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A Study of the Effect of Chromated Copper Arsenate Structures on Adjacent Soil Arsenic Concentrations

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Abstract

The use of Chromated Copper Arsenate as a wood preservative has been banned from use for residential purposes since January 1, 2004 but outdoor structures built before this time are still in use. Out of the three metals, arsenic is the most readily leached and is considered the most harmful because of numerous health problems, including cancer. The objective of this study was to determine if there were any effects on soil arsenic concentrations from wipe concentrations, location and depth from deck, bulk density, deck age, deck size and slope of the ground adjacent the deck. Six decks were randomly chosen within Asheville, North Carolina for this study. Ghost Wipes ™ were used to obtain deck surface concentrations and a 30cm long soil core sample within the yard was obtained with a soil probe. Soil cores were taken at 0cm, 30cm, 60cm and 300cm from the deck and analyzed for soil arsenic concentrations. Soil sample depth, soil sample distance from deck edge and the mean deck wipe's interaction with soil distance all had highly significant effects on soil arsenic concentrations ($p = 0.000$, $p = 0.000$ and $p = 0.000$, respectively.) Soil depth's interactive effects with distance and the mean wipe on soil arsenic concentrations were also significant ($p = 0.032$ and $p = 0.020$, respectively). It was also determined that as soil distance and depth increased, soil arsenic concentrations decreased. The remaining variables, including age, size, bulk density and slope had no significant effects on soil arsenic concentrations.
Keywords: **arsenic, soil, CCA**

1. Introduction

Since the 1970's the use of chromated copper arsenate (CCA) as a chemical wood preservative to prevent rot, insect and microbial decay has been utilized widely throughout the Unites States. Although CCA for treatment of lumber has been banned since January 1, 2004 many homes still have decks, playsets, fences and other wooden structures made with lumber treated with CCA.[1] Although exposure from chromium, copper and arsenic all have negative health effects, arsenic is considered to be the most harmful. [2,3,4]

Not only does arsenic pose a higher health risk, it is also the most readily leached among copper, chromium and arsenic .[5,6,7,8] Many assessments and studies have addressed the concentrations and exposure risks of arsenic on CCA treated surfaces, soil under the structure and in the leachate.[9,10] Less is known about arsenic in soil directly adjacent to the treated lumber. Many factors in both the lumber and the soil affect arsenic concentration within soil. Soil characteristics that may alter arsenic concentrations include; pH, organic matter, cation exchange capacity,[11] presence of Al and Fe, rainfall, humidity and topography. The most influential factors are soil texture, bulk density and water holding capacity [12] three important factors all influence water flow (or leachate), the pathway by which arsenic is spread in soil. Arsenic has been found to be more mobile in sandy soil,[6] and in soil with a low bulk density and that has a higher sorption in soil with more organic matter [5] although according to Balasoiu et al. study, both organic matter and mineral soil demonstrated high levels of sorption.[11]

Studies have demonstrated that arsenic concentrations differ among varying soil depths and distances from the treated structure. Compared to background levels of arsenic, soils directly adjacent the treated structures have been found to contain high levels of arsenic. One study found that the most elevated levels of arsenic were within 0.5m from telephone poles treated with CCA while another found that the closer the soil sample to the structure, the higher the concentrations of arsenic. Studies have also shown that elevated levels of arsenic migrate through soil columns.[5,6,9,13,10] Although distance and depth of contaminated soil is documented for decks, no known research has been done to study the interactive effects between variables such as deck age, deck size, bulk density, ground slope and average deck wipe concentrations.

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 how to plan on using the area around their deck.

2. Materials and Methods

2.1 site determination

Six decks were randomly chosen to sample in Asheville, North Carolina. The randomization method consisted of gridding the greater Asheville area on a map and numbering each cell within the grid. The downtown area was not numbered because of the lack of decks that would be found in the area. Then 18 numbers were randomly chosen from the range of cells using SAS. 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 houses that replied to the flyer were visited. Then it was determined if the decks would be appropriate for our study, i.e.. if they were constructed before January 1, 2004 and if they had not been treated with stain/sealant/paint for the past three years. These factors assured that the decks would have some arsenic content. After verification that the houses met the qualifications, they were sampled. There were difficulties in finding appropriate decks and finding willing participants for the study, therefore only six decks were selected.

2.2 distance, depth slope, bulk density/porosity and other external factors

The deck was first bisected into two equal halves by measuring the width and depth of the surface of each deck. A wipe sample was used to determine the arsenic concentration of the surface of each deck. To produce this wipe sample a Ghost Wipe™ was used to rub the deck in a specific pattern with aid from a rectangular plastic template. First the template was taped down in its position, while using gloves, the wipe was opened fully. The four corners of the inside of the template were then wiped firmly once. Next, the wipe was folded in half and wiped the deck in an "S" shape. Again the wipe was folded and a "S" pattern was used to wipe the area inside of the template in the opposite way of the first "S" pattern. This wipe sample was obtained from the middle of each section which provided an average arsenic level for the deck. From the middle of the deck, four distances from the deck were taken within the yard running a line perpendicular to the longest edge of the deck. These distances included directly under the rim joist of the deck (0cm), 15cm and 60cm from the deck and a background sample at 300cm. Within each distance three depths were measured, 0-10cm, 10-20cm, and 20-30cm. A soil probe was used to obtain the samples. The probe was marked with the three depths needed. The first depth was extracted by pounding the probe into the ground until 10cm of soil was obtained. This first depth was then put into a plastic bag. The probe was then cleaned with a bottle brush to remove soil from the previous sampling. The 10-20cm depth was taken by placing the probe back into the same hole and digging another 10cm. This excavated soil was put into a different bag. The same was done for the 20-30cm sample.

Slope was determined by placing one end of a 2ft level at the 0cm distance on the ground. The distance from the opposite end of the level to the ground was measured. The following equation (1) was used to calculate slope.

$$\text{Slope (\%)} = (H/2\text{ft}) \times 100 \qquad (1)$$

Where H = distance in feet from end of level to the ground

At each site, a bulk density sample was taken directly beside the 60cm plug. This distance was in the middle of the distances for each site. To obtain the samples for analysis, any 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 62.8cm^3 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 it was lifted out of the surrounding soil. Contents of cylinder were placed into a plastic bag.

In the lab, all beakers were cleaned with acid, dried in the oven and then placed in a desiccator for 10min to dry. The glassware was then weighed on a balance. The contents of the cores were then placed in the beakers and dried overnight on an oven at 105° C. The beakers with the soil were then taken out of the oven and placed in the desiccator for 10min to cool. The beakers and soil were then weighed. The following calculation (2) was used to derive the bulk density.

$$\text{Bulk density (g/cm}^3\text{)} = W/V \tag{2}$$

Where W= oven dry soil weight in grams
V= volume of core in cm^3

The square footage of the deck was calculated, not including stairs that may be attached. Age of the deck and treatment history were determined through personal communication with the owner.

2.3 arsenic analysis

Atomic absorption spectroscopy (AAS) was used to determine the concentration amounts of arsenic in both the wipes and the soil samples. Briefly, 0.10g of soil was weighed into 50mL vials. Deck sample wipes were folded up and placed into different vials and 6mL of concentrated HNO_3 and 2mL of 30% H_2O_2 were added to each of the vials. The solution in the vials where then heated in a digestion block to 95°C until 5mL of solution was left. After cooling 3mL concentrated HNO_3 and 1mL 30% H_2O_2 were added and the solution was heated again to 95°C. The vials were then brought to 50mL volume with DI water. A clean wipe was placed in the matrix 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 0.03g NIST Montana Soil Standard Reference Material with a concentration of 105ug/g arsenic. The Method Detection Limit for soil was 1.14µg/g and the MDL for the dust wipes was 0.12µg/wipe to fulfill quality control standards.

An AAS Method-Graphite furnace (Thermo Electron Corporation, M-Series, GF952 Zeeman Furnace) was used to analyze the samples. For quality assurance, runs ended with reagent blank, a 50.0ppb continuing calibration verification (CCV), a 60.0ppb quality control (QC) sample and a duplicate QC sample. A matrix blank was required to be less than half the lowest standard used on curve. The matrix LCS was run two per batch and was required to be within 85-115% recovery. The reagent blank was run at the beginning and end of 10 samples with less than half of the lowest standard used on the curve. The 50.0 ppb CCV and 60.0 ppb QC/duplicate was run at the beginning and end of 10 samples with a required 85-115% recovery.

2.4 Statistical Analysis

A mixed model using the natural log of soil arsenic concentration as the response variable was employed to analyze the data. The natural log was employed to improve normality and homoscedasticity 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 their 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 instead of a value of 0. Any between-site variables or associated interactions found to be significant in those models were included in a joint model. Between-site variables and associated interactions that were significant in those models were included in a final model. Models were fit with the statistical program SAS.

3. Results

Three pairs of between-site variables were highly correlated with each other: log mean deck wipe and site slope (r = -0.81993 , p <0.0001), log mean deck wipe and age (r = -0.64816 , p <0.0001), and site slope and age (r = 0.70948, p <0.0001). 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 = 0.0201) and the interaction of log mean deck wipe arsenic concentration and distance (F = 9.40, p <0.0001), in the model with age the interaction of age and distance (F = 7.77 , p = 0.0002),and in the model with site slope the interaction of site slope and distance (F = 6.14, p = 0.0012). When all of the above factors were combined in a model together only the interaction of log mean deck wipe arsenic concentration and distance was significant (F = 9.40, p = 0.0001).

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 homoscedasticity (no pattern of unequal spread apparent in plot of residuals versus fitted response values).

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

Effect	F value	P value
Location	47.40	<0.001
Depth	17.14	<0.001
Location*Depth	2.54	0.030
Wipe	14.00	0.020
Wipe*Distance	9.40	<0.001
Wipe*Depth	0.56	0.575

Results of fitting the mixed linear model including main effects and two-factor interactions are presented in Table 1. The log mean deck wipe by depth interactive effect was not statistically significant (F = 0.56, p=0.575), which indicates that the slopes of the relationship of log soil arsenic with log mean deck wipe were not significantly different for the different depths. The log mean deck wipe by distance interactive effect was statistically significant (F = 9.40, p<0.001), which indicates that the slopes of the relationship of log soil arsenic with log mean deck wipe were significantly different for the different distances. Individual tests for the difference in slopes of the relationship of log soil arsenic with log mean deck wipe between different distances (Table 2) indicates that slopes, representing the change in log soil arsenic concentration (µg/g) corresponding to an increase of one unit in log wipe arsenic concentration (µg/(100cm^2)), are lower for distances farther from the deck. The interactive effect of depth and distance on log soil arsenic was statistically significant (F=2.54, p=0.032). A plot of estimated mean soil arsenic, including individual 95% confidence limits, (Figure 1) indicates that soil arsenic levels have greater differences between depths at distances closer to the deck.

Table 2. The differences in slopes of log mean deck arsenic concentrations for different distances from the decks.

Distance From Deck (cm)	Estimated Slope	Lower 95% CI Limit	Upper 95% CI Limit
0	1.32	0.79	1.86
15	0.90	0.36	1.43
60	0.58	0.04	1.11
300	0.01	-0.53	0.55

The main effect of log mean wipe arsenic concentration was statistically significant (F=14.00, p=0.020), which indicates that the mean slope of the relationship of log soil arsenic with log mean deck wipe is not zero. The main effect of distance was statistically significant (F=47.40, p<0.001), which indicates that there was evidence of a difference in mean log soil arsenic between different distances at the mean log wipe arsenic concentration. The main effect of depth was statistically significant (F=17.14, p<0.001), which indicates a difference in mean log soil arsenic between different depths at the mean log wipe arsenic concentration. It can be seen from Figure 1 that soil arsenic concentrations are greater at smaller distances and depths.

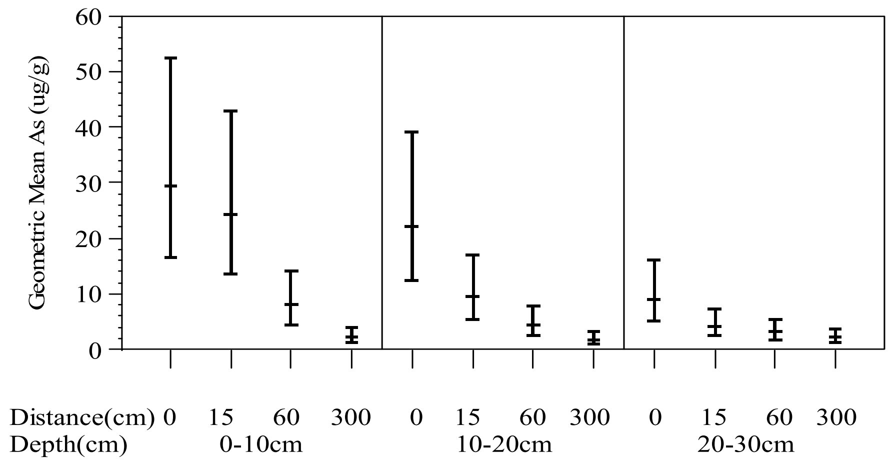

Figure 1. Estimated Geometric Mean Arsenic and 95% Individual Confidence Limits

4. Discussion

This study is congruent with many other studies in that there is a negative relationship between concentrations of arsenic in the soil and the distance from decks [5,7,14] and a negative relationship between arsenic in the soil and depth from the ground surface. [14,6] The only distance that did not exhibit the negative relationship between depth and soil arsenic was the farthest distance four (300cm). This indicates that at a distance of 300cm, the soil is not affected by the arsenic in the deck. It can be seen from Figure 1 that the significant interactive effect of depth and distance on soil arsenic concentrations is due to the fact that the effects of depth are greater at the closer distances than the farther distances. The interactive effect between deck wipes and distance was also significantly different. These findings support the hypothesis that most of the arsenic found in the soil at these sites results from arsenic released from the decks.

Ma et al. suggests that soil arsenic concentrations rapidly decrease within short distances from the deck. [10] This study also found this to be true as shown in Table 2 indicating that the area of greatest concern occurs directly under the outside edge of the CCA treated decks. There is, however, conflicting results as to what area has the greatest soil arsenic concentrations in many studies. Some found higher arsenic concentrations under the deck and some adjacent to the deck.[15] Chirenje et al. suggests the reason why their results showed higher soil concentrations under the deck was because of the lower rainfall that occurs there. The less rain, the less leaching occurs. [5]

Within the between-site variables and within-site variables models, distance from deck is shown to be the variable that has a significant interactive effect with log mean deck wipe, age and slope. The high F value for the final model suggests that distance had the greatest effect on soil arsenic concentrations. Log mean deck wipe also had a significant positive relationship with soil arsenic, which was stronger at closer locations. This is consistent with the hypothesis that the deck is the primary source of arsenic in the soil. The variables age and slope were not significant alone, but they did have significant interactive effects with distance in the models not containing other between-site effects. As the age of the deck increased the difference in soil arsenic concentration between the closer samples and the more distant samples became greater. One other study found that as the age of the deck increased, the amount of arsenic in the soil also increased while another study found that newer CCA treated poles have higher soil arsenic levels associated with them.[9,5] Two other studies found no significant effect between age and soil arsenic concentrations in the final model. [6, 10] The interactive effect between slope and distance was also significant. As the slope of the ground next to the deck increased that difference was less. Both of these results are also consistent with the hypothesis that the deck is the primary source of arsenic in the soil. However when the interactive effects of log mean deck wipe, age of deck and slope of ground with sample distance were combined in a model, only the interactive effect of log mean deck wipe was significant. Because the three predictor variables were highly correlated and there were only 6 sites, it is not possible to determine which factor is primarily responsible for greater differences in soil arsenic concentrations between closer and farther distances; although the data suggest that the log mean deck wipe may be the most important.

It was hypothesized that the larger the deck, the more arsenic is available to leach into the soil but this was not the case because again there was no effect between deck size and arsenic concentrations in the soil. Given that the path of arsenic from the structure to the soil is leachate and water can travel farthest through soil columns with lower bulk densities it was postulated that bulk density would play an important part in migration of arsenic but again, bulk density had no effect. This may also be because the variability between sites was minimal. The lack of significant effects with many of the variables tested could be attributed to the limited number of decks studied, only six, or the inaccuracy of the deck owner's knowledge about the treatment and/or age of their deck. Also the great number of factors not tested, such as soil pH, soil composition, soil particle size distribution, amount of arsenic originally in the lumber and many environmental factors all could play a part in arsenic's mobility. More research is needed to create a more complete picture of the factors that may affect arsenic's mobility in the soil.

All soil samples were over the EPA's Region 6 cancer soil screening level (SSL) of 0.39µg/g, including background samples. [4] The SSL is not a national cleanup standard but where concentrations exceed the SSL, further investigation may be necessary.[1] A study conducted by the Association for the Environmental Health of Soils shows that the soil arsenic ranges for residential areas in various states within the United States vary from less than 1 to greater than1000µg/g.[10] The same study shows that states have widely varying cleanup levels, or levels that require action, that are all based on widely varying criteria. [16] The non-cancer SSL determined by the EPA is 22µg/g. This study's mean concentrations for depths 1-10cm and 11-20cm depths for all sites and distances were 24.0µg/g and 21.1µg/g respectively which are both over the non-cancer SSL. Mean arsenic concentrations at the 300 cm distance were approximately 2µg/g at each depth, which are substantially less than the mean arsenic concentration of 7.2µg/g from background samples taken in a national study in 1984. [17] Therefore, for the decks considered in this study, increases in soil arsenic concentrations from decks appear to be limited to distances less than 300 cm. The results of this study suggest a potential strategy for remediation of soil arsenic near decks. If the top 30cm soil directly under the deck out to a distance of 15cm from the deck and the top 10cm soil out to a distance of 60cm were replaced with new soil the potential for exposure would be reduced significantly.

Other studies have argued that is possible that increases in soil arsenic concentrations near CCA-treated structures may not be from arsenic leaching from the structure but may be from other sources such as saw dust created in building the structure or naturally occurring arsenic.[18] Our findings support the hypothesis that the primary source of arsenic in soil proximate to CCA-treated decks is leaching from the deck. The strong relationship with deck wipe arsenic and strong and consistent relationship of soil arsenic with distance from the deck are indicative of leaching from the deck and not nearby sawdust or other causes.

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