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Contamination of Soil with Copper, Chromium, and Arsenic Under Decks Built from Pressure Treated Wood

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For many centuries wood has been treated with a variety of organic and inorganic additives to protect it from bacterial fungal and insect decay (Warner and Solomon 1990). Presently, the most widely used wood preservative is chromated copper arsenate (CCA), due to its excellent fungicidal (Cu) and insecticidal (As) properties (Dawson et al. 1991). The chromium is used to fix the Cu and As in the wood. In the treatment of wood, up to 250 liters of CCA solution per cubic meter of wood is applied under high pressure, resulting in Cu, Cr, and As wood concentrations in the range of 1000-5000 mg/ kg (Aceto and Fedele 1994; Dawson et al. 1991). In the United States 10.6 million cubic meters of wood treated with preservatives (much of it CCA) was produced in 1986 (Warner and Solomon 1990). Due to the massive amounts of CCA treated wood sold each year, the extent of dispersal of these additives from the wood could have a considerable environmental impact. The potential toxicity of Cu, Cr, and As to humans, animals, and plants is well documented (Seiler and Sigel 1988; Woodbury 1992; Nriagu 1994). According to published studies in controlled laboratory settings, high percentages of CCA can be released from the wood by aqueous solutions. Aceto and Fedele (1994) used simulated rain water (pH 3.0-6.1) to study the release of CCA in wood that was ground to a coarse powder. Between pH 4.5 to 6.1, 21-24% of the Cu, 7% of the Cr, and 6% of As were released after a 72 hour extraction, while at pH 3.0, 100% of the Cu, 14% of the Cr, and 18% of the As were extracted. Warner and Solomon (1990) also concluded that the acidity of aqueous solutions is a major factor in the leaching of CCA from treated lumber. In their study, the percent leached after 40 day immersions in buffered solutions between pH 3.5-5.5 ranged from 92- 100% (Cu), 12-53% (Cr), and 32-68% (As). These findings imply that considerable amounts of Cu, Cr and As could leach from outdoor use of CCA treated wood since rainwater is acidic. The natural pH of rainwater ranges between 4.9-6.5 (Calvert 1983). In many regions worldwide, including the Northeastern US (where this study was conducted) anthropogenic atmospheric sulfur and nitrogen compounds have increased this acidity. The pH of “acid rain” has been measured between 4.1-4.5 in the Northeastern US (Calvert 1983).

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In this field study, the Cu, Cr, and As content in soils under seven decks built with CCA treated wood was determined. The decks ranged in age from 4 months to 15 years. Decks are ideal for the study of the effects of weathering due to rain and solar radiation on the wood. The wood is above ground and the leachate from precipitation tends to flow directly to the soil below.

MATERIALS AND METHODS

A total of 85 soil samples were collected in polypropylene containers from under a total of seven decks built with CCA pressure treated lumber. The deck age, type of coating applied (if any), and the number of soil samples acquired at each site are outlined in Table 1. The decks were numbered 1-7 based on the time since construction. The deck age for decks 3, 4 and 6 were estimated to within two years. Although decks 3 and 4 were situated about 10 m apart in the same residential lot, deck 4 was built 2 years prior to deck 3. The size of the individual decks ranged from 18 to 50 square meters.

Table 1. Deck Descriptions.

Deck #	Size (m^2)	Age (Years)	Coated	No. of Samples* (B)	(C)
1	32	0.3	No	10	5
2	37	2	No	9	5
3	13	5	Yes**	15	5
4	18	7	No	16	5
5	50	7	No	14	4
6	37	8	No	12	5
7	22	15	Yes***	9	4

* B= Beneath decks, C= Control Soils. ** Stained after 5 years.
*** Painted after 1 year

The soil samples were collected in a grid like fashion (Thompson and Maguire 1993), at a frequency of about 1 sample per 2 sq m of deck area. Control soils were acquired at a minimum distance of 5 meters from the decks and at least 4 m apart from each other. All soils were classified as sandy loam (Typic Dystrochrept). Soil samples were a composite of the upper 5 cm soil layer and averaged 100 g. Prior to sampling, any debris on top of the soil was brushed away. After collection, additional debris (such as pebbles, roots, twigs, litter) was picked out, and the samples were dried at 110°C for 15 hours. The soils were homogenized by vigorous shaking of the plastic containers. In addition, three soil core samples were acquired beneath the perimeter of deck #6 using a 2.5 cm diameter soil core sampler. Each core was sliced into 2.5 cm long segments. This deck (#6) was built about 1 m above ground on level land.

The dried soil samples were prepared for analysis by microwave digestion (model MDS 81D, CEM Corp., Matthews NC), as described previously for soil and compost samples (Stilwell 1993). Two replicates from each soil sample, 0.7-0.9 g each, were weighed (± 0.1 mg) into the microwave Teflon vessels 10 ml of concentrated nitric acid was added and the vessels were sealed. The microwave power program was set at 50% for 5 minutes followed by 100% for 30 minutes. The set pressure maximum of 120 psi was achieved approximately 20 minutes into the 100% power cycle. The digests were transferred to 100 ml volumetric flasks, brought up to volume with distilled deionized water and stored in 125 ml polyethylene containers until analysis.

The Cu, Cr, and As content in the digests were determined by inductively coupled plasma atomic emission spectrometry (ICP-AES) using the Atom Scan 16 (Thermo Jarrel Ash, Franklin, MA, USA). The detection limits (mg/kg) in the dried soil were 1.2 (Cu), 1.6 (Cr), and 9 (As). Alternatively, the As content was determined utilizing a PE 5100PC graphite furnace atomic absorption spectrometer (GFAAS) (Perkin Elmer Corp., Norwalk, CT, USA) for soil samples found low in As (<10 mg/kg). Using the GFAAS the As detection limit in the dried soil was 1 mg/kg. All of the chemicals were reagent grade or better, and all aqueous solutions were prepared using distilled deionized water.

For control purposes two procedure blanks were included in each batch of 12, and duplicates of the reference soil sample (NIST 2709, US National Institute Of Standards And Technology, Gaithersburg, MD 20899) were included in every third to fourth batch. Check standards, either AA-1 or QC- 19 (Spex, Edison, NJ, USA) were run after every 5 determinations and the agreement was within 10% of the certified value. The Cu, Cr, and As in all of the procedure blanks (n =62) were all below the detection limits. The amounts found (mg/kg) in the NIST 2709 soil (n=16), were 34 ± 3 (Cu), 99 ± 11 (Cr), and 17 ± 3 (As), compared to the certified values of 34.6 ± 0.7 (Cu), 130 ±4 (Cr), and 17.7 ± 0.8 (As). Incomplete extraction of chromium in these reference soils by nitric acid digestion has been observed by others (Rasberry 1993; Kane et al. 1993).

RESULTS AND DISCUSSION

The range, average, and standard deviation in the amounts of Cu, Cr, and As in the soil samples are given in Table 2. The values for a given soil sample were based on the average result between duplicates. The average relative standard deviation (%RSD) between duplicates was 5% Cu, 3 % Cr, and 6 % As, for soil samples beneath the decks, compared to 5 %. Cu, 3%. Cr, and 11 % As for the control soil samples. These values show that there was good homogeneity within a given soil sample. However, the variability (expressed as %RSD) between samples at a particular deck site was higher. They averaged 43 **%** Cu, 37 % Cr, and 51 **%** As in soils samples beneath the decks, compared to an average of 18 %Cu, 11 % Cr, 25 % As in the control soils. The higher site variability could be due to differences m the amounts of treated wood above the soil sample and its exposure to wear and weather, all of which could effect the CCA leach rate. In addition, variations in the rainwater runoff patterns from the deck surfaces would deposit varying amounts of leachate to the soils. Large within site variations in analytes from soil matrices are frequently encountered, and can be particularly prevalent in contaminated sites (Thompson and Maguire 1993; Lame and Deflze 1993).

At each site, the average Cu, Cr, As content in the soil samples taken beneath the deck was elevated with respect to the average in the control soils. In all cases, except for the Cr content for deck 2, this elevation was statistically significant

Table 2. Range, average and standard deviation (SD) in the amounts (mg/kg) of Cu, Cr, and As in soil samples.

Deck#	Soil Beneath Deck			Control Soil		
	Range	Avg.	SD	Range	Avg.	SD
Copper						
1	22-63	34	12	13-20	16	3
2	23-65	48	14	12-17	14	2
3	38-145	76	25	18-30	22	4
4	41-140	75	27	18-30	22	4
5	26-273	104	74	10-12	11	1
6	60-410	154	87	15-27	20	5
7	17-46	31	10	10-14	13	2
Overall	17-410	75		10-30	17	
Chromium						
1	20-31	26	4	17-24	20	3
2	16-73	26	17	13-19	16	2
3	27-68	42	11	25-30	27	3
4	34-95	58	17	25-30	27	3
5	26-138	64	35	17-18	18	1
6	31-154	59	33	19-23	21	2
7	16-33	23	5	11-19	14	3
Overall	16-154	43		11-30	20	
Arsenic						
1	3-19	9	5	2.2-3.5	2.6	0.4
2	7-91	34	23	3.6-5.2	4.2	0.6
3	34-99	61	20	2.5-8.3	4.9	2.2
4	44-333	139	66	2.5-8.3	4.9	2.2
5	57-215	113	60	2.2-3.9	2.7	0.7
6	50-350	138	77	3.5-5.3	4.4	0.7
7	6-80	40	21	1.3-2.4	1.9	0.4
Overall	3-350	76		1.3-8.3	3.7	

($p<0.025$). Moreover, in the vast majority of samples (100% for Cu, 88%for Cr, and 99% As), the analyte in the soil beneath the deck was greater than the largest value m control soil at that site. These results demonstrate that significant amounts of Cu, Cr, and As leaches from the wood and manifests itself in the soil.

The amounts of analyte in the soil tend to increase with deck age (Table 1), with the exception of deck #7. Deck 7 was painted 1 year after construction and then repainted about 8 years later. Thus the leaching of CCA may be retarded if the decks are coated soon after construction. Deck 3 was constructed 2 years after deck 4, and was stained one year prior to sampling. The Cu in the soil samples beneath decks 3 and 4 were statistically the same, while the Cr and As in soils beneath deck 4 were significantly ($p<0.025$) elevated compared to those beneath deck 3. Indeed, the As beneath deck 4 soils averaged twice those beneath deck 3. In addition to the age and coating effects, location may be an additional factor enhancing As leaching. Deck 3 was more sheltered to the environment, next to the house, while deck 4 was situated in the open. Deck 4 was also built to accommodate a swimming pool and was thereby seasonally exposed to the bleaching action of chlorinated pool-water.

The proportion of Cu, Cr, and As leached from the wood can be obtained by calculating the relative amounts of Cu, Cr, and As expressed as the Cu /Cr /As ratio (by weight) in the soil samples beneath the decks, after subtraction of the background amounts in the control soils. The ratio obtained was overall 1.0/ 0.4 / 1.2, and ranged 1.0 /: 0.3-0.6 / 0.4-2.1, with the relative amounts of As and Cr tending to increase with deck age. The weight ratio of Cu: Cr: As in new treated wood is 1.0 / 1.6-1.9 / 1.2-1.9 (Warner and Solomon 1990; Dawson et al. 1991; Aceto and Fedele 1994). Thus, the relative amounts of Cr, and to lesser extent As, in the soils are less than those normally found in new treated wood, suggesting that these elements are bound more effectively in the wood than is Cu. This finding is consistent with the results of simulated leaching studies where the amounts of metals leached was not proportional to the levels in the wood prior to leaching. For example, using the data in Aceto and Fedele (1994) and in Warner and Solomon (1990), the Cu / Cr / As weight ratio in the wood was 1.0 / 1.6-1.8 / 1.9-2.0, while the amount in the leachate was 1.0 / 0.2-1.0 / 0.4-1.3 (pH 3.0-6.1). In all cases, Cu was released most readily, followed by As and then Cr.

The persistence of Cu, Cr, and As in the soil with depth is indicated by the results given in Figure 1. The Cu and Cr content rapidly decreases with depth, while the As is more mobile in the soil and tends to persist with depth. Concentrations of As persisting up to 15 cm in soil depth were also reported by Elfving et al. (1994) in old orchard soils contaminated with lead arsenate. In addition, an indication of the extent of contamination immediately surrounding the deck perimeter was obtained by comparison of four soil samples taken beneath the deck perimeter to four samples taken 15 cm away from the deck perimeter. The average concentrations (mg/kg) of 4 soil samples taken 15 cm from the deck perimeter

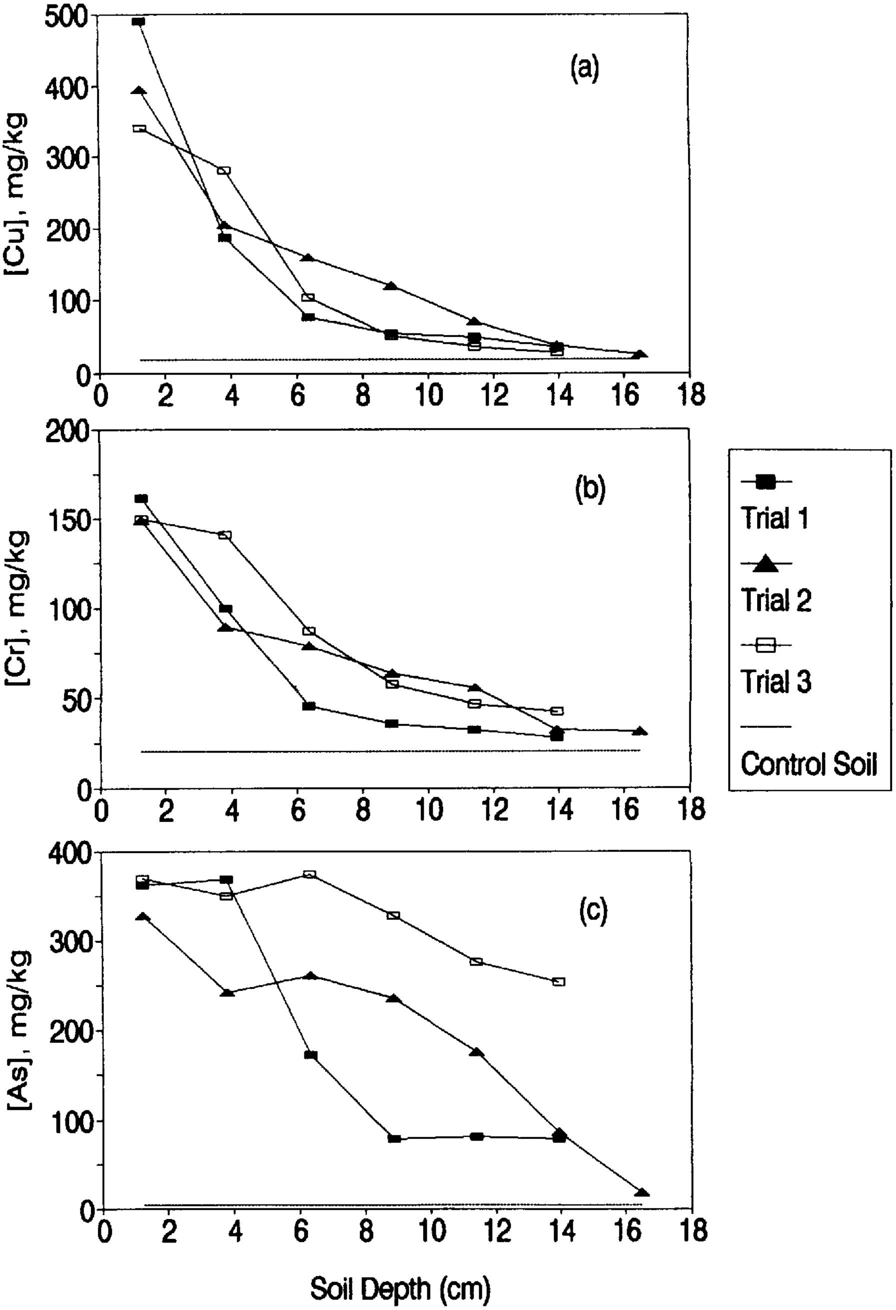

Figure 1. Cu, Cr, and As (a-c) concentrations (mg/kg) as a function of depth in three soil core samples taken beneath the perimeter of deck #6.

Table 3. Average contents in soils (mg/ kg) compared to statutory limits.

	Element			
Location/Limit	Cu	Cr	Cr^{+6}	As
Beneath Decks	75	43	ND	76
Control Soils	17	20	ND	4
EPA 503 (1993)	1500	1200	-	41
State of CT (1996)	2500	3900	100	10

ND - not determined.
*EPA 503 (1993). ** State of Connecticut (1996).

were 67 Cu, 46 Cr and 32 As, compared to 216 Cu, 92 Cr, and 208 As in the 4 perimeter samples. The data from this limited survey suggest that for decks built on level land, the soil contamination can decrease to a great extent a short distance from the deck. Nonetheless, the As levels still exceed State limit of 10 mg/kg (State of Connecticut, 1996).

A perspective, comparing the amounts found in the soils to Federal Guidelines (EPA 503, 1993) and State Regulatory limits (State of Connecticut, 1996) is given in Table 3. The EPA 503 Federal regulation applies to the land application of biosolids, and is used here for guidance limits. The State of Connecticut Statutes are clean-up standards which must be met for the remediation of contaminated soils in residential areas. As shown in Table 3, even though the copper content is up to 10 times higher compared to the control soils, it is still substantially below the limits. The average Cr content does not exceed the 100 mg/kg limit (assuming Cr+6 state, as was present in the wood). However, the upper ranges in the chromium values from surface soil samples from decks 4-6 do approach levels of concern, but these values should decrease with increasing soil depth (Figure 1) to values well below 100 mg/kg. The average As content exceeds both regulatory limits by substantial amounts. Moreover, the As concentrations appear to be persistent with depth (Fig 1). The average As in soil samples from decks 2-7 exceed Connecticut regulatory limits and they surpass the EPA 503 regulatory guidelines from decks 3-6. Clearly, the arsenic levels pose a potential environmental problem.

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