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-----Oorspronkelijk bericht-----
Van: B.R. Boonstra [redacted]
Verzonden: zaterdag 11 maart 2017 0:54
Onderwerp: Chroom-6 en arsenicum in houtrook (kom in actie tegen kanker)

Griffie: Wilt u dit doorsturen? B.v.d.

Geachte raadslid, milieu ambtenaren en het college van B&W,

Wist u dat er over heel Nederland sloophout wordt verbrand in open haarden, allesbranders, vuurkorven of tuinkachels? Volgens de GGD Groningen muteert Chroom VI naar Chroom 3 als je geïmpregneerd hout verbrand (zie bijlage, persbericht dat wij hadden in de Consumenten Gezondheidgids). Maar is dat wel zo?

Wij hebben navraag gedaan bij een milieudeskundige ons dit laat weten:

Attached een aantal artikelen.
In Hingston staat op p 62 een referentie naar een studie van Nyren & Nilsson 1993 waaruit naar voren komt dat tot 20% van Cr in CCA-behandeld hout C6+ is. Daarin ook info over uitloging. Townsend (CCA5)geeft aanvullende info over CCA uitloging uit tuinhout naar de bodem. Nico e.a. (CCA4) over huidcontact met hout. Swietlik e.a. (CCA6) laat zien dat bij verbranding hout met Cr3+ omzetting van
Cr3+ in Cr6+ plaatsvindt.

www.maassluis.nu/nieuws/houtrook-grote-kans-op-kanker-door-chroom-6/

Op Marktplaats ziet u dat 'gratis brandhout' wordt aangeboden. Vaak gaat het hier om behandeld hout. Bedrijven moeten betalen voor het afvoeren van chemisch bewerkt hout. Het is voor hun aantrekkelijk dat hout gratis weg te geven aan bijvoorbeeld hun werknemers. Er is geen enkele controle op wat mensen verbranden in hun houtkachel.

Zie ook: https://www.youtube.com/watch?v=u_ifjBIG1g8 Hierin ziet u de belangen van de overheid parallel lopen en is er sprake van collusie.

De lokale gemeenten gaan uit wat het RIVM zegt. Alsmede de GGD. Maar is deze informatie wel onafhankelijk? Is het RIVM monopolist in de informatie verschaffing aan de Nederlandse overheid? Wie regeert ons land, is dat de politiek, het ministerie van Milieu & Infrastructuur of Milieudefensie?

Het Basisdocument Arseen van het RIVM geeft aan dat 20 tot 80% van het arseen vrijkomt in de lucht. Het bewuste document is (niet) meer online te vinden.

https://www.rijksoverheid.nl/onderwerpen/bestrijdingsmiddelen/vraag-en-antwoord/mag-ik-geimpregneerd-hout-gebruiken

Geïmpregneerd hout nooit verbranden

Gooi geïmpregneerd hout nooit zelf op een vuurtje of in de open haard.
Er komen dan ongezonde en milieuvervuilende stoffen vrij.

De rijksoverheid geeft aan dat er ongezonde stoffen vrijkomen.
Het is niet 'ongezond' (hiermee verkleint de Rijksoverheid de ernstige graad) maar buitengewoon slecht, namelijk levensbedreigend.

Zie ook http://sdnl.nl/tv.html

Zagen in geïmpregneerd hout: Hierbij werden grote concentraties Chroom VI gemeten. Helaas krijgen we dit rapport niet onder ogen.

Klokkenluiders: U kunt zich wenden tot het Meldpunt Rookoverlast. Wij gaan respectvol om met uw gegevens.

Hoe wilt u voorkomen dat er niet meer gestookt wordt op geïmpregneerd hout? Voorlichting? Roken op de werkplek: Dat werd pas opgelost toen er een rookverbod kwam op de werkplek. De GGD geeft aan dat ze niet voor elke houtkachel kunnen gaan liggen. Wij willen u vragen om het artikel van Maassluis door te gaan lezen.

Hoogachtend,
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werkgroep Rookoverlast
[redacted]
www.houtrookoverlast.nl

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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.

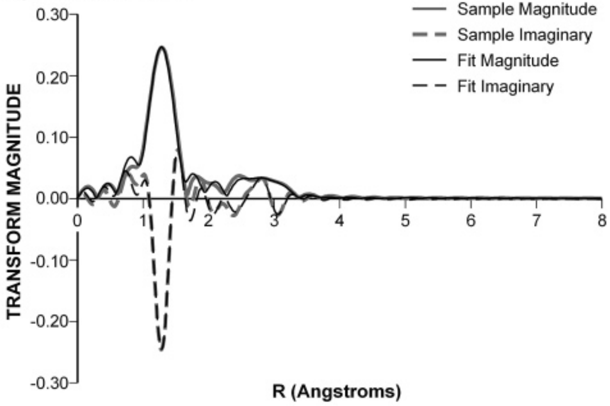
Test samples were submitted to Battelle Pacific NW Lab in Sequim, WA. The samples were analyzed for total arsenic and chromium by inductively coupled plasma/optical emission spectroscopy (ICP/OES), and selected extracts were analyzed for As species in solution by ion chromatography (IC) followed by inductively 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.

1a) Arsenic EXAFS



1b) Chromium EXAFS

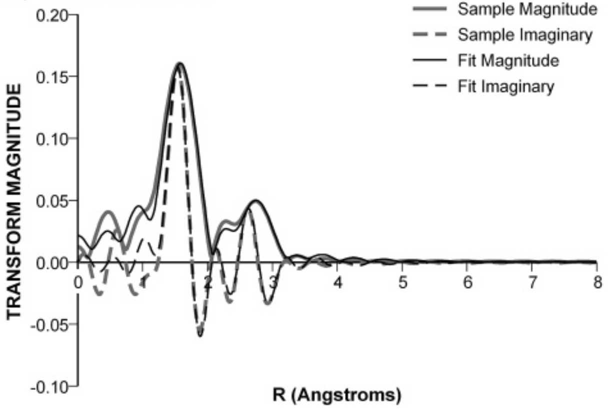


FIGURE 1. Sample data and calculated fits for As and Cr EXAFS of hand-removed residue.

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.

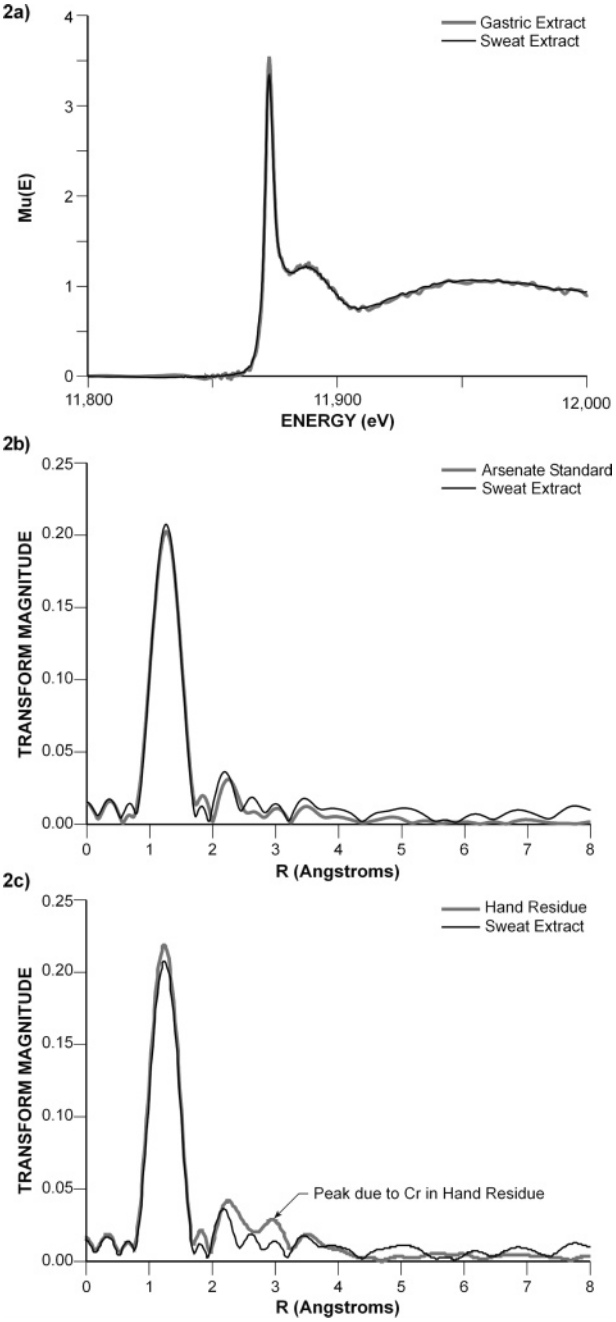


FIGURE 2. (a) Comparison of As XANES spectra for sweat and gastric extract of the brush-removed residue. (b) Comparison of Fourier transformed As EXAFS spectrum of the gastric extract of the brush-removed residue with an arsenate standard spectrum. (c) Comparison of Fourier transformed EXAFS spectrum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

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Chromium, Copper, and Arsenic Concentrations in Soil Underneath CCA-Treated Wood Structures

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Soils below nine structures (decks and foot bridges) in Florida were examined to evaluate potential impacts from chromated copper arsenate (CCA), a common wood preservative. Eight of the nine structures were confirmed to have been treated with CCA. Soils collected were evaluated for arsenic, chromium, and copper concentrations as well as pH, volatile solids content and particle size distribution. Two types of soil samples were collected: a soil core and surface soil samples (upper 2.5 cm). One soil core was collected from below each deck and one control core was collected from an area removed from one of the structures. Eight or nine surface soil samples were collected in a grid-like fashion from beneath each structure. Equal numbers of surface control samples were collected from areas away from the structures. Metal concentrations were elevated in both the soil cores and surface samples collected from below the CCA-treated structures. Core samples showed elevated concentrations of metals at depths up to 20 cm. The arithmetic mean concentrations of arsenic, chromium, and copper in the 65 surface soil samples collected from below CCA-treated structures were 28.5 mg/kg, 31.1 mg/kg, and 37.2 mg/kg, respectively, whereas the mean concentrations of arsenic, chromium, and copper in the control samples were 1.34 mg/kg, 8.62 mg/kg, and 6.05 mg/kg, respectively. Arsenic concentrations exceeded Florida's risk-based soil cleanup target level (SCTL) for residential settings in all 65 surface soil samples. The industrial setting SCTL was exceeded in 62 of the 65 samples.

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KEY WORDS: *chromated copper arsenate, CCA, treated wood, soil contamination, arsenic, chromium, copper, heavy metals.*

INTRODUCTION

THE pesticide chromated copper arsenate (CCA) has been the most widely used wood preservative in the United States in recent years (AWPA, 1999; Solo-Gabriele *et al.*, 1998). Applications for CCA include wood products such as utility poles, marine pilings, fences, decks and walkways. Arsenic, chromium, and copper are known environmental toxins, and their presence in CCA-treated wood raises several human safety and environmental concerns. One environmental concern expressed has been the impact on aquatic ecosystems where CCA-treated wood is used (Weis *et al.*, 1995; Weis and Weis, 1999; Brown *et al.*, 2001). Potential pathways of human exposure include direct contact with individuals working with the wood (Decker *et al.*, 2002; Gordon *et al.*, 2002), exposure by those touching the wood during normal use (Galarneau *et al.*, 1990; Wester *et al.*, 1993), and contact with soil or groundwater contaminated by the wood during its normal use (Fields, 2001). The final disposal of CCA-treated wood products may also result in environmental contamination (Tolaymat *et al.*, 2000; Solo-Gabriele *et al.*, 2002). The degree of risk posed by CCA-treated wood products through these various exposure routes is a topic of debate in the scientific and regulatory community, and it is generally acknowledged that additional research is needed to fully understand the true risks. This paper investigates one pathway of potential environmental exposure: contamination of soil as a result of CCA-treated wood structures.

Soil contamination with arsenic, chromium and copper as a result of the wood preservative CCA has been reported at the locations of former and current wood treatment plants, as well as in the proximity of CCA-treated wood structures. The CCA treatment process involves impregnating wood with the CCA preservative solution using pressurized treatment cylinders. Environmental contamination has resulted from spills of the raw chemical, improper disposal of chemical sludges from treatment, and the dripping of preservative from the wood after the treatment process. Several studies have been conducted on soil contamination at these facilities (Anderson *et al.*, 1996; Balasoiu *et al.*, 2001) and many former and current wood treatment plants have been required to undergo corrective action.

Because of the high concentrations of arsenic, chromium, and copper encountered in CCA preservative solutions, it is not surprising that the improper management of this material often results in contamination at levels that pose a risk to human health and the environment. A fact that is less certain, however, is whether chemicals leached from CCA-treated wood products contaminate soil at concentrations that present a risk. During the CCA treatment process, chemical reactions take place that act to bind the metal compounds to the wood. Wood preservation scientists refer to this process as “fixation,” a reaction dominated by the reduction of hexavalent chromium to trivalent chromium (Cooper and Ung, 1992). While the metals are “fixed” to the wood from a treatment efficacy standpoint, the metals do leach over time to the surrounding environment when exposed to water (Cooper, 1991; Lebow, 1996; Hingston *et al.*, 2001). Most CCA-treated wood products are used outdoors. When rainfall comes in contact with treated wood structures that are located above or in soil (such as a deck or a walkway), some arsenic, chromium and copper will dissolve into the water and travel to the underlying or adjacent soil. The leached metals may then bind to the soil causing an increase in the soil metal concentrations. Arsenic typically poses a greater concern when encountered at elevated levels in the soil (with respect to chromium and copper), as it is harmful at lower concentrations. For example, the generic residential soil cleanup target level (SCTL) for arsenic in Florida is 0.8 mg/kg, compared to 210 mg/kg and 110 mg/kg for chromium and copper, respectively (FAC, 2000). While one might argue whether it is appropriate to compare generic risk levels such as the Florida SCTL to soil underneath a CCA-treated structure, they do provide a benchmark to indicate whether contamination approaches concentrations that might be of concern.

Increased soil arsenic concentrations in the vicinity of CCA-treated structures have been observed in several studies that would raise concern when compared to the Florida SCTL and similar risk-based levels. Stilwell and Gorny (1997) measured soil concentrations under residential decks and found an average arsenic concentration of 76 mg/kg (from 3 to 350 mg/kg). Cooper and Ung (1997) reported soil arsenic concentrations near CCA-treated utility poles at levels as high as 550 mg/kg. Eleven months after the construction of a CCA-treated boardwalk, Lebow *et al.* (2000) found arsenic concentrations in soil underneath the edge of the boardwalk ranging from 5 to 29 mg/kg in the upper 15 cm of soil (compared to background values ranging from 1 to 3 mg/kg). They also observed decreasing arsenic concentrations in deeper soils and soils at distances greater than 15 cm from the structure. Stilwell and Graetz (2001) determined arsenic concentrations in soil immediately adjacent to highway sound barriers to range from 7 to 228 mg/kg, with concentrations dropping dramatically at 80 cm from the barrier.

The research presented in this paper was conducted to assess the degree of soil contamination occurring under typical CCA-structures in Florida. At the time of this study, questions had been raised regarding whether the high soil metal concentrations reported in some of the previous studies were the result of metal leaching from the wood or of poor construction debris management practices (i.e., management of sawdust). Questions were also raised as to how metals would leach from CCA-treated wood structures in a warm and wet environment like Florida. Nine structures (decks and walkways) were examined. Both surface soil samples (upper 2.5 cm) and soil core samples were collected and analyzed for arsenic, chromium and copper. Measured concentrations were then compared to background concentrations at the sites and to Florida's SCTLs. To explore the potential sources of arsenic, chromium and copper in soils underneath CCA-treated structures, a simple mathematical relationship was used to estimate the range of concentration that might occur in the soil based on the fraction of metals leaching from the CCA-treated wood and the depth of soil contamination. Since the time this research was conducted, an agreement was reached between the wood preserving industry and the U.S. EPA that will phase out the use of many, but not all, CCA-treated wood products in the U.S. by the end of 2003 (Federal Register, 2002). CCA-treated wood structures constructed prior to this date will in most cases remain in service until the structure is replaced and thus continue to pose the potential to contaminate underlying soil.

METHODS

Sampling Sites

Nine structures in Florida were selected as sampling sites. Three structures were chosen from three different geographic areas of the state. Sites A, B, and C were located in Gainesville, in north central Florida. Sites D, E, and F were located in Tallahassee, in northwest Florida. Sites G, H, and I were located in Miami, in south Florida. Structures such as decks, walkways or footbridges were selected. Eight of the nine sites were confirmed treated with CCA and one site (site F) was not treated with CCA. To ensure access to the structures, all of the sites sampled were located in public parks or along public right-of-ways. The soil samples were collected in November and December of 1999. A follow-up visit was made to each site in June and July of 2000 to collect additional control samples and to confirm that the structures were indeed constructed of CCA-treated wood.

Table 1 presents a description of the CCA-treated structures sampled. Construction records and personal interviews with park rangers and superintendents were used to determine the approximate age of each of the structures. CCA treatment was confirmed by applying a chemical stain and by using X-ray fluorescence (XRF) to quantify the retention level of CCA within either wood bores or sawdust samples collected from each structure. Sawdust and wood bores utilized for analysis corresponded to the outer 1.5 cm (0.6 inches) of wood. The stain utilized was PAN indicator which, when applied to the surface of the wood, resulted in a distinctive

TABLE 1
Description of Sample Locations

Site	Description	Structure's age when sampled	Stain results	Retention level (pcf)[1]
A	Boardwalk	14 years	Positive	0.477
B	Pedestrian footbridge along roadway	5 years	Positive	0.755
C	Deck	~15 years	Positive	0.206
D	Footbridge	2 years	Positive	0.247
E	Deck	4 years	Positive	0.412
F	Footbridge	19 years	Negative	0.008
G	Playground	9 years	Positive	0.261
H	Lifeguard station	6 years	Positive	0.206
I	Deck	14 years	Positive	(0.005–0.54)

[1] pcf = pounds of CCA per cubic foot of wood.

color change if metals were present (see Blassino *et al.* (2002) for more details concerning this stain). XRF was conducted by an outside laboratory using an ASOMA Model #1503. All sites were confirmed to have been treated with CCA, with the exception of site F.

Sampling Methods

Prior to collection of the surface soil samples, a grid was set up below each of the structures using rope. This provided a uniform distribution of sampling locations below each structure. At each site, eight surface samples were collected, with the exception of site B, where nine surface samples were collected. A detailed description of the sample locations for each site can be found in Townsend *et al.* (2001). The surface samples were collected from the top 2.5 cm (1 inch) of soil. This depth was selected to correspond to the soil that would most likely be encountered by humans. Control samples were collected in the same manner at locations away from the structures. The purpose of the control samples was to determine the naturally occurring concentrations of arsenic, chromium and copper in the soil. Locations at elevations higher than the sampling grid were preferred, at distances ranging from 15 to 30 meters (50 to 100 feet) away.

Soil core samples of approximately 25 cm (10 inches) in depth were also collected at each site to examine the vertical distribution of chromium, copper and arsenic. Each core was collected approximately in the center of the sampling grid. The samples were collected using a 2.8-cm diameter unslotted stainless steel probe fitted with a plastic liner (Forestry Suppliers, Inc., Jackson, MS). A different plastic liner was utilized for each site. After collection, all sample containers were placed in plastic bags and stored in a cooler with ice for transportation to the laboratory.

Analytical Methods

Soil samples were characterized by measuring pH and volatile solids content (standard methods 4500-H and 2540E, APHA, 1995), as well as grain size distribution. Volatile solids content was measured to provide an approximation of the organic matter present in the soil; it was determined as the weight lost from dried soil samples after placement in a muffle furnace at 450°C for 5 hours. The grain size distribution results were used to estimate the gravel, sand, and silt/clay fraction (Das, 1985). Dried soil samples were digested for heavy metal analysis using a Method 3050B (USEPA, 1996a). Method 3050B is an open vessel method requiring the use of acid and oxidizing agents to reflux a sample on a hot plate for a period of 2 to 8 hours. Samples analyzed using a graphite furnace atomic absorption spectrophotometer (AAS) were digested with nitric acid and hydrogen peroxide. Digestions for those samples being analyzed using a flame AAS included the added step of digestion with hydrochloric acid. Analysis of the digestates was performed using a Perkin Elmer model 5100 AAS. This instrument was equipped with both a flame aspiration system and a graphite furnace with Zeeman background correction. Arsenic concentrations were measured using the graphite furnace technique. The graphite furnace was used to measure copper and chromium for the control samples due to the lower concentrations contained in those samples. The flame-AAS technique was employed for all other measurements of copper and chromium.

RESULTS

Surface Soil Samples

A total of 73 surface soil samples were collected under the nine structures in Gainesville, Miami, and Tallahassee. Out of these, 65 were collected from below structures that were confirmed to be made of CCA-treated wood. The remaining 8 samples were collected from below a structure that did not show a positive measurement for CCA using either the stains or XRF (site F). In addition to the surface samples collected below the decks, a total of 73 control soil samples (65 below CCA–treated decks) were collected. Control samples were located at a distance away from the CCA-treated structures and results from these samples were expected to represent background metals concentrations. Table 2 presents a summary of the results for pH, volatile solids content, and percentages of gravel, sand, and silt/clay. All soils were uniformly graded with a grain sizes distribution corresponding to a medium sandy soil (Das, 1985). The volatile solids content of the surface soil samples varied from 2% to 26%, on average, and the pH varied from 5.4 to 7.7.

A summary of measured arsenic, chromium, and copper concentrations is provided in Tables 3, 4 and 5, respectively. While site F is presented, it is not included

TABLE 2
Physical Parameters of Soils Collected Below Each Deck

Site	Description	Avg. soil pH	Avg. volatile solids (%)	Gravel (%)	Sand (%)	Silt/clay (%)
A	Boardwalk	5.4	26	0.3	99.1	0.7
B	Pedestrian footbridge along roadway	7.7	3.5	4.6	92.9	2.5
C	Deck	7.6	5.0	1.0	97.5	1.6
D	Footbridge	6.1	4.6	3.8	93.0	3.3
E	Deck	6.9	4.4	0.6	97.8	1.6
F	Footbridge	7.5	12	2.2	92.9	4.9
G	Playground	6.4	9.7	0.5	97.4	2.1
H	Lifeguard station	7.6	1.9	0.6	98.1	1.3
I	Deck	7.5	4.4	8.6	87.8	3.6

TABLE 3
Arsenic Concentration (mg/kg) in Surface Soils

	Arsenic concentration (mg/kg)					
	Soil beneath structure				Control soil	
Structure	N	Average	Max.	Min.	N	Average
A	8	41.6	87.9	15.6	8	2.61
B	9	10.7	33.2	4.05	9	0.31
C	8	9.56	18.1	3.54	8	0.58
D	8	17.2	31.0	8.59	8	2.31
E	8	34.0	48.8	5.09	8	1.42
F	8	0.48	0.62	0.25	8	0.47
G	8	33.9	81.2	15.5	8	1.98
H	8	4.30	7.47	1.18	8	1.13
I	8	79.1	217	31.7	8	0.66
All locations[1]	65	28.5	217	1.18	65	1.36

[1] Does not include results from site F.

in the statistical analysis of the data. For purposes of statistical analysis, a value of one-half of the detection limit was used for those samples where the concentration was below the detection limit of the analytical instrument. Sample concentrations are reported on a dry weight basis.

TABLE 4
Chromium Concentration (mg/kg) in Surface Soils

	Chromium concentration (mg/kg)					
	Soil beneath structure				Control soil	
Structure	N	Average	Max.	Min.	N	Average
A	8	59.7	113	30.8	8	3.11
B	9	23.4	48.6	10.6	9	7.90
C	8	12.1	28.6	<5.0	8	19.2
D	8	16.4	32.4	6.90	8	8.80
E	8	22.9	44.3	14.3	8	6.98
F	8	<5.0	<5.0	<5.0	8	3.46
G	8	39.5	113	13.8	8	12.7
H	8	4.34	6.85	<5.0	8	6.79
I	8	71.1	198	32.0	8	3.65
All locations[1]	65	31.1	198	<5.0	65	8.62

[1] Does not include results from site F.

TABLE 5
Copper Concentration (mg/kg) in Surface Soils

	Copper concentration (mg/kg)					
	Soil beneath structure				Control soil	
Structure	N	Average	Max.	Min.	N	Average
A	8	106	156	53.0	8	6.00
B	9	20.1	37.0	7.50	9	6.73
C	8	13.6	26.0	<5.0	8	4.60
D	8	18.9	34.0	10.0	8	7.30
E	8	21.8	36.0	12.0	8	3.95
F	8	<5.0	<5.0	<5.0	8	2.54
G	8	44.5	128.5	16.5	8	7.92
H	8	6.13	11.0	<5.0	8	7.36
I	8	68.1	216	18.5	8	4.63
All locations[1]	65	37.2	216	<5.0	65	6.07

[1] Does not include results from site F.

Arsenic was detected in all 65 of the surface soil samples collected from below CCA-treated structures. The arsenic concentrations of these soils ranged from 1.18 mg/kg (site H) to 217 mg/kg (site I), with an arithmetic mean of 28.5 mg/kg. The mean of the corresponding controls was 1.36 mg/kg. Of the 65 soil samples collected from below confirmed CCA-treated structures, 59 were above the detection limit for chromium. For the samples above the detection limit, the surface soil chromium concentrations ranged from a minimum of <5.0 mg/kg (site H) to a maximum of 198 mg/kg (site I), with a mean of 31.1 mg/kg. The mean of the corresponding controls was 8.62 mg/kg. Of the 65 soil samples collected from below confirmed CCA-treated structures, 60 were above the detection limit for copper. For the samples above the detection limit, the surface soil copper concentrations ranged from a minimum of <5 mg/kg (site B) to a maximum of 216 mg/kg (site I), with a mean of 37.2 mg/kg. The mean of the corresponding controls was 6.07 mg/kg.

The mean arsenic concentrations for soil underneath the CCA-treated structures were statistically greater than those of the control samples (95% confidence) for all sites except Site F (the one not treated with CCA). The mean chromium concentrations for soils under the structures were greater than that of the control samples for six of the eight CCA-treated structures, with three of the eight being statistically greater (A, E, I). The mean copper concentrations for soil under the structures were greater than those of the control samples for all eight CCA-treated structures, and were statistically different for 6 sites (A, B, C, E, G, I).

Soil Cores

Soil cores were collected and analyzed from underneath all of the structures. One control soil core sample was collected at site B. Figure 1 presents concentration profiles as a function of depth for the soil cores collected at each site. In general, the highest soil metal concentrations were encountered in the upper soils layers. This observation was more pronounced for arsenic and copper. At a number of sites (B, C, E, G) large chromium concentrations continued to be encountered at deeper locations, possibly a result of the greater natural background concentration of chromium. The greater background concentration of chromium is also illustrated in the soil core profile of site F (the site not treated with CCA).

DISCUSSION

Comparison to Background Levels

The observation that arsenic was found to be statistically different more often than copper and chromium is likely the result of the lower natural occurring background concentrations of arsenic. In a recent study that involved the analysis of 448 Florida surface soils, Chen *et al.* (1999) reported the geometric means (and ranges) of arsenic, chromium, and copper to be 0.42 mg/kg (0.01 to 50.6), 15.9 mg/kg (0.02 to 447) and 6.10 mg/kg (0.1 to 318), respectively. The addition of arsenic to soil from CCA-treated wood was greater relative to the initial total mass of soil arsenic when compared to chromium and copper. A second factor that may account for arsenic being greater than background more frequently is that arsenic often leaches more from CCA-treated wood (especially with respect to chromium). This possibility will be discussed further in a later section (see *Relative Contribution of Metals*).

Intra- and Inter-Site Variability

Surface soil metal concentrations varied from site to site and among the samples at each site. To better illustrate this variability, a histogram showing the distribution of measured metals concentrations for all surface soil samples except those collected at site F is shown in Figure 2. As can be seen from this figure, the range and distribution of metals concentrations varied considerably from site to site. Several factors may contribute to this variability. Factors include soil type, rate of rainfall, age of structure, construction practices, initial treatment conditions of the wood, structure type and infiltration and runoff patterns. While an exhaustive evaluation of all factors impacting site variability was not conducted, several factors were examined to assess possible trends. Surface soil concentrations were not found to correlate with age of the structure. Concentrations also did not show significant

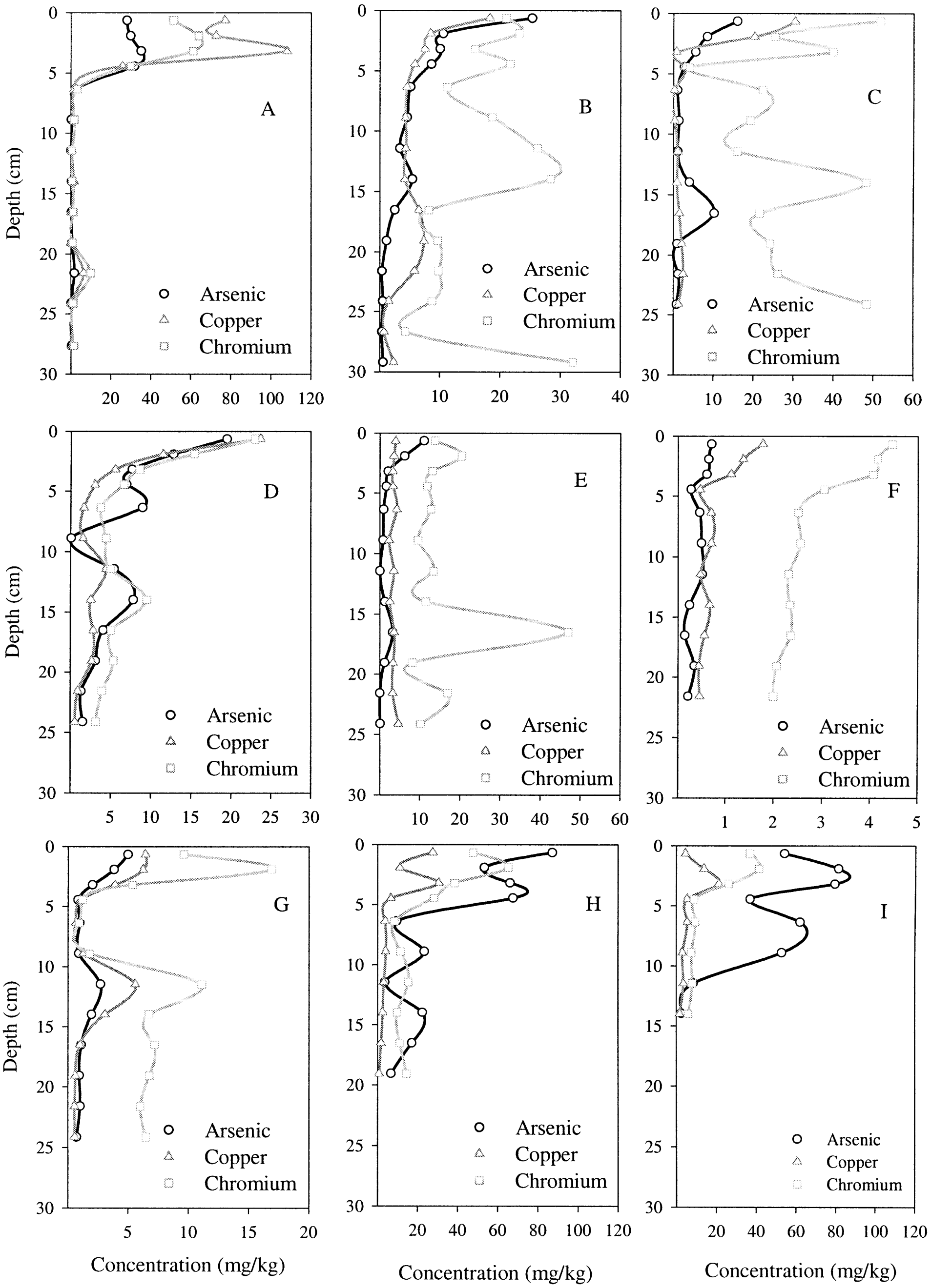

FIGURE 1

Core Soil Profiles.

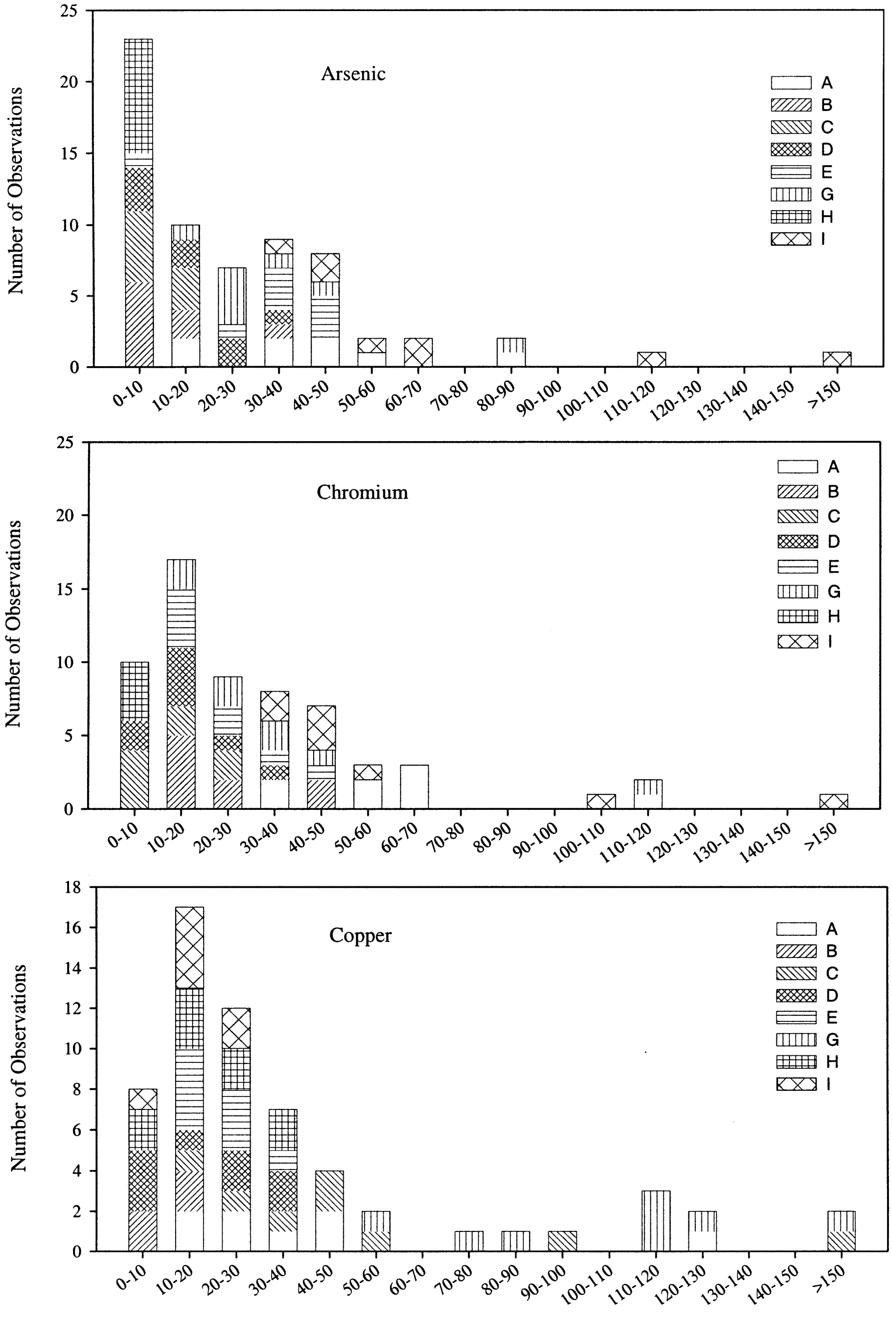

FIGURE 2

Distribution of Metal Concentration (mg/kg) in Soil Under CCA-Treated structures.

correlation with the soil characteristics measured. The lack of significant correlations with these parameters illustrates the diverse factors that impact surface soil metals concentrations.

Surface soil concentrations also varied within a given site. Possible causes of intra-site variation include construction practices, location of different structure components (e.g. above ground versus soil contact), water flow patterns (e.g. drip lines), and retention levels of the different structure components. For example, a large variability in arsenic concentration was observed in the site I samples. For this particular structure, surface soil samples ranged from 31.7 to 217 mg/kg of arsenic. The two highest concentrations measured (112 mg/kg and 217 mg/kg) were found to correspond to the location where two joists intersected. Based on this fact and visual observations of the soil underneath the structure after a rain event, it was concluded that runoff from upper portions of the deck dripped along the joists resulting in a concentrated input of rainwater causing the elevated arsenic concentrations at these two locations. Townsend *et al.* (2001) contains additional details regarding the locations of the samples with respect to the structures and water flow patterns, and discusses the possible relationship between volatile solids and arsenic content.

Relative Contribution of Metals

An examination of the relative concentration of arsenic, chromium, and copper in the soil samples can provide insight regarding the source of the metals. As was previously stated, elevated metals concentrations could result from both the leaching pathway and from wood particles (debris left from construction and abraded wood). The American Wood Preservers Association (AWPA) has standardized three separate CCA formulations, types A, B, and C. CCA type C (CCA-C) is the formulation in current use in the U.S. and contains 47.5% (44.5–50.5%) CrO_3, 18.5% (17.0–21.0%) CuO and 34.0% (30.0–38.0%) As_2O_5(AWPA, 1999). For comparison purposes, the ratio of arsenic to chromium (As:Cr) and the ratio of copper to chromium (Cu:Cr) will be used in this paper. The ratios for CCA-C correspond to 0.9 (0.74–1.1) and 0.6 (0.52–0.72) for As:Cr and Cu:Cr, respectively. Relative soil metal ratios measured in this range could indicate wood particles as the source of contamination.

Previous research has shown that the relative mass of each metal that leaches from a wood product treated with CCA-C in contact with water differs from the relative mass in the treated wood product itself. Most leaching studies on CCA-C treated wood have shown that arsenic and copper leach to a greater extent than chromium when exposed to fresh water (Hingston *et al.*, 2001). The relative amount that leaches is a function of wood species, pH, time of exposure, type of leaching test, and several other factors (Cooper, 1991). Published research differs as to which component, arsenic or copper, leaches more. Crawford *et al.* (2002) found copper to leach more than arsenic in CCA-C exposed to soil, and arsenic to leach more than copper when leached using water. For several different species of wood, Cooper (1991) found As:Cr to range from 5.2 to 16.7 and Cu:Cr to range from 5.8 to 11.7 in batch leaching tests at pH 5.5. When leaching jack pine with deionized water, Warner and Solomon (1990) measured an As:Cr of 23 and a Cu:Cr of 8.6. Townsend *et al.* (2001) leached size-reduced southern yellow pine for 18 hours with simulated rainfall and found average As:Cr and Cu:Cr values of 4.0 and 2.6, respectively. Lebow *et al.* (1996) leached CCA-C southern yellow pine lumber in deionized water and found the As:Cr and Cu:Cr ratios after one month of leaching to be 3.0 and 6.4, respectively. In a study of leaching from a simulated CCA-treated deck, Kennedy and Collins (2001) found that after 300 days of exposure to natural rainfall, metals had leached in the following ratios: 3.4:1 (As:Cr) and 1.2:1 (Cu:Cr).

The above leaching data suggest that soil impacted by rainwater leaching over CCA-treated wood structures should have background-corrected As:Cr and Cu:Cr ratios greater than 1, perhaps many times greater (assuming that the metals are retained in the soil). Since the relative proportions are different between the wood itself and the wood leachate, an analysis of these ratios can possibly help assess whether the source of the metals is from leaching or from wood particles (construction debris, abraded wood). Stilwell and Gorny (1997) and Stilwell and Graetz (2001) reported relative ratios in soil beneath or adjacent to CCA-treated structures that were indicative of leachate from CCA-treated wood and used this to suggest that elevated soil metal concentrations were primarily a result of leaching. Lebow *et al.* (2000) evaluated the relative concentrations of chromium and copper in sediments under a CCA-treated boardwalk to determine if elevated metal concentrations were the result of wood abrasion due to high foot traffic, and determined that abrasion was not the primary source of copper to the underlying sediments.

The relative concentrations of the metals in the soils collected in this study were assessed. Evaluation of all of the surface soil results found that As:Cr and Cu:Cr ratios (without background correction) were 0.98 and 1.2, respectively. The ratios, especially that of As:Cr, are less than might be expected based on typical leaching ratios reported in the literature. When evaluating the soil core profiles in Figure 1, only Site I showed arsenic in greater concentrations throughout the soil profile. Since the background concentrations of metals in the soil differ (Cr > Cu > As), it is important to correct for background. Only three sites had Cr concentrations in the soils under the structures that were statistically greater than background chromium concentrations (A, E, and I). For each of these three sites, background-corrected concentrations were determined by subtracting the average control sample concentration from the concentration of each of the samples collected under the structures. The ratios were then recalculated.

Table 6 presents the background-corrected As:Cr and Cu:Cr ratios for sites A, E, and I. The average ratios, as well as the range, are presented. As a reminder, ratios for CCA-treated wood particles should be approximately 0.9 and 0.6 for As:Cr and Cu:Cr, respectively. Site I most closely resembled a pattern that would correspond to leaching being the primary contributor of metal contamination, with

TABLE 6
Background Corrected As:Cr and Cu:Cr Ratios for Sites A, E, and I

Site	As:Cr	Cu:Cr
A	0.65 (0.46–0.86)	1.9 (1.3–2.5)
E	1.2 (0.62–1.5)	0.88 (0.36–1.1)
I	2.4 (0.45–4.6)	1.2 (0.86–1.7)

most values above the range expected for wood particles. The site I core profile also was indicative of impact by leaching. The site E ratios were more in the range corresponding to wood particles. The site A As:Cr ratios were in the range expected for wood particles, while the Cu:Cr ratios were closer to that which might be expected for leaching.

The large range of observations makes any broad characterization of metal source impossible, but in general the concentration of arsenic in the soil relative to the concentration of chromium in the soil is less than would be expected based on previous leaching results (for all sites except I). While abraded wood and construction debris is one explanation for this, another possibility is that the arsenic was more mobile in the soil relative to chromium. The As:Cr ratios could have at one time been greater, but over time as rainwater moved through the soil, arsenic could have been preferentially leached. The relative degree of leaching would, of course, be strongly dependent on soil type, but in many cases, arsenic would be expected to be more mobile than trivalent chromium (USEPA, 1996b). The soil samples collected in this study were not characterized in great enough detail (e.g. aluminum, iron content) to comment further. The ultimate fate of metals leached from CCA-treated structures into soil is worthy of additional investigation.

Comparison to Soil Cleanup Target Levels

The concentrations of chromium, copper, and arsenic measured in the soil samples from underneath the CCA-treated structures were compared to Florida's risk-based regulatory guidelines for soils. The Florida Department of Environmental Protection (FDEP) has published risk-based SCTLs to serve as an indicator of whether pollutant concentrations in soils exceed acceptable risk in different human contact scenarios (FAC, 2001). For direct human exposure (an aggregate of ingestion, inhalation, and dermal contact), the SCTLs for residential areas are 0.8 mg/kg, 210 mg/kg, and 110 mg/kg for arsenic, chromium, and copper, respectively. For industrial exposure settings, the SCTLs are 3.7 mg/kg, 420 mg/kg, and 76,000 mg/kg, respectively. The arsenic and chromium SCTLs represent a 10^{-6} cancer risk, while the copper SCTL addresses gastrointestinal distress. It should also be noted that the chromium SCTL was derived for hexavalent chromium.

With respect to chromium, no surface soil sample exceeded the residential or industrial SCTL. While no speciation was performed, it is likely that the chromium existed primarily in the reduced chromium (III) state as opposed to the chromium (VI) state. For copper, 7 of 65 surface soil samples (under CCA-treated decks) exceeded the residential SCTL, while none of the samples exceeded the industrial SCTL. For arsenic, all 65 of the surface soil samples exceeded the residential SCTL (0.8 mg/kg) and 62 of the 65 samples exceeded the industrial SCTL. None of the control samples exceeded their respective residential SCTL for chromium or copper. For arsenic, 29 of 65 controls exceeded the residential SCTL and 3 exceeded the industrial SCTL.

From the comparison above, elevated concentrations of arsenic present the greatest direct human exposure risk of the three metals. Several issues deserve additional discussion with respect to the soil samples exceeding the arsenic SCTL. First, as pointed out previously, the Florida SCTL for arsenic is relatively low with respect to natural background. While the Florida SCTL is low, it is in line with risk-based soil concentrations from some other agencies. For example, the U.S. EPA's generic soil screening level for arsenic (for the ingestion pathway) is 0.4 mg/kg (USEPA, 1996b). In a review of different states, arsenic risk-based soil screening levels (SSLs) for residential settings ranged from 0.1 to 250 mg/kg (AEHS, 1998). Ten of 20 states reported a residential arsenic SSL below 1 mg/kg. Those higher than the Florida SCTL were generally derived using a different cancer risk (e.g., 10^{-5}), a non-cancer endpoint, or by setting the screening level to naturally occurring background levels.

A second issue is the applicability of using risk-based screening levels to soils underneath CCA structures. The purpose of these generic levels is to set a threshold below which the soil is considered to pose an acceptable risk. They are used at contaminated sites to help assess the risk posed and to determine whether conditions warrant corrective action. Contamination of soil underneath a CCA-treated structure would not be a "violation," but could require action during future property transactions if contamination was identified as part of the site assessment. One might argue that human exposure to soil underneath a CCA-treated structure would be unlikely, but scenarios can certainly be envisioned where a structure is removed and the likelihood of potential exposure to that soil increases.

Evaluation of Potential Metals Concentrations from the Leaching Pathway

As described earlier, arsenic concentrations were lower relative to chromium concentrations than would be expected from typical ratios measured when CCA-treated wood is leached with water. Stilwell and Gorny (1997) and Stilwell and Graetz (2001) reported that metal leaching was the primary cause of the elevated metal concentrations they observed in soil under CCA-treated structures. The results of the Florida study were inconclusive in this regard. To evaluate whether the soil concentrations measured here would even be possible as a result of leaching, a simple mathematical relationship was developed to predict the average metal concentrations that might occur underneath a CCA-treated structure. The intent was not to model concentrations from any particular structure in this study. A generic structure was assumed.

The concentration of a metal underneath a CCA-treated structure is represented by Equation 1 where C_i is the concentration (mg/kg) of metal "i" in the soil underneath the structure. For a horizontal surface of CCA-treated dimensional lumber (such as a deck or boardwalk), C_i may be calculated as presented in Equation 2 where $F_{i,Leach}$ is the fraction of metal "i" that has leached, A_{Wood} is the area of wood structure exposed to rainfall (m^2), T_{Wood} is the thickness of the wood (m), SRV_i is the standard retention value of metal "i" in the wood (kg-i/m^3), A_{Soil} is the area of soil underneath the structure that is impacted (m^2), D_{Soil} is the depth of soil impacted (m), and ρ_{Soil} is the bulk density of the soil (kg/m^3).

$$C_i = \frac{\text{Mass of Metal Leached from Structure}}{\text{Mass of Soil Impacted}} \tag{1}$$

$$C_i = \frac{F_{i\,Leach}\,A_{Wood}\,T_{Wood}\,SRV_i\,10^6}{A_{Soil}\,D_{Soil}\,\rho_{Soil}} \tag{2}$$

Consider a CCA-treated walkway constructed with 0.038 m thick lumber. Assuming the lumber is treated to a standard retention value of 6.4 kg-CCA/m^3 (0.40 lb-CCA/ft^3), this corresponds to 1.4 kg-As/m^3, 1.6 kg-Cr/m^3 and 0.95 kg-Cu/m^3. As discussed previously, the contamination is usually limited to the area directly underneath the structure, so A_{Wood} is assumed equal to A_{Soil}. Assuming the soil has a bulk density of 1,700 kg/m^3, the arsenic concentration (mg/kg) can be calculated using equation 2 for different F_{Leach} values. Figure 3 represents this relationship in a graphical form. From the graph it can be estimated that if 5% of the CCA were to leach from this generic CCA-treated structure into the upper 0.1 m (4 inches) of the soil underneath the deck, the concentration of arsenic in the soil would be expected to be 16 mg/kg. If 10% were to leach into that depth, the predicted concentration would be 32 mg/kg.

Several simplifications were made in the above approach. Metals were assumed to be uniformly bound in a given depth of soil, when in reality metal concentrations will be distributed according to soil characteristics. Soil core results did indicate that the greatest metal concentrations were found at the surface. The above analysis also only considers a simple structure with wood planks or deck boards, and does not include any support structures or components such as hand railings. All of these additional components would add to the metal loading. Values for F_{Leach} would depend on several factors, including how well the wood was treated, rainfall rates, structure use pattern, and most importantly, time. In most cases the greatest leaching rates of arsenic, chromium and copper from CCA-treated wood occur at the onset of leaching and decrease to lower values over time. In

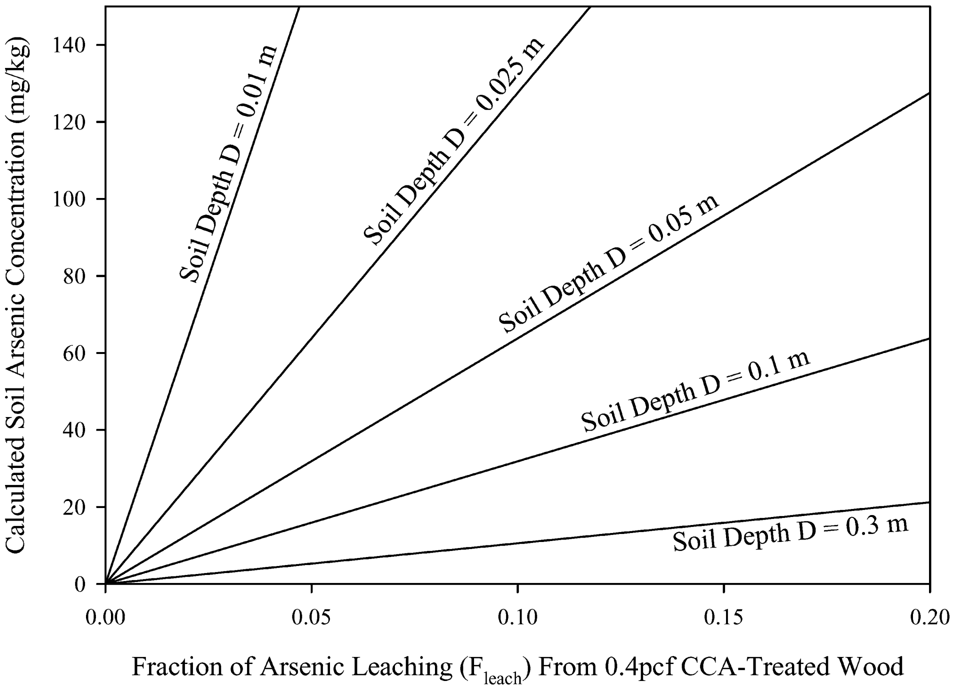

FIGURE 3

Predicted arsenic soil concentrations as a function of F_{Leach}.

18-hour leaching tests with synthetic rainwater, Townsend *et al.* (2001) found that 20-g blocks of CCA-treated wood leached between 0.2% to 2% of the arsenic present, while sawdust leached from 0.5% to 8% of the arsenic present. Results of field tests in aggressive environments have measured typical arsenic depletion amounts from CCA-treated wood in the range of 10% to 25%. Cooper (1993) assumed a 20% loss of chemicals after 20 years of service in assessment of treated wood disposal issues. Kennedy and Collins (2001) exposed CCA-treated deck boards to natural rainfall over a 300-day period. After exposure to 600 mm of rain, the mass of arsenic that leached from the deck boards ranged from 4.0 to 4.4%.

Despite the great number of variables that must be factored into the prediction of the degree of soil contamination underneath a CCA-treated structure, this analysis does indicate that leaching of preservative can result in elevated concentrations of arsenic, chromium and copper. Figure 3, along with the data already discussed, shows that soil arsenic concentrations under CCA-treated wood structures could reasonably be expected to range from 10 to 40 mg/kg above background concentrations. Higher concentrations, or "hot-spots," would occur at locations adjacent to CCA-treated wood buried in the soil and underneath drip lines where metal-concentrated rainwater is focused. Hot spots would also occur if the sample locations coincided with the location of construction debris (e.g., sawdust). While results of this study were inconclusive with regard to the source of elevated metal concentrations (wood particles vs. leaching), simple estimates of what concentrations might be expected as a result of metal leaching from CCA-treated structures fall within the range of the actual metal concentrations measured.

CONCLUSIONS

Wood that is used outdoors, especially in warm, wet environments, must be preserved to deter biological deterioration. Treatment with chromated copper arsenate provides effective resistance to decay, but poses several potential environmental and human health risks. Arsenic, chromium, and copper can become elevated in soils underneath wood structures treated with CCA as a result of rainwater migrating over the wood and infiltrating into underlying soil, and because of wood particles resulting from abrasion or improperly disposed debris. The results of this study were inconclusive as to the source of the metals. The ratio of arsenic to chromium was often less than would be expected for metals found in "leachates" from CCA-treated wood. Given that previous research (Stilwell and Gorny, 1997; Stilwell and Graetz, 2001) found leaching to be the major pathway of metal contamination, and given the range of predicted soil metals concentrations from a theoretical analysis, another possibility that should be considered is that arsenic was at one time found in greater relative concentrations, but leached from the soil with time. This possibility warrants further investigation. The potential for groundwater contamination from CCA-treated wood structures was not examined in this paper.

From a human health risk standpoint, arsenic presented the greatest concern. The concentrations of arsenic underneath CCA-treated structures may exceed risk-based clean soil levels. The arithmetic mean concentration of arsenic underneath eight CCA-treated structures was 28.5 mg/kg, while Florida's generic SCTL is 0.8 mg/kg for residential settings and 3.7 for industrial settings. This presents a dilemma for policy makers, in that soil concentrations underneath these structures are greater than levels that many commercial and industrial sites with arsenic-contaminated soils are being required to reach under remediation.

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Impact of solid fuel combustion technology on valence speciation of chromium in fly ash

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HIGHLIGHTS

- Biomass and high combustion temperature favor enrichment of fly ash with Cr(VI).
- Biomass combustion favor enrichment of fly ash with water soluble Cr(VI).
- Alkali compounds and Fe oxides play a key role in shaping Cr(VI/III) speciation.
- Cr(VI) level in coal fly ash drops in order: PCC boiler ≫ FBC boiler ≈ SF boiler.
- An influence of combustion technologies on Cr speciation in fly ash was explained.

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ABSTRACT

Fly ash (FA) generated in real furnaces was used to evaluate the impact of the kind of the solid fuel burnt and combustion technology on chromium speciation, particularly the presence of Cr(III) and Cr(VI) forms as well as readily and hardly leachable chromium(VI) species in FAs. The FAs originated from a pulverized coal combustion boiler (PCC boiler), a fluidized bed combustion boiler (FBC boiler), a stoker-fired boiler (SF boiler), a municipal solid waste incinerator (MSWI), a cement rotary kiln (CRK) and a modern domestic boiler (DB). The speciation analysis of chromium was carried out by means of extraction followed by catalytic cathodic stripping voltammetry with adsorption of Cr(III)-DTPA complexes (CCSV-DTPA) for determination of Cr(VI) and AAS was used for determination of Cr content.

It has been revealed that the antagonistic action of alkali metal compounds and iron oxides plays a crucial role in shaping valence speciation of chromium. According to the proposed transformation path of oxidation of Cr(III) to Cr(VI), hard coal combustion in an SF boiler, an FBC boiler or a domestic boiler will generate FAs with a low Cr(VI) level. Replacing fuel with biomass should create favorable conditions for generating FA enriched with Cr(VI). Relatively high concentrations of Cr(VI) can also be expected in FA generated in the process of high-temperature combustion of coal in PCC boilers.

1. Introduction

Chromium speciation in fly ash has been studied for a number of years and were focused on the mode of chromium occurrence as well as the mechanism of chromium transformation in a combustion chamber. The determination of chromium(III) and chromium(VI) has been carried out directly in a FA sample by using non-destructive techniques [1–5] or indirectly by extraction followed by determination of released chromium species [2,6–8]. The interest in chromium valence speciation in FA stems from a significant difference in toxicity and bioavailability of the Cr(III)- and Cr(VI)-species. Cr(III) is a bioelement, whereas particulate Cr(VI) is regarded as a factor which increases the severity of ongoing allergic asthma and alters its phenotype [9]. The environmental impact and health effects are related to chromium(VI) load in the environment.

The scale of the problem is large, although it cannot be determined accurately, as Cr(VI) emission is inventoried only in relatively few countries. Within the last twenty years the EU(15) countries produced annually 40 Tg of FA on average, of which 92% was utilized in 2006. The construction industry and underground mining used 20 Tg (concrete addition – 26.7%, cement raw material – 25.8%, road construction and filling applications – 22.5%, blended cement – 11.3%, concrete blocks – 7.1%, infills – 4%, and others – 2.6%) [10]. The remaining FA was used in land reclamation and

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restoration. In that same year in the USA 72 Tg of FA was generated, of which 32 Tg was utilized (the construction industry – 60% and mining and earthworks – 40%) [11]. If we assume that 3 mg/kg is the expected value of Cr(VI) content in FA [2,4,7,8,12] and that utilization of only a half of the FA generated creates conditions for Cr(VI) release, the environment in Europe is loaded annually with 60 Mg of Cr(VI). Although this value is high, it seems to be correct. For comparison, total annual emissions of Cr(VI) in the US were 44 Mg in 2002 [13]. Proportionally lower Cr(VI) emissions to air were found in the UK – 28.6 Mg/year (2008) [14], Australia – 2.5 Mg/year (2011) [15] and Canada – 1 Mg/year (2010) [16].

In order to reduce the Cr(VI) pollution burden on the environment, it is crucial to control oxidation of Cr(III) to Cr(VI) taking place during combustion of solid fuels in such a way that it is possible to reduce the Cr(VI) content or, at least, to limit Cr(VI) elution from FA.

Although Cr valence speciation in various coals and coal combustion products has been covered quite extensively in the literature, and moreover recently a number of papers have been published in which the authors proposed a mechanism of possible chromium transformations [3,5,6,17,18], there is still a lack of a general approach which would explain the essence of shaping Cr speciation in FA generated in real furnaces based on various combustion technologies.

The aim of our work is to examine the speciation of Cr(III/VI) and speciation of Cr(VI) (water leachable and hardly leachable fractions) in FAs depending on which combustion technology of solid fuel has been used. FAs produced in pulverized fuel boilers, stoker-fired boilers, a fluidized bed boiler, an up-draught combustion domestic boiler, a Krüger grate furnace and a cement rotary kiln have been investigated. An attempt has been made to prepare an outline of a chromium transformation model in real solid fuel fired boilers which may explain the differences in chromium valence speciation observed in the generated FAs.

2. Experimental

2.1. Sampling and samples preparation

FA samples (1 kg) were collected from various parts of dust arresting systems. Pulverized fuel combustion FA samples were collected from each of the three fields of an electrostatic precipitator system. Both units, in which hard coal was fired and biomass was co-fired ($C/B = 9:1$), were of the same type and worked in the same coal-fired power plant. The samples were denoted as PCC/FA-I/1-3 and PCC/FA-II/1-3 for coal and coal/biomass combustion, respectively (Table 1). The stoker-fired coal fly ash samples were collected from collection tanks of the multicyclone and a battery of cyclones in two heating plants (I and II) equipped with the same type of stoker-fired boilers. The samples were denoted as SF/FA, 1 – multicyclone and 2 – battery of cyclones and the subscripts *a* and *b* stand for fraction >63 μm (coarse fraction) and $\leqslant 63$ μm (fine fraction), respectively. Three FA samples denoted as FBC/FA-1, FBC/FA-2 and FBC/FA-3 were collected from the ash hopper of the ESP in the FBC boiler system which was supplied with hard coal from three coal mines, one from Lublin Basin (1) and two from Upper Silesian Basin (2 and 3). In this installation dry limestone was injected into the flue gases before the collection of particulate

Table 1
Kind of furnace, fuel, dust collection device and sampling points.

No	Fly ash sample	Furnace	Fuel	Temperature of burning zone	Dust collection device	Sampling point[a]/ remarks
1	PCC/FA-I/1	Pulverized-fuel boiler	Hard coal energy value – 22 MJ/kg, ash – 20%, sulfur – 1.1%. Particle size <0.1 mm.	1800–1935 °C	ESP	1st-field ESP
2	PCC/FA-I/2					2nd-field ESP
3	PCC/FA-I/3					3rd-field ESP
4	PCC/FA-II/1		Hard coal (ditto) + wood waste (10%) energy value of biomass – max. 18 MJ/kg			1st-field ESP
5	PCC/FA-II/2					2nd-field ESP
6	PCC/FA-II/3					3rd-field ESP
7	SF/FA-I/1a	Stoker-fired boiler	Hard coal energy value – 23.2 MJ/kg, ash – 15.1%, sulfur – 0.63%, moisture content – 11.8%	1100 °C	1. Multicyclone	$\varphi > 63$ μm (42%)
8	SF/FA-I/1b					$\varphi \leqslant 63$ μm (58%)
9	SF/FA-I/2a				2. Cyclone	$\varphi > 63$ μm (52%)
10	SF/FA-I/2b					$\varphi \leqslant 63$ μm (48%)
11	SF/FA-II/1a	Stoker-fired boiler	Hard coal energy value – 21.9 MJ/kg, ash – 19.5%, sulfur – 0.62%, moisture content – 10.2%	1100 °C	1. Multicyclone	$\varphi > 63$ μm (40%)
12	SF/FA-II/1b					$\varphi \leqslant 63$ μm (60%)
13	SF/FA-II/2a				2. Cyclone	$\varphi > 63$ μm (57%)
14	SF/FA-II/2b					$\varphi \leqslant 63$ μm (43%)
15	FBC/FA-1	Fluidized-bed boiler	Hard coal energy value – 21.1 MJ/kg, ash – 21.1%, sulfur – 1.04%	850–865 °C	ESP preceded by dry limestone injection	Collection tank
16	FBC/FA-2		Hard coal energy value – 22.1 MJ/kg, ash – 21.4%, sulfur – 0.52%			
17	FBC/FA-3		Hard coal energy value – 22.9 MJ/kg, ash – 20.7%, sulfur – 0.42%			
18	DB/FA-1	Up-draught combustion domestic boiler	Pine wood briquette		Lack	Dead space of flue
19	DB/FA-2		Birch plywood briquette			
20	MSWI/FA	Krüger grate furnace (incinerator)	Sorted municipal wastes	1000–1100 °C	Bag filter preceded by hydrated lime injection	
21	CRK/FA-1	Cement rotary kiln	Hard coal energy value – 27 MJ/kg, ash – 7.0%, sulfur – 1.2%, moisture content – 8.5% + alternative fuel/wood waste	Max. 2000 °C	1. Dust chamber	
22	CRK/FA-2				2. Two parallel bag filters	1st bag filter
23	CRK/FA-3					2nd bag filter

[a] If different than the one given in the dust collection device column.

matter in ESP. A sample of FA generated by incineration of the combustible fraction of municipal solid wastes (denoted as MSWI/FA) was collected from a bag house filter. In this installation hydrated lime was injected into the flue gases before the dust collector. FA generated in a cement rotary kiln fired with a mixture of coal and an alternative fuel was captured in the dust chamber and then in two parallel bag filters. The FA samples are denoted as CRK/FA-1, CRK/FA-2 and CRK/FA-3, respectively. The up-draught combustion boiler (nominal output of 20 kW), commonly used in Poland for individual house heating, was fired with pinewood briquettes and birch-plywood briquettes. The FA samples were collected from the flue at the reversal gas spot where the so-called dead space enabled the accumulation of FA particulates (hereforth designated as DB/FA-1 and DB/FA-2, respectively).

Directly after collection all samples were stored in hermetically sealed plastic containers. The SF/FA samples were sieved through a sieve of 63 μm. In both the SF boilers ca. 40 wt% of FA retained in the multicyclone had a dimension $\leqslant$63 μm, and somewhat below 50 wt% of FA trapped in the cyclone had a dimension $\leqslant$63 μm.

2.2. Determination of the contents of chromium and other metals

The environmentally available metal content in the FA samples (pseudo total metal concentration) was determined via microwave-assisted digestion of the samples with HNO_3/H_2O_2 according to the manufacturer's protocol (Millestone, 1992) [19]. Three subsamples were digested simultaneously for each FA sample.

The concentration of metals in the digest samples was determined using an atomic absorption spectrometer AAS – Agilent Technologies 200 Series AA 240 FS AA. The limits of determination for chromium and other metals being examined were: Cr – 2.7 mg/kg, Ca – 0.9 mg/kg, Fe – 3.8 mg/kg, K – 2.1 mg/kg and Na – 1.4 mg/kg.

2.3. Determination of chromium(VI) content

Leaching of total Cr(VI) from the FA samples was carried out similarly as described in the EPA 3060A method (US EPA, 1996) [20]. A 0.5 g sample was being extracted in 10 mL Na_2CO_3/NaOH for 1 h at 95 °C.

Soluble Cr(VI) was released by shaking a 1 g FA sample in 10 mL of deionised water for 24 h at RT according to the leaching test described in PN-EN 12457-2:2006 [21].

The leachates were filtered through a 0.45 μm nitrate-cellulose membrane filter.

Determination of Cr(VI) in leachates was performed using the technique of CCSV-DTPA. Voltammograms were recorded with a Trace Analyzer Model 394 connected to a hanging mercury drop working electrode Model 303A SMDE (EG&G Princeton Applied Research). LOD (instrumental) was found to be 2.9 μg/L (0.0026 mg/kg of FA).

CMR061-030 (sandy loam) was used as a certified reference material to validate the analytical procedure. Cr(VI) extraction was carried out in the same way as for FA samples. It was found that the content of Cr(VI) was 239.3 mg/kg ($n = 3$), the certified value was 241.00 ± 9.00 mg/kg, hence the recovery was 99.3%.

2.4. ORP and pH determination

The pH of the water extracts was measured using a Mettler Toledo SevenEasy pH-meter (Mettler Toledo, 2006), and the Oxidation–Reduction Potential (ORP) with a single rod electrode (HI-3230, 3.3 mol/L silver chloride electrode, Hanna Instruments, Portugal).

3. Results and discussion

3.1. Occurrence of chromium and other metals

Chromium content in tested samples varies within relatively narrow range limits (Table 2). The lowest concentrations of chromium were found in FA from combustion of wood fuels (DB/FA-1 and DB/FA-2). In the majority of coal-FA samples chromium occurs at the level of 50–100 mg/kg, 81 mg/kg on average. High chromium contents were found in the FA captured at the second stage of dust arresting of flue gases in a cement rotary kiln, 228.3 mg/kg and 242.3 mg/kg. In this case, the presence of chromium only partially has its source in the coal being burnt. The components of burnt clinker and the alternative fuel (a fraction of municipal wastes) have a considerable share in the chromium content. This can be indirectly confirmed by high contents of alkali metals in CRK/FA samples, e.g. potassium content was 15 times higher than its average content in FA generated in power and heating plants. The contents of chromium determined in this work are well within typical values for FA from other power plants: 49–144 mg/kg [8], 18–130 mg/kg [7], 26–50 mg/kg [22], and 71 mg/kg [23]. The chromium content in FA from MSWI (97.3 mg/kg) corresponds to the level of chromium in coal-FA samples and is lower than chromium content given in previous studies on MSWI–FA: 306–341 mg/kg (fraction passed through a # 50 sieve) [24], 127–175 mg/kg [12], 340–770 mg/kg [25], and 407 mg/kg [26]. In this case it is hard to expect a close similarity of results due to the fact that the chemical composition of MSWI–FA, including chromium, was strongly conditioned by the kind of MSW fractions being burnt.

Other metals (K, Na, Ca and Fe) were examined due to the potential role of their compounds in shaping valence speciation of chromium [3,5,6,17,27]. Generally, coal-FA generated in SF boilers and FBC boilers is more enriched in metals regarded as major elements than PCC/FA. As expected, wood-FA was characterized by higher K and Ca contents than coal-FA (PCC/FA and SF/FA). Co-combustion of biomass (10%) in a PCC boiler resulted only in a slight increase in the concentration of K. It is worth noting that the increased concentration of Ca in FBC/FA samples (av. 44 g/kg) and the high concentration in the MSWI/FA sample (306 g/kg) result from desulfurization of flue gases by means of a controlled dosing of limestone and hydrated lime, respectively. The environmentally available Fe varies within a relatively wide range from 3.29 g/kg (MSWI/FA) to 42.0 g/kg (SF/FA). Its concentrations in coal-FA samples from the PCC boiler were lower than those from the SF and FBC boilers.

Some interesting conclusions can be drawn from the results of the distribution of the metals in grain fractions of FA. In order to quantitatively characterize this phenomenon, the values of enrichment factor (EF) for SF/FAs were calculated as a quotient of the concentration of the metal in fine fraction ($\leqslant$63 μm) and in coarse fraction (>63 μm) (Fig. 1), whereas EFs for PCC/FAs as a quotient of metal concentration in the 2nd-field or 3rd-field ESP fraction and in the 1st-field ESP fraction (Fig. 2).

In the process of mid-temperature coal combustion (<1100 °C) the finer fractions become enriched in all the metals of interest, although not to the same degree: Cr > K > Na > Fe ≈ Ca. The distribution of these elements in ESP fractions of PCC–FA were different. The finer FA fractions are enriched in Cr, K and Na and depleted in Ca and Fe. As the condensation of volatile elements on the surfaces of FA particles in the post-combustion zone results in surface enrichment [28], it can be assumed that the surfaces of PCC–FA particles are covered with Cr, Na and K compounds, whereas in SF boilers the compounds of Ca, Cr, K, Na and Fe condense as a coating on FA particles.

Table 2
Metal content in the fly ashes samples and the characteristics its water extracts.

No	Sample	Fly ash							Water extract			
		K (g/kg)	Na (g/kg)	Ca (g/kg)	Fe (g/kg)	Cr (mg/kg)	Cr(VI) (mg/kg)	$Cr(VI)_{sol.}$ (mg/kg)	Cr(VI) (μg/dm^3)	pH	ORP (mV)	rH
1	PCC/FA-I/1	2.94 ± 0.13	2.08 ± 0.15	21.48 ± 0.58	18.2 ± 1.2	30.6 ± 2.8	3.20 ± 0.20	0.504 ± 0.034	50.4 ± 3.4	12.21	−44	29.2
2	PCC/FA-I/2	3.09 ± 0.16	2.42 ± 0.12	16.7 ± 1.3	17.7 ± 1.0	51.9 ± 2.2	5.95 ± 0.18	1.837 ± 0.058	183.8 ± 5.8	12.16	−57	28.7
3	PCC/FA-I/3	4.19 ± 0.14	3.14 ± 0.19	13.71 ± 0.39	16.8 ± 1.0	75.2 ± 3.4	7.20 ± 0.89	3.15 ± 0.11	315.3 ± 11	11.46	−29	28.2
4	PCC/FA-II/1	2.84 ± 0.10	1.94 ± 0.13	16.52 ± 0.27	13.2 ± 0.4	51.8 ± 1.7	4.97 ± 0.54	2.49 ± 0.23	249 ± 23	12.22	−9	30.4
5	PCC/FA-II/2	3.66 ± 0.11	2.26 ± 0.17	13.43 ± 0.16	12.0 ± 0.2	55.1 ± 1.0	5.01 ± 0.11	2.93 ± 0.15	293 ± 15	11.81	−16	29.4
6	PCC/FA-II/3	5.37 ± 0.17	3.43 ± 0.13	9.96 ± 0.14	11.9 ± 0.2	60.8 ± 3.2	4.88 ± 0.37	3.09 ± 0.14	309 ± 14	9.56	80	28.1
7	SF/FA-I/1a	6.45 ± 0.19	5.62 ± 0.19	15.6 ± 2.0	15.8 ± 1.2	67.7 ± 3.1	0.695 ± 0.090	0.0167 ± 0.0076	1.68 ± 0.10	9.59	115	29.4
8	SF/FA-I/1b	17.89 ± 0.26	12.49 ± 0.29	22.91 ± 0.27	25.6 ± 1.0	201.0 ± 6.0	0.939 ± 0.050	0.0423 ± 0.0034	4.23 ± 0.34	8.05	197	29.1
9	SF/FA-I/2a	9.33 ± 0.25	7.87 ± 0.24	18.31 ± 0.32	20.1 ± 1.1	70.9 ± 1.8	0.985 ± 0.092	0.0126 ± 0.0019	1.26 ± 0.19	7.73	161	27.2
10	SF/FA-I/2b	18.96 ± 0.32	13.05 ± 0.20	20.4 ± 1.8	22.6 ± 1.2	228 ± 25	1.237 ± 0.028	0.0463 ± 0.0026	4.64 ± 0.25	7.12	179	26.6
11	SF/FA-II/1a	8.9 ± 1.1	11.58 ± 0.76	27.0 ± 1.1	26.4 ± 3.7	48.7 ± 9.9	0.313 ± 0.011	0.0072 ± 0.0029	0.72 ± 0.22	9.78	94	29.0
12	SF/FA-II/1b	16.10 ± 0.14	17.71 ± 0.95	35.4 ± 1.2	42.0 ± 1.1	100.5 ± 5.1	0.336 ± 0.031	0.0162 ± 0.0079	1.60 ± 0.11	8.71	138	28.4
13	SF/FA-II/2a	7.34 ± 0.98	9.5 ± 1.1	13.9 ± 3.8	14.2 ± 1.2	38.8 ± 1.3	0.398 ± 0.018	0.0065 ± 0.0011	0.65 ± 0.11	9.67	102	29.1
14	SF/FA-II/2b	17.80 ± 0.64	20.45 ± 0.55	27.5 ± 1.4	29.9 ± 4.1	85.1 ± 4.2	0.623 ± 0.049	0.0227 ± 0.0012	2.27 ± 0.11	8.92	132	28.6
15	FBC/FA-1	12.04 ± 0.13	5.25 ± 0.15	36.80 ± 0.97	19.3 ± 1.1	90.7 ± 2.9	0.719 ± 0.052	0.0203 ± 0.0016	2.01 ± 0.16	7.98	121	26.4
16	FBC/FA-2	10.91 ± 0.24	5.41 ± 0.15	48.2 ± 2.1	20.5 ± 1.2	85.3 ± 1.2	0.484 ± 0.030	0.0416 ± 0.0010	4.16 ± 0.10	8.40	95	26.4
17	FBC/FA-3	11.54 ± 0.16	5.31 ± 0.14	45.52 ± 0.31	18.6 ± 1.0	92.2 ± 2.1	0.332 ± 0.010	0.0187 ± 0.0017	1.87 ± 0.17	8.20	117	26.7
18	DB/FA-1	52.2 ± 1.5	5.37 ± 0.18	169.1 ± 3.4	8.75 ± 0.34	20.2 ± 1.1	1.39 ± 0.11	1.280 ± 0.059	128.0 ± 5.9	12.24	−70	28.4
19	DB/FA-2	36.3 ± 1.3	8.99 ± 0.18	89.97 ± 0.57	7.46 ± 0.21	8.62 ± 0.62	2.60 ± 0.18	1.243 ± 0.038	124.0 ± 3.8	11.45	−48	27.6
20	MSWI/FA	31.75 ± 0.29	27.72 ± 0.15	305.8 ± 3.3	3.29 ± 0.24	97.3 ± 6.5	6.30 ± 0.44	1.40 ± 0.10	140 ± 10	12.17	32	31.7
21	CRK/FA-1	137.3 ± 1.7	48.55 ± 0.13	53.96 ± 0.75	–	94.7 ± 2.1	12.05 ± 0.37	7.79 ± 0.23	779 ± 23	10.89	11	28.4
22	CRK/FA-2	162.1 ± 1.8	55.13 ± 0.55	24.65 ± 0.13	–	242.3 ± 2.5	21.3 ± 1.7	0.129 ± 0.024	12.9 ± 2.4	10.05	−9	26.1
23	CRK/FA-3	144.5 ± 4.4	48.24 ± 0.67	34.56 ± 0.16	–	228.3 ± 3.0	11.02 ± 0.59	0.0990 ± 0.0078	9.90 ± 0.75	8.46	90	26.3

3.2. Chromium speciation

The chromium(VI) speciation analysis consisted in determination of two chromium(VI) fractions: leachable by means of a Na_2CO_3/NaOH solution and leachable by water. The first one is defined by other authors as "total content of chromium(VI)" [2], although the term "total leachable chromium(VI)" would be more appropriate. The other fraction is defined as "water soluble chromium(VI)" [26], although taking into account the fact that water extraction in fact consists in an extraction with a solution whose composition depends on chemical properties of the FA examined, we suggest an operational term "water leachable Cr(VI)". This Cr(VI) fraction can be treated as equivalent to the availability of chromium defined by Stam et al. [3].

Keeping in mind the essence of the chromium speciation analysis procedure used, the speciation forms of chromium will be henceforth termed in a simplified manner: Cr – pseudo-total chromium, Cr(VI) – total leachable chromium(VI), Cr(III) – pseudo-total chromium(III) = Cr − Cr(VI), $Cr(VI)_{sol.}$ – water leachable chromium(VI), and $Cr(VI)_{h.leach.}$ – hardly leachable chromium(VI) = Cr(VI) − $Cr(VI)_{sol.}$

Water leachable Cr(VI) can be identified with water soluble chromates, e.g. $(Na,K)_2CrO_4$, $(Ca,Mg)CrO_4$ or $ZnCrO_4$, however, $Cr(VI)_{h.leach}$ should be identified only to a small degree with sparingly soluble chromates, e.g. $BaCrO_4$ or $PbCrO_4$. It is hard to accept the view that hot extraction with a Na_2CO_3/NaOH solution, compared to water extraction, increases the extent of CrO_4^{2-} release only due to digestion of sparingly soluble chromates. Taking into consideration the speciation of Cr(VI) in the FAs studied, the combined concentration of metals whose chromates are sparingly soluble (mainly trace elements: Ba and Pb) should be at least of the same order as the combined concentration of Na, K, Ca and Mg (major elements). Stam et al. [3] have recently paid attention to this aspect of Cr(VI) speciation as well. It is hence justified to accept the assumption that alkali extraction releases primarily Cr(VI) present in the alkali non-resistant target phase (less resistant glass or sinter) which is water-insoluble, e.g. a slagging phase according to Chen et al. [17] or a glassy phase according to Verbinnen et al. [6].

The distribution of chromium species in individual FA samples is shown in Table 3. Valence speciation of Cr(III/VI) and Cr(VI) speciation are presented, with the latter in the form of water leachable and hardly leachable fractions. The results of chromium valence speciation studies for different types of furnaces were obtained by averaging all the results for FA samples collected from the same type of furnaces (Fig. 3).

In the case of the PCC boiler the chromium speciation was evaluated as an average of the results obtained for coal combustion and biomass co-combustion, because the differences appeared to be statistically insignificant. Apart from Cr(VI) determination, pH and ORP were monitored in water leachates (Table 2). The rH values oscillating around rH = 28.6 (from 26.1 to 31.7) in extracts with various Cr(VI) contents, in spite of moderate repeatability of ORP measuring, can be treated as an indication that the extraction method used makes it possible to correctly map Cr(VI) speciation in FA.

The speciation analysis has shown that the level of Cr(VI) in FA from solid fuel combustion (without CRK) was not only considerably lower than the concentration of Cr but also more spread, 2.4 ± 2.4 mg/kg (RSD = 100%), compared with 78 ± 53 mg/kg (RSD = 68%). Cr(VI) concentrations exceeding the mean value were found in FA samples from CRK, MSWI and PCC boilers, 14.8 mg/kg, 6.3 mg/kg and 5.2 mg/kg on average, respectively.

The results obtained for coal-FA are consistent with the reported Cr(VI) contents in Australian coal-FA (0.04–1.4 mg/kg) [7,8], in FA from a Dutch PCC boiler (6–9 mg/kg) [3], and in FA from a

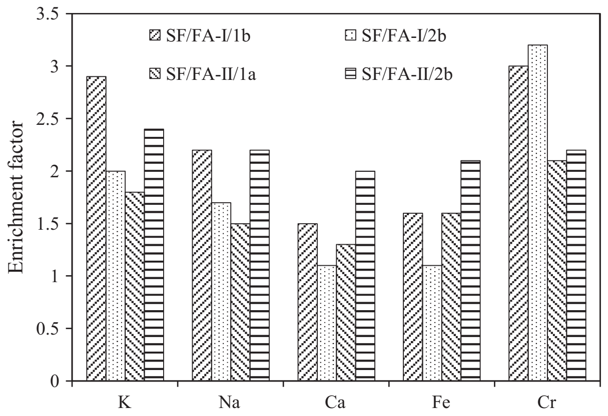

Fig. 1. Enrichment factors of the selected metals in FAs from SF boilers.

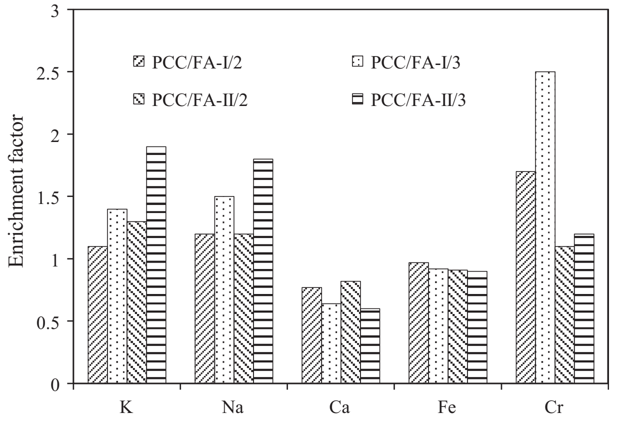

Fig. 2. Enrichment factors of the selected metals in FAs from PCC boilers.

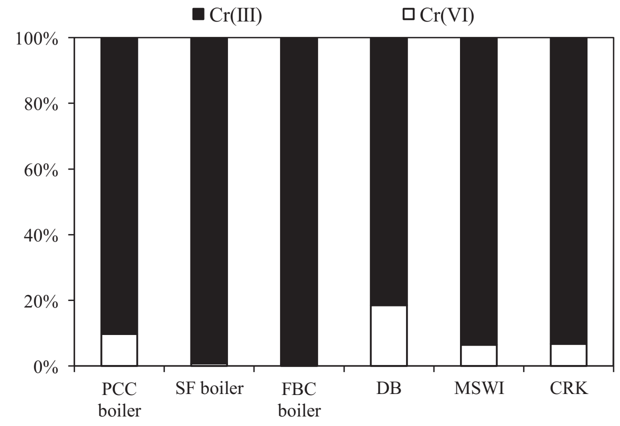

Fig. 3. Chromium valence speciation in fly ashes generated in real solid fuel furnaces based on various combustion technologies.

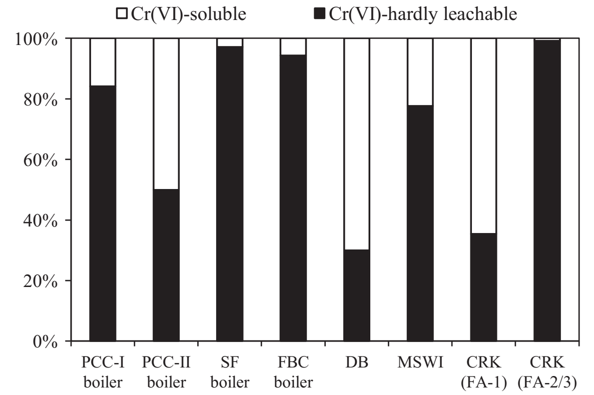

Fig. 4. Chromium(VI) speciation in fly ashes generated in the real solid fuel furnaces.

Table 3
Chromium speciation in the fly ash samples from the different kind of the furnaces.

No	Fly ash sample	Chromium valence speciation (%)		Chromium(VI) speciation (%)	
		Cr(III)	Cr(VI)	$Cr(VI)_{h.leach.}$	$Cr(VI)_{sol.}$
1	PCC/FA-I/1	89.5	10.5	84.2	15.8
2	PCC/FA-I/2	88.5	11.5	69.1	30.9
3	PCC/FA-I/3	90.4	9.6	56.2	43.8
4	PCC/FA-II/1	90.4	9.6	49.9	50.1
5	PCC/FA-II/2	90.9	9.1	41.6	58.4
6	PCC/FA-II/3	92.0	8.0	36.7	63.3
7	SF/FA-I/1a	99.0	1.0	97.6	2.4
8	SF/FA-I/1b	99.5	0.5	95.7	4.3
9	SF/FA-I/2a	98.6	1.4	98.7	1.3
10	SF/FA-I/2b	99.5	0.5	96.3	3.7
11	SF/FA-II/1a	99.4	0.6	97.7	2.3
12	SF/FA-II/1b	99.7	0.3	95.2	4.8
13	SF/FA-II/2a	99.0	1.0	98.4	1.6
14	SF/FA-II/2b	99.0	1.0	97.2	2.8
15	FBC/FA-1	99.2	0.8	97.2	2.8
16	FBC/FA-2	99.4	0.6	91.4	8.6
17	FBC/FA-3	99.6	0.4	94.4	5.6
18	DB/FA-1	93.1	6.9	7.9	92.1
19	DB/FA-2	69.9	30.1	52.2	47.8
20	MSWI/FA	93.5	6.5	77.7	22.3
21	CRK/FA-1	87.3	12.7	35.4	64.6
22	CRK/FA-2	91.2	8.8	99.4	0.6
23	CRK/FA-3	95.2	4.8	99.1	0.9

Turkey Power Plant (0.2–0.3 mg/kg) [29]. The concentration of Cr(VI) in MSWI–FA (6.30 ± 0.44 mg/kg) does not differ from the average Cr(VI) levels reported by other authors: 7.4 mg/kg [12] and ca. 8 mg/kg [30].

High percentage of Cr(VI) distinguishes wood-FA from a domestic boiler (Fig. 3). A moderate share of Cr(VI) (ca. 10%) concerns FA generated in a PCC boiler, MSWI and CRK. FA generated from coal combustion in an SF boiler and an FBC boiler are characterized by only a small (<1%) share of Cr(VI). Hence, it is justified that in mid-temperature combustion boilers the kind of fuel become a crucial factor for chromium valence speciation in the generated FA. Biomass combustion generates FA in which a significant percentage of Cr occurs as a Cr(VI) fraction. This view can also be supported by the results reported by Barbosa et al. [31] who demonstrated that co-combustion of dry sewage sludge with hard coal (1 + 1) in a BFB combustor increases the share of Cr(VI) fraction from 3% to 24% and by the results obtained by Stam et al. [3] for wood-FA from a BFB boiler, Cr(VI) – 29% and 41%.

Thus, the results of $Cr(VI)_{sol.}$ determination turned out to be interesting (Table 2). The highest content of the $Cr(VI)_{sol.}$ fraction can be found in FAs generated in the process of cement production, 7.79 mg/kg (FA captured in a dust chamber). Two to three times lower concentrations of $Cr(VI)_{sol.}$ were found in the PCC–FA. It has been confirmed in studies on FA generated in two PCC boilers of the same type that co-combustion of biomass contributes to a large change in Cr(VI) speciation (Fig. 4).

The biomass/coal-FA captured in the 1st-field ESP (ca. 90% of the total amount of the collected FA) is five times more enriched in $Cr(VI)_{sol.}$ than an analogous coal-FA fraction. The differences diminish with decreasing graining. The finest FA fractions

(3rd-field ESP, ca. 1% total mass) have a similar content of $Cr(VI)_{sol.}$: 3.09 ± 0.14 mg/kg (biomass/coal-FA) and 3.15 ± 0.11 mg/kg (coal-FA). About 40% lower concentrations of $Cr(VI)_{sol.}$ were found in an incinerator-FA sample and wood-FA samples from domestic boilers. The level of the Cr(VI) fraction in coal-FA produced in SF and FBC boilers was similar and very low, from a few to a few dozen µg/kg.

The results of speciation analysis of chromium in FA samples from SF and FBC boilers justify additional remarks. A practically identical pattern of speciation of Cr (Cr(VI) – 0.8%, $Cr(VI)_{sol.}$ – 2.9%) in FA generated in two SF boilers of the same type supplied with coal from the same source but working in different heating plants (Table 3, samples 7–14) shows good reproducibility of chromium speciation in FA generated on industrial scale. On the basis of a similar pattern of speciation of Cr in FBC–FA generated from combustion of coal from three different mines in one installation (Table 3, samples 15–17), it can be concluded that the composition of the hard coal burnt is not a critical parameter for shaping valence speciation of Cr in FA.

3.3. Formation of chromium(VI) during fuel combustion

Based on the speciation analysis of chromium it can be concluded that the technological factors which are conducive to a higher Cr(VI) content in FA are combustion of biomass and a high combustion temperature. The key to explaining these observations is a mechanism of chromium transformations taking place in the process of fuel combustion. The base for a description of the mechanism was to assume that transport of chromium, irrespective of combustion technology, proceeds according to a mixed mechanism in which a major role was played by a volatilization–condensation/adsorption stage. In our work the correctness of this assumption was confirmed by increasing concentrations of chromium in finer fractions of FA generated both in the process of high-temperature coal combustion (PCC/FA samples) and in the stoker-fired boilers (SF/FA samples). Finer particles have larger surface areas, which allows more effective deposition of volatile species on their surface. Our observations are not isolated, although they are not always interpreted identically [8,23]. Following Stam et al. [3] and Chen et al. [17] we assume that organic forms of Cr(III) present in fuels were responsible for volatility of chromium. In a combustion chamber, depending on local oxidizing and temperature conditions, gaseous Cr(III)-org. undergoes pyrolysis to Cr(III)-inorg. and, partially, oxidation to Cr(VI). Cr(III/VI) species which are thermodynamically stable under combustion conditions include $CrOOH_{(g)}$, and $CrO_{3(g)}$ and $CrO_2(OH)_{2(g)}$, respectively [3,18,32]. It has been confirmed experimentally that $CrO_2(OH)_{2(g)}$ was a dominant volatile species when Cr_2O_3 is exposed to H_2O and O_2 at high temperatures [33]. Thereby, one can expect that CrOOH and $CrO_2(OH)_2$ will be the main gaseous species in the combustion zone.

As Cr(VI) concentration in the FA studied also increases with diminishing graining (see also [8,29]), one can justify that Cr(III) undergoes oxidation in the gaseous phase, although it should be kept in mind that oxidation of CrOOH deposited on the surfaces of FA particles, e.g. $2CrOOH + 2Na_2O + 3/2O_2 \rightarrow 2Na_2CrO_4 + H_2O$ was also superficial in nature [17].

It should be noted that there is a divergent tendency for enrichment factors of Cr(III) and Cr(VI) determined for grain fractions of PCC–FA and SF–FA generated during coal combustion (Fig. 5). Similar values of EF-Cr(III) and EF-Cr(VI) directly suggest the oxidation of Cr(III) in the gaseous phase and deposition of the generated Cr(VI) species on FA particles, whereas EF-Cr(VI) < EF-Cr(III) can be interpreted as a result of reduction of Cr(VI) at the surface reaction stage. Hence, the reasons for a low content of Cr(VI) in SF–FA can be related to the chemical composition of the surface layer of FA particles. As demonstrated above, the operating conditions in SF boilers are conducive to the formation of a coating enriched with Ca, Cr, K, Na and Fe, whereas the surface of PCC–FA particles should be enriched only with Na, K and Cr.

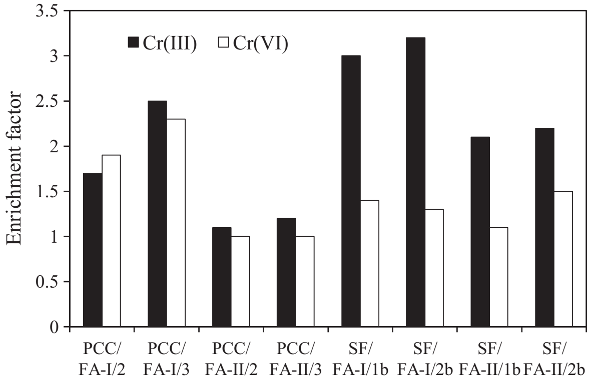

Fig. 5. Enrichment factors of Cr(III) and Cr(VI) in FAs from PCC and SF boilers.

Based on thermodynamic considerations by Fernández et al. [25], it can be assumed that under high-temperature combustion conditions Fe was not volatilized in the combustion chamber, but was mainly present inside the glass matrix or the coating glass matrix of the FA, and its deposition on the surface of FA particles was minimal. These assumptions are consistent with the results of the study by Kutchko and Kim [28] who demonstrated that PCC–FA comprised mainly of amorphous alumino-silicate spheres and a smaller amount of iron-rich spheres, and the majority of the latter exist as mixed iron oxide/alumino-silicate particles.

Transport of Fe should proceed differently in the flue gas of an SF boiler. In this case, it can be expected that the formation–volatilization–condensation of Fe(II) chloride plays an important role (Fe(III) chloride is not stable above 315 °C). Although above 800 °C (typical of an SF boiler combustion chamber) iron can exist as chloride and oxide [25], the surface of FA particles would be enriched primarily with iron oxides due to surface reactions e.g.: $MCl_2 + H_2O = MO + 2HCl$ [34].

Fe oxides accumulated on the surface of SF–FA particles may lead to a low content of Cr(VI) in FA not only by reducing the Cr(VI) species but also by binding the Cr(III) species. The correctness of this reasoning can be confirmed by the results of Jiao et al. [18] who have shown that the percentage of $FeCr_2O_4$ in fine FA particles generated from coal combustion at 1000 °C was considerably higher than in coarse particles. Stam et al. [3] have reported that the spinel phase $(Fe,Mg)(Fe,Al,Cr)_2O_4$ was a dominant form of Cr in FA generated by mid-temperature combustion. Recently, Chen et al. [5] have revealed that Fe_2O_3 effectively inhibits oxidation of Cr(III) by forming the corresponding chromites.

The high level of Cr(VI) in PCC–FAs is a clear indication that high combustion temperature (>1500 °C) during pulverized coal combustion is the factor which significantly shapes chromium valence speciation. The thermal conditions ensuring intensive vaporization of alkali metal compounds (e.g. KOH bp. 1320 °C, NaOH bp. 1390 °C, NaCl bp. 1413 °C and KCl 1500 °C subl.) are thus conducive to both stabilization of Cr(VI) and oxidation of Cr(III) captured in the alkaline aerosol being formed.

The stabilization of Cr(VI) in melted alkalies was probably important in all solid fuel combustion processes. Opila et al. [33] have shown experimentally that in the absence of stabilizing substances, $CrO_2(OH)_2$ condenses at the temperature of $\leqslant$600 °C as hexavalent Cr and at $\geqslant$700 °C as Cr_2O_3. So, one can expect that the Cr(VI) content in FA was a consequence of the stabilizing action of alkali metals and a complex action of iron oxides which, under favorable conditions, can effectively prevent oxidation of Cr(III).

Based on our reasoning presented above, one can expect that the surface composition of PCC–FA should be conducive to oxidation of Cr(III) to Cr(VI) rather than the surface composition of SF–FA. A supplementary experiment was performed in order to positively verify this statement. Two samples of FA ($m = 0.5$ g): the PCC/FA-II/1 and SF/FA-II/1a with similar Cr contents (51.8 mg/kg and 48.7 mg/kg, respectively) were heated in a muffle furnace at 700 °C for 2 h. The concentration of Cr(VI) increased in both samples and there was 10 times more Cr(VI) in the PCC/FA-II/1sample than in the SF/FA-II/1a sample (3.3 mg/kg vs. 0.32 mg/kg). The result corresponds well not only with the Cr speciation in the FA studied, but also with the recent results obtained by Chen et al. [5].

In order to simplify the picture of chromium transformation during solid fuel combustion in real furnaces the attention was put on the factors which are critical for the formation of Cr(VI). The well-known effect of CaO on the formation of Cr(VI) during thermal treatment of wastes was omitted due to a high melting point (m.p. 2572 °C) eliminating the participation of vapor CaO in alkaline aerosol and due to a lower, compared to KOH and NaOH, ability to form chromates under combustion chamber conditions [6].

4. Conclusion

The study of the presence of Cr(III), Cr(VI), water leachable Cr(VI) and hardly leachable Cr(VI) in FAs from 6 types of furnaces used in power industry, heat engineering, municipal waste treatment and cement production allowed for an assessment of the effect of solid fuel combustion technologies on chromium speciation in the generated FAs. It was shown that the technological factors which are conducive to a higher Cr(VI) content in FA were the combustion of biomass and a high combustion temperature. Confronting the results of the Cr speciation analysis obtain with this work with those reported by other it has been shown that hard coal combustion in SF, FBC or domestic boilers should generate FA with a low level of Cr(VI), because, under these conditions, Fe oxides effectively prevent oxidation of Cr(III). Replacing fuel with biomass should promote chromium evaporation while a high content of alkali metals and a low level of Fe, characteristic of biomass, would create favorable conditions for stabilization of Cr(VI) being formed and for oxidation of Cr(III) deposited on the surface of FA particles. As a result, FA has a higher content of Cr(VI). High Cr(VI) concentrations can be expected also in FA generated by high-temperature coal combustion in PCC boilers. Under these conditions oxidation of Cr(III) was favored due to deactivation of Fe oxides and an increase in evaporation intensity of alkali compounds. Municipal solid waste incineration should generate FA in which Cr speciation will be very similar to the one obtained in FA generated during combustion of biomass in heating boilers, although, in this case, the kind and composition of the municipal waste fraction introduce considerable uncertainty to predictions.

Acknowledgment

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Review

Leaching of chromated copper arsenate wood preservatives: a review

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"Capsule": *A review of the existing literature about the wood preservative chromated copper arsenate (CCA) indicates not enough is known about leaching of CCA from treated wood.*

Abstract

Recent studies have generated conflicting data regarding the bioaccumulation and toxicity of leachates from preservative-treated wood. Due to the scale of the wood preserving industry, timber treated with the most common preservative, chromated copper arsenate (CCA), may form a significant source of metals in the aquatic environment. The existing literature on leaching of CCA is reviewed, and the numerous factors affecting leaching rates, including pH, salinity, treatment and leaching test protocols are discussed. It is concluded from the literature that insufficient data exists regarding these effects to allow accurate quantification of leaching rates, and also highlights the need for standardised leaching protocols. © 2000 Elsevier Science Ltd. All rights reserved.

Keywords: Copper; Chromium; Arsenic; Wood preservation; Biocides

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Contents

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1. Introduction

During the development of freshwater, estuarine and marine coastlines, considerable quantities of wood are used in the construction of docks, pilings and bulkheads. Environmental pressures are increasingly inhibiting the continued use of naturally durable hardwood timbers in these structures (Eaton and Hale, 1993). However, many features of wood make it a particularly attractive building material; wood is a renewable resource, has excellent strength-to-weight properties, has a relatively low price and is easily produced (Desch and Dinwoodie, 1996). Timbers that are not naturally durable are treated with preservatives to prevent decay by wood-boring crustaceans, molluscs and fungi.

Currently, the most widely used wood preservative for timbers exposed in aquatic environments is chromated copper arsenate (CCA). CCA belongs to a group of inorganic, waterborne preservatives including chromated copper boron, ammoniacal copper arsenate, acid copper chromate, ammoniacal copper zinc arsenate and ammoniacal copper quaternary. This group has largely replaced alternative organic preservative types such as creosote, coal tars and pentachlorophenol for aquatic use, due to the environmental and human health concerns of these chemical types, as well as rising costs and declining availability of those treatments.

The metal elements in CCA are usually present in the form of oxides, and wood is industrially treated using a vacuum-pressure impregnation process according to British Standard guidelines (BSI, 1987a, b, 1989). The treatment and use of preservative-treated timber is also subject to industry and international guidelines (Environment Canada, 1988; UNEP, 1994; BWPDA, 1995; WWPA, 1996). Three CCA formulations, referred to as types A, B and C, have been developed, although type C is now the most commercially popular (Table 1). Minimum lifespans in fresh and marine water are considered to be 30 and 15 years, respectively (BSI, 1989).

Table 1
Chromated copper arsenate (CCA) formulations (oxides basis) (Cooper, 1994)

Type	CuO	CrO_3 (%)	As_2O_5
CCA-A	18.1	65.5	16.4
CCA-B	19.6	35.3	45.1
CCA-C	18.5	47.5	34.0

Out of the 591 million cubic feet (16.7 million m^3) of wood preserved in the USA in 1996, 467 million cubic feet (13.2 million m^3) (79.1%) were treated with waterborne preservative types. Approximately 144 million lbs (65.3 million kg) of CCA solution was used, while other waterborne preservatives amounted to 4.3 million lbs (1.9 million kg). Nearly 19 million board feet (5.8 million board m) of preserved timber were prepared for marine construction, of which 95% was treated with CCA (AWPI, 1997).

CCA-treated wood has been used extensively for over 60 years and its success as a building material suggests that leaching may not be a problem in terms of long-term efficacy. Wood preservation is an important industry in Europe and North America, with annual gross sales in the USA of around $\$3.91\times10^9$ (3.61×10^9 Euros) in 1996 (AWPI, 1997). However, recent toxicity testing studies have suggested that leaching of preservative components from wood used in aquatic situations may be harmful to the environment, particularly with the proliferation of residential docks around North American coastal waterways.

The toxicity of copper (Cu), chromium (Cr) and arsenic (As) to aquatic organisms is well recorded (Bodek et al., 1988a, b; Fleming and Trevors, 1989; Wong and Chang, 1991; Havens, 1994; Nriagu, 1994a, b; Walley et al., 1996a, b), and all are listed as priority pollutants by the United States Environmental Protection Agency (Weis et al., 1992; Weis and Weis, 1995). The reactions that take place in the wood during the fixation of CCA have a great influence on the metal species that are emitted from the wood, and the subsequent toxicity of these leachates. The toxicity of Cu, Cr and As is highly dependent on the specific form present. Cr in the +6 oxidation state is known to be carcinogenic and mutagenic, but if reduced to Cr (III), as during the CCA fixation process, it may be significantly less harmful (Sanders and Reidel, 1987). As may also be carcinogenic and mutagenic as well as teratogenic and, of the predominant oxidation states, As (V) is thought to be the more prevalent and less toxic form than As (III). Due to its chemical similarity to phosphate, arsenate may have an elevated rate of uptake by phytoplankton (Sanders and Windom, 1980), and it has been suggested that in low phosphate marine environments, arsenate may actually be more toxic than arsenite (W.S. Atkins Environment, 1998). Although Cu is an important micronutrient, it is toxic in the free ionic state above trace levels, though it may be largely partitioned to organic material in the aquatic environment, particularly humic acids (Newell and Sanders, 1986; Fleming and Trevors, 1989; Livens, 1991; Hung et al., 1993).

Studies have been conducted exposing marine organisms to CCA-treated wood or leachate waters and deleterious effects have been shown against a range of aquatic organisms (Weis et al., 1991, 1992). Criticism of this work focused on the unrealistically high ratio between wood and water volume, which allowed the metal concentrations to build up to toxic levels (Albuquerque and Cragg, 1995a; Breslin and Adler-Ivanbrook, 1998). Further work has suggested a decrease in biodiversity close to CCA-treated marine structures, and elevated levels of metal elements in benthic organisms (Weis and Weis, 1994a, b, 1995, 1996; Albuquerque and Cragg, 1995a; Wendt et al., 1996; Cragg and Eaton, 1997; Weis et al., 1998). Although Cu concentrations were found to be significantly elevated in algae growing on CCA-treated wood panels, no increase was found in fish species associated with the same panels (Weis and Weis, 1999). This suggests that trophic transfer to consumers did not occur, although it was possible that the duration of the studies was insufficient to allow accumulation in higher consumers. Similarly, Adler-Ivanbrook and Breslin (1999) found little metal accumulation in blue mussels exposed to treated wood panels in laboratory and field exposures. Again, experimental design may have influenced results, where continuous flushing of the laboratory system may have prevented bioaccumulation.

In contrast, leachates from untreated wood were shown to have a greater toxicity towards fish and invertebrates than leachates from CCA-treated wood. The adverse effects noted were thought to be due to naturally occurring extractives including aldehydes, phenols, terpinene, camphene and pinene (Baldwin et al., 1996; Taylor et al., 1996). These naturally occurring extractives may be leached out somewhat during the treatment process, or may be more strongly bound to wood as a result of complex formation during treatment.

One of the major problems is that due to inadequate understanding of long-term leaching rates, recommended preservative loading is presently set at very high levels. For example, common treated timbers such as Scots pine and Douglas fir have densities between 500 and 550 kg m^{-3} (Desch and Dinwoodie, 1996). Therefore, with a salt loading of up to 50 kg m^{-3} recommended (BSI, 1989; Eaton and Hale, 1993), the preservative may represent around 10% of the final timber weight. It is unclear from the current literature if these levels are based on toxicity thresholds of common decay organisms, or are merely intended to account for losses expected throughout the service period. Preservatives must be persistent enough to allow protection throughout the predicted lifespan of the structure, which may be up to 30 years in fresh water conditions. The active components must be of low solubility to resist leaching, yet soluble enough to continue to be effective against organisms responsible for decay (Hegarty and Curran, 1986).

In addition to the possible environmental problems of losses of preservative components during the life of timber, disposal of timbers still retaining high levels of preservative is also of concern. In Germany and France, around 2.1–2.4 million tons of wood waste is considered dangerous (according to the European Council directive 91/689/EEC on hazardous waste). In France alone, out of 25 million CCA-treated poles, 500,000 (or 50,000 tons) are removed from service annually and must be disposed of (Helsen and Van den Bulck, 1998). Better understanding of losses in service may facilitate a reduction in initial loading, and thus alleviate the problems of disposal.

The wood preserving industry is also engaged in a considerable research and development programme to generate improved biocides. A number of these are based on Cu, with the Cr and As replaced by a triazole biocide in copper azole, or a quaternary ammonium biocide in ammoniacal copper quaternary. The novel biocides, in addition to containing Cu, will bind to wood along the same ion exchange mechanisms, so better understanding of the factors that affect CCA leaching will be of benefit in their further development.

Wood preservatives are also subject to increasingly stringent environmental legislation, particularly within the European Union where they will fall under the control of the new Biocidal Products Directive, which will come into force in the year 2000. As-containing wood preservatives have also recently been scrutinised under the Marketing and Use Directive (W.S. Atkins Environment, 1998).

Wood preservatives must be considered as part of a much wider suite of biocides. Of these, the adverse environmental effects of antifouling paint biocides containing organotins have been widely reported (Gibbs et al., 1987, 1988; Clark et al., 1988). Cu remains an important active ingredient in the antifouling paint industry following legislation against the use of organotin compounds, and is also likely to remain a mainstay of the wood preserving industry in the future. Closer examination of the wood preservatives as an additional source of Cu to the aquatic environment is therefore relevant.

To enable a more realistic assessment of the possible environmental effects of CCA-treated timber accurate quantification of component leaching rates is required.

Leaching involves a number of different processes, including initial loss of surface deposits and unfixed components, penetration of water into wood and hydrolysis or dissolution of the fixed or complexed components and migration of preservative to the surface of the wood (Cooper, 1994). Aspects of the preservative treatment of wood may affect its leachability, in addition to the environment the wood is exposed to in its period of service.

A comprehensive literature review conducted for the United States Department of Agriculture provides a summary of pertinent data available up to 1995 on leaching of a number of preservative types in terrestrial and aquatic environments (Lebow, 1996). This earlier review concluded that despite the numerous laboratory studies that had been conducted, the data generated often had little applicability to in-service leaching rates. It also highlighted the need for further research to address the effects of different environmental exposures, such as fresh water, seawater and highly organic environments, and the need to monitor the overall environmental fate of leached wood preservative components.

The aims of this review are to evaluate the existing data on leaching of CCA, and the principal factors that affect leaching rates in order that releases to different aquatic environments can be predicted and risks assessed. While much of the literature reviewed concerns research conducted with CCA applications in terrestrial as well as aquatic environments, the authors have made every effort to rely upon work which has a specific aquatic focus.

2. Wood preservative treatment

2.1. Fixation

Although the fixation of CCA is still not completely understood, the process is generally defined by the reduction of hexavalent chromium. The reduction of the reactive and mobile Cr (VI) to Cr (III) is crucial in the formation of insoluble complexes in CCA-treated wood. As can be seen in Table 2, there is a direct correlation between the level of unreacted Cr (VI) in treated wood and the leaching concentration of CCA components and complete fixation is essential to minimise leaching (Cooper et al. 1995; Walley et al., 1996b). Fixation of wood at 15°C takes around 14 days (Eaton and Hale, 1993).

Table 2
Effect of chromium (Cr) fixation on chromated copper arsenate (CCA) leaching losses from red pine pole sections following 2 h simulated rainfall (Cooper et al., 1995)

% Cr fixation	Cr (VI)	Leaching ($\mu g\ cm^{-2}$)		
		total Cr	Cu	As
68.2	799	1499	755	120
84.1	200	376	162	96
92.6	53	71	34	4
98.2	0.1	2	4	3

The fixation of multi-component preservative types such as CCA is a complex and active process, and the components are not simply taken up through the conducting tracheid cells and deposited in the lumens of these cells (Hayes et al., 1994). Chou et al. (1973) used analytical electron microscopy techniques to demonstrate component penetration of the primary and secondary cell wall and the presence of coarse deposits of mainly Cu on cellulose microfibrils. Merkle et al. (1993) demonstrated that the highest metal concentrations were found in the porous ring tissues, and granular precipitates were observed in the tracheids. Hager (1969) demonstrated that Cu could fix to wood in the absence of a fixing agent, such as Cr.

Pizzi worked extensively on the chemistry and kinetic behaviour of CCA wood preservatives. Studies of the reactions of mixtures of metal salts with the various constituents of wood, lignin and cellulose and simple model components such as guaiacol and D (+)-glucose were conducted (Pizzi, 1981, 1982a, b, c). The reaction of Cr (VI) was considered to take place in a series of consecutive reactions, involving an initial adsorption by carbohydrates, 'in-situ' reduction and the formation of various complexation reactions such as $CrAsO_4$ with lignin, Cu^{2+} precipitation and complexation with lignin and cellulose and CrO_4^{2-} complexation with lignin. CCA type C was considered to have only ±10% of the total Cr remaining in the hexavalent form, which was totally and irreversibly bound to wood and unable to leach. Cr (III) was considered to be leachable, slowly, along with As. Later work highlighted the presence of chrome arsenates that may be weakly adsorbed or simply precipitated on wood carbohydrates or lignin (Pizzi, 1990a, b). Wood extractives have also been suggested as a potential site for CCA fixation (Pizzi et al., 1986; Ryan and Plackett, 1987; Forsyth and Morrell, 1990; Kennedy and Palmer, 1994).

Developments in the use of techniques such as electron paramagnetic resonance spectroscopy (EPR) and X-ray photoelectron spectroscopy (XPS) have allowed further identification of chemical species and complexes bound to specific sites in the wood anatomy. XPS analysis, for example, has indicated increased carbon–hydrogen bonding and decreased carbon–oxygen bonding, suggesting oxidation of hydroxyl groups on cellulose or lignin and decarboxylation of carbonyl and carboxyl groups during fixation (Ruddick et al., 1993; Kaldas et al., 1998). Evolution of CO_2 resulting from this oxidation and decarboxylation as Cr is reduced has also been monitored as fixation proceeds (Porandowski et al., 1998). EPR techniques have suggested the presence of CuN_2O_2 complexes in amine copper-treated wood, and Cu bound to four oxygen atoms in nitrogen-free formulations, such as CCA (Hughes et al., 1994).

Although these initial reaction steps are generally well characterised, the continuing longer-term reactions, and the effects these have on the distribution of metal species is not so well understood. A general scheme for the different stages of fixation has been proposed (Table 3). The available literature pertaining to CCA fixation suggests that many wood constituents may play a role in the overall reactions. This is to be expected considering the number of potential reactive sites in wood, the tendency of Cu to adsorb strongly to organic matter in general, and the strong reducing capacity of hexavalent Cr (Lebow, 1996).

2.2. Formulation

The ratio of preservative components in CCA formulations is crucial to allow rapid and 'complete' fixation. Fahlstrom et al. (1967) found a clear relationship between the Cr:As ratio and total metal leachability, and proposed a ratio of Cr:As of 1–1.30 as optimum. Smith and Williams (1973a, b) studied a range of CCA formulations and suggested a Cr:As ratio of 1.9 or greater for maximum As fixation. As a consequence of this variation in fixation of different formulations, early leaching studies generated variable results, with As often proving to be the most leached element, presumably due to insufficient Cr available for complexation (Fahlstrom et al., 1967; Henshaw, 1979).

2.3. Wood anatomy

Since lignin is thought to be a primary site for binding of Cr complexes, an increased lignin content may result in improved treatment. Softwood species, high in lignin, are therefore often found to perform better than hardwoods in terms of preservative treatment, and the anatomy of softwoods, with a high proportion of xylem tracheids also results in improved performance (Hayes et al., 1994).

Table 3
General scheme for chromated copper arsenate (CCA) fixation reactions (Murphy, 1998)

Reaction	Description	Products
Initial (minutes)	Cu^{2+}, CrO_4^{2-} adsorption to wood	Cu^{2+}/wood Cr^{6+}/wood
Main (hours/days)	Cr^{6+} reduction	$CrAsO_4$ $Cu(OH)CrAsO_4$ $CuCrO_4$ $Cr(OH)_3$ Cr^{6+}/wood complexes Cr^{3+}/wood complexes Cu^{2+}/wood complexes
Long term (weeks/months)	Fluctuating pH	?

Earlywood tracheid cells of softwood species function primarily as a means of conduction, and consequently have a higher proportion of bordered pits in the cell walls (Desch and Dinwoodie, 1996), and larger volume of lumen (Nicholas et al., 1991). Hayes et al. (1994) suggest that although earlywood is thought to be higher in lignin than latewood, which allows improved fixation, the anatomy of cells may be more important in determining fixation, and allow more rapid preservative movement and increase subsequent losses due to leaching. The distance that solutes such as CCA must diffuse will influence preservative treatment. Hardwoods are penetrated mainly via vessels, and estimated diffusion paths in these species is much longer than softwoods (Cooper and Churma, 1990). It is suspected that long diffusion times may prevent the saturation of the cell wall before the fixation reactions are completed, leading to an altered microdistribution of elements.

Variation in the preservative penetration and retention in sapwood and heartwood of identical species grown in separate areas has been observed, despite the lack of differences in size and number of growth rings, or a consistent relationship between specific gravity and retention (Taylor, 1991).

2.4. Preservative treatment

Physical parameters of the preservative process such as magnitude and duration of vacuum and pressure cycles may influence penetration and retention of preservatives. Increasing the pressure treatment period may reduce the proportion of elements on the surface of the wood, and may thus reduce leaching. Conversely, increasing the length of the vacuum stage may affect the proportion of more readily leached surface components (Cooper, 1994).

The temperature at which the treatment cycle is conducted, and post-treatment drying conditions have been shown to exert a considerable influence on fixation and leaching. Early work in the field of accelerated fixation was pioneered by Peek and Willeitner (1981, 1988). Fixation times are known to be greatly reduced when timbers are exposed to increased temperatures both during and following treatment, with fixation complete within 1 h at temperatures in excess of 85°C (Cooper and Ung, 1992; Eaton and Hale, 1993). However, Dahlgren (1975b) first observed increased leaching of Cu at elevated drying temperatures. Post-treatment drying of wood in kilns at temperatures of 60–80°C resulted in increased leaching of CCA elements compared with wood left to dry at ambient temperature (Dahlgren, 1975a; Lee et al., 1993). Initial leaching rates of Cu were approximately double from steam-fixed wood compared with naturally fixed pine, while Cr losses were substantially reduced by steam fixation (Van Eetvelde et al., 1995a, b). Rapid drying may cause redistribution of chemicals between lignin and cellulose, leading to higher proportions of leach-susceptible components, or deposition of CCA products in the cell lumens, where again they may be more accessible to leaching (Lee et al., 1993; Cooper et al., 1997). Pizzi (1983a) observed that the ratio of CCA components reacting between carbohydrates and lignin increased at increasing temperatures of the preservative solution. Hardwoods subject to accelerated fixation have been shown to be more susceptible to biological decay and the possible causes were postulated to be due to altered Cu complexation that made it less available as a toxicant. Alternatively the diffusion of components to the susceptible cell wall areas may not be able to occur when reaction rates are increased by accelerated fixation, and therefore the microdistribution of CCA may be affected (Preston and McKaig, 1983).

2.5. Loading

Increasing the concentration of the treatment solution has been suggested to increase the rate of fixation and to affect the binding of Cr complexes in favour of lignin, possibly due to the lower pH (Pizzi, 1983b). Conversely, increasing treatment concentrations was observed to lengthen the time period for initial fixation reactions to occur (Dahlgren, 1975a, b). However, in the conditions typically used commercially, solution concentration and retention does not seem to have a major influence on fixation rate (Pizzi, 1983b; Cooper and Ung, 1992).

Preservative loading will affect the absolute concentration of elements leached and the percentage of total leached, although the exact relationship between preservative loading or retention and leaching is not clear (Cooper, 1994; Albuquerque and Cragg, 1995a, b; Albuquerque et al., 1996). Fahlstrom et al. (1967) suggested the effect of retention on leaching was dependent on preservative composition, with percentage leaching decreasing with increasing retention in As-rich formulations. In Cr-rich formulations, leaching increased with retention. Proportional losses have been found to decrease at increased loadings (Archer and Preston, 1994; Hayes et al., 1994). Following 85 months exposure in the marine environment, percentage losses were 52 and 44% from pine-treated to retentions of 24 and 48 mg kg^{-3}, respectively. The reduced leaching was suggested to be due to increased total Cr concentrations in the system available to fix the remaining metal elements (Archer and Preston, 1994). However, other workers have shown increased leaching with increasing retentions (Hager, 1969; Irvine et al., 1972; Albuquerque et al., 1996). Breslin and Adler-Ivanbrook (1998) observed that long-term Cu and Cr leaching rates were highest in CCA-treated wood with retention levels >35 kg m^{-3}, whereas long-term As leaching rates were increased in wood with retention levels <35 kg m^{-3}. These observations may possibly be explained due to competition for binding sites between Cu and Cr, and the role of Cr in the fixation of As.

3. Leaching

There has been a considerable amount of literature published concerning leaching of CCA wood preservatives in aquatic environments. However, the focus of much of the early work has been on monitoring leaching in terms of the durability of wood and the ability of treated timbers to withstand biological decay, rather than quantify releases to, and effects on, the marine environment (Fahlstrom et al., 1967; Hager, 1969; Cherian et al., 1979; Johnson, 1982; Eaton, 1989; Green et al., 1989). Although it is clear that large amounts of preservative do remain in properly fixed wood after prolonged exposure, due to the high loading even small percentage losses may be environmentally significant due to the high toxicity of the components.

3.1. Standard leaching protocols

A number of standard protocols exist for conducting laboratory leaching studies (AWPA, 1983; ANS, 1986; BSI, 1994, 1997). For example, ENV. 1250:2 (BSI, 1994) recommends immersing five end-sealed test blocks (50×25×15 mm) in 500 ml of water or synthetic seawater, and stirring at 20°C, for six leaching periods of increasing duration up to 48 h. Researchers have either followed one of these standard protocols or designed original leaching trials using a range of different parameters, but few studies have been conducted using identical parameters and protocols, making direct comparison of results difficult. Willeitner and Peek (1998) briefly reviewed standard test methods for measuring environmental inputs of waste and other material by leaching and propose general requirements necessary for leaching studies with wood preservatives. Recommendations for the harmonisation toward a single protocol have been made, with modification of the biological efficacy testing protocol B.S. EN. 84 (BSI, 1997) suggested as being the most appropriate (Van Eetvelde et al., 1998; Wegen et al., 1998). The principal advantage of B.S. EN. 84 appears to be the incorporation of a water impregnation stage, where test blocks are immersed in water and maintained in a vaccuum desiccator for 2 h prior to leaching. This may therefore represent the most severe leaching test of all available protocols. Potential drawbacks of this approach are the inability to end-seal test blocks, the use of static water conditions, and the lack of a rigid sampling regime.

ENV. 1250:2 (BSI, 1994) recommends an intermediate drying period of 16 h during the test to simulate natural drying of wood exposed to tidal regimes.

Although these protocols may be regarded to be relatively simple, and therefore easily repeatable, results do not necessarily give an accurate estimation of losses from commercial size timber. This is due to differences in size, physical stresses and environmental conditions. A number of researchers highlight the important point that laboratory results should not be used to interpret losses from commercial size timber, but should only be used as a comparison between preservative types (Cooper, 1994; Albuquerque et al., 1996). However, there is continued reliance on laboratory-based data to make judgements on the acceptability of wood preservatives. Agreement to adopt a single recognised protocol for all leaching studies would certainly aid comparison of laboratory-based data in the future. For the purposes of reducing inter-laboratory variation the methodology of such a single protocol should be kept as simple as possible. One important facet of any leaching protocol is that sampling should be conducted at sufficiently regular intervals to allow quantification of the decline in leaching rates during the early period of exposure. It is also important that the tests are of sufficient duration in order that the longer-term leaching rates be accurately quantified. End-sealing of test blocks will help minimise the effects of high leaching rates from timber end-grains, which may form a significant proportion of standard test blocks. Simulation of water motion and tidal movements, by incorporation of stirring devices and daily drying periods may also be important parameters in any leaching protocol.

Despite a considerable amount of literature available, the leaching rates of common preservative types, such as CCA, from commercial size timber remain poorly defined. The existing literature has indicated that a number of factors may influence the leaching rate of wood preservatives, including pH, salinity, block size and wood surface exposed. These are reviewed below.

3.2. Block size

The size of wooden block used during laboratory leaching trials appears to have a major influence on the leaching rates obtained. The relatively large surface area-to-volume ratio of the typical small sample blocks used in most laboratory studies allows proportionately more wood available for leaching, and distances components must diffuse decreases (Cooper, 1994).

Significant reductions in leaching rates of all CCA elements were observed with a decrease in surface area-to-volume ratio (Hayes et al., 1994), although the exact relationship has not been fully characterised. Attempts have been made to model the three-dimensional transport of organic wood preservatives, taking into account the differential diffusivities of the wood surfaces (Haloui and Vergnaud, 1995, 1997). One trial has attempted to conduct a laboratory study with more realistic timber dimensions, with a pile 250 mm in diameter and 1200 mm long, although sampling did not allow full characterisation of leaching rates (Baldwin et al., 1996).

The proportion of the three wood surfaces exposed may also affect leaching rates. Losses within 24 h have been shown to be greatest from the radial and tangential surface, although long-term leaching was greatest from the end-grain (Orsler and Holland, 1993). End-grain penetration has been shown to be 40 times greater than lateral penetration and may greatly influence leaching rate (Morgan and Purslow, 1973). In commodity size timber, end-grain may represent only a small percentage of exposed surfaces, but may form a significant proportion of standard test blocks. This may lead to laboratory studies grossly overestimating leaching rates (Archer and Preston, 1994; Cooper, 1994; Albuquerque and Cragg, 1995a). However, the advantage of using relatively small blocks, apart from ease of manipulation and relatively high percentage losses, includes the homogeneity of the sample and consistent preservative loading throughout the sample. With increasing size of timber, the heterogeneity of the sample increases, increasing variation in preservative loading. Variations in heartwood and sapwood can significantly alter loading. For example, in wood treated to a specified level of 40.7 kg m^{-3}, outer 1.3 cm sample retention levels ranged from 4.5 to 64 kg m^{-3} (Breslin and Adler-Ivanbrook, 1998). Clearly this magnitude of variation may obscure losses due to leaching. The use of end-matched sections in leaching trials has been recommended to reduce such variability (Rak and Clarke, 1974; Albuquerque et al., 1996).

3.3. Leaching media

A number of features of the leaching media are important in determining leaching rates, particularly salinity and pH. Attention has also been drawn to the importance of the volume of leaching water used, particularly in toxicity studies, where a high wood:water volume ratio allowed toxic concentrations of metals to build up (Weis et al., 1991; Albuquerque and Cragg, 1995a). It is possible that a high wood:water volume ratio, or insufficient replacement of leaching waters may inhibit diffusion of elements into water (Brooks, 1997; Breslin and Adler-Ivanbrook, 1998). Van Eetvelde et al. (1995a, b) quote a wood:water volume ratio of 1–5, as recommended in a Dutch government standard for simulating releases from building materials.

3.3.1. Salinity

Scots pine and beech sapwood blocks treated with CCA were exposed in cooling towers receiving water from fresh water, sewage effluent and marine sources with results indicating increased loss of Cu and Cr with increasing conductivity of the surrounding waters (Irvine et al., 1972). Solutions of higher ionic strength have been shown to leach greater concentrations of CCA, although in the salinity range from 0 to 24‰ no increase in Cu loss was observed. It has been suggested that at low salinities, NaCl has a coagulating effect on the crytallite Cu fixation complexes increasing surface area and decreasing solubility, whilst at salinities above 24‰ the increased formation of complexes between chloride and Cu may explain the increased leaching (Irvine and Dahlgren, 1976). Pine sapwood treated with CCA and leached with varying strengths of salt solutions ($CaCl_2$, $Ca(NO_3)_2$, $Mg(NO_3)_2$ or K_2HPO_4/KH_2PO_4 at 0.03–1.00 M) resulted in increased Cu leaching compared with deionised water controls, and leaching rates increased with salt solution concentration (Plackett, 1984).

3.3.2. pH

Studies investigating the effects of solution pH on preservative loss were conducted using water buffered with sodium hydroxide and citric acid. This study indicated very high leaching rates at low pHs, with losses of Cu of up to 100% at pH 4.5 (Warner and Solomon, 1990). Leaching in dilute sulphuric acid solutions was reduced by up to a factor of 5, and Cooper (1991) later demonstrated that the high losses were due to the use of the citric acid buffer. The carboxylate group of the citric acid acted as a bidentate ligand that bonded with metal ions, forming water-soluble complexes. When pH of solutions was adjusted using a mineral acid with no such chelating properties, no consistent effect on leaching was observed at pH 3.5–5.5. Publication of the initial work resulted in considerable media interest, amid raised concerns over the environmental effects of wood preservative leachates (Cooper, 1990). Van Eetvelde et al. (1995a, b) observed maximum leaching of Cr and As under neutral conditions, with initial losses of Cu increasing with higher acidity. The influence of increased acidity is explained due to the role of the additional hydrogen ions acting in the acid-ion-exchange reactions at the acid adsorption points on wood cell walls (Van Eetvelde et al., 1998). Results of typical leaching trials investigating effects of pH are shown in Table 4.

3.3.3. Temperature

Effects of temperature have also been investigated. Leaching of Cu, Cr and As has been shown to be reduced at lower temperatures, with leaching of Cr at 20°C reported to be 0.119 $\mu g\ m^{-2}\ s^{-1}$ compared with 0.079 $\mu g\ m^{-2}\ s^{-1}$ at 8°C (Van Eetvelde et al., 1995a), although one study has indicated decreased flux of As at 20°C compared with leaching at 4°C (Breslin and Adler-Ivanbrook, 1998).

Table 4
Effects of pH on leaching of copper from chromated copper arsenate (CCA)-treated wood

pH	Percentage leached	Duration	Reference
3.5	3.4	13 days	Cooper (1991)
4.5	2.8		
5.5	2.6		
4.0	4.1	79 hours	Van Eetvelde et al. (1995b)
5.5	3.4		
7.0	2.3		
8.5	1.9		
2.5	145[a]	40 days	Warner and Solomon (1990)
3.5	75		
4.5	21		

[a] Values represent a single replicate, and the percentage loss reported is thought to be an artefact of block-to-block variation and underestimation of initial loading.

3.4. Field trials

A number of field trials have been instigated to better quantify the losses of wood preservatives under more realistic environmental conditions. In long-term marine field trials, CCA-treated pine leached as much as 25% of total active ingredients within 6 months, with total losses only rising to 52% after 85 months (Archer and Preston, 1994). Hayes et al. (1994) also observed losses of Cu from pine submerged in coastal waters occurred most within the first 12 weeks of a 72-week leaching trial. Work on toxicity of leachates indicated a reduction in toxicity of wood used in subsequent trials, suggesting reduced leaching with time (Weis et al., 1991, 1992). Field trials testing the durability of different CCA-treated timbers indicated that the average leaching rates of CCA were 1.8–17.3%, and that those with the highest leaching rates had the minimum lifespan (Cherian et al., 1979).

One of the problems with field trials is that monitoring of leaching is conducted by measuring preservative concentrations remaining in wood after a set period of submergence rather than measuring element concentrations in leaching solutions. Even small variations in the high loading concentrations can obscure trends in losses of preservatives and this has led to apparent negative leaching rates in some studies (Hayes et al., 1994; Albuquerque et al., 1996). Calculation of variation in the As:Cr and Cu:Cr ratio has been used to assess changes in wood recovered from a bulkhead after 13 years exposure (Breslin and Adler-Ivanbrook, 1998). This is based on the assumption that Cr is leached the least. A 53% decrease in both ratios was observed in sections of timber removed from an area that was constantly submerged. Only a 5–7% decrease was seen in samples from wood submerged in sediment. This suggests that even though the sediment may be saturated, the wood was not subject to the constant flushing required to elicit leaching.

Test blocks in the field may be exposed to a more severe leaching environment than in the laboratory due to increased physical stresses leading to abrasion and cracking, and borer attack may increase the surface area available for leaching (Merkle et al., 1993). Due to the effect of pH on leaching rates, it has been postulated that high concentrations of humic acids in surface waters may increase leaching (Cooper, 1994). The growth of fouling organisms on the surface of wood in the field has been considered a possible cause of reduced leaching rates (Hayes et al., 1994). Periodic wetting and drying of CCA-treated wood in seawater, as in tidal flux, has been shown to result in surface separation of tracheids, possibly due to the formation of salt crystals as water evaporates (Johnson et al., 1992) and may result in increased losses of preservative.

3.5. Results of laboratory and field trials

Although direct comparison of results from laboratory and fieldwork is difficult, due to the varying effects of numerous parameters, particularly wood species, loading and environmental conditions, two clear points emerge from the available literature.

Firstly, it is clear that leaching of individual metal elements is not proportional to concentrations in the original formulation. Although Cr losses with some formulations exceed losses of Cu and As (Fahlstrom et al., 1967; Irvine et al., 1972; Hegarty and Curran, 1986), studies with more modern formulations, such as CCA type C, tend to show that Cu and As are lost to the greatest degree, despite being present in the smallest proportions. Total losses released following 28 days exposure in seawater were 530 mg m^{-2} for Cu, 56.2 mg m^{-2} for As, and total Cr loss was equivalent to background concentrations (Baldwin et al., 1996). Following 21 days exposure in seawater, leaching rates for Cu and As were approximately 1 μg cm^{-2} day^{-1} and only 0.01 μg cm^{-2} day^{-1} for Cr (Merkle et al., 1993). In tests with 0.5 g of wood shavings, the increased surface area led to losses of 2060 μg l^{-1} Cu, 720 μg l^{-1} As and 870 μg l^{-1} Cr following submergence for 8 weeks in 50 ml of artificial seawater (Weis et al., 1991).

Studies have also indicated that leaching rates of all metal components are highest initially, and decrease significantly over time. Leaching rates of a variety of CCA formulations were observed to decrease to around one-fifth to one-tenth of initial values within 18 h, and down to one-hundredth within 48 h (Fahlstrom et al., 1967). Breslin and Adler-Ivanbrook (1998) calculated 90-day fluxes for a number of previous studies, and Table 5 shows that though these were consistent for Cu, more variability was seen with As and Cr.

Rates of Cu loss were similarly seen to decrease from 3.6 μg cm^{-2} day^{-1} down to 1.4 μg cm^{-2} day^{-1} after 6 months, with As rates lower, and Cr leaching to the smallest degree (Albuquerque et al., 1996). Of potentially environmental significance was the reported slower decline in flux of As compared to Cu and Cr (Hayes et al., 1994; Breslin and Adler-Ivanbrook, 1998).

In a spreadsheet-based computer model developed to predict Cu concentrations leached from CCA-treated marine structures, based on the results of Putt (1993), non-linear regression techniques were used to produce an equation to describe the decrease in Cu leaching with time:

$$\text{Cu loss } (\mu\text{g cm}^{-2}\text{ day}^{-1}) = 3.566\text{e}^{-0.048\times\text{time(day)}}, \qquad (1)$$

under Eq. (1), Cu leaching rates are reduced to 24% of initial rates within 30 days, and to 1% after 90 days

Table 5
Leaching flux of copper, chromium and arsenic (after Breslin and Adler-Ivanbrook, 1998)

Element	Calculated 12-h flux (μg cm^{-2} day^{-1})	Calculated 90-day flux (μg cm^{-2} day^{-1})
Copper		
(Breslin and Adler-lvanbrook, 1998)	5.7–17.8	0.08–1.4
(Putt, 1993)	7.6	0.8
(Weis et al., 1991)	41.3	0.3
(Merkle et al., 1993)	4.3–5.6	0.5–0.6
Chromium		
(Breslin and Adler-Ivanbrook, 1998)	0.2–1.0	0.004–0.04
(Putt, 1993)	1.5	0.01
(Weis et al., 1991)	0.08	0.0003
(Merkle et al., 1993)	0.03–0.1	0.003–0.006
Arsenic		
(Breslin and Adler-Ivanbrook, 1998)	0.1–3.9	0.04–0.2
(Putt, 1993)	6.9	0.2
(Weis et al., 1991)	0.4	0.001
(Merkle et al., 1993)	3.3–8.2	0.4–0.5

(Brooks, 1996, 1997). It is interesting to note that even though this work takes a relatively conservative approach, Cu concentrations are predicted to exceed marine water quality standards only in very poorly flushed aquatic environments, or where the surface area of the surrounding water body is less than 259 times the surface area of exposed wood.

4. Component redistribution

Work has also been done to try to quantify movement of individual components within the wood during leaching trials. Cu concentrations were observed to increase significantly in the peripheral zones, with large-scale depletion from the inner sections, in long-term trials with marine piles in New Zealand (McQuire, 1976). Similarly, although loss of Cu was greater from the outer zone after just 6 months marine exposure, between 12 and 85 months exposure losses were much greater from the inner zone compared with peripheral zones (outer 8 mm) (Archer and Preston, 1994). Further evidence of redistribution of Cu at the surfaces of CCA-treated wood has been observed, and it has been proposed that treated stakes in seawater may behave as chemical cells and that redistribution be caused electrolytically (Shelver et al., 1992). The phenomenon of transverse movement of Cu ions through wood cell walls has implications for leaching mechanisms, as well as efficacy of treated timber, where redistribution may leave sections of wood vulnerable to decay.

5. Speciation

Although considerable information exists on speciation of the individual elements in CCA, there is little research specific to CCA leachates (Albuquerque and Cragg, 1995a). It is not clear if metals are leached as individual elements, as Cu or Cr arsenates, as inorganic complexes or possibly even as organometallic complexes bound to water-soluble wood extractives (Lebow, 1996).

Baldwin et al. (1996) studied partitioning of metals to sediment during laboratory leaching trials with marine piles, and found that Cu bound to both low and high organic carbon sediment to the same degree, and did not desorb to the overlying waters. Cr exhibited minimal adsorption to a high organic carbon sediment only, and As was found in all cases in the interstitial or overlying waters. Speciation into oxidation states was not possible due to low concentrations.

Some workers have speculated as to the possible mobile species that may be subject to leaching from treated wood. These may include soluble Cu hydroxide ions, CrO_3, $HCrO_4^-$ or $CrAsO_4$, although little data was provided to support this (Hayes et al., 1994). Pizzi (1982c) suggested that of the forms of Cu present in CCA-treated wood, $CuSO_4$ physically adsorbed by the various wood constituents was the likely leachable component.

Analysis of the valence state of As on treated wood has been more widely conducted due to human health concerns. Water-soluble arsenite on the surface of wood was measured and found to be relatively constant at 3–4 μg 100 cm^{-2}, or about 3% of total As in treated wood. Arsenite is inversely proportional to Cr (VI) concentration, indicating that Cr (VI) may oxidise any arsenite in the CCA mixture (Woolson and Gjovik, 1981). Further speciation analysis of preserved wood from commercial supplies indicated no trivalent As to be present, but that up to 20% of the Cr was present in the hexavalent form, suggesting that fixation may not be complete in impregnated timber available on the market (Nygren and Nilsson, 1993).

Table 6
General scheme for leaching of chromated copper arsenate (CCA) from treated timber in aquatic environments

Reaction	Description	Reference	Principal factors affecting rate
Initial (hours)	Loss of surface deposits	Cooper (1994)	Surface area
Mid term (days/weeks)	Capillary absorption and diffusion of H_2O into wood and loss of unfixed components	Cooper (1994)	Timber type Degree of fixation
	Solvation of crytallite CCA fixation products (particularly copper)	Chou et al. (1973)	Post-treatment handling
	Formation of soluble complexes of copper and chromium with chloride and hydroxide ions	Merkle et al. (1993)	Volume of wood
	Disassociation of complexes merely precipitated in lumen of tracheid cells rather than chemically bound to wood carbohydrate or lignin	Hegarty and Curran (1986)	Salinity pH
Long term (months/years)	Reversible disassociation of ion-exchanged metals, redistribution to surface and loss	Irvine and Dahlgren (1976)	Timber type Volume of wood
		Breslin and Adler-lvanbrook (1998)	pH
	Physical or biological decay of timber		Hazard category

6. Leaching mechanism

Just as a general scheme for the fixation of CCA has been developed (Table 3) it is possible to propose a similar scheme to describe the possible leaching mechanism, based on the published literature (Table 6). The principal factors likely to affect each reaction stage are also included.

The mid-term solvation of crytallite forms of Cu may explain the relatively high leaching rate for this element compared with the other metals. The longer-term reactions and redistribution of elements may take place according to the electrolytic cell hypothesis proposed by Shelver et al. (1992).

7. Conclusions

Aspects of both the preservative treatment of wood and the environmental conditions the wood is exposed to may affect its leachability. Factors such as preservative formulation, fixation temperature, post-treatment handling, timber dimensions and leaching media pH, salinity and temperature have been shown to affect leaching rates. However, more rigorous examination of these factors is required if accurate prediction of in-service leaching rates is to be made based solely on results of laboratory studies. Although the fixation reactions greatly reduce leaching, measurable quantities of Cu, As and Cr can be found in leaching solutions from properly treated wood. The toxicity of these leachates will be largely dependent on the speciation of the individual metal elements. In addition, removal of metals from the aqueous phase through partitioning to sediments and dilution by water movements may moderate toxicity.

Examination of the existing information suggests that a number of other areas are worthy of further research in order to gain a more realistic assessment of the risks posed by the use of preservative-treated timber in aquatic environments:

1. establishment of a single laboratory leaching protocol to enable meaningful comparison of all laboratory work conducted in the future; the need for standardisation is increasingly pertinent in light of the forthcoming Biocidal Products Directive;
2. better quantification of effects of surface area: volume ratio and total sample size on leaching rates in order that models may be developed to allow extrapolation of leaching rate data generated from standard laboratory protocols to wood with commercial use dimensions;
3. field trials in both saline and freshwater environments to evaluate losses in-service to allow further refinement of laboratory-based data to losses expected from real environmental exposures;
4. speciation analysis of leached components to determine if metals are lost as individual elements, metal complexes, or bound to inorganic or organic ligands; this will allow further refinement of risk assessments since the toxicities of CCA components, particularly Cr and As, are greatly influenced by valence state;
5. examination of other environmental factors likely to influence leaching rates, including Redox conditions, presence of organic acids in natural waters and growth of fouling communities on timber surfaces; and
6. examination of the long-term fixation reactions, particularly the equilibrium dynamics between Cr (VI) and Cr (III) which may strongly influence leaching over the lifetime of preserved timbers.

In addition, equally rigorous examination of the potential alternative biocides should be made before any further regulatory action against CCA can be recommended.

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Analysis 27 January 2017

Wood-burners: London air pollution is just tip of the iceberg

By **Michael Le Page**

Last week, air pollution in London soared to heights not seen since 2011. The usual suspects were named and shamed, including traffic fumes and a lack of wind. But joining them was a surprising culprit.

“We think about half of the peak was from wood smoke,” says Timothy Baker, part of a team at King’s College London that monitors air pollution.

The trendy log-burning stoves producing much of this pollution are marketed as a source of renewable energy that can cut fuel bills while helping reduce global warming. But recent findings suggest they pose a serious threat to the health of their owners, and are also accelerating climate change in the short term.

If nothing is done to discourage log burning in homes, it could become the biggest source of air pollution in cities like London. In the UK as a whole, wood burning is already officially the single biggest source of an especially nasty form of air pollution.

“I love sitting by a log fire as much as the next person but maybe we need to think again before it’s too late,” says climate scientist Piers Forster of the University of Leeds, UK.

Air pollution is awful for our health. The smallest particles get into our blood and even our brains, increasing the risk of many disorders including heart disease.

Natural killer

Children are especially vulnerable: high pollution levels impair their lung and brain development. Air pollution from all sources is estimated to cause some 10,000 premature deaths a year in London alone, where it frequently exceeds legal limits.

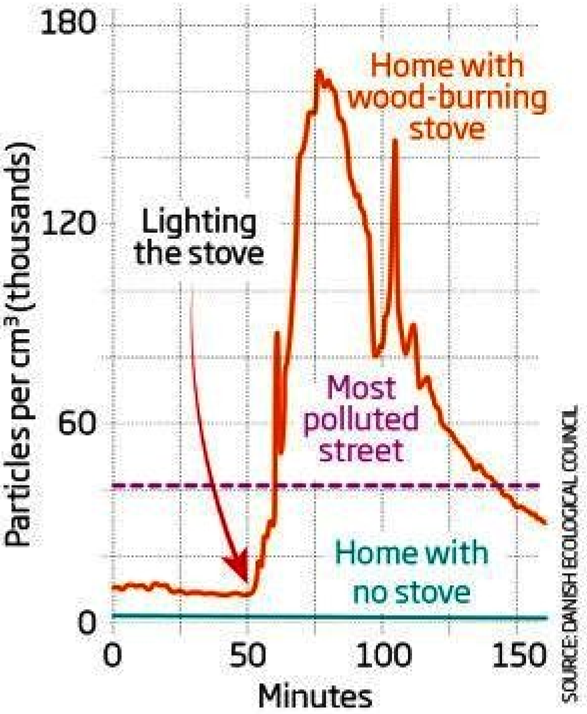
Wood smoke may be natural, but it contains many of the same harmful substances as cigarette smoke. It’s a massive killer worldwide, causing as many as 4 million premature deaths every year through indoor air pollution.

In the UK, however, the problem with pollution from wood fires was thought to have been solved by clean air laws introduced in the 1950s, which banned wood burning in open fires in cities. “The official view is that residential wood burning is a thing of the past,” says Gary Fuller of King’s College London.

Yet logs can still be burned in officially approved stoves in cities. Sales of these stoves have soared in the past decade, rising to nearly 200,000 a year. They are marketed as a way for people to drastically reduce their carbon emissions and save on fuel costs.

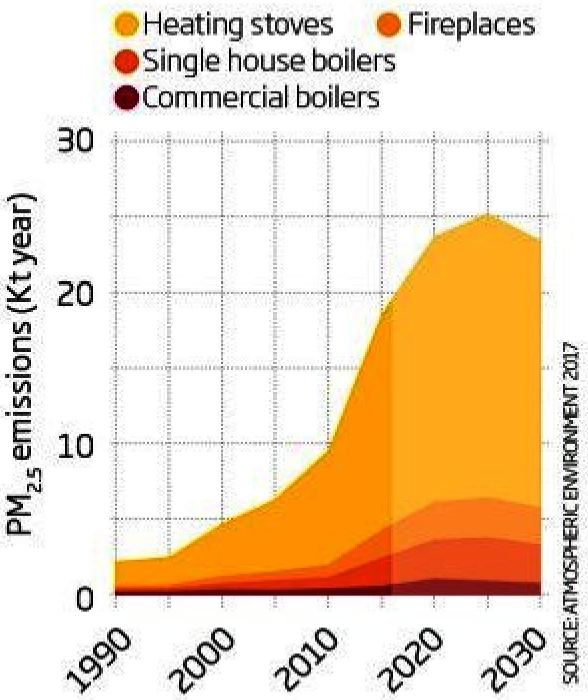
Smoking gun

A correctly installed wood-burning stove has made the air inside one home in Copenhagen more dangerous than the most polluted street there



SOURCE: DANISH ECOLOGICAL COUNCIL

In the UK, particulate emissions from wood-burning stoves have risen steeply and are projected to keep rising



SOURCE: ATMOSPHERIC ENVIRONMENT 2017

Even modern stoves described as “low emission” are highly polluting. And in an echo of the diesel car emissions scandal, measurements during actual use in homes show that the stoves [produce more pollution than lab tests suggest.](#)

In the “smokeless” fumes coming from the chimney of a house with a modern “eco-friendly” wood burner, Kåre Press-Kristensen of the Danish Ecological Council has measured 500,000 microscopic particles per cubic centimetre. The same equipment finds fewer than 1000 particles per cm^3 in the exhaust fumes of a modern truck. The wood stove was certified as meeting Nordic Swan Ecolabel emission standards, which are stricter than the ones stoves in the UK have to meet.

Big in London

What this means is that a small increase in wood-burning stoves can produce a big increase in pollution. In Copenhagen, a city of 600,000 people, just 16,000 wood stoves produce more PM2.5 pollution – the most dangerous particles, smaller than 2.5 micrometres – during winter than traffic does all year round, says Press-Kristensen.

Wood burning is becoming a big problem in London, too. In 2010, when Fuller analysed particulate pollution to discover its source, he found that 10 per cent of all the city’s wintertime pollution was from wood.

There are many reasons to think that figure is higher now. A 2015 government survey found that domestic wood consumption in the UK was three higher than previous estimates, with 7 per cent of respondents reporting that they burned logs. “Wood consumption is increasing substantially,” says Eddy Mitchell at the University of Leeds, UK.

When he, Forster and others fed the data on wood consumption into a computer model of air pollution, their conclusion was disturbing: PM2.5 pollution from residential stoves is soaring in the UK (see diagram, below).

“There is a real risk that if we have a lot more residential wood burning then it could undo our other efforts to control air pollution,” says Fuller.

The harm far exceeds traffic pollution, he says. While people are exposed to high levels of traffic pollution mainly when travelling on busy streets, wood burning produces huge amounts of pollution where people live, when they are at home.

Indoor smog

Press-Kristensen has been measuring that pollution inside homes in Copenhagen. In three out of seven tests done so far, he has found very high levels. In one home with a modern log-burning stove, he found particulate levels several times higher than the highest ever recorded outdoors there (see diagram, above).

So do the health impacts outweigh any climate benefits? Astonishingly, there might not be any climate benefits, at least in the short term.

Burning logs is often touted as being carbon-neutral. The idea is that trees soak up as much carbon dioxide when growing as they release when burned.

In fact, numerous studies show that wood burning is not carbon-neutral, and can sometimes be worse than burning coal. There are emissions from transport and processing. Logs are often pre-dried in kilns, for instance.

Burning wood also emits black carbon – soot – that warms the atmosphere during the short time it remains in the air. Most studies ignore this, but Mitchell and Forster calculate that over 20 years – the timescale that matters if we don’t want the world to go too far above 2°C of warming – soot cancels out half the carbon benefits of all wood burning.

For home wood burning, the figures are even worse. “On a 20-year timescale, wood stoves provide little or no benefit, but they do on the 100-year timescale as they remove some of the long-term warming effect of CO_2 emissions,” says Forster.

Press-Kristensen’s calculations show much the same thing. And both sets of findings almost certainly underestimate the problem, because they assume wood burning is carbon-neutral.

Defenders of wood stoves point out that there is a lot of uncertainty about how much black carbon is emitted when wood is burned and how large its effect is. Patricia Thornley of the University of Manchester, UK, thinks we need more real-world measurements before coming to conclusions.

But the uncertainties cut both ways. For instance, the effects of black carbon can be amplified if it is deposited on snow and melts it, exposing dark land that absorbs more heat. It’s possible soot from wood burning is contributing to the fall in spring snow cover in Europe, but it’s very hard to study.

More research is needed to pin down the precise climatic effects of wood burning, which can vary hugely depending on factors such as the source of wood and where the pollution goes. What is clear, however, is that burning logs in homes in towns and cities is not the best use of the wood we have.

It produces more pollution than wood-burning power plants that can be fitted with expensive filters, it produces that harmful pollution where lots of people live, and it has the least climate benefits, if any. “If we are going to burn biomass to meet climate targets, then we ought to do it in big, remote power stations,” says Martin Williams of King’s College London, who is studying the health impacts of the ways the UK could meet its climate targets.

Most researchers say it isn’t their role to make policy recommendations, but it would be best if cities like London discourage private wood burning before it becomes an even bigger health problem. At the moment, all the focus is on diesel vehicles.

Press-Kristensen doubts governments will ban wood-burning; France recently backtracked on a proposed ban on open fires, for example. Instead, he proposes installing heat sensors in chimneys and taxing people when they burn wood, with the level of tax depending on how polluting the appliance is.

Most importantly, governments must not ignore health impacts when deciding climate policies, says Press-Kristensen. “I like fires, but I have to say they are as polluting as hell,” he says.

Thinking of getting a wood-burner?

Wood-burning stoves are touted as an eco-friendly way to heat your house cheaply. But tests now show that even new, properly installed stoves can produce dangerous levels of outdoor and indoor pollution (see main story). What other options are there?

Consider instead

Stick with gas or oil for heating, and spend your money on insulation. Get a heat pump if you can afford it

Fake it

You can get the same cosy feeling from a log-effect electric or gas fireplace, the best of which are hard to distinguish from the real thing

Already have a wood-burner?

Here’s how to minimise its effects:

Don’t burn scrap wood

Scrap wood or painted wood can release highly toxic substances such as arsenic when burned

Burn wood that’s just right

Burning dry wood with a moisture content of about 20 per cent minimises pollution. But if wood is wetter or drier than that, pollution increases

This article appeared in print under the headline “Where there’s smoke”

Article amended on 1 February 2017

PM2.5 particles measure 2.5 micrometres or less

Tweede Kamer der Staten-Generaal

2

Vergaderjaar 1997–1998

Aanhangsel van de Handelingen

Vragen gesteld door de leden der Kamer, met de daarop door de regering gegeven antwoorden

1220

Vragen van het lid **Hendriks** (Fractie Hendriks) over *arsenicum.* (Ingezonden 7 april 1998)

1
Staat in het rapport «Gezondheidsrisico's van houtverduurzamingsmiddelen: Oriënterende evaluatie voor CCA-zouten»,[1] dat de achterblijvende as na ongecontroleerde verbranding ongeveer 5600 mg arseen per kg bevat en dat daarmee de grens van gevaarlijk afval honderdvoudig wordt overschreden?

2
Kent u het rapport «Basisdocument Arseen»[2] dat bij ongecontroleerde verbranding van met arseen geïmpregneerd hout 20 tot 80 procent van het arseen in de lucht terechtkomt, en dat het arseen nagenoeg volledig aan aërosolen gebonden is?

3
Staat in dat laatste rapport verder, dat het betreffende arseen in aërosolen tot een van de allerfijnste aërosolfracties behoort (massamediaan circa 0,4 µm en 85% beneden 1 µm) en dat dit bij inademing tot diep in de longblaasjes terecht kan komen en zo kanker kan veroorzaken?

4
Kwalificeert het Europese Hof voor de Rechten van de Mens in een uitspraak van 19 februari 1998[3] dat arsenicum in principe in al zijn verbindingen kankerverwekkend is, omdat het in het menselijk lichaam wordt omgezet in arsenaat dat de plaats van fosfaatgroepen in het DNA inneemt, wat leidt tot fouten bij de celdeling en als zodanig tot kanker?

5
Stelt het Hof verder dat de overheid op grond van artikel 8 EVRM een actieve rol moet spelen bij het verstrekken van informatie over de risico's van met arseen geïmpregneerd hout als dat het privé-leven van mensen ernstig nadelig kan beïnvloeden?

6
Is het u bekend dat over geheel Nederland met arseen geïmpregneerd afvalhout wordt verbrand in houtkachels, in open haarden binnenshuis, en op brandstapels in de buitenlucht, zonder dat de Staat de inwoners heeft geïnformeerd over de risico's van de vrijkomende arseenaërosolen in de lucht en de zeer hoge arseenconcentraties in de as?

7
Deelt u de mening, dat de Staat op grond van de genoemde uitspraak van het Europese Hof de plicht heeft tot de actieve verstrekking van informatie aan alle inwoners van Nederland over de grote risico's van het verbranden van met arseen geïmpregneerd hout in kachels, open haarden, op brandstapels, en dergelijke?

8
Hoe gaat u deze informatie concreet verstrekken?

9
Erkent u dat de Staat nalatig is geweest om de Nederlandse bevolking te informeren en dat de Staat op basis van de uitspraak van het Europese Hof verplicht is tot het vergoeden van de aangerichte schade?

10
Bent u bereid alsnog uitvoering te geven aan de door de Tweede Kamer op 12 november 1991[4] en op 19 november 1996 aangenomen moties om arseenhoudende wolmanzouten te verbieden?

11
Bent u bereid, gelet op het bovenstaande, de door u gegeven antwoorden op mijn vragen van 6 augustus 1996[5] en op 7 november 1997[6] betreffende het onmiddellijk verbod op het gebruik van arseenhoudende wolmanzouten te herzien?

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[1] Ministerie van VWS, november 1994.

[2] Rijksinstituut voor Volksgezondheid, januari 1990.

[3] Jurisprudentie Bestuursrecht 1998, nr. 49 (12 maart 1998, afl. 3).

[4] Handelingen Tweede Kamer, 1991–1992, blz. 781 en 1266; Tweede Kamerstuk 22 300, XI, nr. 25.

[5] Aanhangsel Handelingen Tweede Kamer 1996–1997, nr. 33.

[6] Aanhangsel Handelingen Tweede Kamer 1997–1998, nr. 369.

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's-Gravenhage 1998

Antwoord

Antwoord van minister **De Boer** (Volkshuisvesting, Ruimtelijke Ordening en Milieubeheer), mede namens de minister van Justitie en de staatssecretaris van Volksgezondheid, Welzijn en Sport. (Ontvangen 13 mei 1998)

1
In het rapport «Gezondheidsrisico's van houtverduurzamingsmiddelen: oriënterende evaluatie voor CCA-zouten» van het RIVM staat dat de achterblijvende as na ongecontroleerde verbranding ongeveer 5600 mg arseen per kg bevat. Er wordt geen uitspraak gedaan over gevaarlijk afval.

2
Ja.

3
Het is correct dat het «Basisdocument arseen» van het RIVM vermeldt dat arseen in aërosolen tot de fijnste aërosolfracties behoort, met dien verstande dat dit geldt voor een *landelijke* omgeving. In een *stedelijke en industriële* omgeving zijn de aërosolfracties met arseen aanzienlijk grover (tot 3 μm).
Het basisdocument gaat ook in op de kankerverwekkendheid van anorganisch arseen wanneer dit wordt ingeademd. Op grond van het werkingsmechanisme is hiervoor een drempelwaarde aan te geven. Voor de algemene bevolking wordt een veilige concentratie in lucht afgeleid van 500 ng/m^3. In zijn advies van 19 februari 1993 stemt de Gezondheidsraad hiermee in.
De gemiddelde concentratie van arseen in lucht is in ons land veel lager, 1–50 ng/m^3. De bijdrage van verbranding van arseenhoudend hout aan het gemiddelde arseengehalte in lucht is gering vergeleken met die van andere bronnen zoals kolengestookte elektriciteitscentrales en de metaalindustrie.

4
Neen. De uitspraak d.d. 19 februari 1998 van het Europese Hof voor de Rechten van de Mens inzake Guerra e.a. versus Italië betrof een chemische fabriek, gelegen op 1 kilometer afstand van de stad. De fabriek stootte giftige gassen uit en deze dreven in de richting van de stad. Het Hof gaat in zijn uitspraak niet in op de kankerverwekkendheid van arseen.

5
Het Hof heeft zich in deze uitspraak niet uitgelaten over met arseen geïmpregneerd hout. In meer algemene zin stelt het Hof evenwel het volgende:
a. Ernstige milieuverontreiniging kan een nadelige invloed hebben op het welbevinden van een individu en het genot van diens omgeving en maakt daarmee inbreuk op het recht op privé-leven;
b. Alhoewel artikel 8, tweede lid, van het ERVM inmenging van het openbaar gezag in de uitoefening van het recht op privé-leven niet toestaat, tenzij bij wet anders is voorzien, kan artikel 8 positieve verplichtingen voor de Staat met zich mee brengen om inbreuken op dat recht te voorkomen of tegen te gaan.
In voornoemde zaak had Italië volgens het Hof omwonenden van de chemische fabriek de essentiële informatie moeten verschaffen, zodat omwonenden in staat waren geweest de risico's van het op die plaats wonen voor zichzelf en hun gezinnen in te schatten. In de uitspraak wordt erop gewezen dat het gaat om een fabriek die valt onder de Seveso-richtlijn inzake de risico's van zware ongevallen. Deze richtlijn brengt ook verplichtingen voor de Staat met betrekking tot het informeren van de omwonenden met zich mee.

6 en 8
Het is mij bekend dat het voorkomt dat men verduurzaamd afvalhout verbrandt in bijvoorbeeld open haarden en houtkachels. Dit is een ongewenste situatie, zoals ik al eerder heb aangegeven in het beleidsplan Niet-landbouwbestrijdingsmiddelen (okt. 1996). Dat men verduurzaamd hout (maar ook andere materialen zoals geverfd hout, spaanplaat, etc.) niet in open haarden en houtkachels moet verbranden wordt door het Ministerie onder de aandacht van burgers gebracht door middel van de folder «Verstandig stoken».
Daarnaast zal er in de toekomst ook informatie worden meegeleverd bij de aanschaf van verduurzaamd hout met een KOMO-keur. Deze eis is opgenomen in de kortgeleden herziene beoordelingsrichtlijn voor certificering van verduurzaamd hout. Onder het vernieuwde KOMO-keur zal de producent van verduurzaamd hout bij iedere partij een instructie voor de gebruiker meeleveren. In deze instructie wordt onder meer aangegeven hoe men met het hout in de afvalfase om moet gaan. Hout met het vernieuwde keurmerk zal naar verwachting vanaf begin 1999 geleverd worden.
Ook aan het bredere probleem van de overlast die het stoken van open haarden en houtkachels aan omwonenden kan bezorgen zal in de toekomst aandacht worden besteed. Hiertoe zal een handboek worden samengesteld waarin de problematiek van alle kanten wordt belicht. Dit handboek heeft een voorlichtende functie voor alle betrokkenen en zal mogelijke oplossingen naar verwachting een groter bereik geven.

7
Op grond van de eerder genoemde uitspraak van het Europese Hof alsmede op grond van een eerdere uitspraak van het Hof van 9 december 1994 (Lopez Ostra – Spanje) valt af te leiden dat een geval waarin een industriële bedrijvigheid ernstige milieuvervuiling veroorzaakt een inbreuk op het recht op een privé-leven van de omwonenden kan opleveren. In die gevallen kan voor de Staat een positieve verplichting bestaan om informatie ten aanzien van eventuele risico's te verstrekken.
Uit deze uitspraken valt niet af te leiden dat er een positieve verplichting bestaat tot informatieverstrekking aan alle inwoners van Nederland met betrekking tot het verbranden van met arseen geïmpregneerd hout in open haarden, houtkachels en brandstapels. De situaties zijn daarvoor te veel verschillend.
Dit laat onverlet dat de Staat wel informatie verstrekt over de risico's van het verstoken van geïmpregneerd hout in open haarden en allesbranders, zoals in het antwoord op vraag 6 is aangegeven.

9
Neen. Zoals reeds in het antwoord op vraag 7 is aangegeven is de situatie met betrekking tot het verbranden van met arseen geïmpregneerd hout een andere dan de situatie die in eerder genoemde uitspraken van het Hof aan de orde is.

10
Reeds eerder is aan de Kamer meegedeeld hoe met beide moties zal worden omgegaan. Ik verwijs

hiervoor naar de brief van mijn voorganger Alders aan de Kamer van 28 mei 1993 (kamerstukken II, 1992–1993, 23 176, nr. 3) en mijn brief aan de Vaste Kamercommissie voor VROM van 18 december 1996. De genoemde uitspraken van het Europese Hof brengen hierin geen verandering.

11
Neen.