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Chemical Speciation and Bioaccessibility of Arsenic and Chromium in Chromated Copper Arsenate-Treated Wood and Soils

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This research compares the As and Cr chemistry of dislodgeable residues from chromated copper arsenate (CCA)-treated wood collected by two different techniques (directly from the board surface either by rubbing with a soft bristle brush or by rinsing from human hands after contact with CCA-treated wood) and demonstrates that these materials are equivalent in terms of both the chemical form and bonding of As and Cr and in terms of the As leaching behavior. This finding links the extensive chemical characterization and bioavailability testing that has been done previously on the brush-removed residue to a material that is derived from human skin contact with CCA-treated wood. Additionally, this research characterizes the arsenic present in biological fluids (sweat and simulated gastric fluid) following contact with these residues. The data demonstrate that in biological fluids the arsenic is present primarily as free arsenate ions. Arsenic-containing soils were also extracted into human sweat to evaluate the potential for arsenic dissolution from soils at the skin surface. For soils from field sites, only a small fraction of the total arsenic is soluble in sweat. Based on comparisons to reference materials that have been used for in vivo dermal absorption studies, these findings suggest that the actual relative bioavailability via dermal absorption of As from CCA residues and soil may be well below the current default value of 3% used by U.S. EPA.

Introduction

Chromated copper arsenate (CCA) has been used to treat lumber for over 60 years (*1*), owing to the extended lifetime of CCA-treated wood as compared to its untreated counterparts (*2*−*5*). Since the late 1980s, U.S. production of CCA-treated lumber has averaged approximately 5×10^8 ft^3/year (*6*). Because of the inherent toxicity of arsenic and chromium, regulatory and public attention has become focused on the potential risks from this exposure source. In particular, exposure of children to arsenic from CCA-treated wood used in decks and play sets has received considerable attention, and the U. S. EPA Office of Pesticide Programs is currently preparing a human health risk assessment for direct-contact exposures to CCA-treated wood (www.epa.gov).

The chemical and structural environment of As and Cr in CCA-treated wood has been studied by several researchers (*2*, *3*, *7*−*9*). Bull et al. (2000) concluded that As and Cr are present in the (V) and (III) oxidation states, respectively, and that all of the As and half of the Cr was present as the solid $CrAsO_4$. They further reasoned that the remaining Cr must be present as $Cr(OH)_{3(s)}$. X-ray diffraction analysis of CCA-treated material showed no detectable crystalline phases other than that of the wood cellulose (*8*, *9*).

The most detailed study of the As and Cr form in CCA-treated materials evaluated three types of CCA-treated materials: new CCA-treated wood, aged CCA-treated wood, and an easily dislodgeable residue removed from the surface of aged CCA-treated wood. In all cases, the dominant oxidation states of the two elements are As(V) and Cr(III) and the local chemical environment of the two elements was best represented as a Cr/As cluster consisting of a Cr dimer bridged by an As(V) oxyanion (*10*).

The study reported herein was undertaken to answer several important questions that remained unresolved in the existing literature. First among them is whether the CCA residue that has been extensively examined in these previous investigations is representative of that to which humans are actually exposed in the environment. In contrast to the previously studied residue, which was collected with a soft bristle brush (brush-removed residue), the material examined in this work was collected directly from human hands after contact with CCA wood (hand-removed residue).

Second, we address the leaching characteristics of both of these residues when extracted with biologically relevant solvents, namely human sweat and simulated gastric solution.

Third, we determine the leaching behavior of four different As-containing soils in human sweat.

Finally, the data collected are interpreted in terms of the mechanism of As and Cr leaching from CCA-treated materials. They are also evaluated in light of previously published relative As bioavailability data and EPA exposure estimates.

Materials and Methods

Two environmental matrices were evaluated in this study: (1) dislodgeable residues from CCA-treated wood and (2) test soils that were collected from around CCA-treated wood and from other types of arsenic sources.

Brush-Removed Residue. The brush-removed residue was derived from CCA-treated boards by gently brushing the board with a soft bristle test tube brush while rinsing with deionized water. Details of the collection procedure, the X-ray absorption spectroscopy (XAS) analysis, and the As bioaccessibility of this material can be found in previous studies (*10*, *11*).

Hand-Removed Residue. The hand-removed residue was collected from nine weathered CCA-treated boards that were removed from decks in either Florida or Pennsylvania. Removal of the residue was conducted using a hand-wiping protocol developed by the Consumer Product Safety Commission (*12*), with the addition of a wash step to remove the CCA residue from the subject's hands. The hand was washed in a minimal amount of deionized water and a soft-bristle bottle brush was used to ensure complete removal of the CCA residue. To maximize the amount of material collected,

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each board was wiped, using this protocol, three times. The wash solution was then frozen and lyophilized. This procedure was employed in order to collect material that is representative in terms of the type of the material collected by incidental contact with CCA-treated wood. The resulting data cannot be used to calculate risk estimates derived from the quantity of material collected on a human hand from CCA wood contact. That question has been addressed in previous studies (*13*, *14*).

CCA-Treated Wood Surface. The surface of a weathered CCA-treated board (from a historical deck) was removed, to a depth of approximately 0.3 cm, as small wood chunks. This was accomplished by using a small hobby knife to cut a 1 cm by 1 cm grid in the wood surface, to an approximate depth of 0.3 cm. The hobby knife was then used to cut out small wood chunks that measured approximately 1 cm^2.

Test Soil Collection and Preparation. Test soils consisted of three field-collected soils that represented different arsenic sources and one synthetic substrate that consisted of soluble arsenic spiked onto a clean soil. Each soil was oven dried (45 °C) and sieved to <150 μm (100 mesh), unless otherwise indicated. The <150 μm size fraction was selected for this study because hand-press trials have indicated that the bulk of soil particles that adhere to human skin are of this size fraction (*15*) and also because this size fraction is being used for in vivo studies of dermal arsenic absorption from these soils (*16*).

The "utility pole soil" (CCA-impacted) was collected adjacent to a CCA-treated utility pole and contains As of CCA origin (based on the mineralogical forms of As present). Soil was collected near the base of utility poles treated with CCA type C wood that had been installed in a field service plot in Conley, GA, in 1998. Soil samples were then taken from several locations adjacent to the pole, extending outward approximately 12 in. and at depths of 1/4 to 2 in. Full details can be found in the Utility Pole Soil Collection Procedure section of the 2003 report submitted to U.S. EPA (*17*).

The "Colorado residential soil" was collected from a site in Colorado that has been impacted by arsenical pesticide application and contains elevated levels of both arsenic and lead. The "New York pesticide facility soil" sample was collected from Middleport, NY, and contains arsenic that originated from a pesticide production plant. The "Yolo County soil" is a reference soil, with a background As concentration of 0.05 mmol/kg, that was spiked with a sodium arsenate solution to obtain a soil arsenic concentration of 46.7 mmol/kg. The Colorado residential soil and the NewYork pesticide facility soil samples are currently being evaluated for dermal arsenic absorption using the nonhuman primate model described in Wester et al. (2004), while the Yolo County soil is the same substrate evaluated for dermal arsenic absorption in Wester et al. (1993) but is studied here in two separate size fractions: the 180−300 μm fraction used by Wester et al. (1993) and a <150 μm fraction to be consistent with the other soils used in this study (*11*, *18*). The 180−300 μm fraction was spiked with an arsenate solution 1 h prior to extraction, and the <150 μm fraction was spiked 15 min prior to extraction.

X-ray Absorption Spectroscopy . Bulk-phase Cr and As K-edge spectra, of both the near-edge (XANES) and extended fine-structure (EXAFS), were collected on the hand-removed residue and extracts; results for the brush-removed residue were reported in Nico et al. (2004) (*10*). The data were collected using GSECARS beamline 13-BM, with a beam size of approximately 1.5 × 6.0 mm, at the Advanced Photon Source at Argonne National Laboratory, Argonne, IL. The storage ring was operating in "top-up" mode so beam current remained relatively constant at ~100 mA. Spectra were collected in fluorescence mode using a Canberra 16-element Ge detector and a Si (111) monochromator. Incident and transmitted intensities were measured with in-line ionization chambers. Energy calibration was achieved by analyzing a Cr metallic foil before collecting a sample, in the case of Cr, and by recording the transmission and fluorescence spectra for an As(V) standard, Na_3AsO_4, in the case of As. Fluorescence spectra were processed in a manner described previously (*10*).

Electron Microprobe Analysis. The brush-removed residue was examined by electron microprobe analysis (EMPA). The EMPA work was conducted at the Laboratory for Environmental and Geological Studies at the University of Colorado, Boulder, using a JEOL 8600 electron microprobe equipped with four wavelength spectrometers (including an LEDC spectrometer crystal for carbon and an LDE-1 crystal for oxygen analyses), an energy-dispersive spectrometer, a BEI detector, and a Geller Microanalytical data processing system. Details regarding sample preparation and handling, and instrument operating conditions, are available in Link et al. (1994) (*19*).

Sweat Collection. Human sweat was collected from four volunteers, two male and two female, by having the subjects shower, rinse off with deionized water, don a Tyvek suit with collection bags taped around the feet, and then exercise for approximately 1 h (stationary bike was the preferred method). Fluid that pooled in the bags was collected at the end of the exercise session. Each individual sweat sample was filtered through a 0.45 μm cellulose acetate filter, and all the samples were combined into a single container to generate a composite sweat (420 mL of sweat at a pH of 7.2, specific conductivity of 6.31 mS/cm, and background As concentration 0.15 μmol/L). This sweat was used for the leaching tests conducted on the brush-removed residue, the CCA-treated wood, the utility pole soil, and the Yolo country soil (<150 μm fraction). Because additional sweat was needed to complete the experiments, a second sweat composite was created, which involved the participation of new male volunteers (the same females contributed to the second sweat composite). The second composite consisted of 785 mL at a pH of 7.8, and a specific conductivity of 6.43 mS/cm, and background As concentration 0.29 μmol/L. This second sweat sample was used for the remaining leaching tests. All sweat samples were stored at 4 °C. The reported extract As concentrations are background subtracted.

Sweat Leaching Procedure. The two CCA residues were tested without any further preparation beyond the collection procedures described. For the arsenic-bearing soils, the <150 μm size fraction was tested in the sweat extraction. For the reference soil (Yolo County soil; the same substrate evaluated in Wester et al. 1993), both the <150 μm and 180−300 μm size fractions were tested (*18*). The residue tests consisted of combining 5 mL of filtered sweat and 0.2 g of air-dried solid ($1{:}25_{(m/v)}$); the soil tests consisted of combining 1.0 g of soil in 25 mL of sweat ($1{:}25_{(m/v)}$). Leach tests were run at 30 °C for 8 h in a water bath equipped with a shaker table. The leachate was separated from the solid fraction by centrifugation, filtered through a 0.22 μm cellulose acetate syringe filter, and preserved with 0.02 mL of hydrochloric acid. Each of the sweat extraction tests was conducted in triplicate.

Test samples were submitted to Battelle Pacific NW Lab in Sequim, WA. The samples were analyzed for total arsenic and chromium by inductively coupled plasma/optical emission spectroscopy (ICP/OES), and selected extracts were analyzed for As species in solution by ion chromatography (IC) followed by inductively coupled plasma/mass spectrometry (ICP/MS). Based on retention times for As eluting from the ion column, and coelution of other elements, the presence of "free" As in extraction fluid (i.e., as As(III) or As(V) oxyanions in solution), or As complexed with other metals such as Cr or Fe, was established.

TABLE 1. Total Metal Concentration Data for Solid Matrixes

material type (solid matrixes)	arsenic (μmol/g)	chromium (μmol/g)	Cr:As molar ratio	iron (μmol/g)	copper (μmol/g)
brush-removed residue[b]	47.4	78.8	1.66	269	35.3
hand-removed residue[b,c]	9.92	19.6	1.98	57.4	8.47
wood surface (0.3 cm)	22.7	51.7	2.28	42.3	11.0
utility pole soil (CCA impacted)	4.56	3.38	0.74	543	3.40
NY pesticide facility soil[b]	21.5	0.333	0.02	304	0.946
Colorado residential soil	16.4	0.996	0.06	244	
Yolo County soil (spiked, <150 μm)[d]	46.3	6.06	0.13	720	0.677
Yolo County soil (spiked, 180−300 μm)[e]	48.5			664	

[a] Tables reporting values in both μmol/g and μg/g units are included in the Supporting Information for comparison to previous studies. [b] Average of duplicate samples. [c] Concentration in pre-extraction solid was back-calculated from the sweat extract and post-test residue concentrations and masses. [d] Yolo County soil was spiked with approximately 46.7 μmol/g arsenic 15 min before the extraction test was performed. [e] Yolo County soil was spiked with approximately 46.7 μmol/g arsenic 1 h before the extraction test was performed.

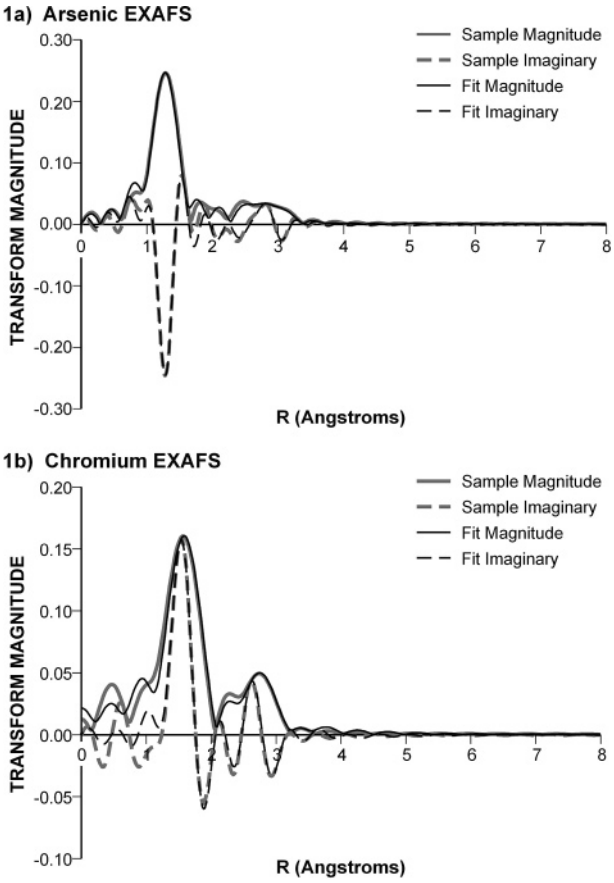

FIGURE 1. Sample data and calculated fits for As and Cr EXAFS of hand-removed residue.

Gastric Leaching Procedure. The gastric extraction method consisted of a 1 h extraction in simulated stomach fluid (pH value of 1.5) at physiological temperature (37 °C), with mixing by end-over-end rotation. The extraction involved 1 g of test substrate that had been sieved to <250 μm in 100 mL of buffered extraction fluid (glycine/HCl buffer). After the 1 h extraction, an aliquot of extract was filtered through a 0.45 μm cellulose acetate disk filter. Each of the gastric extractions was conducted in triplicate. A detailed description of this method is available in Kelley et al. (2002) (*20*). Gastric extracts were analyzed in the same way as sweat extracts. All extracts were frozen after the extraction procedure was complete and kept frozen until analysis.

Results and Discussion

Residue Comparison. The bulk elemental compositions of the two residues are shown in Table 1. The total metals concentrations of the two materials are quite different; however, the various metal ratios are relatively similar between the two materials. Therefore, the remaining mass of the hand-removed residue must consist of substances mostly free of As, Cr, Cu, or Fe. Potential substances would include Al- or Si-based soil minerals or metal-free organic material derived either from the surface of the wood or from the hands of the subjects. Since it seems unlikely that the hand-removal process would have dislodged more soil minerals than the brush-removal process and since the subjects' hands were brushed in order to ensure complete removal of the CCA material, dislodged skin cells are a likely source of this extra material.

The EMPA analysis of the brush-removed residue indicated that it is composed primarily of wood particles, consistent with a previous estimate of only 4% inorganic material in the residue based on elemental analysis (*21*). The wood residue particles exhibit broadly distributed As at concentrations ranging from 6.67 to 40.0 μmol/g by EMPA. The inorganic fraction consists primarily of common soil minerals such as quartz, pyroxene, microcline, and iron oxides (hematite and goethite). The inorganic fraction also contains small numbers of discrete grains, 1−2 μm, of an arsenic−chromium−oxygen compound averaging 41% arsenic in the grain, and As containing iron oxide minerals, 1−45 μm in size, averaging 2.9% arsenic. The percentage of As in the discrete grains is consistent with these particles being $CrAsO_4$, which are likely remnants of the "sludging" reactions known to produce $CrAsO_4$ particles on the surface of treated wood (*22*). Scanning electron microscopy conducted by Battelle on an aliquot of the brush-removed residue identified arsenic-enriched iron oxide particles in the matrix but did not identify any pure chromium arsenate particles (*21*). Attempts to quantify the fraction of As associated with each phase (wood, Cr−As particles, and Fe−As particles) during the EMP analysis by multiplying the concentration in each phase by the area micrograph occupied by that phase suggested that the majority of the As was associated with the wood particles.

The fitting parameters for the As and Cr EXAFS spectra of the hand-removed residue are shown in Table 2, and the actual fits in Figure 1a,b.

The universal similarity of the fitting parameters for the hand-removed residue and those previously established for the brush-removed residue, Table 3, clearly demonstrates that the As exists in a similar, if not identical, local chemical environments in the two materials, despite the difference in total metals concentrations (*10*). This indicates that the two materials are expected to have similar chemical behaviors.

Arsenic and Chromium Leaching from Residue. The releases of As and Cr under sweat and gastric leaching conditions are shown in Table 4. The data in Table 4 show, both in absolute terms and as a percentage of mass, that more As and Cr are leached from the CCA residues than

TABLE 2. Final Cr and As EXAFS Fitting Parameters for Hand-Removed Residue

	As EXAFS ($S_0^2 = 0.96$)				Cr EXAFS ($S_0^2 = 0.82$)			
scattering pair	As−O	As−Cr	As−O−O	As−O−As−O	Cr−O	Cr−C	Cr−As	Cr−Cr
coordination number (N)	3.95	1.89	12	4	5.99	4.31	1.24	1.11
distance R (Å)	1.69	3.28	3.05	3.36	2.00	3.03	3.25	3.48
σ^2	0.0019	0.0078	0.0038	0.038	0.0030	0.004	0.004	0.0044
E_0	2.35	2.35	2.35	2.35	0.83	0.83	0.83	0.83

TABLE 3. Final Cr and As EXAFS Fitting Parameters for Brush-Removed Residue

	As EXAFS ($S_0^2 = 0.99$)				Cr EXAFS ($S_0^2 = 0.64$)			
scattering pair	As−O	As−Cr	As−O−O	As−O−As−O	Cr−O	Cr−C	Cr−As	Cr−Cr
coordination number (N)	3.9	1.9	12	4	6.0	4.74	1.27	1.18
distance R (Å)	1.68	3.25	3.06	3.36	1.97	3.08	3.25	3.47
σ^2	0.0022	0.0094	0.0053	0.01	0.0016	0.011	0.0018	0.0017
E_0	0.82	0.82	0.82	0.82	−2.41	−2.41	−2.41	−2.41

TABLE 4. Metal Concentrations in Extract Solutions[a]

	arsenic				chromium			iron		copper	
	extracted				extracted			extracted		extracted	
material type	(μmol/L)	(%)	As(V) (%)	As(III) (%)	(μmol/L)	(%)	Cr:As molar ratio	(μmol/L)	(%)	(μmol/L)	(%)
Sweat Extraction Fluid											
brush-removed residue	246	12 ± 0.3	92 ± 0.5	7.8 ± 0.4	152	4.7	0.62	17.0	0.15	377	26
hand-removed residue[b,c]	43.7	11 ± 2.2			66.8	8.8	1.53	50.4	2.3	157	48
wood surface (0.3 cm)	21.2	2.3 ± 0.7	98 ± 0.2	1.7 ± 0.2	26.0	1.2	1.23	5.00	0.29	217	49
utility pole soil (CCA impacted)	2.65	1.4 ± 0.2	82 ± 0.8	18 ± 0.8	0.0450	0.031	0.02	0	∼0	0.169	0.12
NY pesticide facility soil	15.3	1.8 ± 0.1									
Colorado residential soil	71.1	11 ± 0.3									
Yolo County soil (spiked, <150 μm)[d]	879	45 ± 20									
Yolo County soil (spiked, 180−300 μm)[e]	1414	72 ± 2.7									
Gastric Extraction Fluid											
brush-removed residue	99.1	22 ± 2.4	93 ± 0.1	7.1 ± 0.1	62.9	8.2	0.63	98.5	3.8	249	73
wood surface (0.3 cm)	14.3	6.2 ± 0.4	99 ± 0.8	0.93 ± 0.8	9.99	1.9	0.70	13.0	3.0	99.8	90

[a] Unless otherwise stated, values represent the average of three samples. If concentration in the sweat blank or the matrix was greater than concentration in the sample extract, the sample extract concentration was set to zero. Tables reporting values in both μmol/g and μg/g units are included in the Supporting Information for comparison to previous studies. [b] Average of duplicate samples. [c] Concentration in pre-extraction solid was back-calculated from the sweat extract and post-test residue concentrations and masses. [d] Yolo County soil was spiked with approx 46.7 μmol/g arsenic 15 min before the extraction test was performed. [e] Yolo County soil was spiked with approx 46.7 μmol/g arsenic 1 h before the extraction test was performed.

from the CCA-treated wood. This was expected, given the finely divided nature of the residues and, therefore, the much larger leachable surface area compared to the wood sample, which was tested in the form of wood chips (i.e., approximately 1 cm^2 pieces of wood).

However, the percent of extractable As is almost identical between the two residues: the brush-removed averages 12% ($N = 3$), and the hand-removed averages 11% ($N = 2$). This similarity in chemical behavior is consistent with the conclusions reached from the XAS data.

The other major metals, Cr, Fe, and Cu, are more easily extracted from the hand-removed residue. The result is most dramatic for iron, with 0.15% extracted from the brush-removed residue, compared to 2.3% from the hand-removed residue. With Cr and Cu, while the percent extracted is greater, the total leachate concentration is actually less in the hand-removed versus the brush-removed residue. The increased relative solubility of the Cr, Cu, and Fe from the hand-removed residue is consistent with the hypothesis that it contains a larger fraction of organic material derived from skin cells. This material would tend to increase metal solubility through chelation (*23*). The effect is expected to be larger for Fe than for Cr or Cu because of the susceptibility of Fe to reductive dissolution as well as chelation. This trend is born out in the data shown in Table 4 where the percent extractable Cr and Cu both increase by roughly a factor of 2 while the percent extractable Fe increases by over an order of magnitude.

Extraction in simulated gastric fluid, versus in sweat, results in a greater percent extraction of As and Cr; however, the final solution concentrations of As and Cr are actually lower in the gastric extraction due to the greater mass to volume extraction ratio. Since As and Cr should be more soluble in the gastric solution as compared to the sweat solution, it is clear that the gastric extraction was not limited by solution saturation. In this way, the gastric extracts may represent a maximum leachable fraction of As and Cr, even under relatively harsh conditions. Therefore, in the dislodgeable residues ∼11%−12% of the As and ∼5%−9% of the Cr are more easily leachable, an additional ∼9% of the As and ∼3% of the Cr are available under harsher gastric leaching conditions, and finally, the remaining ∼80% of As and ∼90% of Cr are unavailable even under the gastric leaching conditions.

Form of Extracted Arsenic. The chemical form of the As present in the biological fluids was established by XAS analysis of the extraction fluids and confirmed by IC−ICP. Independently, each establishes that the dominant solution-phase arsenic form is a free arsenate ion. These results are consistent with the work of Khan et al. (2004) who also found that

arsenate was the dominant species extracted from CCA-treated wood samples (*24*).

One sweat and one gastric extract of the brush-removed residues were examined by XAS spectroscopy. The XANES spectra of the two solutions are identical, indicating that the form of the As is the same in both samples, Figure 2a. Because the absolute concentration of As was lower in the gastric extract than in the sweat extract, the data collected for the gastric extract were too noisy for the EXAFS to be analyzed. However, since the form of As appears to be the same in both species by XANES, detailed analysis of one of the solutions should be sufficient. The Fourier transforms of the As EXAFS of the sweat extract are shown in Figure 2b. Also shown in Figure 2b is the Fourier transform of an arsenate standard. The similarities between the two spectra are obvious, indicating that the form of As in the sweat extract is that of free arsenate. By way of contrast, the sweat extract spectrum is compared to that of the hand-removed residue in Figure 2c. The second peak in the hand-removed residue spectra at approximately 3.00 Å (uncorrected for phase shift) is caused by the Cr atoms that complex the As in this material. A peak similar to this would be expected in the sweat extract solution if the As in that solution were bound to elements such as Cr or Fe; however, no indication of any significant backscatter in the 3.00 Å region (uncorrected for phase shift) is observed. These data confirm that, once in solution, the As is no longer complexed with the Cr or Fe.

As a corraboration of the XAS analysis, the leachates were also analyzed by IC−ICP/MS. For all the leachate samples tested, free arsenate ion was the dominant form of As in solution (see Table 4). The sweat and gastric extracts of the brush-removed samples were also examined for dimethyl arsenate (DMA), but DMA concentrations were found to be 0.05% or less. The ICP/MS analysis of the As-bearing IC peaks showed no indication of coeluting elements such as Cr or Fe. Again, these data support the conclusion drawn from the XAS analysis that the form of the As in the sweat and gastric extracts is free arsenate ion.

The release of As into solution as free arsenate ion is consistent with the fact that As is preferentially leached with respect to Cr. For all CCA samples tested, the leaching solution is enriched in arsenic relative to the solid substrate tested, Tables 1 and 4. For example, the ratio (molar basis) of Cr to As is 1.66 and 1.98 in the brush-removed and hand-removed residues, respectively, but these ratios change to 0.62 and 1.53 for the sweat extract solutions. (The higher Cr-to-As ratio in the hand-removed residue leachate is due to the larger percentage extraction of Cr, which, as mentioned above, could be due to a greater concentrations of small organic chelators in the hand-removed residue.)

Nature of the Labile Arsenic Pool. One possible source of the sweat-extractable As and Cr is the dissolution of the $CrAsO_4$ particles identified by EMPA. The sweat extract solutions are over 6 orders of magnitude under-saturated with respect to $CrAsO_4$ (the degree of under-saturation was assessed using MINTEQ, sweat extract metal concentrations and pH, and a $CrAsO_4$ K_{sp} of 7.8×10^{-21}). This means that any $CrAsO_4$ present in the residue should have dissolved during the sweat extraction procedure. This assumes that there are not kinetic limitations on the dissolution of these particles, but given their small size (1−2 μm), large surface areas, and the 8 h extraction time, kinetic limitations seem unlikely. This calculation places a conservative upper limit on the fraction of As present in the EMPA-detected $CrAsO_4$ particles at ∼12% (the percent As released in the sweat extraction). However, the data from the brush-removed residue do not support $CrAsO_4$ particles as the major source of arsenic because the Cr concentrations in the resulting extraction solutions are not large enough to account for the observed concentrations of As. Therefore, either the $CrAsO_4$ undergoes incongruent dissolution, liberating the As and re-forming $Cr(OH)_3$, or there is another source of labile As. The former, while possible, seems unlikely to be true because even in the gastric extraction solutions where the pH is low enough to make $Cr(OH)_3$ soluble, there is still not enough Cr in the extraction solutions to account for the observed As concentrations.

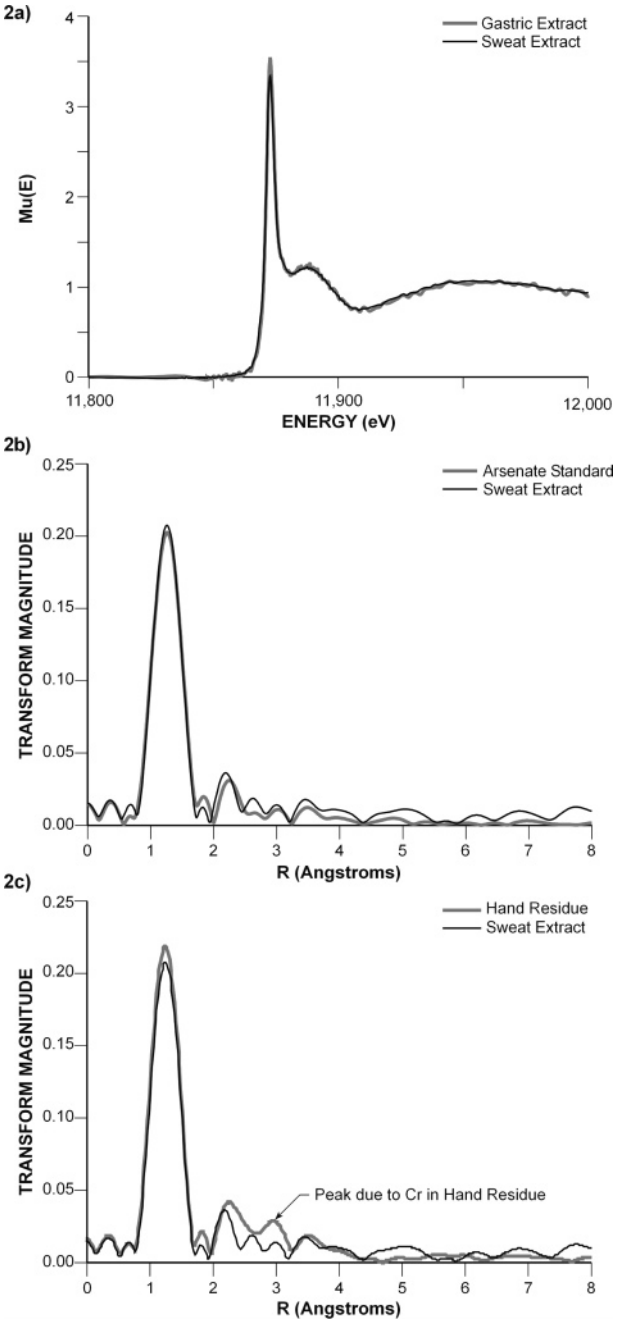

FIGURE 2. (a) Comparison of As XANES spectra for sweat and gastric extract of the brush-removed residue. (b) Comparison of Fourier transformed As EXAFS spectrum of the gastric extract of the brush-removed residue with an arsenate standard spectrum. (c) Comparison of Fourier transformed EXAFS spectrum of the gastric extract of the hand-removed residue with the spectrum of the hand-removed residue.

Another likely source of extractable As in wood is arsenate ions sorbed onto Fe oxides and/or the other soil minerals in the dislodgeable residues. The EMP analysis of the brush-removed residue specifically identified Fe oxide particles containing As. A small percentage of As, <12%, being bound to Fe instead of Cr would not be detectable in the XAS analysis

because of the similarities of Cr and Fe as backscattering elements. The fact that greater Fe extraction from the hand-removed residue, as opposed to the brush-removed, did not result in greater As extraction implies that almost all of the Fe-associated As is removed in the sweat extraction.

If the sweat-extractable pool of labile As is a combination of loosely sorbed free arsenate and $CrAsO_4$, then the next question concerns the nature of the additional As liberated during the gastric extraction. The two most likely possibilities are that the harsher extraction conditions accomplish the dissolution of some remaining recalcitrant $CrAsO_4$ particles or, more likely, that the high acid concentrations favor hydrolytic release of the As still bound to Cr binding sites in the wood. Either way, as stated above, the harsher conditions only liberate an additional ~9% of the total As in the residues, leaving >80% of the As unavailable.

Arsenic Leaching from Soil. The total metals concentrations for the studied soils are shown in Table 1, and the sweat extraction results are shown in Table 4. Both Yolo County soil fractions show As concentrations that are quite similar to the intended spike value of 46.7 μmol/g, implying that the As spike has been uniformly distributed throughout the sample. Between the two Yolo County soil size fractions, particle size had the expected effect on As retention with the <150 μm fractions leaching less As than the 180−300 μm fraction, 45% vs 72%, respectively. This is most likely due to a lower expected surface area of the particles in the larger size fraction. However, the most important result is that the the percentage of As released from the Yolo County soils is 40−50 times greater than any of the field-collected soils. (It should also be pointed out that the leaching results discussed above, for residues and soil samples, represent conservative measurements of As availability because the extraction conditions, which include high fluid-to-solid ratio, continuous mixing, and long extraction period, would tend to bias the results toward a greater percent extraction than would occur under real human exposure conditions.)

Environmental Significance. These data indicate that, independent of extraction fluid or substrate-extracted, the solubilized form of As is predominantly that of free arsenate ion. Consequently, this is the relevant form of arsenic to which a biological receptor would be exposed.

Furthermore, while there is a difference in total metals concentration between the two CCA residues, they are equivalent in terms of As and Cr oxidation state, binding environment, and As leachability. The residues are made up primarily (96%) of wood particles containing As and Cr bound together in an As−Cr complex. Within the residues ~12% of the As is available to the relatively mild conditions of leaching in human sweat and an additional 9% is available to the harsher simulated gastric conditions. The remaining ~80% of the As and 90% of the Cr appear to be resistant to even the harsher conditions, presumably remaining bound within wood particles as the Cr/As cluster described above. The labile fraction of As is likely composed of either weakly sorbed arsenate ions or $CrAsO_4$ particles that are present in small amounts in the residue.

The availability of As from the field soils when leached in human sweat ranged over an order of magnitude (1.4% to 11%) but was much less than in either size fraction of the As spiked soils, 45% and 72%, <150 μm and 180−300 μm, respectively. The greater extractability of As in the spiked soils is likely due to the short period of time between the addition of As to the soil and the attempt to extract the As. In general, it would be expected that the longer the As remains in contact with the soil before extraction the less available this As would be. While it is true that soils receiving As leached from CCA-treated wood would always have some fraction of "recent" As, it is equally true that the majority of the As in the soil will have had a significant amount of time (months to years) to equilibrate with the soil. It should also be pointed out that the utility pole soil, which is the one soil directly impacted by CCA-treated wood, had the lowest extractable As of any of the soils test, 1.4%.

A sample of Yolo County soil treated in an identical manner to our Yolo Country (180−300 μm) sample was used as the solid substrate in the Wester et al. (1993) study to try to understand dermal absorption of arsenic "from soil" (*18*). The data gathered from the Wester et al. (1993) research was interpreted by the EPA to support the assumption that 3% of arsenic "in soil" would be dermally absorbed (*18*). However, the percent As extraction from environmental soils and CCA residues was ~1/6 −1/100 of that extracted from spiked Yolo County soil (180−300 μm). Because the solubilization of As into biological fluids, i.e., sweat, is likely a key step in the dermal absorption of As, it is reasonable to suggest that actual dermal absorption of arsenic from environmental soils and CCA residues is likely to scale, roughly, with the sweat extractability of As from these materials. This implies that the currently accepted 3% dermal absorption value, derived from the spiked Yolo County soil, may significantly overestimate the availability of As from CCA-treated wood residues and arsenic-affected soils. Given that the sweat extraction procedure used in this research is far more aggressive than actual conditions at the skin surface, these data should not be considered a direct index of how much As might be available for dermal absorption, but rather they provide a sense of the relative solubility of As from the different substrates.

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Supporting Information Available

Further details of this study. This material is available free of charge via the Internet at http://pubs.acs.org.

Literature Cited

(1) Hingston, J. A.; Collins, C. D.; Murphy, R. J.; Lester, J. N. Leaching of chromated copper arsenate wood preservatives: a review. *Environ. Pollut.* **2001**, *111*, 53−66.

(2) Bull, D. C.; Harland, P. W.; Vallance, C.; Foran, G. J. EXAFS study of chromated copper arsenate timber preservative in wood. *J. Wood Sci.* **2000**, *46*, 248−252.

(3) Bull, D. C. The Chemistry of chromated copper arsenate II. Preservative-wood interactions.*Wood Sci. Technol.* **2001**, *34*, 459−466.

(4) Zagury, G. J.; Samson, R.; Deschenes, L. Occurrence of metals in soil and ground water near chromium copper arsenate-treated utility poles. *J. Environ. Qual.* **2003**, *32*, 507−514.

(5) Balasoiu, C. F.; Zagury, G. J.; Deschenes, L. Partitioning and speciation of chromium, copper, and arsenic in CCA-contaminated soils: influence of soil composition. *Sci. Total Environ.* **2001**, *280*, 239−255.

(6) Solo-Gabrielle, H.; Townsend, T. *Generation, use, disposal and management options for CCA-treated wood*; Florida Center for Solid and Hazardous Waste Management: Gainsville, FL, 1998.

(7) Woolson, E. A.; Gjovik, L. R. The Valence state of arsenic on treated wood. **1981**, *77*, 15−22.
(8) Kamdem, D. P. ESEM of CCA Type C *Treated Southern Pine; Osmose Inc.*: Buffalo, NY, 2001.
(9) Kamdem, D. P.; Cui, W. *X-ray Diffraction of CCA Treated Wood Surface; Osmose Inc.*: Buffalo, NY, 2001.
(10) Nico, P. S.; Fendorf, S. E.; Lowney, Y. W.; Holm, S. E.; Ruby, M. V. Chemical structure of arsenic and chromium in CCA-treated wood: implications of environmental weathering. *Environ. Sci. Technol.* **2004**, *38*, 5253−5260.
(11) Wester, R. C.; Hui, X.; Barbadillo, S.; Maibach, H. I.; Lowney, Y. W.; Schoof, R. A.; Holm, S. E.; Ruby, M. V. In vivo percutaneous absorption of arsenic from water and CCA-treated wood residue. *Toxicol. Sci.* **2004**, *79*, 287−295.
(12) Briefing package associated with Petition to Ban Chromated Copper Arsenic (CCA)-Treated Wood in Playground Equipment; Consumer Product Safety Commission, U.S. Government Printing Office: Washington, DC, 2003.
(13) Hemond, H. F.; Solo-Gabriele, H. M. Children's exposure to arsenic from CCA-treated wooden decks and playground structures. *Risk Anal.* **2004**, *24*, 51−64.
(14) Kwon, E.; Zhang, H.; Wang, Z.; Jhangri, G. S.; Lu, X.; Fok, N.; Gabos, S.; Li, X.-F.; Le, X. C. Arsenic on the hands of children after playing on playgrounds. *Environ. Health Perspect.* **2004**, *112*, 1375−1380.
(15) Duggan, M. J.; Inskip, M. J.; Rundle, S. A.; Moorcroft, J. S. Lead in playground dust and on the hands of school children. *Sci. Total Environ.* **1985**, *44*, 65−79.
(16) Lowney, Y. W.; Ruby, M. V.; Wester, R. C.; Schoof, R. A.; Holm, S. E.; Hui, X.; Barbadillo, S.; Maibach, H. I. Percutaneous absorption of arsenic from environmental media. *Toxicol. Ind. Health* **2005**, *21*, 1−14.
(17) *Relative Bioavailability of Arsenic in Soil Affected by CCA-Treated Wood*; American Chemistry Council: Arlington, VA, 2003.
(18) Wester, R. C.; Maibach, H. I.; Sedik, L.; Melendres, J.; Wade, M. In vivo and in vitro percutaneous absorption and skin decontamination of arsenic from water and soil. *Fundam. Appl. Toxicol.* **1993**, *20*, 336−340.
(19) Link, T. E.; Ruby, M. V.; Davis, A.; Nicholson, A. D. Soil lead mineralogy by microprobe: an interlaboratory comparison. *Environ. Sci. Technol.* **1994**, *28*, 985−988.
(20) Kelly, M. E.; Brauning, S. E.; Schoof, R. A.; Ruby, M. V. *Assessing oral bioavailability of metals in soil*; Battelle Press: Columbus, 2002.
(21) Sass, B. *Chemical Characteristics and Morphology of Particulate in Dislodgeable Residue*; Battelle Press: Columbus, 2003.
(22) Bull, D. C. The chemistry of chromated copper arsenate I. Characterisation of timber plant chemical sludge. *Wood Sci. Technol.* **2000**, *34*, 367−376.
(23) Dubbin, W. E. Influence of organic ligands on Cr desorption from hydroxy-Cr intercalated montmorillonite. *Chemosphere* **2004**, *54*, 1071−1077.
(24) Khan, B. I.; Solo-Gabriele, H. M.; Dubey, B. K.; Townsend, T. G.; Cai, Y. Arsenic speciation of solvent-extracted leachate from new and weathered CCA-treated wood. *Environ. Sci. Technol.* **2004**, *38*, 4527−4534.

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