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Chromium, Copper, and Arsenic Concentrations in Soil Underneath CCA-Treated Wood Structures

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Soils below nine structures (decks and foot bridges) in Florida were examined to evaluate potential impacts from chromated copper arsenate (CCA), a common wood preservative. Eight of the nine structures were confirmed to have been treated with CCA. Soils collected were evaluated for arsenic, chromium, and copper concentrations as well as pH, volatile solids content and particle size distribution. Two types of soil samples were collected: a soil core

and surface soil samples (upper 2.5 cm). One soil core was collected from below each deck and one control core was collected from an area removed from one of the structures. Eight or nine surface soil samples were collected in a grid-like fashion from beneath each structure. Equal numbers of surface control samples were collected from areas away from the structures. Metal concentrations were elevated in both the soil cores and surface samples collected from below the CCA-treated structures. Core samples showed elevated concentrations of metals at depths up to 20 cm. The arithmetic mean concentrations of arsenic, chromium, and copper in the 65 surface soil samples collected from below CCA-treated structures were 28.5 mg/kg, 31.1 mg/kg, and 37.2 mg/kg, respectively, whereas the mean concentrations of arsenic, chromium, and copper in the control samples were 1.34 mg/kg, 8.62 mg/kg, and 6.05 mg/kg, respectively. Arsenic concentrations exceeded Florida's risk-based soil cleanup target level (SCTL) for residential settings in all 65 surface soil samples. The industrial setting SCTL was exceeded in 62 of the 65 samples.

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INTRODUCTION

THE pesticide chromated copper arsenate (CCA) has been the most widely used wood preservative in the United States in recent years (AWPA, 1999; Solo-Gabriele *et al.*, 1998). Applications for CCA include wood products such as utility poles, marine pilings, fences, decks and walkways. Arsenic, chromium, and copper are known environmental toxins, and their presence in CCA-treated wood raises several human safety and environmental concerns. One environmental concern expressed has been the impact on aquatic ecosystems where CCA-treated wood is used (Weis *et al.*, 1995; Weis and Weis, 1999; Brown *et al.*, 2001). Potential pathways of human exposure include direct contact with individuals working with the wood (Decker *et al.*, 2002; Gordon *et al.*, 2002), exposure by those touching the wood during normal use (Galarneau *et al.*, 1990; Wester *et al.*, 1993), and contact with soil or groundwater contaminated by the wood during its normal use (Fields, 2001). The final disposal of CCA-treated wood products may also result in environmental contamination (Tolaymat *et al.*, 2000; Solo-Gabriele *et al.*, 2002). The degree of risk posed by CCA-treated wood products through these various exposure routes is a topic of debate in the scientific and regulatory community, and it is generally acknowledged that additional research is needed to fully understand the true risks. This paper investigates one pathway of potential environmental exposure: contamination of soil as a result of CCA-treated wood structures.

Soil contamination with arsenic, chromium and copper as a result of the wood preservative CCA has been reported at the locations of former and current wood treatment plants, as well as in the proximity of CCA-treated wood structures. The CCA treatment process involves impregnating wood with the CCA preservative solution using pressurized treatment cylinders. Environmental contamination has resulted from spills of the raw chemical, improper disposal of chemical sludges from treatment, and the dripping of preservative from the wood after the treatment process. Several studies have been conducted on soil contamination at these facilities (Anderson *et al.*, 1996; Balasoiiu *et al.*, 2001) and many former and current wood treatment plants have been required to undergo corrective action.

Because of the high concentrations of arsenic, chromium, and copper encountered in CCA preservative solutions, it is not surprising that the improper management of this material often results in contamination at levels that pose a risk to human health and the environment. A fact that is less certain, however, is whether chemicals leached from CCA-treated wood products contaminate soil at concentrations that present a risk. During the CCA treatment process, chemical reactions take place that act to bind the metal compounds to the wood. Wood preservation scientists refer to this process as "fixation," a reaction dominated by the reduction of hexavalent chromium to trivalent chromium (Cooper and Ung, 1992). While the metals are "fixed" to the wood from a treatment efficacy standpoint, the metals do leach over time to the surrounding environment when exposed to water (Cooper, 1991; Lebow, 1996; Hingston *et al.*, 2001). Most CCA-treated wood products are used outdoors. When rainfall comes in contact with treated wood structures that

are located above or in soil (such as a deck or a walkway), some arsenic, chromium and copper will dissolve into the water and travel to the underlying or adjacent soil. The leached metals may then bind to the soil causing an increase in the soil metal concentrations. Arsenic typically poses a greater concern when encountered at elevated levels in the soil (with respect to chromium and copper), as it is harmful at lower concentrations. For example, the generic residential soil cleanup target level (SCTL) for arsenic in Florida is 0.8 mg/kg, compared to 210 mg/kg and 110 mg/kg for chromium and copper, respectively (FAC, 2000). While one might argue whether it is appropriate to compare generic risk levels such as the Florida SCTL to soil underneath a CCA-treated structure, they do provide a benchmark to indicate whether contamination approaches concentrations that might be of concern.

Increased soil arsenic concentrations in the vicinity of CCA-treated structures have been observed in several studies that would raise concern when compared to the Florida SCTL and similar risk-based levels. Stilwell and Gorny (1997) measured soil concentrations under residential decks and found an average arsenic concentration of 76 mg/kg (from 3 to 350 mg/kg). Cooper and Ung (1997) reported soil arsenic concentrations near CCA-treated utility poles at levels as high as 550 mg/kg. Eleven months after the construction of a CCA-treated boardwalk, Lebow *et al.* (2000) found arsenic concentrations in soil underneath the edge of the boardwalk ranging from 5 to 29 mg/kg in the upper 15 cm of soil (compared to background values ranging from 1 to 3 mg/kg). They also observed decreasing arsenic concentrations in deeper soils and soils at distances greater than 15 cm from the structure. Stilwell and Graetz (2001) determined arsenic concentrations in soil immediately adjacent to highway sound barriers to range from 7 to 228 mg/kg, with concentrations dropping dramatically at 80 cm from the barrier.

The research presented in this paper was conducted to assess the degree of soil contamination occurring under typical CCA-structures in Florida. At the time of this study, questions had been raised regarding whether the high soil metal concentrations reported in some of the previous studies were the result of metal leaching from the wood or of poor construction debris management practices (i.e., management of sawdust). Questions were also raised as to how metals would leach from CCA-treated wood structures in a warm and wet environment like Florida. Nine structures (decks and walkways) were examined. Both surface soil samples (upper 2.5 cm) and soil core samples were collected and analyzed for arsenic, chromium and copper. Measured concentrations were then compared to background concentrations at the sites and to Florida's SCTLs. To explore the potential sources of arsenic, chromium and copper in soils underneath CCA-treated structures, a simple mathematical relationship was used to estimate the range of concentration that might occur in the soil based on the fraction of metals leaching from the CCA-treated wood and the depth of soil contamination. Since the time this research was conducted, an agreement was reached between the wood preserving industry and the U.S. EPA that will phase out the use of many, but not all, CCA-treated wood products in the U.S. by the end of 2003 (Federal Register, 2002). CCA-treated wood structures constructed prior to this date will in most cases remain in service

until the structure is replaced and thus continue to pose the potential to contaminate underlying soil.

METHODS

Sampling Sites

Nine structures in Florida were selected as sampling sites. Three structures were chosen from three different geographic areas of the state. Sites A, B, and C were located in Gainesville, in north central Florida. Sites D, E, and F were located in Tallahassee, in northwest Florida. Sites G, H, and I were located in Miami, in south Florida. Structures such as decks, walkways or footbridges were selected. Eight of the nine sites were confirmed treated with CCA and one site (site F) was not treated with CCA. To ensure access to the structures, all of the sites sampled were located in public parks or along public right-of-ways. The soil samples were collected in November and December of 1999. A follow-up visit was made to each site in June and July of 2000 to collect additional control samples and to confirm that the structures were indeed constructed of CCA-treated wood.

Table 1 presents a description of the CCA-treated structures sampled. Construction records and personal interviews with park rangers and superintendents were used to determine the approximate age of each of the structures. CCA treatment was confirmed by applying a chemical stain and by using X-ray fluorescence (XRF) to quantify the retention level of CCA within either wood bores or sawdust samples collected from each structure. Sawdust and wood bores utilized for analysis corresponded to the outer 1.5 cm (0.6 inches) of wood. The stain utilized was PAN indicator which, when applied to the surface of the wood, resulted in a distinctive

TABLE 1
Description of Sample Locations

Site	Description	Structure's age when sampled	Stain results	Retention level (pcf) ¹
A	Boardwalk	14 years	Positive	0.477
B	Pedestrian footbridge along roadway	5 years	Positive	0.755
C	Deck	~15 years	Positive	0.206
D	Footbridge	2 years	Positive	0.247
E	Deck	4 years	Positive	0.412
F	Footbridge	19 years	Negative	0.008
G	Playground	9 years	Positive	0.261
H	Lifeguard station	6 years	Positive	0.206
I	Deck	14 years	Positive	(0.005–0.54)

¹pcf = pounds of CCA per cubic foot of wood.

color change if metals were present (see Blassino *et al.* (2002) for more details concerning this stain). XRF was conducted by an outside laboratory using an ASOMA Model #1503. All sites were confirmed to have been treated with CCA, with the exception of site F.

Sampling Methods

Prior to collection of the surface soil samples, a grid was set up below each of the structures using rope. This provided a uniform distribution of sampling locations below each structure. At each site, eight surface samples were collected, with the exception of site B, where nine surface samples were collected. A detailed description of the sample locations for each site can be found in Townsend *et al.* (2001). The surface samples were collected from the top 2.5 cm (1 inch) of soil. This depth was selected to correspond to the soil that would most likely be encountered by humans. Control samples were collected in the same manner at locations away from the structures. The purpose of the control samples was to determine the naturally occurring concentrations of arsenic, chromium and copper in the soil. Locations at elevations higher than the sampling grid were preferred, at distances ranging from 15 to 30 meters (50 to 100 feet) away.

Soil core samples of approximately 25 cm (10 inches) in depth were also collected at each site to examine the vertical distribution of chromium, copper and arsenic. Each core was collected approximately in the center of the sampling grid. The samples were collected using a 2.8-cm diameter unslotted stainless steel probe fitted with a plastic liner (Forestry Suppliers, Inc., Jackson, MS). A different plastic liner was utilized for each site. After collection, all sample containers were placed in plastic bags and stored in a cooler with ice for transportation to the laboratory.

Analytical Methods

Soil samples were characterized by measuring pH and volatile solids content (standard methods 4500-H and 2540E, APHA, 1995), as well as grain size distribution. Volatile solids content was measured to provide an approximation of the organic matter present in the soil; it was determined as the weight lost from dried soil samples after placement in a muffle furnace at 450°C for 5 hours. The grain size distribution results were used to estimate the gravel, sand, and silt/clay fraction (Das, 1985). Dried soil samples were digested for heavy metal analysis using a Method 3050B (USEPA, 1996a). Method 3050B is an open vessel method requiring the use of acid and oxidizing agents to reflux a sample on a hot plate for a period of 2 to 8 hours. Samples analyzed using a graphite furnace atomic absorption spectrophotometer (AAS) were digested with nitric acid and hydrogen peroxide. Digestions for those samples being analyzed using a flame AAS included the added step of digestion with hydrochloric acid. Analysis of the digestates was

performed using a Perkin Elmer model 5100 AAS. This instrument was equipped with both a flame aspiration system and a graphite furnace with Zeeman background correction. Arsenic concentrations were measured using the graphite furnace technique. The graphite furnace was used to measure copper and chromium for the control samples due to the lower concentrations contained in those samples. The flame-AAS technique was employed for all other measurements of copper and chromium.

RESULTS

Surface Soil Samples

A total of 73 surface soil samples were collected under the nine structures in Gainesville, Miami, and Tallahassee. Out of these, 65 were collected from below structures that were confirmed to be made of CCA-treated wood. The remaining 8 samples were collected from below a structure that did not show a positive measurement for CCA using either the stains or XRF (site F). In addition to the surface samples collected below the decks, a total of 73 control soil samples (65 below CCA-treated decks) were collected. Control samples were located at a distance away from the CCA-treated structures and results from these samples were expected to represent background metals concentrations. Table 2 presents a summary of the results for pH, volatile solids content, and percentages of gravel, sand, and silt/clay. All soils were uniformly graded with a grain sizes distribution corresponding to a medium sandy soil (Das, 1985). The volatile solids content of the surface soil samples varied from 2% to 26%, on average, and the pH varied from 5.4 to 7.7.

A summary of measured arsenic, chromium, and copper concentrations is provided in Tables 3, 4 and 5, respectively. While site F is presented, it is not included

TABLE 2
Physical Parameters of Soils Collected Below Each Deck

Site	Description	Avg. soil pH	Avg. volatile solids (%)	Gravel (%)	Sand (%)	Silt/clay (%)
A	Boardwalk	5.4	26	0.3	99.1	0.7
B	Pedestrian footbridge along roadway	7.7	3.5	4.6	92.9	2.5
C	Deck	7.6	5.0	1.0	97.5	1.6
D	Footbridge	6.1	4.6	3.8	93.0	3.3
E	Deck	6.9	4.4	0.6	97.8	1.6
F	Footbridge	7.5	12	2.2	92.9	4.9
G	Playground	6.4	9.7	0.5	97.4	2.1
H	Lifeguard station	7.6	1.9	0.6	98.1	1.3
I	Deck	7.5	4.4	8.6	87.8	3.6

TABLE 3
Arsenic Concentration (mg/kg) in Surface Soils

Structure	Arsenic concentration (mg/kg)					
	Soil beneath structure				Control soil	
	N	Average	Max.	Min.	N	Average
A	8	41.6	87.9	15.6	8	2.61
B	9	10.7	33.2	4.05	9	0.31
C	8	9.56	18.1	3.54	8	0.58
D	8	17.2	31.0	8.59	8	2.31
E	8	34.0	48.8	5.09	8	1.42
F	8	0.48	0.62	0.25	8	0.47
G	8	33.9	81.2	15.5	8	1.98
H	8	4.30	7.47	1.18	8	1.13
I	8	79.1	217	31.7	8	0.66
All locations ¹	65	28.5	217	1.18	65	1.36

¹Does not include results from site F.

in the statistical analysis of the data. For purposes of statistical analysis, a value of one-half of the detection limit was used for those samples where the concentration was below the detection limit of the analytical instrument. Sample concentrations are reported on a dry weight basis.

TABLE 4
Chromium Concentration (mg/kg) in Surface Soils

Structure	Chromium concentration (mg/kg)					
	Soil beneath structure				Control soil	
	N	Average	Max.	Min.	N	Average
A	8	59.7	113	30.8	8	3.11
B	9	23.4	48.6	10.6	9	7.90
C	8	12.1	28.6	<5.0	8	19.2
D	8	16.4	32.4	6.90	8	8.80
E	8	22.9	44.3	14.3	8	6.98
F	8	<5.0	<5.0	<5.0	8	3.46
G	8	39.5	113	13.8	8	12.7
H	8	4.34	6.85	<5.0	8	6.79
I	8	71.1	198	32.0	8	3.65
All locations ¹	65	31.1	198	<5.0	65	8.62

¹Does not include results from site F.

TABLE 5
Copper Concentration (mg/kg) in Surface Soils

Structure	Copper concentration (mg/kg)					
	Soil beneath structure				Control soil	
	N	Average	Max.	Min.	N	Average
A	8	106	156	53.0	8	6.00
B	9	20.1	37.0	7.50	9	6.73
C	8	13.6	26.0	<5.0	8	4.60
D	8	18.9	34.0	10.0	8	7.30
E	8	21.8	36.0	12.0	8	3.95
F	8	<5.0	<5.0	<5.0	8	2.54
G	8	44.5	128.5	16.5	8	7.92
H	8	6.13	11.0	<5.0	8	7.36
I	8	68.1	216	18.5	8	4.63
All locations ¹	65	37.2	216	<5.0	65	6.07

¹Does not include results from site F.

Arsenic was detected in all 65 of the surface soil samples collected from below CCA-treated structures. The arsenic concentrations of these soils ranged from 1.18 mg/kg (site H) to 217 mg/kg (site I), with an arithmetic mean of 28.5 mg/kg. The mean of the corresponding controls was 1.36 mg/kg. Of the 65 soil samples collected from below confirmed CCA-treated structures, 59 were above the detection limit for chromium. For the samples above the detection limit, the surface soil chromium concentrations ranged from a minimum of <5.0 mg/kg (site H) to a maximum of 198 mg/kg (site I), with a mean of 31.1 mg/kg. The mean of the corresponding controls was 8.62 mg/kg. Of the 65 soil samples collected from below confirmed CCA-treated structures, 60 were above the detection limit for copper. For the samples above the detection limit, the surface soil copper concentrations ranged from a minimum of <5 mg/kg (site B) to a maximum of 216 mg/kg (site I), with a mean of 37.2 mg/kg. The mean of the corresponding controls was 6.07 mg/kg.

The mean arsenic concentrations for soil underneath the CCA-treated structures were statistically greater than those of the control samples (95% confidence) for all sites except Site F (the one not treated with CCA). The mean chromium concentrations for soils under the structures were greater than that of the control samples for six of the eight CCA-treated structures, with three of the eight being statistically greater (A, E, I). The mean copper concentrations for soil under the structures were greater than those of the control samples for all eight CCA-treated structures, and were statistically different for 6 sites (A, B, C, E, G, I).

Soil Cores

Soil cores were collected and analyzed from underneath all of the structures. One control soil core sample was collected at site B. Figure 1 presents concentration profiles as a function of depth for the soil cores collected at each site. In general, the highest soil metal concentrations were encountered in the upper soils layers. This observation was more pronounced for arsenic and copper. At a number of sites (B, C, E, G) large chromium concentrations continued to be encountered at deeper locations, possibly a result of the greater natural background concentration of chromium. The greater background concentration of chromium is also illustrated in the soil core profile of site F (the site not treated with CCA).

DISCUSSION

Comparison to Background Levels

The observation that arsenic was found to be statistically different more often than copper and chromium is likely the result of the lower natural occurring background concentrations of arsenic. In a recent study that involved the analysis of 448 Florida surface soils, Chen *et al.* (1999) reported the geometric means (and ranges) of arsenic, chromium, and copper to be 0.42 mg/kg (0.01 to 50.6), 15.9 mg/kg (0.02 to 447) and 6.10 mg/kg (0.1 to 318), respectively. The addition of arsenic to soil from CCA-treated wood was greater relative to the initial total mass of soil arsenic when compared to chromium and copper. A second factor that may account for arsenic being greater than background more frequently is that arsenic often leaches more from CCA-treated wood (especially with respect to chromium). This possibility will be discussed further in a later section (see *Relative Contribution of Metals*).

Intra- and Inter-Site Variability

Surface soil metal concentrations varied from site to site and among the samples at each site. To better illustrate this variability, a histogram showing the distribution of measured metals concentrations for all surface soil samples except those collected at site F is shown in Figure 2. As can be seen from this figure, the range and distribution of metals concentrations varied considerably from site to site. Several factors may contribute to this variability. Factors include soil type, rate of rainfall, age of structure, construction practices, initial treatment conditions of the wood, structure type and infiltration and runoff patterns. While an exhaustive evaluation of all factors impacting site variability was not conducted, several factors were examined to assess possible trends. Surface soil concentrations were not found to correlate with age of the structure. Concentrations also did not show significant

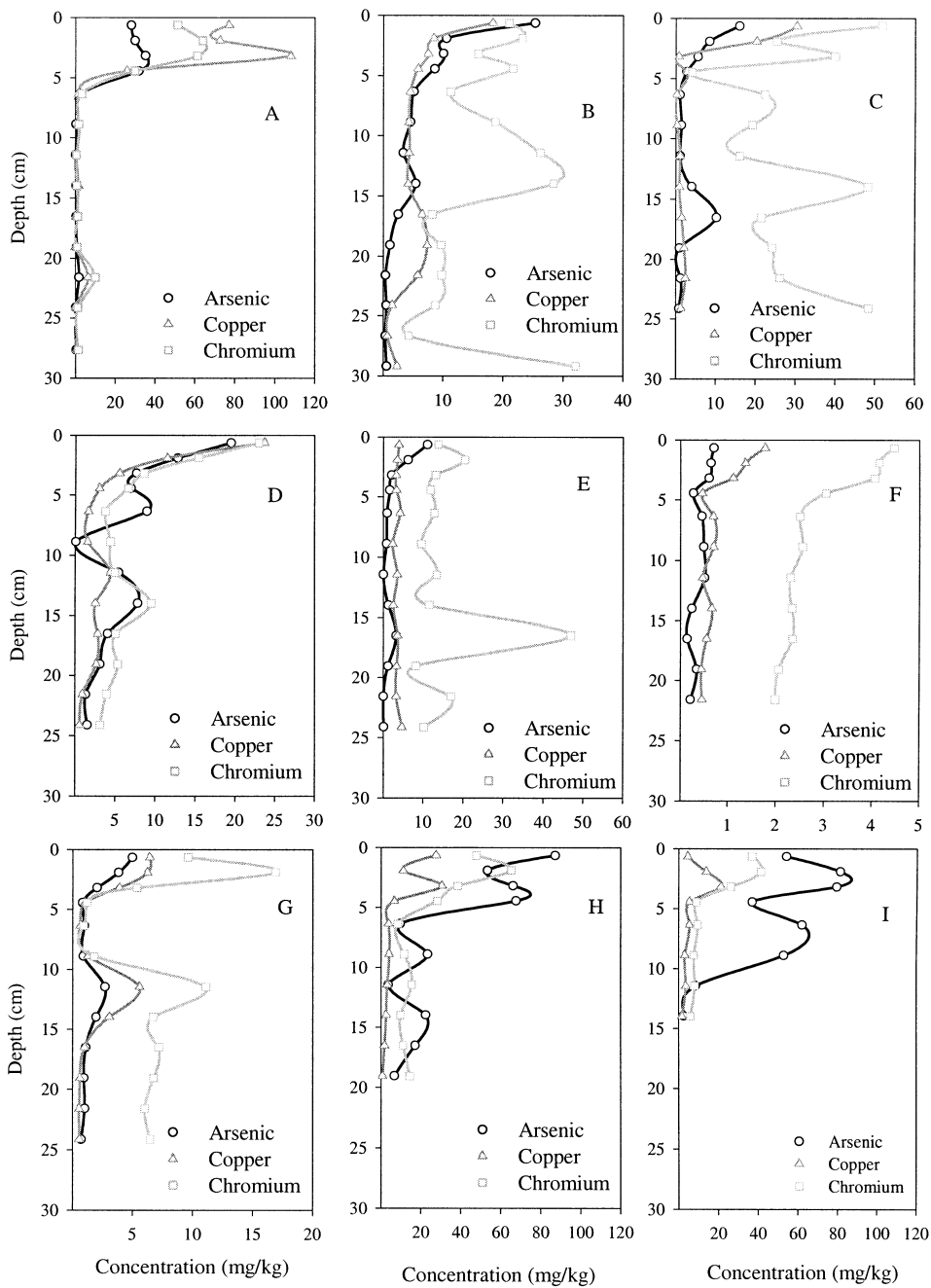


FIGURE 1
Core Soil Profiles.

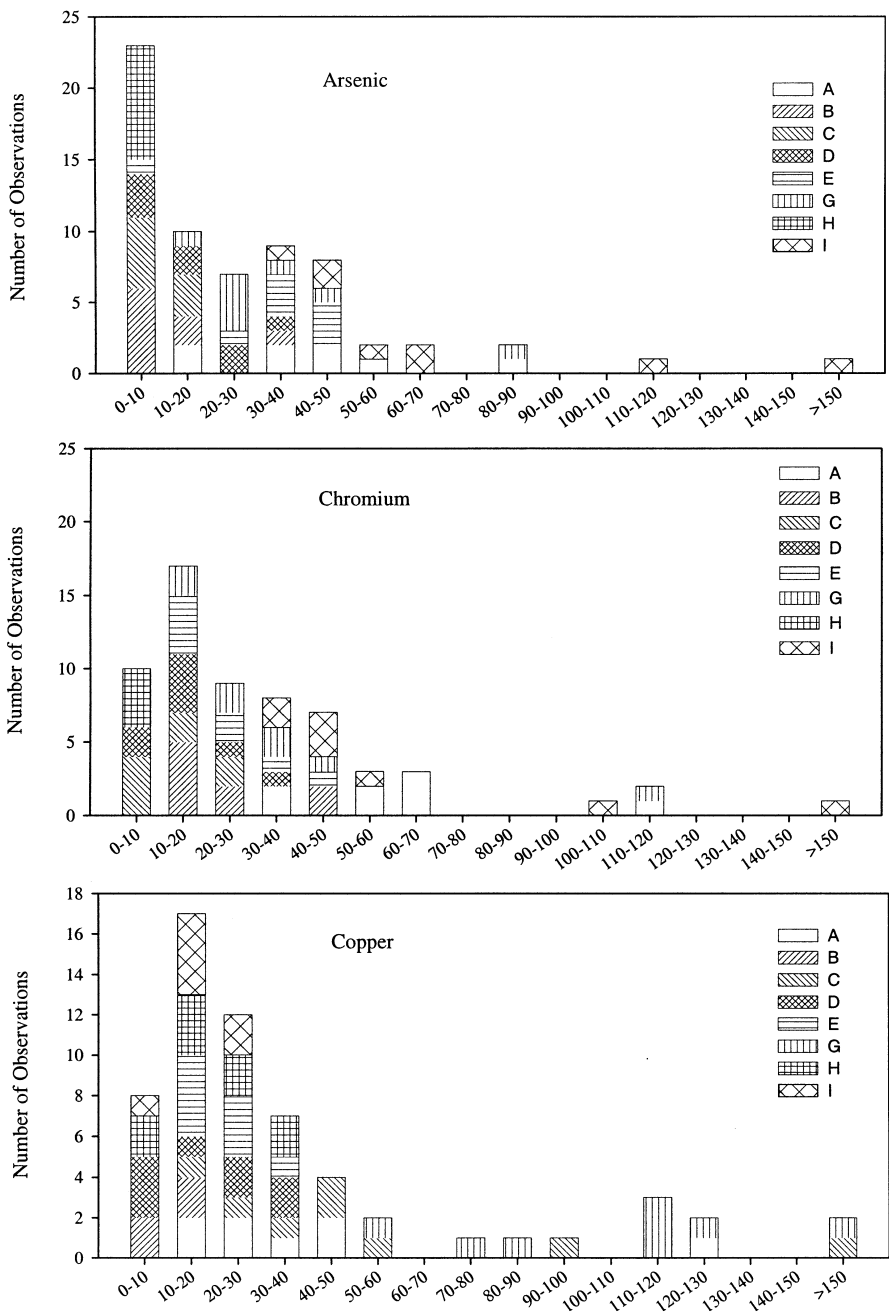


FIGURE 2

Distribution of Metal Concentration (mg/kg) in Soil Under CCA-Treated structures.

correlation with the soil characteristics measured. The lack of significant correlations with these parameters illustrates the diverse factors that impact surface soil metals concentrations.

Surface soil concentrations also varied within a given site. Possible causes of intra-site variation include construction practices, location of different structure components (e.g. above ground versus soil contact), water flow patterns (e.g. drip lines), and retention levels of the different structure components. For example, a large variability in arsenic concentration was observed in the site I samples. For this particular structure, surface soil samples ranged from 31.7 to 217 mg/kg of arsenic. The two highest concentrations measured (112 mg/kg and 217 mg/kg) were found to correspond to the location where two joists intersected. Based on this fact and visual observations of the soil underneath the structure after a rain event, it was concluded that runoff from upper portions of the deck dripped along the joists resulting in a concentrated input of rainwater causing the elevated arsenic concentrations at these two locations. Townsend *et al.* (2001) contains additional details regarding the locations of the samples with respect to the structures and water flow patterns, and discusses the possible relationship between volatile solids and arsenic content.

Relative Contribution of Metals

An examination of the relative concentration of arsenic, chromium, and copper in the soil samples can provide insight regarding the source of the metals. As was previously stated, elevated metals concentrations could result from both the leaching pathway and from wood particles (debris left from construction and abraded wood). The American Wood Preservers Association (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 U.S. and contains 47.5% (44.5–50.5%) CrO₃, 18.5% (17.0–21.0%) CuO and 34.0% (30.0–38.0%) As₂O₅ (AWPA, 1999). For comparison purposes, the ratio of arsenic to chromium (As:Cr) and the ratio of copper to chromium (Cu:Cr) will be used in this paper. The ratios for CCA-C correspond to 0.9 (0.74–1.1) and 0.6 (0.52–0.72) for As:Cr and Cu:Cr, respectively. Relative soil metal ratios measured in this range could indicate wood particles as the source of contamination.

Previous research has shown that the relative mass of each metal that leaches from a wood product treated with CCA-C in contact with water differs from the relative mass in the treated wood product itself. Most leaching studies on CCA-C treated wood have shown that arsenic and copper leach to a greater extent than chromium when exposed to fresh water (Hingston *et al.*, 2001). The relative amount that leaches is a function of wood species, pH, time of exposure, type of leaching test, and several other factors (Cooper, 1991). Published research differs as to which component, arsenic or copper, leaches more. Crawford *et al.* (2002) found copper to leach more than arsenic in CCA-C exposed to soil, and arsenic to leach more than

copper when leached using water. For several different species of wood, Cooper (1991) found As:Cr to range from 5.2 to 16.7 and Cu:Cr to range from 5.8 to 11.7 in batch leaching tests at pH 5.5. When leaching jack pine with deionized water, Warner and Solomon (1990) measured an As:Cr of 23 and a Cu:Cr of 8.6. Townsend *et al.* (2001) leached size-reduced southern yellow pine for 18 hours with simulated rainfall and found average As:Cr and Cu:Cr values of 4.0 and 2.6, respectively. Lebow *et al.* (1996) leached CCA-C southern yellow pine lumber in deionized water and found the As:Cr and Cu:Cr ratios after one month of leaching to be 3.0 and 6.4, respectively. In a study of leaching from a simulated CCA-treated deck, Kennedy and Collins (2001) found that after 300 days of exposure to natural rainfall, metals had leached in the following ratios: 3.4:1 (As:Cr) and 1.2:1 (Cu:Cr).

The above leaching data suggest that soil impacted by rainwater leaching over CCA-treated wood structures should have background-corrected As:Cr and Cu:Cr ratios greater than 1, perhaps many times greater (assuming that the metals are retained in the soil). Since the relative proportions are different between the wood itself and the wood leachate, an analysis of these ratios can possibly help assess whether the source of the metals is from leaching or from wood particles (construction debris, abraded wood). Stilwell and Gorny (1997) and Stilwell and Graetz (2001) reported relative ratios in soil beneath or adjacent to CCA-treated structures that were indicative of leachate from CCA-treated wood and used this to suggest that elevated soil metal concentrations were primarily a result of leaching. Lebow *et al.* (2000) evaluated the relative concentrations of chromium and copper in sediments under a CCA-treated boardwalk to determine if elevated metal concentrations were the result of wood abrasion due to high foot traffic, and determined that abrasion was not the primary source of copper to the underlying sediments.

The relative concentrations of the metals in the soils collected in this study were assessed. Evaluation of all of the surface soil results found that As:Cr and Cu:Cr ratios (without background correction) were 0.98 and 1.2, respectively. The ratios, especially that of As:Cr, are less than might be expected based on typical leaching ratios reported in the literature. When evaluating the soil core profiles in Figure 1, only Site I showed arsenic in greater concentrations throughout the soil profile. Since the background concentrations of metals in the soil differ ($Cr > Cu > As$), it is important to correct for background. Only three sites had Cr concentrations in the soils under the structures that were statistically greater than background chromium concentrations (A, E, and I). For each of these three sites, background-corrected concentrations were determined by subtracting the average control sample concentration from the concentration of each of the samples collected under the structures. The ratios were then recalculated.

Table 6 presents the background-corrected As:Cr and Cu:Cr ratios for sites A, E, and I. The average ratios, as well as the range, are presented. As a reminder, ratios for CCA-treated wood particles should be approximately 0.9 and 0.6 for As:Cr and Cu:Cr, respectively. Site I most closely resembled a pattern that would correspond to leaching being the primary contributor of metal contamination, with

TABLE 6
Background Corrected As:Cr and Cu:Cr
Ratios for Sites A, E, and I

Site	As:Cr	Cu:Cr
A	0.65 (0.46–0.86)	1.9 (1.3–2.5)
E	1.2 (0.62–1.5)	0.88 (0.36–1.1)
I	2.4 (0.45–4.6)	1.2 (0.86–1.7)

most values above the range expected for wood particles. The site I core profile also was indicative of impact by leaching. The site E ratios were more in the range corresponding to wood particles. The site A As:Cr ratios were in the range expected for wood particles, while the Cu:Cr ratios were closer to that which might be expected for leaching.

The large range of observations makes any broad characterization of metal source impossible, but in general the concentration of arsenic in the soil relative to the concentration of chromium in the soil is less than would be expected based on previous leaching results (for all sites except I). While abraded wood and construction debris is one explanation for this, another possibility is that the arsenic was more mobile in the soil relative to chromium. The As:Cr ratios could have at one time been greater, but over time as rainwater moved through the soil, arsenic could have been preferentially leached. The relative degree of leaching would, of course, be strongly dependent on soil type, but in many cases, arsenic would be expected to be more mobile than trivalent chromium (USEPA, 1996b). The soil samples collected in this study were not characterized in great enough detail (e.g. aluminum, iron content) to comment further. The ultimate fate of metals leached from CCA-treated structures into soil is worthy of additional investigation.

Comparison to Soil Cleanup Target Levels

The concentrations of chromium, copper, and arsenic measured in the soil samples from underneath the CCA-treated structures were compared to Florida’s risk-based regulatory guidelines for soils. The Florida Department of Environmental Protection (FDEP) has published risk-based SCTLs to serve as an indicator of whether pollutant concentrations in soils exceed acceptable risk in different human contact scenarios (FAC, 2001). For direct human exposure (an aggregate of ingestion, inhalation, and dermal contact), the SCTLs for residential areas are 0.8 mg/kg, 210 mg/kg, and 110 mg/kg for arsenic, chromium, and copper, respectively. For industrial exposure settings, the SCTLs are 3.7 mg/kg, 420 mg/kg, and 76,000 mg/kg, respectively. The arsenic and chromium SCTLs represent a 10^{-6} cancer risk, while the copper SCTL addresses gastrointestinal distress. It should also be noted that the chromium SCTL was derived for hexavalent chromium.

With respect to chromium, no surface soil sample exceeded the residential or industrial SCTL. While no speciation was performed, it is likely that the chromium existed primarily in the reduced chromium (III) state as opposed to the chromium (VI) state. For copper, 7 of 65 surface soil samples (under CCA-treated decks) exceeded the residential SCTL, while none of the samples exceeded the industrial SCTL. For arsenic, all 65 of the surface soil samples exceeded the residential SCTL (0.8 mg/kg) and 62 of the 65 samples exceeded the industrial SCTL. None of the control samples exceeded their respective residential SCTL for chromium or copper. For arsenic, 29 of 65 controls exceeded the residential SCTL and 3 exceeded the industrial SCTL.

From the comparison above, elevated concentrations of arsenic present the greatest direct human exposure risk of the three metals. Several issues deserve additional discussion with respect to the soil samples exceeding the arsenic SCTL. First, as pointed out previously, the Florida SCTL for arsenic is relatively low with respect to natural background. While the Florida SCTL is low, it is in line with risk-based soil concentrations from some other agencies. For example, the U.S. EPA's generic soil screening level for arsenic (for the ingestion pathway) is 0.4 mg/kg (USEPA, 1996b). In a review of different states, arsenic risk-based soil screening levels (SSLs) for residential settings ranged from 0.1 to 250 mg/kg (AEHS, 1998). Ten of 20 states reported a residential arsenic SSL below 1 mg/kg. Those higher than the Florida SCTL were generally derived using a different cancer risk (e.g., 10^{-5}), a non-cancer endpoint, or by setting the screening level to naturally occurring background levels.

A second issue is the applicability of using risk-based screening levels to soils underneath CCA structures. The purpose of these generic levels is to set a threshold below which the soil is considered to pose an acceptable risk. They are used at contaminated sites to help assess the risk posed and to determine whether conditions warrant corrective action. Contamination of soil underneath a CCA-treated structure would not be a "violation," but could require action during future property transactions if contamination was identified as part of the site assessment. One might argue that human exposure to soil underneath a CCA-treated structure would be unlikely, but scenarios can certainly be envisioned where a structure is removed and the likelihood of potential exposure to that soil increases.

Evaluation of Potential Metals Concentrations from the Leaching Pathway

As described earlier, arsenic concentrations were lower relative to chromium concentrations than would be expected from typical ratios measured when CCA-treated wood is leached with water. Stilwell and Gorny (1997) and Stilwell and Graetz (2001) reported that metal leaching was the primary cause of the elevated metal concentrations they observed in soil under CCA-treated structures. The results of the Florida study were inconclusive in this regard. To evaluate whether the

soil concentrations measured here would even be possible as a result of leaching, a simple mathematical relationship was developed to predict the average metal concentrations that might occur underneath a CCA-treated structure. The intent was not to model concentrations from any particular structure in this study. A generic structure was assumed.

The concentration of a metal underneath a CCA-treated structure is represented by Equation 1 where C_i is the concentration (mg/kg) of metal “i” in the soil underneath the structure. For a horizontal surface of CCA-treated dimensional lumber (such as a deck or boardwalk), C_i may be calculated as presented in Equation 2 where $F_{i,Leach}$ is the fraction of metal “i” that has leached, A_{Wood} is the area of wood structure exposed to rainfall (m^2), T_{Wood} is the thickness of the wood (m), SRV_i is the standard retention value of metal “i” in the wood ($kg-i/m^3$), A_{Soil} is the area of soil underneath the structure that is impacted (m^2), D_{Soil} is the depth of soil impacted (m), and ρ_{Soil} is the bulk density of the soil (kg/m^3).

$$C_i = \frac{\text{Mass of Metal Leached from Structure}}{\text{Mass of Soil Impacted}} \quad (1)$$

$$C_i = \frac{F_{i,Leach} A_{Wood} T_{Wood} SRV_i 10^6}{A_{Soil} D_{Soil} \rho_{Soil}} \quad (2)$$

Consider a CCA-treated walkway constructed with 0.038 m thick lumber. Assuming the lumber is treated to a standard retention value of $6.4 \text{ kg-CCA}/m^3$ ($0.40 \text{ lb-CCA}/ft^3$), this corresponds to $1.4 \text{ kg-As}/m^3$, $1.6 \text{ kg-Cr}/m^3$ and $0.95 \text{ kg-Cu}/m^3$. As discussed previously, the contamination is usually limited to the area directly underneath the structure, so A_{Wood} is assumed equal to A_{Soil} . Assuming the soil has a bulk density of $1,700 \text{ kg}/m^3$, the arsenic concentration (mg/kg) can be calculated using equation 2 for different F_{Leach} values. Figure 3 represents this relationship in a graphical form. From the graph it can be estimated that if 5% of the CCA were to leach from this generic CCA-treated structure into the upper 0.1 m (4 inches) of the soil underneath the deck, the concentration of arsenic in the soil would be expected to be 16 mg/kg. If 10% were to leach into that depth, the predicted concentration would be 32 mg/kg.

Several simplifications were made in the above approach. Metals were assumed to be uniformly bound in a given depth of soil, when in reality metal concentrations will be distributed according to soil characteristics. Soil core results did indicate that the greatest metal concentrations were found at the surface. The above analysis also only considers a simple structure with wood planks or deck boards, and does not include any support structures or components such as hand railings. All of these additional components would add to the metal loading. Values for F_{Leach} would depend on several factors, including how well the wood was treated, rainfall rates, structure use pattern, and most importantly, time. In most cases the greatest leaching rates of arsenic, chromium and copper from CCA-treated wood occur at the onset of leaching and decrease to lower values over time. In

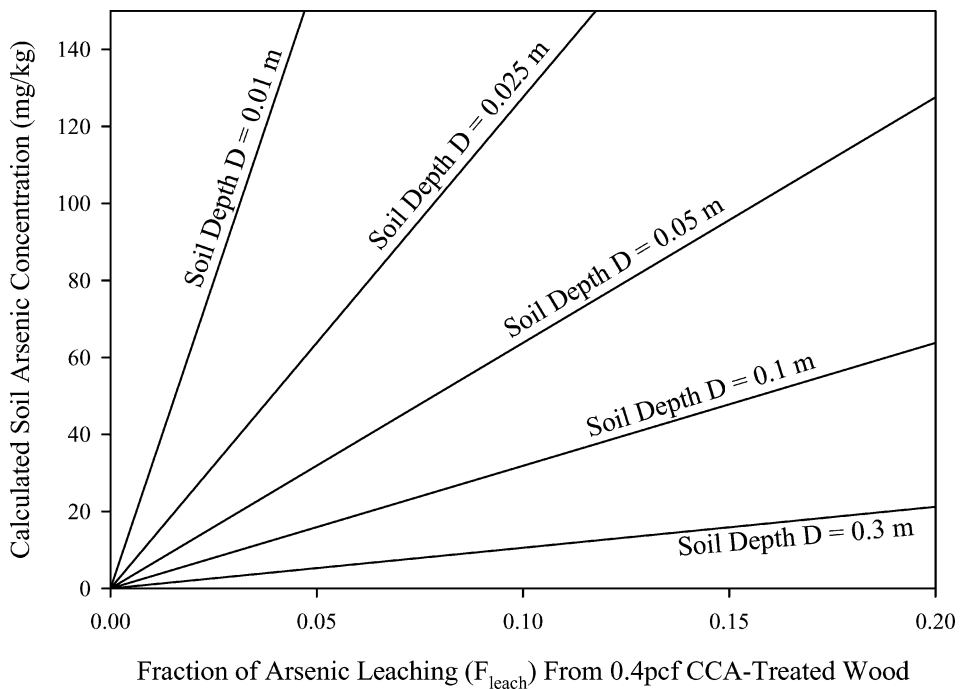


FIGURE 3

Predicted arsenic soil concentrations as a function of F_{Leach} .

18-hour leaching tests with synthetic rainwater, Townsend *et al.* (2001) found that 20-g blocks of CCA-treated wood leached between 0.2% to 2% of the arsenic present, while sawdust leached from 0.5% to 8% of the arsenic present. Results of field tests in aggressive environments have measured typical arsenic depletion amounts from CCA-treated wood in the range of 10% to 25%. Cooper (1993) assumed a 20% loss of chemicals after 20 years of service in assessment of treated wood disposal issues. Kennedy and Collins (2001) exposed CCA-treated deck boards to natural rainfall over a 300-day period. After exposure to 600 mm of rain, the mass of arsenic that leached from the deck boards ranged from 4.0 to 4.4%.

Despite the great number of variables that must be factored into the prediction of the degree of soil contamination underneath a CCA-treated structure, this analysis does indicate that leaching of preservative can result in elevated concentrations of arsenic, chromium and copper. Figure 3, along with the data already discussed, shows that soil arsenic concentrations under CCA-treated wood structures could reasonably be expected to range from 10 to 40 mg/kg above background concentrations. Higher concentrations, or “hot-spots,” would occur at locations adjacent to CCA-treated wood buried in the soil and underneath drip lines where metal-concentrated rainwater is focused. Hot spots would also occur if the sample locations coincided with the location of construction debris (e.g., sawdust). While results of this study

were inconclusive with regard to the source of elevated metal concentrations (wood particles vs. leaching), simple estimates of what concentrations might be expected as a result of metal leaching from CCA-treated structures fall within the range of the actual metal concentrations measured.

CONCLUSIONS

Wood that is used outdoors, especially in warm, wet environments, must be preserved to deter biological deterioration. Treatment with chromated copper arsenate provides effective resistance to decay, but poses several potential environmental and human health risks. Arsenic, chromium, and copper can become elevated in soils underneath wood structures treated with CCA as a result of rainwater migrating over the wood and infiltrating into underlying soil, and because of wood particles resulting from abrasion or improperly disposed debris. The results of this study were inconclusive as to the source of the metals. The ratio of arsenic to chromium was often less than would be expected for metals found in "leachates" from CCA-treated wood. Given that previous research (Stilwell and Gorny, 1997; Stilwell and Graetz, 2001) found leaching to be the major pathway of metal contamination, and given the range of predicted soil metals concentrations from a theoretical analysis, another possibility that should be considered is that arsenic was at one time found in greater relative concentrations, but leached from the soil with time. This possibility warrants further investigation. The potential for groundwater contamination from CCA-treated wood structures was not examined in this paper.

From a human health risk standpoint, arsenic presented the greatest concern. The concentrations of arsenic underneath CCA-treated structures may exceed risk-based clean soil levels. The arithmetic mean concentration of arsenic underneath eight CCA-treated structures was 28.5 mg/kg, while Florida's generic SCTL is 0.8 mg/kg for residential settings and 3.7 for industrial settings. This presents a dilemma for policy makers, in that soil concentrations underneath these structures are greater than levels that many commercial and industrial sites with arsenic-contaminated soils are being required to reach under remediation.

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