STATISTICAL ANALYSIS OF INFLUENCE OF SOIL SOURCE ON LEACHING OF ARSENIC AND COPPER FROM CCA-C TREATED WOOD

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ABSTRACT

Leaching of wood preservatives affects the long-term efficacy and environmental impact of treated wood. Soil properties and wood characteristics can affect leaching of woad preservatives, but these effects are not well understood. This paper reports a statistical analysis of the effects of soil and wood properties on leaching of arsenic (As) and copper (Cu) from southern yellow pine sapwood treated with chromated copper arsenate (CCA-C). Specimens were leached by an accelerated laboratory method for 12 weeks in soil obtained from different locations or in water. Loss of Cu and As was measured using X-ray fluorescence and correlated with various physical and chemical soil properties. Leaching was greater from specimens with higher initial As and Cu retentions. Average Cu loss was approximately equal to or greater than As loss for specimens exposed to soil: for specimens leached in water, As loss was about twice that of Cu loss. Generally, more Cu leaching occurred from specimens in soil contact compared to specimens in water, suggesting that ground-contact leaching studies of the new copper-rich systems should employ soil-based methods for realistic depletion measurements. The amount of As and Cu leached was influenced by soil properties. Depletion of Cu and As from CCA-treated woad appears to be differentially related to various soil properties as well as to initial As and Cu retention in the wood. This research will help develop a standard laboratory method for soil-contact leaching of metals from CCA and other copper-based preservative systems.

Keywords: CCA-C, depletion, leaching. soil, wood preservative.

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INTRODUCTION

Leaching and depletion caused by biological and chemical reactions lower the retention of metallic or organic biocides when treated wood is placed in exterior applications. Although extremely difficult to predict, biocide depletion is important since it affects the long-term efficacy of treated wood and can be an environmental concern.

One reason for the difficulty in predicting depletion is that it is influenced by many factors. For wood placed in ground contact, soil characteristics appear to have some influence on leaching. For example, greater leaching of metallics usually occurs when treated wood is placed in soil as opposed to water (Nicholas 1988; Cooper and Ung 1992; Wang et al. 1998), indicating that the chemical and physical properties of a particular soil have an effect. The type of microbes present, which is heavily influenced by the soil, can also affect depletion. Collection methods in laboratory studies, including experimental setup, experimental methods, sampling, and microbial determination methods, can contribute to variability in depletion. Even under careful control, depletion among replicate samples can vary widely (Schultz et al. 2002), and wood itself is extremely variable (Lebow et al. 2004; Schultz et al. 2004) resulting in erratic data that are difficult to interpret.

The development of an effective wood preservative requires considerable laboratory and outdoor exposure tests, including leaching studies. When this study was initiated, there was no standard laboratory accelerated leaching protocol for treated wood in soil contact; only a short-term laboratory water leach was required by the American Wood-Preservers' Association (AWPA) for new system proposals (AWPA 2002).

In this study, we further explored the roles of two factors in leaching, treatment variability and soil properties, by conducting a full statistical analysis of leaching from samples exposed to five soils with a range of properties. Sapwood samples were cut from five different southern yellow pine hoards, All samples were treated together with CCA-C, and matched samples from each board were then leached in water or one of five soils collected by government, university, and industry cooperators. We chose southern yellow pine because it is the major species group treated in the United States. Prior to 2004, CCA-C was the major U.S. wood preservative (Micklewright 1999), and it is still widely used for treatment of poles, piles, and timbers.

Our primary objective was to identify which soil and properties significantly affect CCA leaching; this knowledge could then be used to help develop a laboratory protocol for leaching of metallic-preservative-treated wood. A second objective was to determine if leaching is significantly influenced by the particular board from which a sample is cut.

MATERIALS AND METHODS

Wood samples

Small stakes, 14 mm square by 250 mm long, were cut from kiln-dried, defect-free southern yellow pine (*Pinus* spp.) sapwood. Thirty specimens were cut from each of five different boards, for a total of 150 specimens. The five boards were randomly selected from boards used to prepare field stakes or small wafers for laboratory decay tests. The specimens were equilibrated to approximately 10% moisture content before treating with CCA-C to a target retention of 6.4 kg m^{-3} (0.4 lb/ft^3) by a full-cell process (15 min vacuum at -95kPa, followed by 1,050 kPa pressure for 60 min). Treated specimens were stored in plastic bags for 7 days at room temperature to prevent redistribution of the biocide during air-drying/free water movement (Schultz et al. 2004), then unbagged and air-dried. A 100-mm-long section was then cut from each specimen to determine the initial CCA retention prior to leaching. The retention sample was removed from the cut end of the section to avoid the possibly higher retention at the ends of the treated specimen (Schultz et al. 2004).

Soil leaching

Researchers in Wisconsin (USDA Forest Service, Forest Products Laboratory), Georgia

(Arch Wood Protection Inc.), Michigan (Michigan State University), New York (Osmose, Inc.), and Mississippi (Mississippi State University at Dorman Lake) obtained soil locally and conducted the leaching trials. Specimens were also leached in deionized water at Mississippi State University. A common leaching protocol was developed prior to the experiment to minimize variation in the laboratory methodology.

At each laboratory, five replicate specimens cut from one specific board were inserted vertically into the soil of one pot, so that the end of each specimen was flush with the top of the soil. This process was repeated for other subsets of five specimens from each of the remaining 4 boards, for a total of 25 specimens leached in 5 pots at each laboratory. The bottom of each pot was covered with a plastic screen prior to adding the soil, and the drain hole was plugged with a rubber stopper. After the soil and specimens were added to the pot, distilled water was slowly added until the soil was saturated. After 24 h, the excess water was drained from the bottom of the pot by removing the stopper. Additional water was added twice a week to maintain high soil moisture content; a loose-fitting cover was placed over the pot to prevent drying. Pots were maintained at room temperature throughout the 12-week exposure period.

The samples leached in deionized water were immersed for 12 weeks using five replicate specimens cut from each of the same five boards used for the soil tests. Because each laboratory evaluated only one soil type, the effect of soil and any unknown variations in laboratory methodology were confounded. Further procedural details can he found in a report by Crawford et al. (2002).

A representative soil sample from each of the five participating laboratories was analyzed at Mississippi State University (MSU) for physical and chemical properties by previously described procedures (Schultz et al. 2002) for particle size distribution, pH, and organic matter (Table 1), chemical (Table 2). and heavy metal (Table 3) content.

A 50-mm section from the initial (unleached) sample and a leached 50-mm sample from each specimen were individually ground in a Wiley mill to pass through a 20-mesh (0.85-mm) screen. Each ground wood sample was analyzed three times, using different wood subsamples each time, to determine individual CCA components (chromium (Cr), copper (Cu), and arsenic (As), oxide basis) by X-ray fluorescence (XRF, ASOMA model 8620 bench-top instrument, SPECTRO Analytical Instruments, Inc. Marble Falls, Texas). Unfortunately, some soil iron and/or manganese leached into some specimens and interfered with Cr measurement (Schultz et al. 2003). Consequently, Cr depletion is not reported. This problem could be avoided by the use of other analytical techniques, such as ICP or atomic adsorption spectroscopy, hut such tests are not routinely used in the wood treatment industry.

Statistical analysis

The contributions of different experimental aspects (board, pot, specimen, specimen subsample for XRF) to the total variation in a pre-exposure retention measurement were studied using variance component models (specifically nested random effects models, Montgomery 1997). This assumed that assignments of speci-

TABLE 1. *Soil characteristics.*

Soil location	Lab[a]	Soil texture (%)			pH (H₂O)	pH (KCl)	Organic matter (%)
		Sand	Silt	Clay			
Wisconsin	FPL	17.9	67.2	14.9	6.68	5.82	2.13
Georgia	Arch	75.5	21.2	3.3	4.34	3.99	2.91
Michigan	MI	74.0	22.2	3.8	5.49	5.03	3.89
New York	Osmose	44.6	39.4	16.0	7.59	6.84	4.78
Mississippi	MSU	11.4	56.0	32.6	4.81	3.72	2.40

[a] FPL is Forest Products Laboratory; MI, Michigan State University; MSU, Mississippi State University.

TABLE 2. *Exchangeable cations and base saturation of soils.*

Soil location	Lab	Exchangeable cations (Cmol/kg)							
		Ca	Mg	K	Na	Exch H+	Exch Al[a]	Sum of bases	Base saturation (%)
Wisconsin	FPL	7.59	4.10	0.16	0.05	3.50	0.00	15.40	77.27
Georgia	Arch	2.11	0.93	0.07	0.03	6.15	0.32	9.29	33.80
Michigan	MI	4.27	0.97	0.37	0.06	5.91	0.06	11.58	48.96
New York	Osmose	16.26	2.03	0.80	0.03	2.58	0.00	21.70	88.10
Mississippi	MSU	5.66	4.49	0.39	0.12	15.60	5.45	26.26	40.31

[a] Not included in sum of bases.

TABLE 3. *Heavy metal content of soils.*

Soil location	Lab	Soil heavy metal content (ppm)								
		Fe	Mn	Zn	As	Cd	Cr	Ni	Pb	Cu
Wisconsin	FPL	16,111	1,248	50	7	0.047	20	18	15	11
Georgia	Arch	16,611	579	31	2	0.006	89	18	8	15
Michigan	MI	6,882	80	46	3	0.182	7	5	12	4
New York	Osmose	17,267	612	306	10	0.337	22	35	297	32
Mississippi	MSU	43,436	1,489	46	23	0.390	43	13	40	11

mens from a particular board to pots were from random selection within the board. Random effect and residual plots were examined for non-normality and independence. Based on this analysis of the pre-exposure measurements, each specimen was assigned a pre- and post-exposure measurement by averaging the three XRF measurements on the pre- and post-exposure material.

Randomized block models with covariates were used to better understand the influence of initial retention effects within and between boards and to evaluate soil type effects on leaching considering those influences. The appropriateness of including initial retention (pre-exposure measurement) as a covariate was evaluated in SAS v8.2 (SAS Institute 1999) following the general approach given by Littell et al. (1996) and Milliken and Johnson (2002). The biocide elements As and Cu were modeled separately using the same model forms.

Initially, models for post-exposure retention at the specimen level were fit to assess if at least one set of responses for each soil type/location had a nonzero relationship with initial retention. A nonzero relationship between the pre- and post-exposure retentions would indicate that inclusion of pre-exposure measurements in the model would help in understanding soil expo-

sure differences as well the extent of the relationship between pre- and post-exposure retentions. Evidence of nonzero initial (pre-exposure) retention effects was then followed by an overall test of a common initial retention effect within each chemical element, that is, a test of slope homogeneity. Results from this test would indicate that a common underlying coefficient could sufficiently explain the relationship between initial retention and exposure retention. For each biocide, an additive model with terms for treatment, common-slope covariate, and three error terms was fit. The error terms included board error, pot (board by soil) error, and specimen error. This model assumes that for a fixed initial retention, a soil/location effect can be modeled as an additive term. For these models, the effect of soil location on leaching can then be compared at a common initial retention value. Least squares means were compared using the simulation adjustment method option in SAS v8.2 using a family-wise error rate of 0.05.

From these models, the percentage of As or Cu leaching, P_i, at soil/location i ($i = 1,...,6$ for Georgia, Michigan, Mississippi, New York, Wisconsin, and water, respectively) was estimated by first defining a common initial retention of the appropriate biocide, $\bar{U}$, evaluating

the exposure retention $\hat{R}_i$ at the appropriate $\overline{U}$, and then calculating

$$\hat{P}_i = 100(1 - \hat{R}_i/\overline{U}) \qquad (1)$$

At a common fixed (non-random) initial biocide retention, mean comparison of percentage of leaching reduces to mean comparison of the exposed biocide retention values.

   Relationships between leaching and soil properties were examined graphically by Friendly's corrgrams (Friendly 2002) and statistically by regression procedures with additional random effects for boards, pots, and specimens in the statistical package S-PLUS (Insightful Corporation, Seattle, WA, 2001) following methods in Pinheiro and Bates (2000). For the retention of each biocide (As or Cu) after exposure at the specimen level, R_{ijk}, the final regression model, fit as mixed effect model, was generally of the form

$$R_{ijk} = \beta_0 + \beta_1 * S_{1i} + \beta_2 * S_{2i} + \beta_3 * U_{ijk}$$
$$+ w_{ij} + \varepsilon_{ijk} \qquad (2)$$

where

   β_0, β_1, β_2, β_3 are fixed regression parameters,
   S_{1i}, S_{2i} are specific soil property values for soil type i,

   $U_{,,}$ is initial retention of specimen ijk before exposure to leaching,

   $w_{ij} \sim$ iid $N(0,\sigma_w^2)$ (pot (board by soil) error), and

   $\varepsilon_{ijk} \sim$ iid $N(0,\sigma_\varepsilon^2)$ (specimen error).

   Unlike the randomized block models with covariates used for assessing mean differences, these models do not explicitly model soil type as a factor. Essentially we would like to capture the variations due to soil source methodology by associating them with differences in the initial soil properties. Depending on the model, certain

random effects (error terms) may be estimated as zero. In particular, for these regression models a random effect for boards was initially included but was excluded in the final models based on likelihood ratio tests.

RESULTS AND DISCUSSION

Board effect and relationship to initial retention and leaching extent

Variation in initial retention.–The largest contribution to variation in initial As and Cu retention (50%) was due to board-to-board differences, followed by specimen-to-specimen (within pot) variation. Average initial retention was estimated based on the variance component models, with estimated initial retention of 2.02 kg/m^3 for As and 1.27 kg/m^3 for Cu. Table 4 gives the variance breakdown for As and Cu measurements before exposure. Figures (not shown) of initial retentions showed initial As retention was higher in the Mississippi (MSU) and New York specimens than in the other specimens, whereas initial Cu retention was lower in the MSU specimens relative to the other specimens. Initial retentions for the different boards form clusters along the primary axis of the relationship, indicating that the particular board from which a sample was cut, influenced initial biocide retention. Furthermore, retention levels in specimens from the same board appeared to be more similar than retention levels in specimens from different boards. This was confirmed by the fit of the variance component model. Greater similarity in retention within than between boards was not unexpected. Schultz et al. (2004) found that biocide retention for samples treated in a laboratory cylinder was

TABLE 4. *Variance component (VC) estimation for milled wood Cu and As concentrations before exposure.*[a]

Variance component	Arsenic VC est. ($\times 10^{-2}$ –(kg/m^3)^2)	Contribution (%)	Copper VC est. ($\times 10^{-2}$ –(kg/m^3)^2)	Contribution(%)
Board-to-board, σ_b^2	2.89 (2.22)	50	1.29 (0.96)	54
Pot (board), σ_w^2	1.13 (0.42)	19	0.29 (0.13)	12
Specimen (pot), σ_ε^2	1.65 (0.22)	28	0.74 (0.10)	31
Within specimen, σ_ξ^2	0.16 (0.01)	3	0.05 (0.00)	2

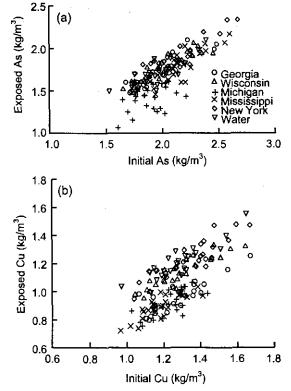   [a] Values in parentheses are standard errors.

highly correlated to the specific gravity of the particular wood sample. Samples from a particular board would likely have relatively more uniform specific gravity compared to samples cut from different boards, which suggests that initial retention will be strongly influenced by the particular board from which a sample is obtained.

Smaller contributions to variation in initial retention were due to between-pot variation and repeat measurements on specimens. The triplicate XRF analysis of subsamples made only a minor contribution (3%) to the overall variation in biocide retention (Table 4). Thus, the triplicate subsample measurements were averaged and further analyses were based on the average for each specimen.

Assignment to pots would not be expected to contribute to the variation in retention in unexposed specimens, yet variations were found in both As and Cu measurements. The variation between pots was due in part to differences in the initial retention measurements for specimens exposed at MSU. The MSU specimens were analyzed on a different date than those from other laboratories, and this time difference caused slight changes in XRF response. In analyzing the leaching results from exposed specimens, the analysis of covariance models described earlier and discussed below sheds light on possible effects.

Initial retention as a covariate in leaching analysis. — The average percentage of Cu and As leached from the CCA-C treated specimens after exposure to different soils and water was published previously (Crawford et al. 2002). Each individual board value was the average percentage leached from the five replicate specimens. The revised models result in different estimators and estimates of these values and are available from the first author of this paper.

Average final retention of As and Cu versus initial retention for each specimen is shown in Fig. 1. Not surprisingly, Fig. 1 indicates a positive relationship between initial and final exposed retention for individual specimens. Including initial retention as a covariate allowed the comparison of soil source effects at a com-

FIG. 1. Final versus initial biocide retention per specimen for As (a) and Cu (b).

mon initial retention level and provided information about the underlying relationships.

Following the methodology in Milliken and Johnson (2002), sequences of models were fit to determine the appropriateness of including the covariate and its forms in the models. For both As and Cu, a common underlying coefficient sufficiently explains the relationship between initial and exposure retentions for all exposure types. Table 5 shows the breakdown in the error estimates, which had substantial reductions from a model that did not include the covariate. The slope estimate, giving the relationship between initial and exposed retention, was 0.71 (S.E. = 0.05) for As and 0.65 (S.E. = 0.04) for Cu. Although not readily apparent from Fig. 1, the model estimated slight increases in the percentage of As and Cu leaching with an increase in initial As and Cu retention.

Mean comparisons of exposed retentions evaluated at a common initial retention level for

TABLE 5. *Influence of soil location on retained As and Cu based on randomized block models with covariate (initial retention).*

Model component	Retained As (R_{As})		Retained Cu (R_{Cu})	
	p-value (F-value, df_{num}, df_{den})	Error estimate ($\times 10^{-2}$ –(kg/m^3)^2)	*p*-value (F-value, df_{num}, df_{den})	Error estimate ($\times 10^{-2}$ –(kg/m^3)^2)
Soil type	<0.0001 (14.60,5,20)		<0.0001 (69.15,5,20)	
Covariate	<0.0001 (199.08,1,118)		<0.0001 (222.32,1,119)	
Board		$\hat{\sigma}_b^2 = 0.1105$		$\hat{\sigma}_b^2 = 0.0211$
Experimental error (pot = board × soil type)		$\hat{\sigma}_w^2 = 0.2858$		$\hat{\sigma}_w^2 = 0.0444$
Specimens (pot)		$\hat{\sigma}_\varepsilon^2 = 0.6589$		$\hat{\sigma}_\varepsilon^2 = 0.2647$
	$n = 149$[a]		$n = 150$	

[a] One exposed specimen for Wisconsin, cut from board 59, was missing

As ($U_{As} = 2.0223$ kg/m^3) and Cu ($U_{Cu} = 1.2675$ kg/m^3) were broken down to look at differences in soil exposures. Least squares means were compared using the simulation adjustment method as described in the Statistical Analysis section. The multiple comparisons for differences in percentage of As and Cu leached are listed in Table 6 (using a family-wise error rate of 0.05). The adjusted means sharing the same grouping label were not declared significantly different at the 0.05 level, indicating that specimens exposed in the Michigan soil experienced statistically significant greater As leaching than specimens exposed in the other four soils or water. Specimens exposed in the Michigan, Mississippi, and Georgia soil experienced statistically significant greater Cu leaching than specimens exposed elsewhere, while the Wisconsin exposure appeared intermediate to exposures to New York soil and water.

As can be seen with the adjusted average percentage of Cu and As leached, the amount of Cu and As leached varied greatly among five soils examined. Wang et al. (1998) reported that more Cu than As was lost from wood exposed to soil, whereas more As than Cu was lost from wood exposed to water, In the study reported here, more As than Cu was leached from samples exposed to New York soil, but for the other four soils Cu loss was greater than or equal to As loss. For water, the amount of As leached was about twice the Cu loss.

Other forms of the randomized complete block model could be considered, although they have different underlying assumptions and interpretations (for general discussion, see chapter 7 in Senn 1997). For example, using the percentage of leaching as the response variable in a randomized complete block design (without a covariate) results in mean comparisons similar to those in the randomized block model with covariate given in Table 5. With this implicit adjustment, the board effect is marginally significant (likelihood ratio tests, $p = 0.08$ for both

TABLE 6. *Mean comparisons for percentage of leaching of As and Cu.*

Treatment (soil location)	Arsenic leaching (%)	Multiple comparison grouping		Copper leaching (%)	Multiple comparison grouping		
Michigan	25.67	A		25.92	A		
Mississippi	15.94		B	25.64	A		
Georgia	13.72		B	24.50	A		
Water	13.34		B	6.28			C
Wisconsin	11.91		B	11.73		B	
New York	10.00		B	7.11		B	C

[a]Percentage of leaching estimated from randomized block with covariate models with estimates adjusted to common initial retention level ($P_{Ax,i}$ = 100 * $(1 - R_{As,i}/U_{As})$ with U_{As} = 2.02 kg/m^3, $P_{Cu,i}$ = 100 * $(1 - R_{Cu,i}/U_{Cu})$ with U_{Cu} = 1.27 kg/m^3), Initial retentions estimated from variance components models with 25 replicates per board.

As and Cu). Randomized complete block models based on the exposure retentions (i.e., without initial retention as a covariate) indicate highly significant board effects (likelihood ratio tests, $p = 0.0001$ for As and $p < 0.0001$ for Cu). Also, randomized complete block models based on the leached amounts (initial retention minus final retention) indicate highly significant board effects (likelihood ratio tests, $p = 0.0036$ for As and $p = 0.0005$ for Cu). Thus, while the amount leached is significantly related to the particular board from which a sample is cut, the initial retention explains much of the leaching variation, as confirmed by the inclusion of the initial retention as a covariate in the randomized complete block models. The randomized complete block with covariate model further allows the comparison of treatment differences at a common initial retention.

Essentially, differences in leaching by exposure to different soil types have been modeled effectively by differences in estimates of the intercept. It should be kept in mind that only a single target retention was evaluated in this study, and drawing inferences concerning leaching beyond this target retention level must be done with care. Other studies using a range of treatment solutions have found that the percentage of leaching typically declines with increased initial retention level (Cooper 2003).
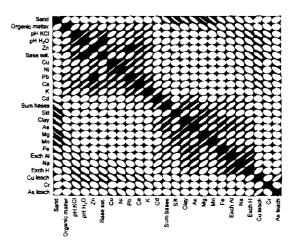
Soil properties associated with leaching

The physical and chemical properties of soils, which vary greatly among different soils, influence biocide leaching from wood (see references in Introduction, Schultz et al. 2002). However, the complex, inherently heterogeneous matrix of treated wood in combination with the complex nature of soil make it difficult to experimentally determine the dominating soil factors and their interactions. To study the association of leaching extent with soil properties, the chemical and physical properties of the five soils were measured (Tables 1 to 3).

Given the large number of soil properties relative to the small number of soils examined, the data set has low dimensionality, which limits

inferences. However, general associations between the percentage of As and Cu leached and soil properties, shown in the corrgram in Fig. 2, appear to offer some help in interpreting possible relationships: corrgrams provide a visual pattern of correlations based on low dimensionality due to the limited number of soils examined.

The corrgram illustrates two clusters of properties that appear positively related amongst themselves but not to the other cluster, with a few exceptions. As mentioned earlier, many soil properties are correlated with each other. Exceptions to the clustering are that sodium (Na), exchangeable hydrogen (Exch H), and exchangeable aluminum (Exch Al) have negative associations with the pH cluster, sand content is negatively related to one cluster, and chromium (Cr) content is not strongly associated with either cluster, although it appears to have some negative association with the pH cluster. Soil properties with the highest correlations with the percentage of As and Cu leached are potential initial candidates for simple regressions.
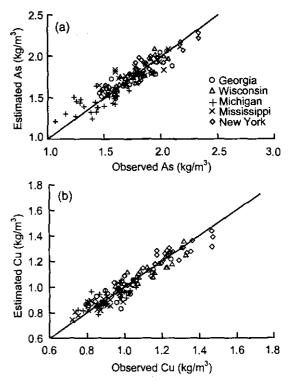
Initially, the exposed As retention, the initial As retention, and each of a select group of soil properties were individually modeled as simple regressions with nested random effects. The estimated random effects from the simple exposed As retention regression model were graphed against various soil properties (similar to re-

Fig. 2. Corrgram for percentage of leaching of As and Cu.

sidual graphs). Models evaluated as a mixed effect model in terms of the exposed As retention (kg/m^3), including a term for a random pot effect, are summarized in Table 7; random board effects in these models were insignificant. The corrgram in Fig. 2 suggests that soil Cu levels have the second highest correlation with percentage of As leached but are also highly correlated with soil nickel (Ni) levels. The inclusion of the soil Ni levels in the regression model appears to explain the relationship between exposed As retention levels and soil Cu levels. See models A–As, C–As, and D–As.

Figure 3 shows the ability of the mixed regression model A–As (Table 7) to estimate the final exposed As retention values for the specimens; random pot effects were set to zero for this graph. Interestingly, although it appears that soil iron (Fe) content was not singly related to the extent of As leaching, a model that includes initial As retention, soil Fe content, and exchangeable aluminum (Exch Al) is statistically comparable to results with the chosen model (model A–As versus model B–As). Previous research (Ruddick and Moms 1991; Moms et al. 1993) has indicated that Fe uptake could reduce As leaching.

FIG. 3. Final fit of mixed effect models (as determined by stepwise regression) in Table 7 for predicting retentions of exposed As (a) and Cu (b) specimens (random effects set to zero).

TABLE 7. *Nested regression models for exposure retentions of As and Cu as fit by mixed-effects models.[a]*

Model	Response R	β₀ est. (SE,df)	β₁ est. (SE,df)	S_1	β₂ est. (SE,df)	S_2	β₃ est(SE,df)	U	$\dot{\sigma}_w^2$	$\dot{\sigma}_\varepsilon^2$
									Random effects ($\times 10^{-2} \cdot (kg/m^3)^2$)	
A–As	As	0.2774 (0.1088,98)	0.0126 (0.0017,22)	Ni	–0.0669 (0.016622)	Organic matter	0.7041 (0.0479,98)	Initial retention	0.3936	0.6551
B–AS	As	–0.1211 (0.1036,98)	0.0294 (0.0039,22)	Fe($\times 10^{-3}$)	–0.1626 (0.0221,22)	Al	0.7079 (0.0488,98)	Initial retention	0.3888	0.6554
C–As	As	0.0982 (0.1078,98)	0.0095 (0.001923)	Ni			0.7131 (0.0531,98)	Initial retention	0.7415	0.6563
D–As	As	0.1383 (0.1108,98)	0.0088 (0.0022,23)	Cu			0.7134 (0.0531,98)	Initial retention	0.9477	0.6567
A–Cu	Cu	–0.1540 (0.0552,99)	0.0056 (0.0004,22)	Base saturation	0.0012 (0.0003,22)	Cr	0.6407 (0.0422,99)	Initial retention	0.0693	0.2514
B–Cu	Cu	0.5624 (0.0652,99)	–0.0751 (0.0059,22)	H	0.1354 (0.0125,22)	Al	0.6420 (0.0425,99)	Initial retention	0.0695	0.2515
C–Cu	Cu	–0.0578 (0.0593,99)	0.0046 (0.0004,23)	Base saturation			0.6483 (0.0464,99)	Initial retention	0.1503	0.2522
D–Cu	Cu	–0.2449 (0.0719,99)	0.0786 (0.0087,23)	pH(H_2O)			0.6450 (0.0483,99)	Initial retention	0.2102	0.2521

[a]Refer to Equation (2) for nomenclature.

These procedures were repeated for Cu retention of the specimens after exposure, and these results are summarized in Table 7. Figure 3b shows the ability of the mixed model A–Cu (Table 7) to estimate the final exposed Cu retention values for the specimens: random pot effects were set to zero for this graph.

As previously mentioned, many soil properties are interrelated. One example is soil base saturation and acidity. Any of these values would have been reasonable regressors in the regression models. After adjusting for initial retentions, retention after exposure and soil pH apparently have a fairly positive linear relationship, implying that more Cu is retained at higher pH levels; i.e., less leaching occurs with less acidic soils (data not shown). Other researchers have also reported soil pH to be a significant factor associated with Cu leaching from wood (Wang et al. 1998; Edlund and Nilsson 1999). However, the effect of soil acidity on leaching is likely more complex than indicated. For example, organic acids, which can complex with Cu to result in greater leaching than expected with inorganic acids (Warren and Solomon 1990; Cooper 1991; Lebow 1996), may also play a part. Cation exchange capacity has also been correlated with leaching of copper (Archer and Jin 1994). However, it needs to be emphasized that soils can vary widely, and the limited number of soils examined — as well as the inherent variability of wood — made it difficult to definitively assign one or two soil properties as important factors in metallic biocide leaching.

Soil Cu content had a negative relationship with the percentage of Cu leached (Fig. 2), implying that the higher the soil Cu content, the less percentage of Cu leached. This result is similar to results reported by Wang et al. (1998). We theorize that the lower the soil Cu content, the greater the diffusion gradient and, consequently, the greater the potential for Cu migration from wood.

The portion of variation in the retention level of exposed wood explained by the initial retention appears to he about 57% for As and 52% for Cu, based on maximum likelihood fits to the same models and following the procedures in Xu (2003). Total variation in the exposed retentions attributed to the fixed portions of the model was 83% for A–As and 89% for A–Cu.

CONCLUSIONS

Replicate XRF analysis was found to make only a minor contribution to the variation in initial retention measurements. Initial retention was highly correlated to the particular hoard from which a sample was cut, and the extent of As and Cu leached (kg/m^3) was highly dependent on the pre-exposure retention. Significantly more As was leached from samples exposed to the Michigan soil than from samples exposed to the other four soils or water. Significantly more Cu was leached from samples exposed to Michigan, Mississippi, and Georgia soils, with the least Cu leached from samples exposed to New York soil or leached with water. Cu loss was always greater when the leaching test was run with soil than water, although the losses attributed to the New York soil were not statistically different than those attributed to water. While the limited number of soils examined and the wide variation possible in soil chemical and physical properties make it difficult to identify statistically the most important soil properties associated with leaching, models associating the extent of As and Cu leached were developed that explained over approximately 80% of the variation in retention for both of these biocides.

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