

Effect of Chromated Copper Arsenate Structures on Adjacent Soil Arsenic Concentrations

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Received: 4 December 2010 / Accepted: 29 March 2011 / Published online: 20 April 2011
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Abstract Structures made of chromated copper arsenic (CCA) have been shown to leach arsenic into the surrounding soil. Soil cores were taken adjacent to six CCA decks at 0, 15, 60 and 300 cm from the deck at depths of 0–10, 10–20, and 20–30 cm, and were analyzed for soil arsenic concentrations. Median soil arsenic concentrations ranged from 1.8 µg/g at a depth of 10–20 cm and a distance of 300 cm to 34.5 µg/g at a depth of 0–10 cm and a distance of 30 cm. Soil arsenic concentrations taken at depths of 0–10 and 10–20 cm decreased as distance from the deck increased. Soil arsenic concentrations close to the deck were higher at lower soil depths and at homes with greater deck wipe arsenic concentrations. Age of deck and slope of land had significant effects on the differences in arsenic concentrations between samples taken at different distances when evaluated in models by themselves, but not in models adjusting for deck wipe concentrations. Size of deck and bulk density of soil did not have significant effects on soil arsenic concentrations.

Keywords Arsenic · Soil · Chromated copper arsenate · Lumber · Decks

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Since the 1970s, chromated copper arsenate (CCA) has been used as a chemical wood preservative to prevent rot, insect and microbial decay throughout the United States. Although CCA for treatment of lumber has not been used for most residential uses since January 1 2004, many homes still have decks, playsets, fences and other wooden structures made with CCA-treated lumber (US Environmental Protection Agency (EPA) 2008). Although exposure from chromium, copper and arsenic all may have negative health effects, arsenic is considered to be the most harmful (US Consumer Product Safety Commission 2003). Arsenic is also the most readily leached among copper, chromium and arsenic (Dagan et al. 2006; Chirenje et al. 2003; Kim et al. 2007). Based on unpublished studies in the United States and Canada, Zartarian et al. (2005), estimated the mean soil arsenic concentration to be 37.3 µg/g near CCA decks in warm climates and 83.7 µg/g near CCA decks in cold climates. Based on these and several other estimated inputs into the model Zartarian et al. (2005) estimated the mean additional exposure to children who have frequent contact with CCA-treated playsets and decks from contact with soil adjacent to playsets and decks to be 11.0×10^{-6} mg/kg/day in warm climates and to be 1.3×10^{-6} mg/kg/day in cold climates. EPA Region 6 has a cancer soil screening limit of 0.39 µg/g and a non-cancer limit of 22.3 µg/g. These limits are not a national cleanup standard but suggest that further investigation may be necessary (US Environmental Protection Agency 2011).

Studies have demonstrated that arsenic concentrations tend to be greater at smaller distances and depths from treated structures (Stilwell and Gorny 1997; Townsend et al. 2003; Chirenje et al. (2003); Stilwell and Graetz 2001), but have not focused on decks and systematically explored the interrelations between distance and depth and

site characteristics such as removable arsenic concentrations on the structure itself.

The objective of this study was to determine the effect that distance from CCA treated deck and depth from the ground's surface, along with bulk density, slope and age had on the concentrations of arsenic found in the soil adjacent to the decks. The results from this study may inform homeowners with CCA-treated decks about the amount and extent of arsenic exposure from their decks.

Materials and Methods

Six decks in Asheville, North Carolina were randomly selected by gridding the greater Asheville area on a map and numbering each cell within the grid. The downtown area was not included because of the lack of decks that would be found in the area. Then 18 numbers were randomly chosen from the range of cells. The area within the 18 cells was then visited and each house that had a deck was then given a flyer asking for participation in our study. All eligible houses that replied to the flyer were included in the study. Decks were eligible for the study if they were constructed before January 1, 2004 and if they had not been treated with stain/sealant/paint for the past 3 years. The study was approved by the University of North Carolina Asheville IRB.

Decks were first bisected into two equal halves. A wipe sample was taken following the US Department of Housing and Urban Development (1995) method for lead dust-wipe clearance testing but sampling a smaller area (100 cm²) was used to determine the arsenic concentration dislodged on the surface from the center of each half. A plastic template having a 100 cm² opening was taped down in its position and, using gloves, a Ghost WipeTM was used to rub the deck in an "S" shaped pattern three times with approximately 1 kg of pressure, folding the wipe in half between each time.

From the middle of the deck, samples were taken at four distances from the deck in a line running perpendicular to the longest edge of the deck. These distances included directly under the band of the deck (0 cm), 15 and 60 cm from the deck and a background sample at 300 cm. Within each distance three depths were measured, 0–10 cm, 10–20 cm, and 20–30 cm. A soil probe was used to obtain the samples. The probe was marked with the three depths needed. The first depth was extracted by inserting the probe into the ground until 10 cm of soil was obtained and placed in a plastic. The probe was then cleaned with a bottle brush to remove soil from the previous sampling. The 10–20 cm depth was taken by placing the probe back into the same hole and digging another 10 cm. This excavated soil was put into a different bag. The same was done for the 20–30 cm sample.

Percent slope was determined by placing one end of a 2 ft level at the 0 cm distance on the ground and measuring the height at the opposite end of the level. The square footage of the deck was calculated, not including stairs. Age of the deck and treatment history was determined through personal communication with the owner. At each site, bulk density was taken directly beside the 60 cm plug. Any leaf litter was cleaned from the surface of the soil. If there was grass on the surface, a hand trowel was used to dig under the roots and discard the root mat. A 62.8 cm³ PVC pipe sampler was driven into the soil. Once the cylinder was in the soil a knife was used to excavate around the cylinder and then the cylinder was lifted out of the surrounding soil. Contents of cylinder were placed into a plastic bag. The bulk density soil sample was dried in the laboratory and then weighed. Density was calculated by taking the dry weight of the sample divided by the volume of the core.

Atomic absorption spectroscopy (AAS) was used to determine the amounts of arsenic in both the wipes and the soil samples. First, 0.10 g of soil was weighed into 50 mL vials. Wipes were folded up and placed into the vial. Then 6 mL of concentrated HNO₃ and 2 mL of 30% H₂O₂ were added to the vials. The solution was then heated in a digestion block to 95°C until 4–5 mL of solution was left. When cooled, 3 mL concentrated HNO₃ and 1 mL 30% H₂O₂ were added and the solution was again heated to 95°C until 4–5 mL of solution was left. The vials were then brought to 50 mL volume with DI water. A clean wipe was placed in the blank, laboratory control sample (LCS) and a duplicate LCS for the control assurances with the wipes. Also, soil quality assurances were used by digesting using approximately 0.03 g NIST Montana Soil Standard Reference Material with a concentration of 105 µg/g arsenic. The lowest reporting limit was 1.3 µg/g.

An AAS Method-Graphite furnace (Thermo Electron Corporation, M-Series, GF952 Zeeman Furnace) was used to analyze the samples. Reagent blanks and Standard Reference Material samples using NIST Montana Soil having a nominal concentration of 105 µg/g were analyzed in each run. For soil samples, the Method Detection Limit (MDL) was 1.3 µg/g and the mean (standard deviation) percent recovery was 94.8% (3.9%). For wipe samples, the MDL was 2.55 µg/g and the mean (standard deviation) percent recovery was 91.6% (3.1%).

Mixed models using the natural log of soil arsenic concentration as the response variable were used to analyze the data. The natural log was used to improve normality and stabilize the variance of the residuals. Site was considered as a random factor. There were five potential between-site quantitative predictor variables: natural log deck wipe, site slope, soil bulk density, size of deck, and age of deck. There were two categorical within-site

variables, depth and distance from the deck. Because there were only 6 sites, each between-site variable was considered separately in a model including the variable, its interaction effects with depth and distance, depth, distance and the depth $\times$ distance interactive effect. Numeric variables were centered by subtracting the mean so that main effects of categorical variables were estimated at the mean level of the quantitative variable to allow interactive effects to be estimated independently of main effects. Any between-site variables or associated interactions with depth or distance found to be significant in those models were included in a joint model. If a between-site variable or any of its associated interactions were significant in the joint model then the variable and its interactions were included in the final model. Calculations were performed using the statistical program SAS.

Results and Discussion

Median soil arsenic concentrations ranged from 1.8 $\mu\text{g/g}$ at a depth of 10–20 cm and a distance of 300 cm to 34.5 $\mu\text{g/g}$ at a depth of 0–10 cm and a distance of 30 cm (Fig. 1). All soil samples were over the EPA's Region 6 cancer soil screening limit of 0.39 $\mu\text{g/g}$. The samples taken at depths of 0–10 cm and 10–20 cm under the edge of the deck and the samples take at a depth of 0–10 cm at 15 cm from the deck had median arsenic concentrations above EPA's Region 6 non-cancer soil screening limit of 22.3 $\mu\text{g/g}$. Median concentrations of samples taken close to the decks in this study were not inconsistent with the estimates used in Zartarian et al. (2005), especially considering that the top 1–5 cm of soil may have greater arsenic concentrations than soil 5–10 cm deep (Kim et al. 2007).

Three pairs of between-site variables were highly correlated with each other: log mean deck wipe and site slope ($r = -0.820$, $p < 0.001$), log mean deck wipe and age ($r = -0.648$, $p < 0.001$), and site slope and age ($r = 0.709$,

$p < 0.001$). For the models with a single between-site variable, the following factors involving between-site factors and their interactions with within-site factors were statistically significantly related to soil arsenic: in the model with log mean deck wipe arsenic concentration the factors log mean deck wipe arsenic concentration ($F = 14.00$, $p = 0.020$) and the interaction of log mean deck wipe arsenic concentration and distance ($F = 9.40$, $p < 0.001$), in the model with age the interaction of age and distance ($F = 7.77$, $p < 0.001$), and in the model with site slope the interaction of site slope and distance ($F = 6.14$, $p = 0.001$). When all of the above factors were combined in a joint model only the interaction of log mean deck wipe arsenic concentration and distance was significant ($F = 9.40$, $p < 0.001$).

The final model included log mean deck wipe arsenic concentration, its interactions with distance and depth, distance, depth and their interactions. Residuals from the model meet standard linear model assumptions of normality (Shapiro-Wilks $W = 0.975$, $p = 0.155$) and homoskedasticity (no pattern of unequal spread apparent in plot of residuals versus fitted response values). In the final model, distance ($p < 0.001$), depth ($p < 0.001$), the distance $\times$ depth interaction ($p = 0.030$), log wipe concentration ($p = 0.020$), and the log wipe concentration $\times$ distance interaction ($p < 0.001$) were significantly related to log soil arsenic concentration but the log wipe concentration $\times$ depth interaction ($p = 0.575$) was not (Table 1). It can be seen from Fig. 1 that soil samples that were farther from the deck had lower arsenic concentrations and soil samples that were deeper had lower arsenic concentrations overall, but that the arsenic concentrations are closer for the different depths at the larger distances. Log mean deck wipe was positively related to mean log soil arsenic concentration overall ($p = 0.020$), but there was an interactive effect with distance ($p < 0.001$). Pearson correlations between log deck wipe concentration and mean log soil concentration are very high for the two smaller distances but not significant for the two larger distances (Table 2).

The result of that soil farther from the structure have lower concentrations of arsenic in the soil agrees with

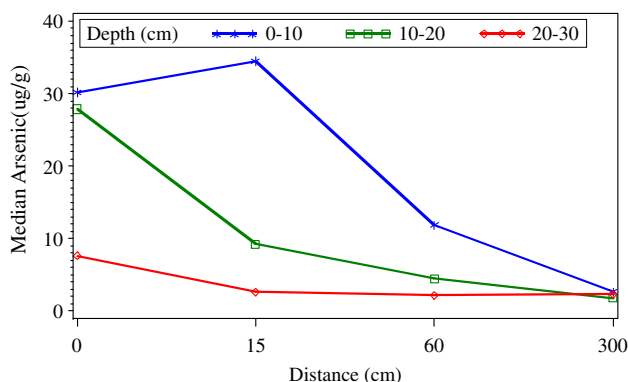


Fig. 1 Median arsenic concentrations at each distance and depth

Table 1 Results of the final linear model of both main and two-factor interactions

Effect	<i>F</i> value	<i>p</i> value
Distance	47.40	<0.001
Depth	17.14	<0.001
Distance $\times$ depth	2.54	0.030
Log wipe	14.00	0.020
Log wipe $\times$ distance	9.40	<0.001
Log wipe $\times$ Depth	0.56	0.575

Table 2 Pearson correlations between mean log deck wipe arsenic concentrations and mean log soil arsenic concentration averaged over depths for each distance with associated *p*-values

Distance				
	0 cm	15 cm	60 cm	300 cm
Correlation	0.984	0.922	0.548	0.020
(<i>p</i> -value)	(0.0004)	(0.0087)	(0.2599)	(0.9695)

Chirenje et al. (2003), Kim et al. (2007) and Stilwell and Gorny (1997), and that deeper soil has lower concentrations agrees with Stilwell and Gorny (1997), Kim et al. (2007) and Dagan et al. (2006). Coupled with the fact that the correlations between deck wipe arsenic concentration and soil arsenic concentration are very high at the lower distances this indicates that most of the arsenic found in soil close to decks comes from the deck itself. However, the facts that concentrations at 300 cm were not much less than those at 60 cm and that there were no differences in concentrations between the depths at 300 cm suggest that typically the effect of arsenic from decks on soil are limited to 300 cm or less. Therefore potential exposure could be significantly reduced by either restricting access or replacing soil closer than 300 cm from the deck down to a depth of 30 cm.

Two factors did not have a significant main or interactive effect with soil arsenic concentration: bulk soil density and size of deck. Because these were between-site factors, they were based on only six sites and there was only limited statistical power for finding differences within between-site variables. Two other factors had a significant interaction with distance when in the model by themselves: slope and age. Sites that had yards that were more steeply sloped away from the deck and sites that had older decks had smaller differences in arsenic concentrations between the closer distances and the farther distances when yard slope and age were considered in individual linear models, respectively. However, those relationships became insignificant when combined with a model including log deck wipe concentrations so it may be that those relationships are just artifacts of the negative correlations of yard slope and age of deck with log deck wipe concentration. Because this study was designed to focus on the effects of depth of soil and distance from the deck, other studies would be

needed to be able to sort out the relationships between deck wipe arsenic concentration, age of deck and slope of yard on arsenic concentrations at various distances from the deck.

Acknowledgments We thank Anne Marie Traylor for her help in analyzing the samples for arsenic.

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