

Emissions of Chromium, Copper, Arsenic, and PCDDs/Fs from Open Burning of CCA-Treated Wood

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Aged and weathered chromated copper arsenate (CCA) treated wood was burned in an open burn research facility to characterize the air emissions and residual ash. The objectives were to simulate, to the extent possible, the combustion of such waste wood as might occur in an open field or someone's backyard; to characterize the composition and particle size distribution (PSD) of the emitted fly ash; to determine the partitioning of arsenic, chromium, and copper between the fly ash and residual ash; and to examine the speciation of the CCA elements. This work reports preliminary air emission concentrations and estimated emission factors for total particulate matter, arsenic (As), chromium (Cr), copper (Cu), and polychlorinated dibenzodioxins/dibenzofurans (PCDD/F) totals and toxic equivalents (TEQs). The partitioning of As, Cr, and Cu between the emitted fly ash and residual ash is examined and thermochemical predictions from the literature are used to explain the observed behavior. Results indicate a unimodal fly ash PSD between 0.1 and 1.0 μm diameter. In addition to a large carbonaceous component, between 11 and 14% of the As present in the burned CCA treated wood was emitted with the air emissions, with the remainder present in the residual ash. In contrast, less than 1% of both the Cr and Cu present in the wood was emitted with the air emissions. PCDD/F levels were unremarkable, averaging 1.7 ng TEQ/kg of treated wood burned, a value typical for wood combustion. Scanning electron microscopy (SEM) was unable to resolve inorganic particles consisting of Cu, Cr, or As in the wood samples, but X-ray absorption fine structure (XAFS) spectroscopy confirmed that the oxidation states of the CCA elements in the wood were Cu^{2+} , Cr^{3+} , and As^{5+} . SEM examination of the fly ash samples revealed some inorganic microcrystals within the mostly carbonaceous fly ash, while XAFS spectroscopy of the same samples showed that the oxidation states after combustion

were mixed Cu^+ and Cu^{2+} , Cr^{3+} , and mixed As^{3+} and As^{5+} . Estimates of the ratios of the mixed oxidation states based on the XAFS spectra were $\text{As}^{3+}/(\text{total As}) = 0.8\text{--}0.9$ and $\text{Cu}^+ / (\text{total Cu}) = 0.65\text{--}0.7$. The Cu and Cr present in the fly ash were determined to coexist predominantly in the two oxide phases CuCrO_2 and CuCr_2O_4 . These results indicate that the open burning of CCA-treated wood can lead to significant air emissions of the more toxic trivalent form of As in particle sizes that are most respirable.

Introduction

Until being discontinued for consumer applications in 2003, aqueous solutions containing chromated copper arsenate (CCA) were the most common wood preservatives used in the United States. CCA preservatives were introduced in the 1940s, and since the late 1970s CCA formulations have dominated the wood preservation market (1, 2). CCA solutions are applied to wood through a pressure treating process. This batch process involves loading wood into a pressure vessel, applying a vacuum to the wood to remove trapped air, and then introducing the CCA solution under high pressure. The vacuum step facilitates the pressurized penetration and incorporation of the CCA solution into the cellular structure of the wood (3). In current formulations, Type C CCA solutions (those most commonly used for residential applications) contain by weight $47 \pm 3\%$ CrO_3 , $19 \pm 2\%$ CuO , and $34 \pm 4\%$ As_2O_5 (3–5). Depending on its intended application, wood is treated to CCA retention levels of between 4.0 and 40 kg/m^3 (0.25 and 2.5 lb/ft^3) (5). However, most CCA treated wood sold to consumers is treated to 6.4 kg/m^3 (0.40 lb/ft^3) (3).

Although a voluntary agreement between the U. S. Environmental Protection Agency and the preservative registrants resulted in the cancellation and termination of the use of CCA formulations in virtually all products available for consumer purchase after December 31, 2003 (2, 6), a large volume of CCA-treated wood products remains in service. Between 1985 and 1997, an estimated 113 million m^3 (48 billion board feet) of wood products were treated with CCA preservatives (1). On the basis of a 30-year service life, researchers at the Forest Products Laboratory in Madison, WI, estimated that 6 million m^3 (or 2.5 billion board feet) of treated wood products (including all preservative formulations) entered the solid-waste stream in 1997, and this amount is likely to increase to 19 million m^3 per year by the year 2020 (1). In addition to its disposition in landfills, management and disposal options under development for waste CCA-treated wood currently include methods of reuse and recycling; chemical, physical, and biological processes to recover the CCA elements; and high-temperature processes involving pyrolysis, gasification, combustion, and incineration. Helsen and Van den Bulck (7) present an excellent review of these management options and disposal technologies, including their status and limitations, and conclude that after reuse and recycling options have been exhausted, co-incineration, pyrolysis, and gasification are currently the most promising disposal technologies. Jambeck et al. (8) seem to agree, but present a life-cycle assessment comparing landfill and waste-to-energy options that identify a number of issues complicating this decision. While incineration is currently the preferred method of disposal in Europe, most CCA-treated wood waste in the United States is disposed of in landfills. Currently, discarded CCA-treated wood products are not defined as hazardous wastes (either listed or characteristic)

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and can be disposed of as municipal solid waste when discarded by the user (9).

While open burning of CCA-treated wood is banned in a number of states (10–13), and discouraged elsewhere, it remains a route of disposal either in ignorance, or clandestinely as a way to avoid landfill tipping fees. The Consumer Safety Information Sheet for Inorganic Arsenical Pressure-Treated Wood (14) cautions that CCA treated wood “should not be burned in open fires or in stoves, fireplaces, or residential boilers because toxic chemicals may be produced as part of the smoke and ashes”. Further, “treated wood from commercial or industrial use (e.g., construction sites) may be burned only in commercial or industrial incinerators or boilers in accordance with state and Federal regulations”. Peters et al., (15, 16) report on a clinical case of arsenic (As) poisoning of a family living in rural Wisconsin who had used CCA-treated plywood as a source of fuel for their woodstove. Samples from a California beach revealed As concentrations of 20 000 and 70 000 ppm in the sand within two fire rings where CCA-treated wood was likely burned (17). Dobbs and Grant (18, 19) and McMahon et al. (5) first examined CCA element concentrations in the emission of very small quantities of CCA sawdust burned in bench-scale glass tube reactors. Dobbs and Grant report ~20% of the As was vaporized when the wood was burned in air, whereas only negligible amounts of copper (Cu) and chromium (Cr) (0.7 and 0.2%, respectively), were vaporized. McMahon et al. report ~22% vaporized As at temperatures between 400 and 800 °C, but showed larger amounts, up to 77%, as the reactor temperature and heating times were increased. More recent efforts (20) are continuing similar bench-scale reactor experiments designed to determine if high-temperature processes can be used to recover both the wood’s energy content and CCA elements. Preliminary results indicate increasing depletion of As from the residual ash (from 10 to 80%) as process temperatures increase from 600 to 1050 °C, with little effect on Cu and Cr depletion. However, increasing temperatures result in greater stability of the residual ash, as measured by the relative solubility of these elements in different solvents. Clearly, both the fly ash and residual ash generated during CCA-treated wood combustion can contain significant quantities of As. Acute levels of inhaled As can cause death while chronic exposure can cause cancer (21, 22). Even though CCA-treated wood wastes are not regulated as hazardous waste, ash from burning these materials may fail the relevant leaching tests and be thus classified. Solo-Gabriele et al. (23) examined residual ash from mixtures of CCA-treated and non-CCA-treated wood. Their results indicate that all the ash samples from the combustion of mixtures containing as little as 5% CCA treated wood leached sufficient As, and sometimes Cr, to be characterized as hazardous wastes as defined by U.S. regulations.

In addition to the small-scale combustion experiments described above, a number of full-scale studies have attempted to characterize the emissions from the combustion of wood wastes including construction and demolition debris, railroad ties, and other pressure-treated wood wastes. Atkins and Donovan (24) describe the industrial practices of processing waste wood for use as fuel in industrial boilers and report on emissions from a number of field studies. However, these studies examined actual operating combustors burning mixtures of clean wood and treated wood. As a result, the amounts of CCA wood in the waste streams were not typically known. Emissions were reported for three facilities burning construction and demolition wood waste and four facilities burning railroad ties. In general, these studies indicate increased As emissions while burning mixtures containing treated wood.

In this study, we expand upon the work of Dobbs and Grant (18, 19) and McMahon et al. (5). However, instead of

burning gram quantity samples in an externally heated laboratory reactor, we examined kilogram charges of CCA-treated wood samples burned in a controlled-flow, open burn research facility. Our intent was to simulate, to the extent possible, the unauthorized combustion of waste wood as might occur in an open field or someone’s backyard. The objectives were to characterize the composition and particle size distribution (PSD) of the emitted fly ash; determine the partitioning of As, Cr, and Cu between the fly ash and residual ash; examine the speciation of the CCA elements emitted; and provide preliminary emission factor data for the emitted particles and toxic elements. Further, because of the known catalytic potential of Cu to promote the formation of polychlorinated dibenzo-*p*-dioxins and dibenzofurans (PCDDs/Fs), samples were taken and analyzed to characterize these pollutants. Measurement of the air in the facility, coupled with the dilution rate of the incoming combustion air and the loss-in-weight combustion platform, allowed for emission factors to be estimated in terms of pollutant mass/mass of CCA-treated wood burned.

Experimental Section

Test Facilities. Tests were conducted in a 3.0 m wide × 2.8 m deep × 2.1 m high shed (Figure S1, Supporting Information) modified to serve as an open burn facility (25). This arrangement has been used previously to examine emissions from the open burning of residential waste (26, 27), wheat straw (28), and forest biomass (29). The building’s sheet metal walls have been finished with sheetrock wallboard and lined with aluminum foil. High-volume air handlers provided metered dilution air (18 m³/min) into the building, resulting in approximately 1 volume change per minute. Internal fans and flow deflectors were positioned to enhance air circulation, while preventing the incoming air from blowing directly on the burning wood. Gases and particles exited the facility at the roof peak above a metal deflection panel, designed to insulate the roof from the fire below. An induced draft fan pulled all the dilution air and combustion emissions through a 20.3-cm diameter transfer duct and through a MAC 72RT21 baghouse with 18.2 m² of singed Dacron polyester bags before being discharged to the atmosphere. Extractive samples to characterize the gas, particle, and CCA element air emissions were taken from the transfer duct. PCDD/F air emission samples were taken using a modified ambient sampler set up within the burn facility.

The Type C CCA-treated wood used for these combustion experiments was taken from a dismantled southern yellow pine deck approximately 10 years old. This lumber has a nominal retention level of 6.4 kg/m³ (0.4 lb/ft³) of CCA preservative (3–5). The CCA wood charges (nominally 7 kg) were burned in a 112 × 112 × 15 cm sand-filled pan sitting on top of an electronic balance. Lengths of “as received” 25-mm (after dressing) deck board were split to approximately 2.5 × 2.5 × 100 cm pieces and arranged around crumpled office paper (~45 g) in a conical shape. Thermocouples were positioned to continuously monitor the ash bed temperature as well as the transfer duct temperature.

Emission Measurements. Continuous gas-phase samples were extracted from the transfer duct through a temperature-controlled (120 °C) heated Teflon sample line and heated filter. A portion of this sample was directed hot to a total hydrocarbon (THC, model 300HFID, California Analytical, Anaheim, CA) continuous emission monitor (CEM). The remaining portion was directed through a refrigeration drier and silica desiccant to carbon monoxide (CO, model VIA510, Horiba, Irvine, CA), carbon dioxide (CO₂, model VIA510, Horiba, Irvine, CA), and oxygen (O₂, model 755, Rosemount Analytical, Solon, OH) CEMs.

Particulate samples were collected isokinetically from the transfer duct by Method 29 (M-29) (30). Additional particle

samples were directed to a micro orifice uniform deposition impactor (MOUDI, MSP Inc. Minneapolis, MN). The M-29 samples, collected at a nominal flow rate of 20 L/min (dry standard conditions) on "as received" quartz filters, provided information on total particulate matter (PM) emissions and element concentrations. The MOUDI samples, collected at a nominal flow rate of 28 L/min (dry standard conditions) on polycarbonate membrane substrates, were used to add additional size dependent analysis. Nine experiments alternated M-29 (5 samples) and MOUDI (4 samples) sampling. It should be noted that M-29 collects and maintains PM samples at 121 °C (250 °F), while the MOUDI samples were collected and maintained at room temperature (~20 °C). This may affect any comparison of total PM concentrations if substantial quantities of the emitted organic matter condense at temperatures between 20 and 121 °C. In addition to analysis for PM mass, two of the M-29 samples, including the probe rinse solution, filter, and impinger solutions, were combined, digested with a 60/40 (% by volume) solution of concentrated nitric acid and hydrofluoric acid, and analyzed by a commercial laboratory using inductively coupled plasma mass spectroscopy (ICP-MS, method SW846-6020, model Elan 6000, Perkin-Elmer, Boston, MA) (31) for the presence of As, Cr, and Cu. The MOUDI polycarbonate substrates were covered with 4- μ m Prolene film (Chemplex Industries, Stuart, FL), mounted in polyethylene holders, and analyzed in-house using a wavelength dispersive X-ray fluorescence (WD-XRF) spectrometer (Philips model 2404 Panalytical, Natick, MA). Two 41-mm diameter punches cut from each of the three remaining 100-mm M-29 quartz filter samples were analyzed flat in stainless steel sample holders by WD-XRF. The data were collected by Panalytical's SuperQ software and analyzed by UniQuant 5 (Omega Data Systems, Veldhoven, The Netherlands) using the AnySample calibration. The WD-XRF analysis was used to quantify the concentrations of As, Cr, and Cu, as well as other fly ash elements present. Following WD-XRF analysis, the same three M-29 filter samples (as well as a sample of the CCA-treated wood) were examined by scanning electron microscopy/energy-dispersive X-ray spectroscopy (Hitachi model S-3200 SEM/EDX) and X-ray absorption fine structure (XAFS) spectroscopy. XAFS analysis provided detailed information about the speciation of the three added elements, including identification of elemental oxidation states, which is often most important for assessing the toxicity of an element.

XAFS spectroscopy was conducted at the K-edges of the three elements of interest, As, Cr, and Cu. Copper and As XAFS spectra were collected at beam-line X-18B at the National Synchrotron Light Source (NSLS) at Brookhaven National Laboratory, Long Island, NY, whereas the Cr XAFS data were collected at beam-line 10-ID-B (MRCAT) at the Advanced Photon Source (APS) at Argonne National Laboratory, near Chicago, IL. Operating conditions at NSLS during the experiments were a ring voltage of 2.8 GeV and a ring current that varied between 150 and 220 mA. Corresponding quantities were 6.0 GeV and between 80 and 100 mA at APS. A multi-element Ge detector was used to collect the X-rays fluoresced from the samples at both synchrotrons (32). Such detectors can be gated to accept only X-rays within a narrow energy interval (± 300 eV) centered on the energy of the K_{α} emission line of the element of interest. In this way, the signal/noise ratio is enhanced for the element of interest at dilute concentrations. Soller slits and/or a 6 μ (Z-1) filter were also employed to increase the signal-to-noise ratio (33). Calibration of the energy scales was achieved by obtaining spectra of Cu or Cr metal foils and of As₂O₃ simultaneously with the spectra of the unknown samples in a second XAFS experiment either behind (NSLS) or in front (APS) of the fluorescence experiment. For Cr and Cu, the zero-points of energy were defined by the position of the lowest-energy major inflection

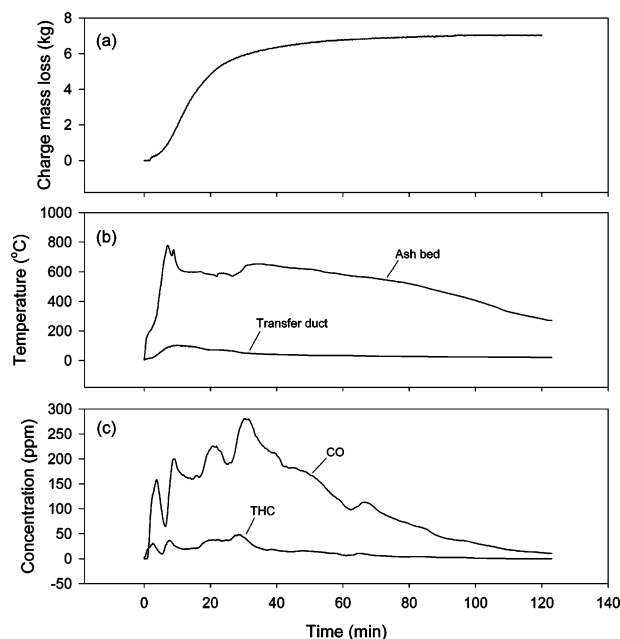


FIGURE 1. Representative profiles of (a) charge mass loss; (b) transfer duct and ash bed temperatures; and (c) carbon monoxide and total hydrocarbon (vapor phase) concentrations. Presented profiles are for test 1120a.

point on the absorption edge in the spectrum of the metal foil, whereas for As the peak position of the sharp white line of As₂O₃ was used as the calibration point. These zero-points of energy are taken by definition to occur at 5989, 8979, and 11 867 eV, for Cr, Cu, and As, respectively. Analysis of the XAFS data followed conventional practice (34–37).

PCDD/F measurements were made via a Graseby PS-1 sampler by EPA's ambient TO-9 method consisting of an open-faced filter holder followed by polyurethane foam (PUF) surrounding an XAD-2 sorbent (38). Sample volumes were 59 and 47 m³ (dry standard conditions) collected at a nominal flow rate of 70 L/min. The TO-9 filter and PUF/XAD-2 module were analyzed by Alta Analytical Perspectives, Wilmington, NC, using an Autospec high-resolution gas chromatography and mass spectrometry (HRGC/HRMS) instrument and a modified Method 8290A for PCDD/F (39). In this paper, all references to PCDD/F concentrations include tetra- to octa-homologues only. Background field blank tests (sampling without CCA wood combustion) were conducted to ensure that the sampling and analysis methods, potential facility contamination, and ambient feed air PCDD/F concentrations were not biasing the tests.

CCA Wood and Ash Analysis. In addition to the analysis of the air emission samples, WD-XRF analysis of the CCA wood and wood ash was also performed. The CCA wood was crosscut on a band saw and the collected sawdust was passed through a 100-mesh screen. Next, 562 mg of the sawdust was mixed with 50 mg of Spectroblend Binder (Chemplex Industries) and pressed onto a 2-g pellet of X-ray Mix (Chemplex Industries). Samples of the CCA wood ash were mixed with Liquid Binder (Chemplex Industries) in a 10:1 ratio (2000 mg ash to 200 mg solids from binder) and pelletized. A sample of the CCA wood ash was also analyzed for evidence of crystalline components using a Siemens D-500 X-ray diffractometer (XRD) (Bruker AXS, Inc., Madison, WI). The ash was prepared for XRD analysis by mixing and grinding using a boron-carbide mortar and pestle, then passing it through a 200-mesh screen.

Procedure. The CCA-treated wood ignited easily from the paper. Burn cycles, as characterized by the charge weight loss, temperatures, and gas CEM measurements, showed

TABLE 1. Elemental Composition of the Type C CCA-Treated Wood ($\mu\text{g/g}$)

element	WD-XRF ^a	ICP-MS	ICP-MS ^b	nominal formulation ^c
As	1920 (31.0%)	1500 (27.5%)	1761 (32.6%)	2230 (36.0%)
Cr	2520 (40.6%)	2520 (46.2%)	2699 (50.0%)	2480 (40.0%)
Cu	1760 (28.4%)	1440 (26.4%)	940 (17.4%)	1480 (24.0%)
Si	557			
Ca	588			
Fe	558			
Al	276			
Mg	242			
Na	230			
K	205			
Mn	118			
S	62			
P	20			
Zn	28			
Ti	20			
Cl	32			
unidentified ^d	986900			

^a The sum of inorganic elements (as oxides) indicates an ash content of 1.31%. ^b Aged wood (ref 40). ^c Calculated concentrations based on the formulation of Type C CCA preservative and a retention level of 6.4 kg/m³ (0.40 lb/ft³) (refs 3–5). ^d Assumed cellulose.

similar behavior. Figure 1a, b, and c present representative plots of charge mass loss, ash bed and duct temperatures, and CO and THC concentrations versus time for 1 of the 9 combustion experiments (test 1120a). O₂ and CO₂ profiles (Figure S2, Supporting Information) are unremarkable, showing O₂ and CO₂ peaks between 5 and 15 min with O₂ and CO₂ concentrations always greater than 19% and always less than 2%, respectively.

While temperature and gas CEM measurements were recorded continuously, M-29, MOUDI, and TO-9 samples collected integrated samples over all, or a large portion of, the burn cycle. All integrated samples were started immediately after the paper tinder was ignited and the door was sealed ($t = 0$ min). The M-29 samples were typically collected for 60 min, and MOUDI samples were typically collected for 30 min to prevent overloading the stages. The TO-9 samples were collected for 60 min, and the same TO-9 sampling train was used for four combustion cycles in an attempt to collect sufficient sample for PCDD/F analysis. As a result, only two composite TO-9 samples were collected and analyzed for PCDDs/Fs.

Results and Discussion

CCA-Treated Wood Fuel. Elemental concentrations measured in the Type C CCA-treated wood (sawdust) used are presented in Table 1. Both WD-XRF analysis for 16 elements and ICP-MS analysis for As, Cr, and Cu are presented. Also presented for comparison is an analysis performed by ICP-MS taken from the literature (40) as well as calculated concentrations using the nominal industry formulation for Type C CCA solution and a retention level of 6.4 kg/m³ (0.40 lb/ft³) (3–5). Evident from Table 1 is that As, Cr, and Cu each constitute between 0.1 and 0.3% of the treated wood mass, and comparison between the WD-XRF, ICP-MS, and literature data indicates reasonable agreement. The WD-XRF data indicate that the identified ash elements suggest a total ash content of 1.3%, with As, Cr, and Cu contributing over 60% of this mass. This suggests an ash content of the original non-CCA treated wood of approximately 0.5%, and this value is within the range of values (0.12–2.2) reported for softwoods in the literature (41). Table 1 also presents the relative percentages of As, Cr, and Cu (normalized to 100%) and can be compared to the nominal formulation. Our data using weathered wood (WD-XRF and ICP-MS) as well as the ICP-MS literature data (40) indicate lower As concentrations compared to the nominal formulation. However, it is unclear if these data indicate preferential leaching of As via weather-

ing, or may indicate that the elemental composition of CCA-impregnated wood is somewhat variable and may not necessarily reflect the nominal composition of the impregnating pressure-treating solution.

CCA-treated wood has been thoroughly characterized in a number of previous studies using a variety of characterization methods (40, 42–44). We present some brief, confirmatory observations by SEM/EDX and XAFS spectroscopy on the wood itself in order to provide background for the characterization of the combustion fly ash emissions. XAFS spectroscopy was used to determine the oxidation states of Cr, Cu, and As in pieces of the CCA-treated wood. X-ray absorption near edge structure (XANES) and extended X-ray absorption fine structure/radial structure function (EXAFS/RSF) spectra for the three elements in the wood samples (Figure S3, Supporting Information) clearly showed the absence of any significant preedge peak in the Cr XANES spectra peak indicating that all (>97%) of the Cr in these samples was in the Cr³⁺ oxidation state (45). Similarly, the positions and shapes of the main peaks in both the As XANES and EXAFS/RSF spectra indicated that all (>90%) of the As in the sample was pentavalent and most likely present as arsenate (AsO₄³⁻) species. As the observed Cr oxidation state is quite different from that in which Cr was initially impregnated into the wood, the initial Cr⁶⁺ species must be reduced during or just after the impregnation process. Furthermore, as has been noted previously (43), reduction of the Cr⁶⁺ in the preservative solution during the pressure treating process most likely occurs by reaction with lignin components in the wood, as both the As and Cu species present in the preservative solution are already fully oxidized. Once formed, the Cr³⁺ ion may interact with AsO₄³⁻ species and form a hydrated chromium arsenate as has been previously suggested (43). The absence of a sharp preedge in the Cu XANES spectra shows that the oxidation state of Cu is mostly Cu²⁺. The XAFS spectra observed here for Cu, Cr, and As in the CCA treated wood are very similar to spectra recently reported by Nico et al. (40) and Bull et al. (46) for other samples of CCA treated wood. Bull et al. (46) interpreted their data in terms of the formation of a hydrated chromium arsenate (CrAsO₄·nH₂O), with Cu²⁺ isolated from the other elements due to its association with binding sites in the wood. Nico et al. (40) did not record Cu XAFS data. However, their interpretation of their Cr and As XAFS data was essentially similar to that of Bull et al. (46). Our analysis of the XAFS data on aged CCA-treated wood obtained in this study is also in agreement with these earlier published interpretations.

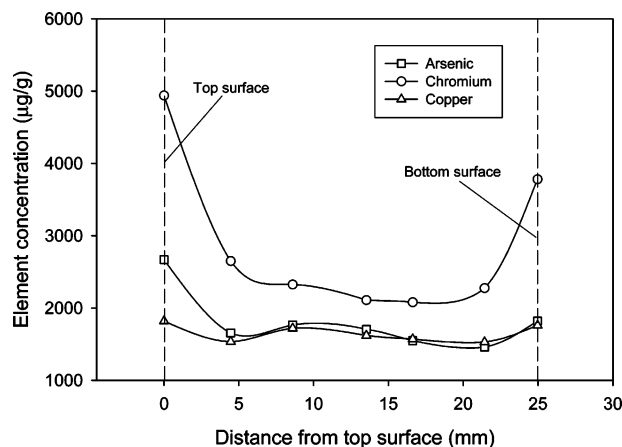


FIGURE 2. Measured element concentration profiles through the width of CCA treated wood. Concentrations determined by WD-XRF analysis of the surfaces of six slices from a 25-mm-thick deck board. Top (weathered) and bottom (sheltered) surfaces are indicated.

The wood samples were briefly examined by SEM equipped with an energy-dispersive X-ray (EDX) spectrometer (Figure S4, Supporting Information). All SEM micrographs and EDX spectra were more or less identical, indicating no metal-rich particles. These observations confirm that at the microscale, all three of the CCA elements are distributed more or less uniformly at low levels (<1%) throughout the wood. Any compound formation between the elements, if it occurs at all, must only result in extremely small particles that cannot be resolved by the SEM.

A specimen of the tested deck wood was segmented into 6 layers (top to bottom) in an attempt to determine uniformity in the concentrations of As, Cr, and Cu at the macro-scale, across the thickness of the weathered boards. The surfaces of each approximately 40 mm × 30 mm × 3 mm thick segment were analyzed by WD-XRF. The elemental concentration profiles are shown in Figure 2. As expected, the outer surfaces showed the highest concentration of CCA elements with the weathered top surface slightly higher in concentration compared to the bottom surface. This could be the result of the inability of the pressure treating process to distribute the CCA solution uniformly throughout the lumber, or perhaps the result of element mobility as a result of weathering. These results indicate that surface concentrations may be notably higher than the average concentrations and this may have implications for risk assessments determined by other routes of exposure. Attempts to determine the species present on the wood surface or in the wood sawdust by XRD showed only broad amorphous diffraction patterns typical of cellulose wood structure and did not indicate the presence of identifiable elemental crystalline phases. These results are consistent with previously reported results (40).

Fly Ash Emissions and PSDs. Table 2 presents a summary of the experimental and sampling parameters for the nine replicate experiments and the calculated particulate matter (PM) mass concentrations and emission factors. The CCA-treated wood charged during each experiment was 7.00 ± 0.33 kg for every test except test 1117a. The sampling time was approximately 60 min for all the Method 29 samples and 30 min for all of the MOUDI samples except for test 1118a (60 min). The mass of wood burned was determined by the difference in the balance readings between time zero and time at the end of the test except for tests 1117a and 1118a where this information was not available, and therefore, no emission factor estimates could be calculated. Further, due to failure of the induced draft fan during test 1118b, PM and elemental emissions and emission factor estimates could

not be determined. Particle mass was analyzed from the front end of the M-29 trains (probe wash plus filter) and from the ten MOUDI stages. M-29 filters are collected hot (121 °C) and, may therefore, be expected to collect less semi-volatile organic compounds than the MOUDI samples which operate at room temperature. Table 2 indicates that the particle mass concentrations determined from the MOUDI samples are notably larger than those determined from the M-29 samples. This may be partially due to differences in their operating temperatures. However, these concentrations are also influenced largely by the fact that the two methods are sampling integrated samples over different portions of the test burn. Emissions were not produced uniformly over the course of the tests, and it is evident from Figure 1 that the 30-min MOUDI samples collected material during the most intense portion of the combustion cycle, while the 60-min M-29 samples included both high-intensity and low-intensity burnout portions of the cycle. However, when presented in terms of emission factors, the two approaches indicate better agreement. PM emission factors for the M-29 samples range from 1.46 to 1.95 g/kg, while those for the MOUDI samples range from 2.10 to 2.43 g/kg. These values were determined by dividing the PM emission rate (PM mass concentration × the chamber flow rate, g/min) by the CCA wood consumption rate (CCA wood burned divided by the sampling time, kg/min). Considering that the purpose of the MOUDI samples was primarily to determine the resulting PSDs, and that the M-29 samples collected emissions over the entire burn cycle, we believe that the M-29 results are likely more applicable to emission factor estimates.

Analysis of the size-segregated MOUDI impactor substrates indicates that most of the fly ash (particulate) mass reports to the respirable size range, between 0.1 and 1.0 µm aerodynamic diameter. Figure 3a shows the relative mass distribution of particulate matter compared to the mass distributions of As, Cr, and Cu. The data indicate that the air emissions comprise primarily carbonaceous material. However, as shown in Figure 3b, notable submicrometer As emissions are also present, especially compared to emissions of Cr and Cu. This is not surprising and is likely related to the relatively high volatility of As. In coal combustion, As enrichment of the submicrometer aerosol emissions is often reported. This is believed to occur via a mechanism of vaporization and homogeneous nucleation to form nanometer-scale particles that grow in size via coagulation and agglomeration, or preferential heterogeneous condensation on the surfaces of existing submicrometer particles that offer the bulk of the available surface area for condensation (47–49). Arsenic is often considered a semi-volatile element (boiling point of 613 °C) while both Cr and Cu are typically considered nonvolatile (boiling points of 2672 and 2567 °C, respectively) (50). In fact, both Cr and Cu are often reported as being depleted in the submicrometer fraction of coal fly ash. In practice, however, As chemistry is much more complex. Arsenic is known to form nonvolatile arsenate compounds with iron (Fe) and calcium (Ca), and the extent of these interactions is dependent on a number of variables including concentrations of As, Ca, Fe, and sulfur (51). Arsenic volatility during CCA-treated wood combustion may also be affected by the presence of these elements. Table 1 indicates that the CCA-treated wood burned had Ca and Fe contents between 500 and 600 ppm.

Sandelin and Backman (52, 53) reported on the predicted equilibrium distributions of As, Cr, and Cu from the “hypothetical” combustion of CCA-treated wood. These authors used a commercially available equilibrium program (ChemSage) and thermochemistry available from the literature. Their results indicate that substantial quantities of As are predicted to vaporize at temperatures as low as 600

TABLE 2. Experimental Parameters and Fly Ash (PM) Emissions Data

run	CCA wood charge kg	sample time min	CCA wood burned kg	chamber flow rate dsm ³ /min	filter or impactor mass mg	sample volume dsm ³	PM mass concn mg/dsm ³	PM emission factor ^a g/kg
M-29 Samples								
1117a	4.52	60	<i>b</i>	18.7	12.30	1.228	10.01	<i>b</i>
1118b	6.87	~20	<i>c</i>	19.8	6.3	<i>c</i>	<i>c</i>	<i>c</i>
1120a	6.85	70	6.85	15.0	12.73	1.337	9.52	1.46
1124a	6.90	60	6.83	19.2	16.07	1.390	11.56	1.95
1125a	7.33	60	6.56	19.1	11.89	1.284	9.26	1.62
MOUDI Samples								
1118a	6.85	60	<i>b</i>	15.7	37.79	1.603	23.58	<i>b</i>
1120b	6.85	30	5.47	18.0	17.11	0.805	21.26	2.10
1124b	7.05	30	5.67	17.5	15.63	0.686	22.79	2.11
1125b	6.69	30	5.90	17.8	18.40	0.684	26.89	2.43

^a PM emission factors in units of g of PM per kg of CCA treated wood burned. ^b Wood charge weight loss data were not recorded for runs 1117a and 1118a. ^c Test 1118b experienced induction fan failure after approximately 20 min. PM concentration and emission factor information could not be determined.

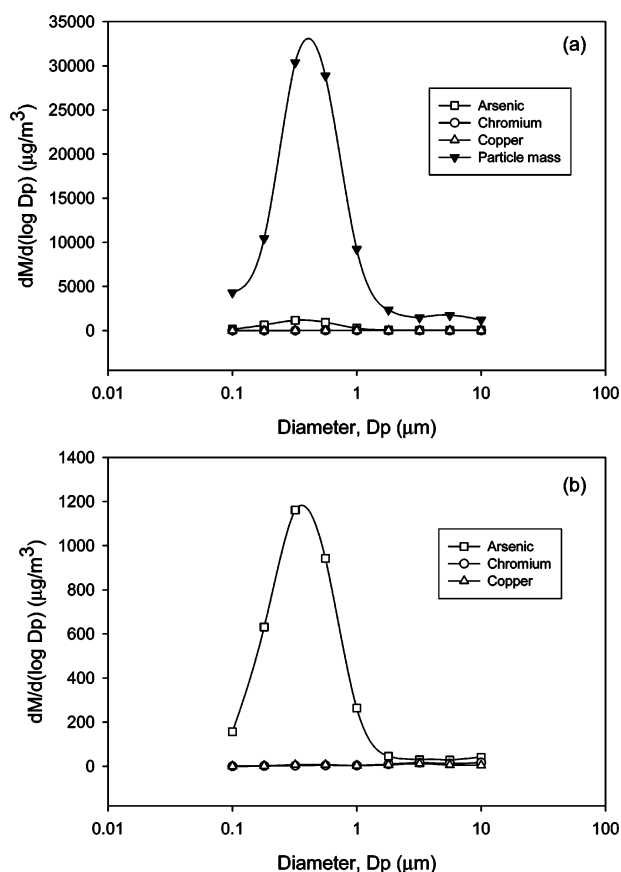


FIGURE 3. Average PSDs from four MOUDI samples of air emissions from the open burning of CCA treated wood. Panel (a) compares total particle mass emissions with emissions of As, Cr, and Cu. Panel (b) presents a magnification of the PSDs for the three CCA elements.

°C, but that the formation of calcium arsenate is predicted to limit As vaporization. Copper and Cr vaporization are negligible below 1200 and 1500 °C, respectively. At temperatures below 1200 °C the vapor-phase As species predicted by the authors include As_2O_5 (As^{5+}) and As_4O_6 (As^{3+}). It should be noted that equilibrium predictions represent an ideal state, and that kinetic and mixing limitations are likely to affect the ash chemistry. In addition, equilibrium predictions will be erroneous if the thermochemistry of all significant species is not accurately included in the database. However, when used cautiously, equilibrium calculations can provide a

TABLE 3. Elemental Composition ($\mu\text{g/g}$)^a of Emitted Fly Ash (M-29 Samples)^b

element	1117a	1118b ^c	1120a
As	116500	111350	129300
Cr	980	29500	12000
Cu	1060	17800	6710
Ca	200	7600	3510
K	740	2810	1730
Na	60	1240	1050
S	740	1160	480
Cl	110	270	190
P	70	340	140
unidentified ^d	838000	757000	791100

^a Elemental concentrations are presented in units of μg element per g of PM (dry). ^b WD-XRF analysis of M-29 quartz filters did not allow quantification of Si, Al, and Fe. ^c Test 1118b experienced fan failure after approximately 20 min. ^d Assumed carbon.

powerful tool to help explain experimental results and predict trace element behavior.

Table 3 presents the elemental composition of the emitted fly ash determined by WD-XRF analysis of the M-29 quartz filters. Note that the use of quartz filters precluded analysis for some elements present in the filter media [i.e., silicon (Si), Fe, and aluminum (Al)]. Results indicate that the emitted fly ash contained large amounts of As (between 110 000 and 130 000 $\mu\text{g/g}$ or 11–13%) and smaller amounts of Cr (0.1–3.0%) and Cu (0.1–1.8%). Other identified elements, predominantly alkali and alkaline earth elements, are present in smaller concentrations. These results also indicate that between 76 and 84% of the fly ash mass was unidentified and assumed to be carbonaceous. Table 4 presents these data for As, Cr, and Cu along with similar M-29 samples analyzed by ICP-MS, and relates air emissions of As, Cr, and Cu as emission factors (mg/kg CCA-treated wood burned). Except for the case of Cr, there is good agreement between the two analytical methods. Emission factors for As, Cr, and Cu range from 190 to 240, 8 to 22, and 9 to 13 mg/kg of CCA-treated wood burned, respectively.

Residual Ash. Averaged WD-XRF analyses of residual ash samples from five experiments are presented in Table 5. These results indicate that the residual ash contains approximately 8.4% As, 15.9% Cr, and 9.2% Cu. Note that the ash also contains percent levels of several other elements including Ca and Fe. Unidentified material (assumed carbonaceous) comprises approximately 35% of the residual ash mass. Attempts to characterize the composition of the residual ash by XRD indicated that most ordered or crystalline materials were nondetectable. The diffraction patterns from each ash

TABLE 4. Fly Ash Element Concentrations and Calculated Emission Factors^a (M-29 Samples)

run	arsenic			chromium			copper		
	WD-XRF μg/g	ICP-MS μg/g	emission factor mg/kg	WD-XRF μg/g	ICP-MS μg/g	emission factor mg/kg	WD-XRF μg/g	ICP-MS μg/g	emission factor mg/kg
1117a	116500		<i>b</i>	980		<i>b</i>	1060		<i>b</i>
1118b	111350		<i>b</i>	29500		<i>b</i>	17800		<i>b</i>
1120a	129300		188	12000		22	6710		9.8
1124a		110800	218		7600	14.9		6700	13.4
1125a		146200	237		5700	8.4		5200	8.7

^a Elemental concentrations are presented in units of μg element per g of PM (dry). Emission factors are presented in units of mg element per kg of CCA treated wood burned. ^b Wood charge weight loss data were not recorded for runs 1117a or 1118b.

TABLE 5. Measured Element Content of the CCA Treated Wood Residual Ash (μg/g)^a

element	WD-XRF		ICP-MS
	average	std. dev.	
As	84260	7130	85900
Cr	158740	4500	86700
Cu	91620	4180	90000
Si	20060	5160	
Ca	50580	9530	
Fe	7260	1730	
Al	6920	2350	
Mg	12380	2230	
Na	1700	230	
K	11500	2030	
Mn	5240	770	
S	1180	100	
P	1700	300	
Zn	1350	100	
Ti	620	190	
Cl	570	670	
unidentified ^b	349500	15900	

^a WD-XRF results indicate the average and standard deviation from the analysis of five samples (1117a, 1118b, 1120a, 1124a, 1124b). Sample 1125a was analyzed by ICP-MS. ^b Assumed carbon.

TABLE 6. Arsenic, Chromium, and Copper Partitioning between Fly Ash and Residual Ash (wt %) (M-29 Samples)

run	arsenic		chromium		copper	
	fly ash	residual ash	fly ash	residual ash	fly ash	residual ash
1120a	11.0	89.0	0.87	99.13	0.61	99.38
1124a	12.7	87.3	0.59	99.41	0.84	99.16
1125a	13.9	86.1	0.33	99.67	0.54	99.46

were very similar, showing only trace amounts of crystalline silica superimposed on the broad amorphous peaks of incompletely burned cellulose.

Residual ash from one experiment was also analyzed by ICP-MS. Analyses for As and Cu agreed well with those analyzed by WD-XRF. However, similar to the fly ash samples, the ICP-MS Cr analysis was somewhat lower than the WD-XRF analysis, and may be related to known problems with digesting insoluble Cr species in CCA-treated wood pyrolysis residues described by Van den Broeck et al. (54). Linak et al. (55) describe similar problems analyzing Cr samples from incineration experiments, and indicate that conventional approaches using nitric and hydrofluoric acids were insufficient to dissolve Cr₂O₃. They used an aggressive caustic fusion procedure to dissolve the Cr in their samples for ICP-MS analysis.

Table 6 examines the partitioning of As, Cr, and Cu between the fly ash and residual ash. These calculations indicate that a substantial portion of the As (between 11 and

14% of the As mass present in the burned CCA-treated wood) is emitted with the fly ash. In contrast, both Cr and Cu report predominantly to the residual ash (between 99.1 and 99.7%). Less than 1% of both the Cr and Cu is emitted with the fly ash. This is not surprising considering the thermochemical predictions and temperature measurements (see Figure 1). While the ash bed temperature monitored may not be indicative of peak temperatures in other locations of the burning wood, the bed temperatures measured (between 600 and 800 °C) are much too low to vaporize substantial amounts of Cr or Cu. These temperatures, however, are sufficiently high to promote the vaporization of As, the extent of which is likely controlled by local temperatures and oxidizing environments within the burning wood as well as complex chemistry that include As interactions with other ash constituents. These results are also consistent with the bench-scale reactor studies described above (5, 18, 19).

Element Speciation. XAFS data from this investigation and others (40, 46) have shown that the oxidation states of the added elements in aged CCA-treated wood are predominantly, if not entirely, As⁵⁺, Cr³⁺, and Cu²⁺ and that the Cr and As may be present as an amorphous chromium arsenate species. On the basis of the equilibrium predictions of Sandelin and Backman (52, 53), most of the Cr is expected to remain as trivalent Cr₂O₃ during combustion at temperatures below 1400 °C. However, depending on temperature, vapor-phase As is predicted to form pentavalent As₂O₅ or trivalent As₄O₆. In fact, McMahon et al. (5) reported the emission of both trivalent arsenites and pentavalent arsenates from their bench-scale reactor.

XANES spectra of As, Cr, and Cu in the fly ash emission samples are shown in Figures 4, 5, and 6. Whereas As exhibits three strong and similar spectra (Figure 4) for each emission sample examined, Cu (Figure 5) and Cr (Figure 6) yield two strong spectra for samples 1118b and 1120a and a weak spectrum for sample 1117a, correlating qualitatively with the variation in Cu and Cr concentrations in the WD-XRF analyses shown in Table 4. Furthermore, as shown for Cu, the shape of the spectrum of the low-Cu sample is significantly different from those of the high-Cu samples. Basically, by comparison of the XANES spectra in Figures 4, 5, and 6 with published compilations of As, Cu, and Cr XANES standard spectra (45, 56, 57), it is readily concluded that As is principally present as a mixture of As³⁺ and As⁵⁺ forms, that Cu is mostly present as Cu⁺, and that Cr is present almost entirely as Cr³⁺. Further, based on simulated spectra involving As³⁺ and As⁵⁺ species (58), it would appear that the As³⁺/(total As) ratio has to be between 0.8 and 0.9 in order to generate the As XANES profiles shown in Figure 4. In addition, many simple phases of both Cu and Cr can be eliminated from consideration as being significant in the ash samples: these include the simple oxides, Cu₂O, CuO, and Cr₂O₃, as well as many non-oxide phases (sulfides, chlorides, etc.).

The corresponding EXAFS/RSF spectra for the three elements in the fly ash samples are shown in Figure 7. Both Cu and Cr exhibit two major peaks in their RSF spectra; the

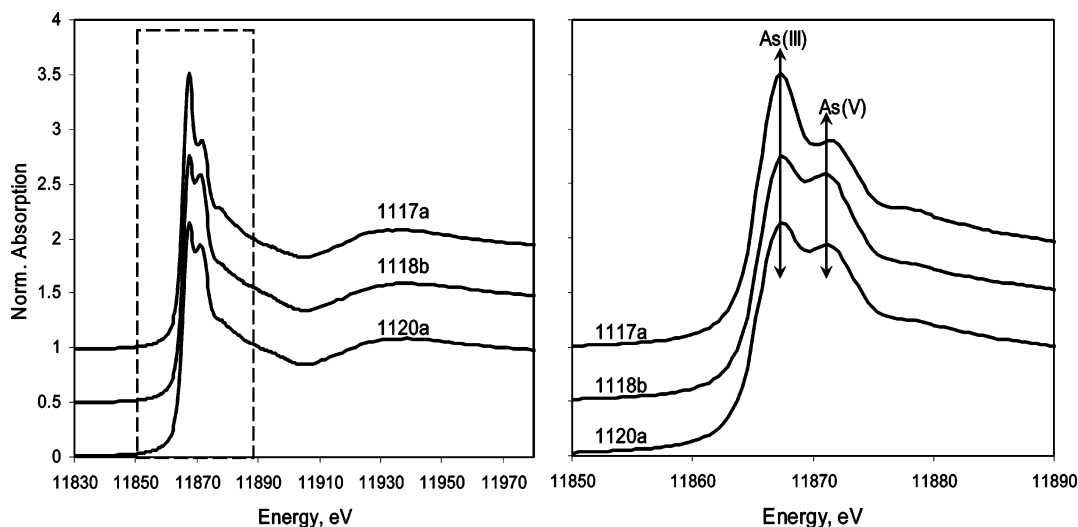


FIGURE 4. Arsenic K-edge XANES spectra for three fly ash samples from open burning of CCA treated wood. The region enclosed by the dashed oblong box in the left panel is shown expanded in the right panel and the white lines due to both the As^{3+} and As^{5+} oxidation states are indicated.

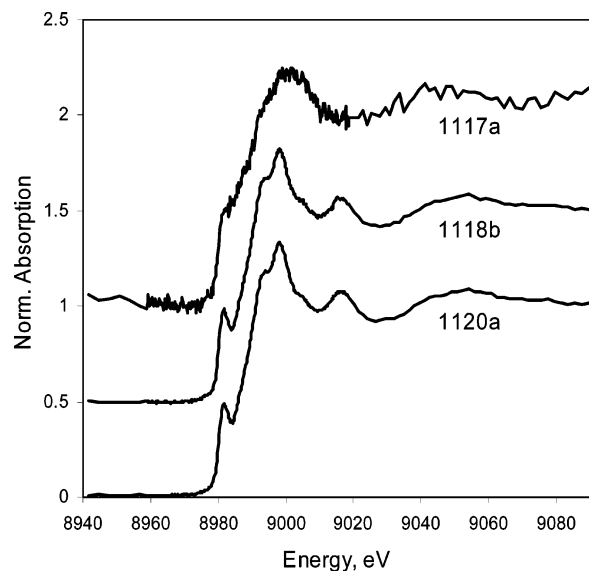


FIGURE 5. Copper K-edge XANES spectra for three fly ash samples from open burning of CCA treated wood. The sharp feature on the edge at about 8982 eV in the lower two spectra indicates that the oxidation state is principally Cu^+ .

peaks at shorter distances arise from the nearest neighbor shell of oxygen anions around the metal cation, whereas the peaks at larger distances arise from the next-nearest neighbor shell of metal cations that surround the absorbing metal cation. Arsenic, in contrast, exhibits one major peak at a position of $\sim 1.35 \text{ \AA}$. The position of this peak is compatible with $\text{As}^{3+}\text{-O}$ bond distances in arsenite compounds, after allowance is made for the arsenic–oxygen phase shift (34–37). Peak positions for $\text{As}^{5+}\text{-O}$ in EXAFS/RSF spectra of arsenates are normally significantly shorter, at about $1.25 \pm 0.05 \text{ \AA}$. The presence of two peaks in the EXAFS/RSF spectra for both Cu and Cr indicates that both elements occur predominantly in relatively simple, high-symmetry structures. As mentioned above, the XANES data rule out the significant presence of simple single-metal end-member oxides such as Cu_2O or CuO or Cr_2O_3 and, because primarily of differences in valence state, substitution of Cu^+ or Cu^{2+} in Cr_2O_3 or of Cr^{3+} in either of the copper oxides is minimal in these phases (59). Consequently, the likelihood is that these elements are present in mixed oxide phases and the

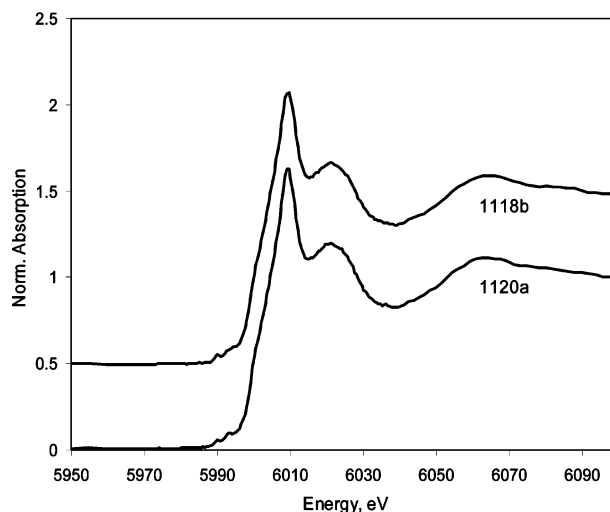


FIGURE 6. Chromium K-edge XANES spectra of two fly ash samples from open burning of CCA treated wood. The lack of a significant peak at 5993 eV indicates the absence of significant Cr^{6+} . The third sample (1117a) gave a much noisier spectrum (not shown).

two simplest such compounds are Cu^+CrO_2 and $\text{Cu}^{2+}\text{Cr}_2\text{O}_4$, both of which can form in air at high temperatures (59).

Figure 8 shows the Cu XANES spectrum of one fly ash sample. As indicated in the figure, the spectrum can be adequately simulated using least-squares fitting by the weighted addition of the Cu XANES spectra for the standard compounds CuCrO_2 (68%) and CuCr_2O_4 (31%), leaving only 1% unaccounted. Although almost all the spectral features are accounted for in this simulation, the simulated spectrum from the summation of the two components is notably sharper in detail than the spectrum of the fly ash. This may indicate that the ideal two-element mixture may be somewhat more complex and that other elements (e.g., Fe, Ca, etc.) are minor components substituting for either Cu or Cr. However, it appears clear that these two phases account for most, if not all, of the Cu and Cr, leaving little of either to bond with As. Similar least-squares analysis for Cr was not nearly as precise because the Cr XANES spectra for CuCrO_2 and CuCr_2O_4 are quite similar due to the fact that both the oxidation state and coordination number of Cr are the same in both phases.

Evidence for the presence of mixed chromium–copper oxides is also apparent from SEM studies. SEM examination

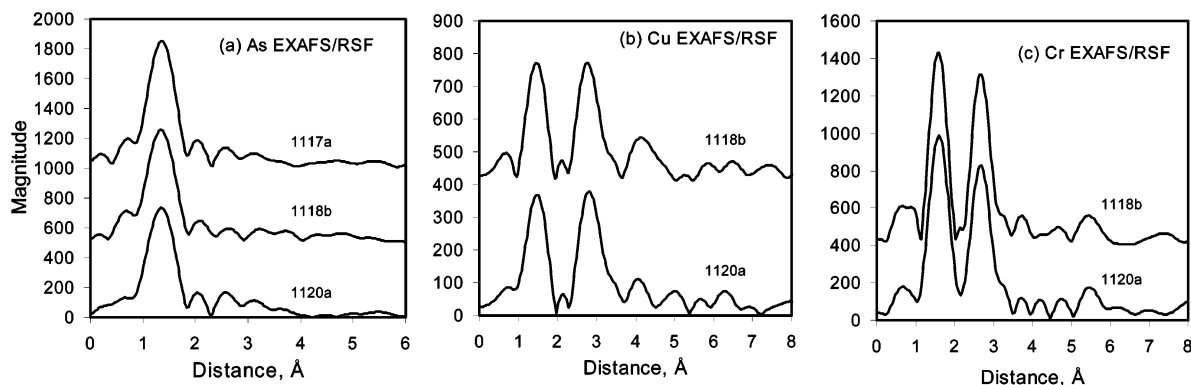


FIGURE 7. Comparison of the EXAFS/RSF spectra for As, Cu, and Cr in the fly ash samples. Copper and Cr in sample 1117a were too dilute to give rise to useful EXAFS/RSF spectra.

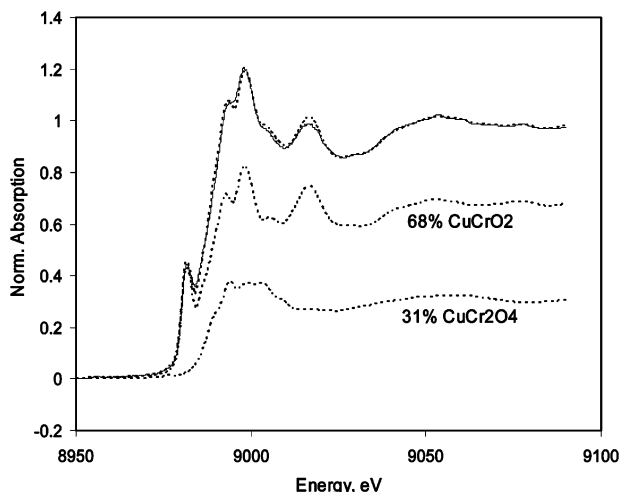


FIGURE 8. Example of least-squares fitting of Cu XANES of fly ash samples 1120a to weighted contributions of the spectra from the standard oxide compounds, CuCrO_2 and CuCr_2O_4 . The experimentally determined XANES data are indicated by the solid line, and the fit and individual oxide components are indicated by dashed lines.

of the fly ash samples (Figures S5 and S6, Supporting Information) indicates that most of the samples consist of carbonaceous material (soot aggregates) with minor amounts of Ca, Cr, Cu, and As present in large area EDX scans. Generally, at the limit of resolution of the SEM, these elements appeared to be distributed rather uniformly throughout the carbonaceous matrix. Occasionally, specific particles would be observed that appeared to contain somewhat higher amounts of some combination of Ca, Cr, Cu or As; typically such particles were less than $3\ \mu\text{m}$ in diameter.

PCDD/F Emissions. Due to the presence of large quantities of Cu and notable quantities of chlorine in the CCA-treated wood, gas phase and fly ash emissions were examined for the presence of PCDD/F compounds. Copper is a known catalyst for PCDD/F formation and chlorine is essential for PCDD/F formation, whether in organic or inorganic form. Samples were collected as described above, and further method details are described elsewhere (28, 29). Emission factors were determined in a manner similar to those for the particles and elements presented above. Two simultaneous samples were taken and analyzed for homologue-specific PCDD/F total emissions and the 17 congeners that comprise the PCDD/F toxic equivalence (TEQ) measure. Individual isomeric emissions are depicted in Figure 9a. The isomer pattern, shown as moles of the isomer divided by the molar sum of the toxic PCDD or PCDF isomers, is distinctive from other industrial sources, while being most similar to the pattern from industrial boiler wood combustion. Principal

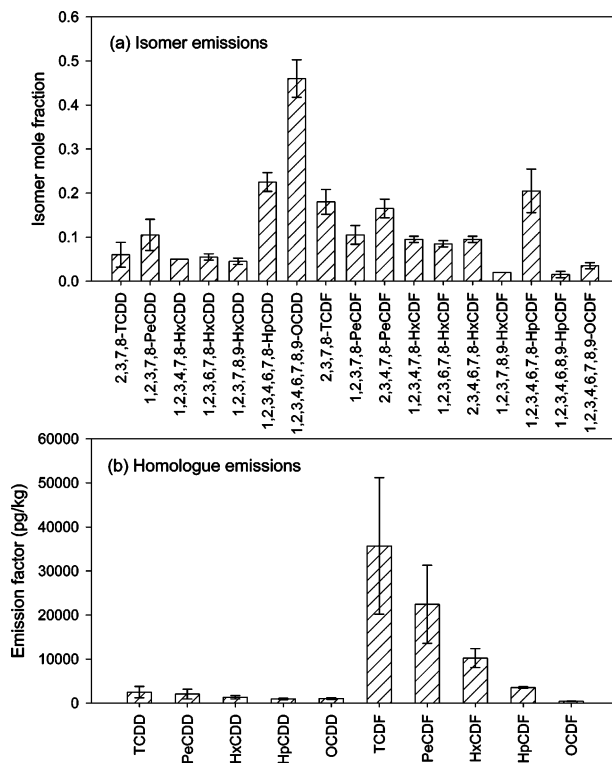


FIGURE 9. PCDD/F emission patterns and factors for the open burning of CCA treated wood. The upper panel (a) presents the 2,3,7,8-Cl-substituted PCDD/F isomer pattern, as moles of the isomer divided by total molar sum of the PCDD or PCDF 2,3,7,8-chlorine-substituted congeners. The lower panel (b) presents the PCDD/F emission factor homologue profile as mass of the homologue divided by mass burned. The columns represent averages and the ranges indicate the standard deviations.

component analysis (PCA) of the molar fractions of the 2,3,7,8-chlorine substituted compounds show that their distribution pattern is quite similar to those of other biomass types including wheat, rice, and straw stubble; forest fires; and prairie grass. PCDFs dominated the PCDDs, comprising over 90% of the emissions for both samples. The homologue profiles were skewed toward the lower chlorinated congeners, as shown in Figure 9b.

Total PCDD/F emissions averaged $80\ \text{ng/kg}$, with a precision between the replicate samples of 37%. The TEQ value was derived from toxic equivalent factors (TEFs) for the 2,3,7,8-chlorine-substituted congeners termed "WHO98" (60). Application of the WHO98 TEFs to the concentrations of the 17 2,3,7,8-Cl-substituted congeners results in TEQ values of 2.3 and $1.4\ \text{ng TEQ/kg}$ of CCA-treated wood burned

for the two samples. All of the isomer concentrations exceeded the detection limit. The TEQ value around 2 ng TEQ/kg has been found elsewhere for combustion of common wood (61). This suggests that CCA wood, despite the presence of the Cu PCDD/F catalyst, has PCDD/F emission factors similar to those of other wood combustion. Almost 50% of the TEQ measure is composed of the 2,3,4,7,8-pentachloro dibenzo furan (PeCDF) isomer, which is typical for combustion sources (62). Analysis of the residual ash (<2% of the original mass) showed PCDDs/Fs at levels of 0.07 ng TEQ/kg of CCA-treated wood burned. This value is less than 4% of that in the gas phase and fly ash emissions. These PCDD/F levels appear to be about 5–15 times lower than results from a bench-scale test (63). Differences in wood type, initial CCA treatment, and combustion conditions could explain this difference. Our values suggest that about 20–30 times more PCDD/F TEQ is emitted than remains in the residual ash. These results, however, are based on only two samples. A more thorough study of potential CCA wood emissions would consider variations in burning conditions and combustion efficiency, as well as moisture content, grade, and age of the CCA wood.

Combustion of aged CCA-treated wood in an open burn simulation facility allowed sample collection and the estimation of emission factors. Characterization of the emitted fly ash indicated a predominantly submicrometer PSD and an estimated particulate emission factor of between 1.5 and 2.0 g/kg of CCA-treated wood burned. While a large fraction of the emitted particle mass was unidentified (by WD-XRF) and assumed to be carbonaceous, a notable fraction, between 11 and 13%, was As. Although present in the CCA-treated wood in approximately the same concentrations, both Cr and Cu represent less than ~1% of the emitted particle mass. This behavior can be explained by the relative volatility of As compared to both Cr and Cu and is consistent with the measured PSD. Even with high Cu (a known catalyst) concentrations and notable chlorine concentrations, emissions of PCDD/F indicate unremarkable TEQ concentrations that are consistent with emissions from the combustion of other biofuels. These emission factors will be useful for generating internationally mandated national PCDD/F inventories as well as in prioritizing regulatory and policy actions to open burning of CCA-treated wood. In addition, these emission factors along with activity, exposure, and toxicity information may help quantify the risks associated with the open burning of CCA-treated wood. Analyses of the residual ash indicate large concentrations of Cr (~16%), Cu (~9%), and As (~8%), as well as percent levels of Si, Ca, Fe, Al, magnesium, and potassium. Comparison of the fly ash and residual ash compositions suggest that while over 99% of the Cr and Cu partition to the residual ash, between 11 and 14% of the As partitions to the fly ash. This general behavior is consistent with thermodynamic predictions, which also suggests air emissions of both trivalent and pentavalent As species. These predictions are also consistent with the XAFS spectroscopy results that indicate that the oxidation states after combustion were mixed Cu⁺ and Cu²⁺, Cr³⁺, and mixed As³⁺ and As⁵⁺. Estimates of the ratios of the mixed oxidation states based on the XAFS spectra are As³⁺/(total As) = 0.8–0.9 and Cu⁺/(total Cu) = 0.65–0.7. The Cu and Cr present in the fly ash were determined to coexist predominantly in the two oxide phases, CuCrO₂ and CuCr₂O₄.

Acknowledgments

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(APS) National Laboratories where the XAFS measurements were made. The research described in this article has been reviewed by the Air Pollution Prevention and Control Division, U.S. EPA, and approved for publication. The contents of this article should not be construed to represent agency policy nor does mention of trade names or commercial products constitute endorsement or recommendation for use.

Supporting Information Available

Schematic of EPA open burn test facility, representative profiles of O and CO₂ concentrations, XAFS spectral data, typical SEM images, and EDX spectra. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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