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Leaching of Arsenic, Chromium, and Copper in a Contaminated Soil at a Wood Preserving Site

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For over 50 years in the U.S., wood products have been treated with many types of chemicals (organic and inorganic) to prevent bacterial, insect and fungal attack. These wood products are extensively used to build structures such as decks, fences, poles, pilings, playgrounds, and picnic tables. Wood preserved with chromated copper arsenate (CCA), the most commonly used wood preservative, represents approximately 75 % of the U.S. treated wood market by volume. In 1997, approximately 65,000 metric tons of CCA-solution were utilized in the U.S. to produce 1.27 million cubic meters of treated wood (AWPI, 1996). The copper in the wood serves as the fungicide, while the arsenic protects against insects. The chromium is used to assist fixation of the copper and arsenic into the wood. The metals in CCA-solution are introduced into the pore space of the wood under high pressure. Soil contamination as a result of concentrated CCA-solution has occurred near wood preserving facilities due to accidental spills, leakage, or dripping from newly made wood (Lund & Fobian, 1991; Woodward-Clyde, 1992; Anderson et al., 1996; Allinson et al., 2000). Because of the high concentrations of metals in the CCA-solution, relatively small leaks or spills may result in high concentrations of the metals in soil that are potentially harmful to human health and the environment.

When soil is contaminated with high levels of metals, an investigation to determine the risk posed by the contamination may be necessary (e.g., the nature and extent of contamination, the identification of hazards and routes of exposure, and the evaluation of the risks to the surrounding environment). During the risk assessment, three different routes of risk exposure are typically considered: direct human exposure (ingestion, inhalation, and dermal absorption), leaching to groundwater, and ecological risk. If direct human contact is possible, the total recoverable concentration of metals (mg/kg) is compared to soil screening levels (SSLs). The total recoverable concentration is the amount that is extracted in an aggressive acid digestion. The SSLs are risk-based concentrations derived from standardized equations that combine exposure assumptions with toxicological information (US EPA, 1996b). The evaluation of the risk of metal leaching to groundwater is somewhat more complicated. The amount of metal that leaches from the soil is typically much less than the total recoverable amount. Leaching

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risk may be evaluated either by theoretical predictions of the total fraction of the metal concentration expected to leach, or by conducting leaching tests. The commonly employed leaching tests used in the U.S. include the toxicity characteristic leaching procedure (TCLP) and the synthetic precipitation leaching procedure (SPLP) (US EPA SW-846 method 1311 and 1312, respectively, US EPA, 1996c). While the TCLP was designed to simulate the leaching of metals (and organics) from wastes disposed in a municipal solid waste landfill, the SPLP simulates the leaching of chemicals under conditions of infiltrating acidic rainfall. The data obtained when applying both tests may be used by environmental regulators and generators of contaminated materials to determine possible disposal or reuse options (e.g., land application). Although leaching tests are routinely used in risk assessments and for regulatory purposes, many parameters that affect the release of metals from contaminated soils are not well addressed in the current leaching tests. These parameters include pH, leaching time, redox, solid to liquid ratio, particle size, mode of contact with water/air, and reaction kinetics. Additional leaching tests can provide information that help better characterize risks from contaminated soil.

The objectives of this work were to measure the leaching behavior of arsenic, chromium, and copper from CCA-contaminated soil at a wood preserving site, by means of the two common batch leaching tests (toxicity characteristic leaching procedure and synthetic precipitation leaching procedure), and to evaluate some of the parameters affecting the release of the metals. The parameters examined during the leaching tests included pH, leaching time, and liquid/solid ratio. Results from the leaching tests and total recoverable metal tests were compared to regulatory risk levels to assess whether the CCA-contaminated soil presents a risk to human health. The leaching tests were also used to assess potential ecological risk by conducting a series of aquatic toxicity tests on the TCLP and SPLP leachates. It is important to note that this study was not designed to represent a complete risk assessment; the entire extent of site contamination was not determined. Rather, this study demonstrates the potential utility of additional leaching tests when conducting risk assessments.

MATERIALS AND METHODS

CCA-contaminated soil was collected from an abandoned CCA wood preservation site located in Archer (40 miles west of Gainesville), Alachua County, Florida. In the 1950's, this site was operated to treat wood with an aqueous solution of arsenic pentoxide, copper sulfate, and sodium or potassium chromate (Woodward-Clyde, 1992). During the operation, the site was heavily contaminated with arsenic, chromium and copper. Soil samples were collected from surface soil to a depth of approximately 15 cm at five different sampling locations. The samples were placed in five 19-liter plastic containers, transported and stored in the Solid and Hazardous Waste Laboratory at the University of Florida until the experiment began. Approximately 3 kg of soil from each container were collected and thoroughly mixed in a 19-liter plastic container to obtain a composite sample before the experiment.

Several physical and chemical parameters were measured in this soil in parallel with the leaching experiments. Samples of the contaminated soil (approx. 20 g) were dried at 105 °C for overnight, and the moisture content was calculated from the weight loss. The pH and oxidation reduction potential (ORP) were determined in a suspension of 20 g of soil in 10 ml of deionized water (EPA SW 846-9045C and Standard Method 2580, respectively). A combination platinum electrode was used for the ORP measurement (mV). The diameter of soil particles was less than 0.7 mm (greater than 90%), based on a particle size distribution analysis. The Walkley-Black method was used to determine the total organic carbon (TOC) in the contaminated soils. All measurements were carried out in triplicate. The results are summarized in Table 1. Total recoverable metal concentrations were measured using a hot plate digestion following the U.S. EPA Method SW-846 3050B (US EPA, 1996c). After digestion, the concentrations of metals (As, Cr, and Cu) were measured by a Perkin-Elmer Model 5100 atomic absorption graphite furnace spectrophotometer. Samples with high concentrations of metal were diluted to fit within the linear region of the calibration curve.

Table 1. Physical and chemical properties of chromated copper arsenate-contaminated soil.

Parameters	Physical and chemical properties
pH	8.52
Eh (mV)	552
TOC	0.48 %
Moisture Content	22 %

The TCLP and SPLP tests have been used as standardized batch leaching tests in the United States (US EPA, 1996c). The leaching procedures are very similar with the exception of the leaching fluid. For each test, a 100-gram sample was placed in a 2.2-liter polyethylene container. Two liters of extraction fluid were then added to the container. The extraction fluid of TCLP depends on the alkalinity of the waste material. Very alkaline waste materials are leached with a fixed amount of glacial acetic acid without buffering system (pH 2.88 ± 0.05), while other waste materials are leached with glacial acetic acid buffered at pH 4.93 ± 0.05 with 1-N sodium hydroxide. Since contaminated soil samples in this study were only slightly alkaline, the buffered extraction fluid (pH 4.93 ± 0.05) was used. For the SPLP test, an extraction fluid was prepared by adding a 60/40 weight percent mixture of sulfuric and nitric acids to deionized water to simulate mildly acidic rain (pH 4.20 ± 0.05). In each test, the container was placed in a rotary extraction vessel (Analytical Testing Inc.) and leached for 18 ± 2 hours at 30 rpm. After rotation, the mixture was filtered using a pressurized filtration apparatus with a 0.7-μm borosilicate microfiber filter (Environmental Express). The filtered leachates were transferred to a 250-ml plastic bottle (Nalgene HDPE bottle), acidified with nitric acid to a pH < 2, and stored prior to digestion. A liquid extract was digested following the US EPA SW-846 Method 3020A before atomic absorption analysis.

The SPLP leachates were also evaluated using a battery of aquatic toxicity assays. The assays used included Microtox™ (*Vibrio fischeri*, Beckman Instruments, 1982), MetPLATE™ (*Escherichia coli*, Bitton et al., 1994), and an invertebrate assay (*Ceriodaphnia dubia*, US EPA, 1993). Detailed experimental procedures of each test can be found in the references above. Microtox™, MetPLATE™, and the *C. dubia* assay measure the acute toxicity of the leachates. MetPLATE™ is a rapid bacterial assay that is specific for the detection of heavy metal toxicity (Bitton et al., 1994).

Other leaching tests were also carried out to examine the effect of pH, leaching time, and liquid to solid (L/S) ratio on metal leaching. Only chemical concentrations were measured during these leaching tests (i.e., no toxicity assays were performed). To determine the effect of pH on metal leaching from the contaminated soil, a pH static test was conducted at different pH values (ranged from 2 to 13). The static test was carried out at a L/S ratio of 20 with a leaching duration of 18 hrs. A 10-g sample was placed in a 250-ml plastic container (Nalgene HDPE bottle) with 150 ml deionized water. The amount of deionized water initially added was adjusted in order to achieve an approximate L/S = 20 after addition of diluted nitric acid or sodium hydroxide needed at the specific pH. The mixing was carried out the same as the standardized leaching tests described above. The pH was periodically monitored and adjusted to the appropriate pH value with either 0.1 N - 1 N nitric acid or 0.1 N – 1 N sodium hydroxide during the mixing. After mixing, the sample was filtered through a Gelman glass fiber filter (pore size 1.0 µm), digested and analyzed for arsenic, chromium, and copper.

The L/S ratio is defined as the amount of a leaching solution in contact with the amount of waste tested (e.g., liter/kg). The following L/S ratios were evaluated using the SPLP: 200:1, 100:1, 40:1, 20:1, 10:1, and 5:1. The volume of the SPLP leaching solution was two liters for the entire L/S ratio leaching tests. Only the amount of the contaminated soil was varied to achieve the desired L/S ratios. For example, for L/S 100:1, 20 g of contaminated soil were added to two liters of the SPLP leaching solution in an extraction vessel. The remaining procedures were the same as the SPLP test.

The amount of time during which a leaching solution is in contact with a soil may influence the quantity of contaminant leached unless equilibrium conditions are established. The leaching process was performed on 10 g of the soil in a 250-ml plastic bottle. Each sample was treated with 200 ml of SPLP leaching solution (i.e. L/S = 20). The leaching test was performed by rotating the mixture for different periods of time (30 min., 1 hr., 2 hr., 4 hr., ..., 16 days, and 30 days). After rotation, the remaining procedures were the same as the pH static test.

To implement quality assurance practices during the laboratory analysis, laboratory blanks were performed as appropriate. Metals were not detected above the detection limits for any of the blanks (10 µg/L). Triplicate samples were run for all samples with an exception of the time study leaching samples (only duplicate analysis conducted). All reagents used were of analytical grade.

RESULTS AND DISCUSSION

To assess the direct exposure risk of the contaminated soils, the total recoverable metal concentration was measured in mg/kg (Table 2). The highest heavy metal content of the contaminated soil was arsenic (100.2 mg/kg) followed by chromium (75.2 mg/kg). A relatively small amount of copper (10.4 mg/kg) was present in the soil. The heavy metal concentrations in the soil samples were compared to risk-based exposure standards (e.g., US EPA Soil Screening Levels, US EPA, 1996b) to determine what reuse or disposal options are appropriate. Metal concentrations in the soil samples were also compared to Florida's Soil Cleanup Target Levels (SCTLs) (FAC, 1999). It should be noted that the direct exposure concentrations such as Soil Screening Levels and Soil Cleanup Target Levels are not regulations, but goals that may be used for several purposes. Table 2 presents the results of the total metal concentrations along with the risk-based levels. Among the three metal evaluated in this study, the average total concentration of arsenic exceeded the soil screening levels (both Florida SCTLs and U.S. SSLs). For chromium and copper, the average concentrations in the soil were less than the risk-based guidelines. The arsenic and chromium screening levels for leaching to groundwater (based on the groundwater standards of arsenic and chromium) are 29 mg/kg and 38 mg/kg, respectively. The mean arsenic and chromium concentrations were greater than the Florida SCTLs for leaching. Thus, groundwater contamination may be another potential problem due to metal leaching to groundwater other than direct exposure of arsenic.

Table 2. Comparison of total metal concentrations in chromated copper arsenate-contaminated soil with soil screening levels (dry weight) in mg/kg.

Element	Total concentration	U. S. SSLs [a]	Direct exposure [b]			Detection limit
			Residential	Industrial	Leaching [b]	
As	100.2 (14.2)[c]	0.4	0.8	3.7	29	0.25
Cr	75.2 (10.4)	390	210	420	38	0.5
Cu	10.4 (1.8)	--	110	39,000	40	0.5

[a] US EPA, 1996b, [b] Florida SCTLs, [c] Standard deviation

Table 3 presents the results of the toxicity characteristic leaching procedure (TCLP) and synthetic precipitation leaching procedure (SPLP) tests on the soil. The concentrations of arsenic and chromium in the TCLP leachate extracted from the contaminated soil did not exceed the TCLP limit of 5 mg/L. Therefore, this soil would not be considered a hazardous waste. The arsenic concentration in the SPLP leachate (0.25 mg/L) exceeded five times the drinking water standard (or Florida Groundwater Cleanup Target Level) for arsenic (0.05 mg/L). Therefore, the soil would still be viewed as a possible risk regarding groundwater contamination.

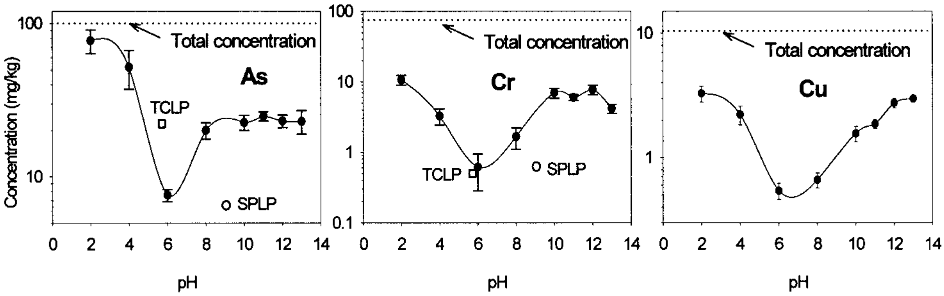

Figure 1. Metal leaching from chromated copper arsenate -contaminated soil as a function of pH.

Table 3. Results of leaching tests for chromated copper arsenate-contaminated soil (mg/L).

Element	TCLP	SPLP	TCLP limits [a]	FGWCTL[b]	Detection limit
As	0.88 (0.1) [c]	0.25 (0.04)	5.0	0.05	0.005
Cr	0.02 (0.002)	0.02 (0.01)	5.0	0.1	0.01
Cu	< 0.01	< 0.01	-	1.0	0.01

[a] US EPA, 1996a, [b] Florida groundwater cleanup target levels (FAC, 1999), [c] Standard deviation

The average concentration of arsenic leached from TCLP was greater than SPLP. The higher arsenic concentrations in TCLP can be explained by the ability of acetate ion to complex metals. The TCLP leaching fluid contained the monodentate ligand acetate, while the SPLP extraction fluid contained nitrate and sulfate ions. Another probable reason is the effect of pH on arsenic leaching. Further detail can be found in the next section. For both leaching tests chromium and copper leached into the solution at the relatively low levels (0.02 mg/L) or below the detection limits. This suggests that most chromium and copper were bound to the soil and would not be expected to leach readily. For the TCLP leaching test, the percent leaching of chromium and copper was also less than 1 %, but a higher leaching percentage of arsenic (22.2 %) was observed. The percentage of metal extracted from the soil averaged less than 1 % of chromium and copper, and 6.5 % of arsenic using the SPLP extraction procedure. The percent leaching was calculated by leaching results divided by total metal concentrations.

One of the significant factors influencing the release of metals from soil is pH. It has been widely known that pH is a crucial parameter in determining the solubility of metal in soil (van der Sloot et al., 1997). In Figure 1, the results of the pH static tests are presented for arsenic, chromium, and copper. All three metals showed strong pH dependence of leaching. In general, the metals exhibited a marked increase in leachability at both low and high pH values, and at neutral pH values, relatively low leachability of the metals was observed.

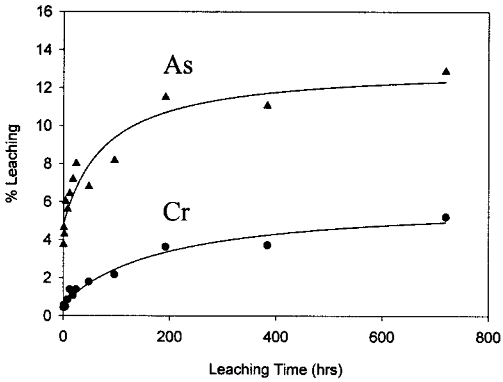

Figure 2. Arsenic and chromium leaching from chromated copper arsenate-contaminated soil as a function of leaching time

Similar results were found in other studies (van de Sloot et al., 1997; Fytianos et al., 1998). At pH 2, the arsenic concentration was close to total concentration of arsenic present in the chromated copper arsenate-contaminated soil. The increase in the leachability of the metals at lower pH values may be attributed to an increase in the metal solubility under these conditions. The results of the pH static tests were compared to TCLP and SPLP results at final pH values (Figure 1). It was observed that arsenic leached more in TCLP than in the pH static test. One explanation for this is that the higher arsenic leaching in TCLP was caused by metal complexation with acetate ion rather than simply by pH. However, the arsenic concentration of SPLP was much less than that of the pH static test because of two probable reasons. One is that, unlike TCLP, no metal complexation is involved in the SPLP. Another reason is that the pH might have affected both leaching tests differently; the pH of the SPLP solution started at 4.20 ± 0.05, as described previously, and ended up with pH 9.06 after 18 hr mixing, while the initial pH of the pH static test was maintained throughout the test. For chromium leaching, the chromium concentration of the TCLP is very close to that of the pH static test, while the SPLP chromium is much lower than the pH static chromium concentration. It appears to be that chromium leaching is strongly dependent upon the pH. The lower SPLP chromium concentration can be explained by the same rationale described above.

Figure 2 presents the results of the experiment conducted to evaluate the impact of leaching time. The percent of the total arsenic and chromium concentrations that leached into solution was plotted over time for a period of up to 720 hrs (30 days). In agreement with previous results, arsenic leached a greater amount than chromium. The arsenic equilibrium time appears to be faster than the chromium equilibrium. This result indicates that a considerable amount of arsenic could be mobilized in a relatively short time and made available to the surrounding environment. The 18-hr leaching results were similar to those measured using

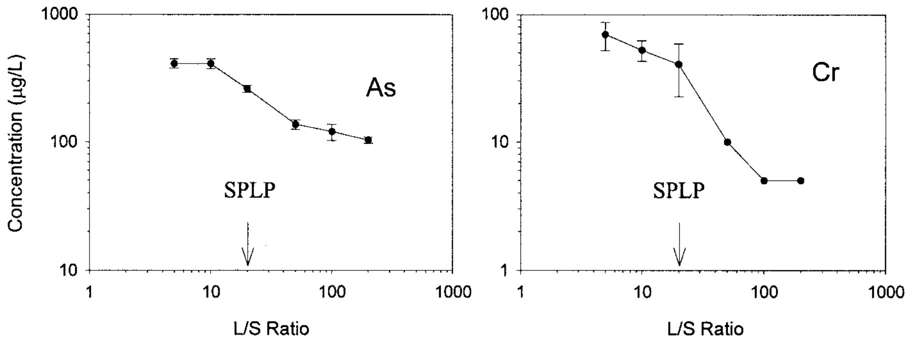

Figure 3. Arsenic and chromium leaching from chromated copper arsenate - contaminated soil as a function of L/S ratio

the SPLP, falling within one standard deviation (288 μg/L compared 250 μg/L for arsenic, and 35 μg/L compared with 24 μg/L for chromium). The concentration at 720 hrs was approximately double times greater than the concentration at 18 hrs for arsenic, and approximately five times greater for chromium. From a leaching to groundwater risk assessment perspective, this indicates that for long exposure times, the concentration in the soil water may increase beyond that predicted by the SPLP.

Figure 3 demonstrates the impact of liquid to solid ratio on metal leaching. The arsenic and chromium concentrations are greater at lower L/S and decrease as the L/S increases. As noted in Figure 3, the synthetic precipitation leaching procedure (SPLP) employs a 20:1 L/S. The typical practice when interpreting SPLP results as part of a risk assessment is to compare the leachate concentration of SPLP directly to appropriate groundwater risk-based concentrations (e.g., Florida groundwater cleanup target levels). This approach does not take into account any dilution in the underlying groundwater. The leaching SCTL presented earlier includes a default dilution factor of 20. Since the SPLP is conducted under much more dilute concentrations than that found in soil water, many risk assessors assume that dilution is already accounted for. Figure 3 shows, however, that the arsenic concentration at a 20:1 L/S ratio of the SPLP is not 20 times less than arsenic concentrations measured lower L/S ratios (more representative of soil water). A more appropriate approach would be to use the arsenic concentration at the low L/S and apply an appropriate dilution factor. For arsenic, if a dilution factor of 20 was applied to the average concentration at a 5:1 L/S (410 μg/L), the diluted concentration would be 20.5 μg/L. This concentration would be less than the current groundwater cleanup target level for Florida (50 μg/L). Copper did not leach from the soil at L/S greater than 5.

The invertebrate assay and the Microtox™ test both revealed slight toxicity in the SPLP leachate, while no toxicity was found with the MetPLATE™ test. There was less than 20% mortality in the undiluted SPLP leachate when the invertebrate assay was used. The inhibition measured by the Microtox™ assay was slightly less than 50% inhibition (48.3% ± 4.9) for the SPLP leachate. According to the levels of arsenic, chromium, and copper in CCA-contaminated soil samples from various leaching tests, groundwater contamination may be a potential problem as a result of arsenic mobility. The expanded leaching test results presented here could be used with site specific data to provide a more thorough assessment of risk.

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