached relatively more overall arsenic and was attributed to increased inorganic As(III) leaching. The greater presence of As(III) in the weathered wood samples as compared to the new wood samples may be due to natural chemical and biological transformations during the weathering process. CCA-treated wood ash leached more arsenic than unburned wood using the SPLP and TCLP, and ash samples leached more inorganic As (III) than the unburned counterparts. Increased leaching was due to higher concentrations of arsenic within the ash and to the conversion of some As(V) to As(III) during combustion.

Introduction

Chromated-copper-arsenate (CCA) is an inorganic water-borne pesticide widely used in the wood preservation industry to extend the useful service life of wood as a building material. Through 2003, millions of cubic meters of CCA-treated wood were produced annually for the construction of many outdoor structures including decks, picnic tables, playground equipment,

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telephone poles, and docks. The chemical CCA, made up of hexavalent chromium, divalent copper, and pentavalent arsenic, is formulated to be leach-resistant when fixed to wood. Complete fixation of CCA to wood is defined by the reduction of hexavalent chromium to trivalent chromium resulting in the formation of insoluble complexes in the CCA-treated wood (1,2). CCA-Type C is the most common type used, consisting of 47.5% as CrO_3 , 18.5% as CuO , and 34% as As_2O_5 by weight. The amount of CCA utilized to treat wood or “retention level” depends on the particular application of the wood. Typical standard retention levels utilized by the wood preservative industry are 4.0, 6.4, 9.6, 12.8, and 40.0 kg/m^3 (3) where kg refers to the mass of CCA on an oxide basis and m^3 corresponds to the volume of wood. Low retention levels, 4.0 and 6.4 kg/m^3 , are permissible for above-ground applications. Wood treated to a higher retention, 9.6 kg/m^3 , is used for load-bearing structures, such as pilings and structural poles, while retention levels of 12.8 and 40.0 kg/m^3 are used for foundations and saltwater applications.

Migration of chromium, copper, and arsenic from discarded CCA-treated wood and the possible environmental impacts upon disposal raise concern, most notably for arsenic. When CCA-treated wood is burned, arsenic can be released to the air, and when it is landfilled, arsenic can migrate to the leachate and possibly the groundwater. Discarded CCA-treated wood in the United States is typically disposed of in three ways: (i) disposal in landfills including construction and demolition (C&D) debris and municipal solid waste (MSW) landfills, (ii) combustion, and (iii) inadvertent land application as landscape mulch (4–6). In Florida, as well as several other states, C&D debris landfills do not require liner systems; thus, arsenic leaching from CCA-treated wood may pose a risk to groundwater. In the case of lined landfills, elevated concentrations of arsenic from CCA-treated wood could create leachate disposal problems. Leaching of arsenic from land-applied mulch or combustion ash could result in soil and groundwater contamination. An understanding of the rates and mechanisms of arsenic leaching is thus important.

Several studies have been conducted to evaluate the leaching of total arsenic from CCA-treated wood as a whole, but there are limited data pertaining to the speciation (7–11) and ash from the combustion of CCA-treated wood (12). Speciation is of interest because the different forms of arsenic exhibit different levels of toxicity. Inorganic forms of arsenic, arsenites (As(III)) and arsenates (As(V)), are generally more toxic than the organic forms, monomethylarsinic acid (MMAA) and dimethylarsinic acid (DMAA) (13,14); inorganic As(III) is reported as more toxic than As(V) (15,16). The research reported in this paper builds from previous work by the authors where the total concentration of arsenic leached from CCA-treated wood and ash were measured (11,12). This study focuses on arsenic leachability in terms of speciation. Unlike conventional methods that analyze for total arsenic concentrations, speciation sheds light on environmental conditions that promote arsenic leaching and more accurately identifies potential health risks from soil and groundwater contamination. As part of the current study, new and weathered CCA-treated wood as well as CCA-treated wood ash were leached using several different solvents, and the leachates generated were analyzed for the inorganic arsenic species, As(III) and As(V) , and the organoarsenic species, MMAA and DMAA.

Materials and Methods

Two sets of solvent-extraction leaching experiments were conducted. The first investigated arsenic species leaching from CCA-treated wood as a function of extraction pH. The second evaluated the leachability of arsenic species from both CCA-treated wood and ash from the combustion of CCA-treated wood using several different solvents.

Sample Selection and Preprocessing

Samples of new and weathered CCA-treated wood were used in both types of leaching experiments. New treated and untreated southern yellow pine (SYP) wood samples (A–L) were obtained from home improvement stores. The “rated” retentions of the new treated wood purchased were 4.0, 6.4, 9.8, and 40 kg/m³. The rated retention refers to the level of treatment as established by the manufacturer based upon the treatment conditions at the plant. The weathered wood samples (M–V) included wood taken from a playground demolition (14 yr of age at the time of the experiments), a utility pole (18 yr of age at the time of the experiments), mulch samples from C&D debris recycling facilities that were mixtures of different types of untreated and treated wood, and from other demolished structures including a fence, wood used in highway guardrails, and wood from a park. The age of the C&D debris wood and the other demolished structures was unknown. The manufacturer’s rated retention level was not available for the weathered wood samples.

Prior to the leaching experiments, samples from both the outer 1.52 cm and the full cross-section of each wood sample were collected and analyzed to determine the “true” retention levels. The rated retentions reported by the wood industry correspond to the outer 1.52 cm (3). The retention of the entire cross-section of the wood was needed for mass balance computations. Wood samples were drilled to generate sawdust capable of passing through a 9.5 mm (0.95 cm) standard sieve. The sawdust was analyzed by one or more of the following analytical methods: (i) X-ray fluorescence spectroscopy (XRF) (Asoma model 100) using an industry standardized method (Method A9-99) (3), (ii) open digestion followed by flame atomic absorption (FAA) (Perkin-Elmer AAnalyst 800 spectrometer) analysis, or (iii) open digestion followed by inductively coupled plasma atomic emission spectrometry (ICP-AES) (Thermal Jarrel Ash, model Enviro 36). The open digestion method (SW-846 Method 3050B) (17) requires addition of acids and hydrogen peroxide under heated conditions. The “measured” retentions of these wood samples and the corresponding arsenic concentrations are tabulated in Table 1. Table 2 provides specific details regarding the source of each wood sample.

Retention analysis of the new wood samples showed that for many of the samples the measured outer 1.52 cm retentions differed appreciably from the rated outer 1.52 cm retentions. Differences between the rated and measured retentions have been reported in other studies (18) and result from several factors. During the treatment process, several pieces of wood are stacked together exposing different parts of the wood to different amounts of the chemical. Furthermore, the degree of penetration and retention of preservative is a function of the permeability of the wood, which in turn is dependent upon the type, quantity, and size of the wood cells. Consequently, not all of the wood accepts the same amount of preservative; hence, deviations from the rated retention can occur between samples.

Wood samples for the pH experiment included new and weathered wood, designated as pH-N and pH-W, respectively. Samples A–V were used for the SPLP, rainwater, TCLP, deionized water, and seawater leaching tests. The ash samples utilized in this research were previously derived as part of another study on leaching of preservative compounds from ash from the combustion of CCA-treated wood (12). No arsenic speciation was carried out in this original work. In short, the ash samples were generated by placing several wood samples (new wood: samples A, B, G, and J; weathered wood: samples M, T, and V) in an industrial furnace (Al-Jon/United Inc.) for approximately 1.5 h. Ashing temperatures ranged from 427 to 649 °C. Upon ashing, the samples were removed from the incinerator and permitted to cool for 45 min, after which they were stored in labeled pre-acid-washed containers. The ash samples were leached using the SPLP and TCLP tests.

Leaching Experiments

The arsenic speciation provided in this study corresponds to the speciation of the leachate and not necessarily to the speciation within the original wood sample. The leaching tests were conducted following standardized procedures as outlined by the TCLP (Method 1311) and SPLP (Method 1312) (17). These two tests were developed by the U.S. Environmental Protection Agency (EPA) and are often used for assessing the leachability of wastes and contaminated soils. Additional leaching experiments were performed using the basic approach of the TCLP and SPLP and differed only by the type of solvent used. The leaching procedure required adding the sawdust sample to the solvent in a 1:20 ratio. This mixture was rotated for 18 ± 2 h. The resulting leachate was filtered and analyzed for arsenic. All samples were extracted in duplicate.

The leaching solvent used for the pH experiment consisted of deionized water, to which 1 N nitric acid (HNO_3) or 1 N sodium hydroxide (NaOH) was added to obtain the desired pH. Nitric acid was selected for use in this experiment after careful assessment of similar leaching tests conducted by other researchers (9,19). Unlike acetic, citric, and hydrochloric acids, nitric acid is less likely to cause complexation with heavy metals that can lead to increase metal leaching beyond the effects of pH.

The leaching solvent for the SPLP ($\text{pH } 4.20 \pm 0.05$) consisted of a mixture of deionized water to which a solution of sulfuric acid/nitric acid (60/40 wt %) was added. The SPLP simulates conditions where infiltrating rainfall can result in the leaching of chemicals from recycled waste that is intended for land application and is used to assess if leaching poses a threat to groundwater contamination.

For the TCLP, the leaching solvent was buffered acetic acid ($\text{pH } 4.93 \pm 0.05$). The TCLP test was designed to simulate the acidic conditions generated from decomposing waste under anaerobic conditions as found within a municipal solid waste landfill.

The rainwater ($\text{pH } 4.50$) was collected during August 2002 in Miami, FL. The deionized water ($\text{pH } 5.71$) was produced using a Millipore RiOs 8 deionizer, and the seawater ($\text{pH } 8.11$) was taken from Key Biscayne in Miami, FL, in January 2003.

Arsenic Analysis

Speciation analysis was determined by HPLC coupled with on-line hydride generation (HG) and AFS detection. The species measured using this method were inorganic As(III) and As(V), MMAA, and DMAA. The HPLC (SpectraSYSTEM P4000 with an AS 3000 autosampler) used was fitted with an anion-exchange column (Hamilton PRP-X100, 250 mm $\pm$ 4.6 mm i.d., 10 μm particle size). The flow rate of mobile phase (15 mM KH_2PO_4 /15 mM K_2HPO_4 , $\text{pH } 5.81$) was 1.0 mL/min. Sample injection volume was 100 μL . The HG-AFS (Millenium Excalibur, PS Analytical, Kent, UK) fitted with an arsenic lamp pumped solutions of HCl (12.5% v/v) at 2 mL min^{-1} and NaBH_4 (1.4% m/v in 0.1 M m/v NaOH) at 1 mL min^{-1} , with argon as the carrier gas and nitrogen as the dryer gas. Final results were graphically displayed using the computer integrator software Avalon. The detection limit for arsenic was 2 $\mu\text{g/L}$ and was calculated based upon 3σ of the baseline noise. Total arsenic was determined by summing the concentrations of the individual arsenic species. The coefficient of variation, computed by dividing the standard deviation by the mean, was $\pm 10\%$ for total arsenic in the pH experiment. For the SPLP and TCLP, the coefficient of variation for the unburned samples was $\pm 13\%$ and for the ash samples was $\pm 9\%$.

Results and Discussion

Effect of pH on Arsenic Leaching from CCA-Treated Wood

During the pH experiment, inorganic As(V) was the only species detected from the new wood (Figure 1). Inorganic As(III) and the organoarsenic species MMAA and DMAA were not detected. The total arsenic concentration for the new wood leachates (by HPLC–HG-AFS) ranged from 2 to 40 mg/L. The highest concentrations of arsenic were seen at the extreme pH values, those less than 2 and greater than 12, with concentrations up to 40 mg/L at pH 1 and an average of 10 mg/L at pH 12.7. The results from speciation analysis presented in the current paper are consistent with the total arsenic values previously reported for this particular sample (11). Other leaching studies have also noted higher levels of arsenic releases at the extreme pH values from soils (20) and CCA-treated wood (9,21); this increased arsenic leaching may be attributed to the degradation of the wood as a result of the low pH (22). In the pH range of 6–10, where environmental samples are generally found, the mean arsenic concentration was 3 ± 0.3 mg/L at the 95% confidence limit (student's *t* test).

Both inorganic As(III) and As(V) were present in the leachate of the weathered wood samples, with no trace of the organoarsenic species. The total arsenic concentrations for the weathered wood samples ranged from 5 to 28 mg/L (Figure 2). Inorganic As(III) was observed to occur up to a pH of about 9.5, after which no inorganic As(III) was observed. Inorganic As(V), however, was detected across the entire pH range (Figure 2). In a similar fashion as new wood, the highest concentrations of arsenic for the weathered wood were seen at the lowest and highest pH values, with an average of 27.8 mg/L at pH 1 and 26.4 mg/L at pH 12.8. Within the environmental pH range of 6–10 for the weathered wood, inorganic As(III) and As(V) concentrations were 1.4 and 4.9 mg/L, respectively, on average with inorganic As(V) as the predominant species. The mean for the total arsenic concentration within this pH range was 6.3 ± 0.6 mg/L at the 95% confidence limit.

At low pH values (pH 1–3), arsenic leaching was greater from the new wood than the weathered wood, even though the measured retention value was lower for the new wood (5.1 kg/m^3) than the weathered wood (6.6 kg/m^3). Above pH 3, there was more arsenic leaching from the weathered wood than the new wood with increased leaching as the solvent became more alkaline. Further testing would have to be conducted to determine why leaching is greater from lower retention new wood than weathered wood at low pH values. However, the increased arsenic leaching from the weathered wood at the other pH values can be attributed to the following: (i) the As(III) present in the leachate may be due to arsenic as As(III) in the wood, with inorganic As(III) as a more soluble and more mobile species which may not bind as strongly to the wood as inorganic As(V); (ii) over time, biological and environmental conditions may contribute to the breakdown of wood's natural structure thus allowing more of the fixed arsenic to be readily released; and (iii) the mere fact that the measured retention of the weathered wood is somewhat higher than that of the new wood could account for the higher arsenic leaching. There is limited information about the mechanism for conversion of inorganic As(V) to As(III) in CCA-treated wood, and further study of this occurrence is needed.

Arsenic Leaching from Unburned CCA-Treated Wood

Arsenic concentrations leaching from the SPLP, rainwater, TCLP, deionized water, and seawater tests ranged between 2 and 10 mg/L for the new wood, from 1 to 13 mg/L for the weathered wood, and averaged 0.02 mg/L for the untreated new wood (Table 3). These results are consistent with other laboratory studies that utilized various solvents including deionized water (7), freshwater (8–10,23), saltwater (8,23), and a variety of acids (9,19,24). The concentrations also fall within the typical range reported previously for TCLP and SPLP (11). For the C&D debris mulch samples, which were mixtures of treated and untreated wood,

the arsenic concentration was less than 1 mg/L. Townsend et al. (6) measured arsenic leaching from C&D debris mulch samples and found most SPLP arsenic concentrations to range from 0.05 to 0.55 mg/L.

Speciation analysis revealed that inorganic As(III) and As(V) were the only species detected in the leachate, with inorganic As(V) predominating (Table 3). There was no noticeable association between the amount of inorganic As-(III) leaching to that of inorganic As(V). The organoarsenic species, MMAA and DMAA, were not detected in any of the leachates.

At comparable retention levels, results show that more total arsenic leached from weathered wood relative to new wood in many cases. In the SPLP, for example, the weathered sample with a high retention value (e.g., sample M, 24.1 kg/m³) leached significantly more arsenic than new wood samples L, H, and K, which are characterized by similar retention levels as sample M (Figure 3). Similarly, the weathered wood samples with intermediate retention levels (e.g., samples N, Q, and O with retention levels between 5.3 and 6.3 kg/m³) leached more arsenic than the new wood samples of similar retention (e.g., samples D and C). The same was observed for samples within the 3 kg/m³ retention range.

For samples in the 3–9.1 kg/m³ retention level range, weathered wood leached more total arsenic than new wood at 95% confidence limits. This increase in arsenic leaching in the weathered samples was attributed to the increased leaching of arsenic as inorganic As(III). The As(III) concentration leaching from new and weathered wood with retentions greater than 5 kg/m³ under the SPLP were significantly different at 99% confidence limits. One possible explanation for these results is that inorganic As(V) can be reduced to inorganic As(III) while CCA-treated wood is in service and that this transformation may occur biologically or chemically if natural occurring elements in the wood serve as electron donors. As a result, more As(III) and total arsenic was observed in the leachates from the weathered wood samples.

Inorganic As(III) was also noted leaching from some of the new wood samples, although at a lower concentrations than in weathered wood. While the form of arsenic in the chemical CCA is inorganic As(V), its presence in new wood is puzzling. One theory to explain its occurrence is the possible chemical transformation of the species during the treatment process of new wood, which involves high temperature and high pressure. Another possibility is conversion of the arsenic during storage at the lumber yard or retail store. Further experimentation is necessary to evaluate these possibilities.

No distinct relationship was observed between arsenic leaching and retention for new wood (Figure 4). However, some new wood samples with higher retention leached less arsenic than new wood with lower retention (Table 3). For example, in the SPLP, sample J (46.0 kg/m³) leached slightly less arsenic than sample G (13.0 kg/m³), although the retention level of sample G was almost 4 times less than that of sample J. The retention level of sample E (3.9 kg/m³) was 2–7 times less than that of samples H (24.6 kg/m³), L (27.5 kg/m³), I (9.1 kg/m³), and C (5.6 kg/m³), but sample E leached more arsenic (Table 3). In the SPLP, the arsenic concentration leaching from new wood with retentions ranging from 3 to 48 kg/m³ was 3–7 mg/L with no distinct relationship between the amount of arsenic leached and retention value. Other researchers have also noted arsenic losses to be independent of retention for wood structures made from new southern pine CCA-treated wood and have suggested that the higher the CCA loading to the wood the better the fixation and the lower the metal leaching (25,26).

Unlike new wood, weathered wood samples showed a tendency to leach more arsenic with increasing retention (Figure 5). Since the treatment process leaves behind a layer of CCA residue on the surface of freshly treated new wood, the general thought is that CCA losses are highest soon after installation and attenuate with time (19,27,28). However, results of this study suggest that, as wood ages, deterioration allows once well-fixed arsenic (and other CCA

components) to be readily released. This process accounts for the increased arsenic leaching observed from the weathered wood samples. A presumed arsenic leaching curve from CCA-treated wood would then possess two leaching peaks, one peak soon after installation resulting from excess arsenic residue from the treatment process or incomplete fixation and a second peak resulting from the natural aging of wood. In the SPLP, arsenic leaching from weathered samples M (10 300 mg/kg) > N (2700 mg/kg) > Q (2500 mg/kg) > O (2300 mg/kg) > P (850 mg/kg). However, samples R and S, with similar arsenic loading (1500 and 1400 mg/kg, respectively) leached about the same amount of arsenic as samples N (2700 mg/kg) and Q (2500 mg/kg), whose arsenic loading was twice that of R and S, implying higher arsenic losses from lower retention wood. Similar results were also noted from the rainwater test.

The type of leaching solvent also played a role in arsenic leaching (Table 3). For instance, the amount of arsenic leaching from sample M decreased from 12 mg/L (rainwater) to 10 mg/L (SPLP) to 8 mg/L (TCLP) and then to 5 mg/L (deionized water). Additionally, weathered samples N, Q, and R with similar retentions leached almost 2 times more arsenic under the SPLP than during the rainwater test, implying that the SPLP may be a more aggressive solution. When new wood samples J (46.0 kg/m³), L (27.5 kg/m³), and K (20.4 kg/m³) were leached with seawater, regardless of the differences in retention, the total arsenic concentration leached was relatively constant (ranging from 1.2 to 1.7 mg/L); whereas, for the SPLP, rainwater, TCLP, and deionized water tests, it ranged from 4 to 9 mg/L (Table 3). The pH of the seawater was approximately 8.0; whereas, the pH of the other leaching solvents ranged between 4.0 and 6.0. Other researchers studying the leaching of CCA metals in seawater have suggested that the higher pH of seawater may be a significant factor when studying arsenic leaching from CCA-treated wood (25). Results from the pH experiment in this study indicate that arsenic leaching from new wood decreases from pH 4.0 to a low at pH 8.0 before increasing again after pH 8 (Figure 1). In addition, since salinity (26 ppt of seawater) is the most distinguishing feature between freshwater and seawater, few studies examining the leaching effects of CCA-treated wood with seawater have suggested that some components of seawater possess the capability to alter the leaching rate of the CCA metals. Of the three CCA metals, arsenic has been observed to leach less in seawater than deionized water (25) and distilled water (29). Moreover, when CCA-treated wood was subjected to seawater of varying salinities (30) and solutions of different amounts of sodium chloride concentrations (31), fluctuations in the leaching rate of the three CCA metals were observed. It is therefore believed that the presence of dissolved ions, including species of sulfur, magnesium, calcium, and other elements, could play a role in the immobilization of soluble arsenic in seawater (32).

As a benchmark, the arsenic concentrations were compared to Florida's risk-based groundwater cleanup target level (GWCTL) of 0.05 mg/L. Regulatory agencies often compare the results of leaching tests directly to groundwater standards or target levels when assessing the potential for a waste or soil to contaminate groundwater. In this case, SPLP results are most commonly used. All CCA-treated wood samples tested in this study surpassed the 0.05 mg/L GWCTL. This has also been observed previously (11). In addition, the TCLP arsenic concentrations in many cases exceeded or were close to the 5 mg/L toxicity characteristic (TC) regulatory limit for arsenic. As described in previous work examining the leaching of CCA-treated wood using the TCLP (11), exceeding the 5 mg/L TC limit implies that CCA-treated wood leaches enough arsenic in many cases that it would frequently have to be managed as hazardous waste. Discarded CCA-treated wood is, however, excluded at the Federal level from being classified as a hazardous waste; thus, this material is often disposed in nonhazardous landfills. The relatively high leachability of arsenic raises concerns over potential impacts on ground-water at unlined landfills and leachate quality at lined landfills, especially given the large quantities of CCA-treated wood that have been projected to come out of service (4).

Arsenic Leaching from CCA-Treated Wood Ash

Some of the unburned treated wood samples (A, B, G, J, M, T, and V) were ashed and subjected to the TCLP and SPLP tests. The arsenic concentration leaching from the untreated sample A averaged 0.05 mg/L for both SPLP and TCLP. The total arsenic concentrations for the new wood samples B, G, and J and the weathered wood sample M ranged between 100 and 600 mg/L for both tests (Figure 6); whereas, for the unburned counterparts, it was no greater than 10 mg/L (Table 3). Arsenic leaching for the mulch ash samples T and V was greater under the TCLP than the SPLP tests and greater than the unburned counterparts. During incineration, metals are concentrated within the ash and the particle size decreased thus facilitating greater leaching of the metals. Leaching from generated CCA-treated wood ash can therefore result in large amounts of arsenic being leached once the residual ash is landfilled or land applied.

For the TCLP, incineration proved to be an enhancement factor for arsenic leaching, where arsenic concentrations were 7 times greater than the unburned T and V samples. The leachate from the ash control (A, untreated wood) showed similar arsenic concentrations (0.02 for the SPLP and 0.07 mg/L for the TCLP) to that of its unburned counterpart (0.03 mg/L for SPLP and 0.02 mg/L for TCLP) (Table 3). Whereas, the arsenic in the ash leachate of samples B, G, J, and M showed concentrations almost 40–100 times greater under the SPLP and 30–60 times greater under the TCLP than the unburned counterpart.

Speciation analysis again showed inorganic As(III) and As(V) as the major arsenic species. The ratio of inorganic As(III) to As(V) for the ash samples from new wood (B, G, and J) showed that there was more inorganic As(III) leaching from the ash samples when compared to the unburned samples. The greater concentrations of inorganic As(III) in the ash can be attributed to the transformation of inorganic As(V) to As(III) during the incineration process. Although one would expect the oxidation of arsenic during incineration, the opposite has been observed in this study and in others. Helsen and Van den Bulck (33) note that inorganic As(V) can be reduced to inorganic As(III) under low oxygen pyrolysis and that this reduction may be facilitated by the organic compounds contained within the wood matrix. The conversion toward As(III) was not observed for the weathered wood ash sample M, which was composed of 100% CCA-treated wood and which had a relatively high proportion of As(III) prior to incineration. In this case, the ratio of As(III) to As(V) in the ash was lower than for the unburned wood, suggesting that some of the As(III) in sample M was oxidized to As(V) during incineration. Apparently species conversion during burning is dependent upon the age of the wood or the initial distribution of arsenic species prior to burning.

All ash samples tested exceeded Florida's GWCTL (0.05 mg/L) and TCLP regulatory limit (5 mg/L) for arsenic. Unlike unburned CCA-treated wood, CCA-treated wood ash is not excluded from the definition of hazardous waste, and thus ash that exceeds the TC limit of 5 mg/L will be much more expensive to manage. As discussed in Solo-Gabriele et al. (12), ash from the combustion of CCA-treated wood alone should in nearly all cases be a TC hazardous waste because of arsenic (and in some cases chromium). The results also show that the ash from C&D debris-derived wood fuel may also end up being a TC hazardous waste because of the presence of CCA-treated wood. The speciation work reported here demonstrates that one possible reason the leaching of arsenic from the ash increased is due to the higher relative levels of inorganic As(III) in the ash as compared to the original wood. Inorganic As(III) is more mobile than As(V) and thus more likely to leach from the ash. Caution should therefore be applied when disposing of the treated wood residual ash, and efforts to remove this material from the waste should be maximized wherever possible.

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FIGURE 1.

As(V) concentrations leached from new CCA-treated wood subjected to different pH values. Samples extracted in duplicates. Error bars correspond to the standard deviation between both duplicates.

FIGURE 2.

As(III) and As(V) concentrations leached from weathered CCA-treated wood subjected to different pH values. Samples extracted in duplicates. Error bars correspond to the standard deviation between both duplicates.

FIGURE 3.

Arsenic species concentrations from new and weathered CCA-treated wood subjected to the SPLP test. Retentions are in decreasing order for new wood and weathered wood samples. Samples extracted in duplicates. Error bars correspond to the standard deviation between both duplicates.

FIGURE 4. Total arsenic concentrations from new CCA-treated wood subjected to the SPLP, rainwater, TCLP, deionized water, and seawater tests.

FIGURE 5. Total arsenic concentrations from weathered CCA-treated wood subjected to the SPLP, rainwater, TCLP, deionized water, and seawater tests.

FIGURE 6.

Arsenic species concentrations leaching from the ash samples subjected to the TCLP and SPLP tests. Sample A is untreated.

TABLE 1

Measured Retention Values for New and Weathered CCA-Treated Wood

wood sample	“rated” retention (kg/m ³)	“measured” retention (kg/m ³)		avg As concn for full cross- section (mg/kg)
		outer 1.52 cm	full cross- section	
pH Experiment				
pH-N (new)	6.4	5.1 ^a	3.1 ^b	1 300
pH-W (weathered)		6.6 ^a	4.9 ^b	2 100
Other Solvents				
new wood				
A			<0.02 ^b	<5
B	4.0	5.4 ^c	4.1 ^a	1 800
C	4.0	6.0 ^a	5.6 ^a	2 400
D	4.0	6.2 ^a	5.9 ^a	2 500
E	6.4	4.0 ^a	3.9 ^a	1 700
F	6.4	3.7 ^a	3.6 ^a	1 600
G	9.6	14.7 ^c	13.0 ^a	5 600
H	9.6	24.7 ^a	24.6 ^a	10 600
I	9.6	9.2 ^a	9.1 ^a	4 000
J	40.0	54.8 ^c	46.0 ^a	19 800
K	40.0	23.1 ^a	20.4 ^a	8 700
L	40.0	28.4 ^a	27.5 ^a	11 800
weathered wood				
M		14.3 ^c	24.1 ^a	10 300
N		13.3 ^c	6.3 ^a	2 700
O		9.7 ^c	5.3 ^a	2 300
P		3.9 ^c	2.0 ^a	800
Q		8.3 ^c	5.8 ^a	2 500
R			3.5 ^a	1 500
S			3.2 ^a	1 400
T			1.4 ^a	600
U			1.4 ^a	600
V			1.9 ^a	800
new wood ash				
A				11 ^b
B				12 000 ^b
G				30 400 ^b
J				90 400 ^b
weathered wood ash				
M				48 200 ^b
T				2 000 ^b
V				1 600 ^b

^a AA, atomic absorption.^b ICP-AES, inductively coupled plasma-atomic emission spectroscopy.^c XRF, X-ray fluorescence.

TABLE 2

Sample ID for Wood Sample in Table 1

sample id	notes
A, B, G, J	new wood: sample A untreated new wood; samples B, G, and J new wood treated with CCA; all samples purchased in 1998 from a home improvement store and remained in storage until the leaching experiment was carried out August 2001
C, D, E, F, H, I, K, L	new wood: all samples CCA treated and purchased in 2002 from a home improvement store; leaching experiment carried out between September and November 2002
M	weathered wood: 15-yr-old sample from a utility pole from a pole barn owned by a utility company in West Palm Beach, FL; sample obtained in 1998 and kept in storage; leaching experiment carried out in August 2001; estimated age of wood at time of experiment was 18 yr old
N, O, P, Q, R, S	weathered wood: samples N, O, P, and Q originated from a county park and were collected from a public works department; sample R originated near an interstate highway; sample S was a demolished fence; age and storage time of these samples prior to the leaching tests was unknown; leaching experiment carried out in 2002
T, U, V	weathered wood mixture: mulch obtained from three separate C&D recycling facilities in 1998 and consisted of a mixture of untreated and CCA-treated wood waste of varying retention levels; CCA-treated portion was very low; samples remained in storage until leaching experiment in August 2001; age of these samples unknown

TABLE 3

Arsenic Concentrations from Solvent-Extraction Tests^a

sample	SPLP (mg/L)			rainwater (mg/L)			TCLP (mg/L)			DI water (mg/L)			seawater (mg/L)		
	avg As(III)	avg As(V)	total	avg As(III)	avg As(V)	total	avg As(III)	avg As(V)	total	avg As(III)	avg As(V)	total	avg As(III)	avg As(V)	total
A	bdl	0.03	0.03	bdl	0.01	0.01	bdl	0.02	0.02	bdl	0.01	0.02	bdl	bdl	bdl
B	0.37	3.32	3.69	0.48	4.65	5.13	0.84	3.58	4.42	na	2.29	2.54	na	na	na
C	0.02	3.10	3.12	na	na	na	na	na	na	na	na	na	na	na	na
D	0.77	3.05	3.82	na	na	na	na	na	na	na	na	na	na	na	na
E	0.06	4.32	4.37	na	na	na	na	na	na	na	na	na	na	na	na
F	0.02	4.01	4.03	na	na	na	na	na	na	na	na	na	na	na	na
G	0.45	6.52	6.75	0.06	9.02	9.08	0.23	5.27	5.38	0.04	4.24	4.28	na	na	na
H	0.03	3.30	3.33	na	na	na	na	na	na	na	na	na	na	na	na
I	bdl	3.39	3.39	na	na	na	na	na	na	na	na	bdl	na	na	na
J	bdl	5.73	5.73	0.03	4.49	4.52	0.06	8.97	9.02	0.02	3.61	3.89	nd	1.70	1.70
K	0.07	4.67	4.74	na	na	na	na	na	na	na	na	na	0.26	1.06	1.32
L	0.06	2.99	3.05	na	na	na	na	na	na	na	na	na	0.20	0.99	1.19
A	bdl	0.02	0.02	na	na	na	bdl	0.08	0.07	na	na	na	na	na	na
B	56.0	56.2	112.2	na	na	na	0.08	126.2	126.3	na	na	na	na	na	na
G	160.7	179.5	340.1	na	na	na	22.45	167.2	189.6	na	na	na	na	na	na
J	227.0	324.5	551.4	na	na	na	117	240.2	357.1	na	na	na	na	na	na
M	3.48	6.50	9.98	2.52	9.74	12.25	3.46	4.82	8.28	0.85	4.24	5.08	na	na	na
N	2.29	4.49	6.77	2.56	3.45	6.01	na	na	na	na	na	na	na	na	na
O	0.30	3.63	3.93	0.67	3.60	4.26	na	na	na	na	na	na	na	na	na
P	0.08	0.71	0.78	0.27	0.48	0.74	na	na	na	na	na	na	na	na	na
Q	1.50	5.13	6.63	0.35	2.78	3.13	na	na	na	na	na	na	na	na	na
R	0.64	6.80	7.44	0.63	3.23	3.86	na	na	na	na	na	na	na	na	na
S	0.16	6.43	6.58	0.19	3.26	3.45	na	na	na	na	na	na	na	na	na
T	0.16	0.30	0.46	0.004	0.68	0.72	0.18	1.10	1.27	0.01	0.17	0.20	na	na	na
U	na	na	na	0.31	0.03	0.40	na	na	na	0.09	0.06	0.17	na	na	na
V	bdl	0.03	0.03	na	na	na	bdl	0.18	0.18	na	na	na	na	na	na
M	2.73	125.2	128.0	na	na	na	Weathered Wood Ash	212.9	218.6	0.85	4.24	5.09	na	na	na
T	bdl	0.30	0.30	na	na	na	0.003	7.46	7.46	na	na	na	na	na	na
V	bdl	2.07	2.07	na	na	na	0.01	7.94	7.94	na	na	na	na	na	na

^a bdl, below 0.002 mg/L detection limit; na, not analyzed.