

# Migration of iron and manganese into CCA-treated wood in soil contact and the resulting error in leaching results when using energy dispersive x-ray fluorescence spectrometers

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## Abstract

In a laboratory leaching study, we found that chromated copper arsenate (CCA) treated wood, which had been exposed to one of five soils examined, unexpectedly appeared to gain significant Cr (47%) when measured with an energy-dispersive x-ray fluorescence instrument (American Wood-Preservers' Association (AWPA) Method A9-01 2001). Analysis of some of the leached samples exposed to all five soils by inductively coupled plasma (ICP) spectrometry showed that Fe migrated into the CCA-treated samples from four of the five soils and Mn migrated into wood exposed to two of the five soils. The presence of Fe and Mn interfered with measurement of Cr retention using two different bench-top energy dispersive x-ray fluorescence spectrometers. It has been previously shown that Mn and/or Fe can migrate from soil into wood, and we conclude that this may result in a significant error in determining the amount of metals that leach from CCA-treated wood. Thus, AWPA Method A9-01 may need to be modified to indicate this potential error, and leaching data from prior studies that used energy dispersive instruments may need to be reexamined.

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Standard methods, such as the American Wood-Preservers' Association (AWPA) Standards (AWPA 2001), ensure that any person can run a particular test or analyses without needing an expert knowledge of the instruments or methods involved. While being developed, these methods are typically subjected to extensive review by experts who are aware of potential pitfalls and problems that an average scientist may not be aware of. Thus, by following a standard method a laboratory can be assured that any data obtained, and the resulting conclusions, are sound. However, in a recent study we found that a significant error apparently occurred when using a stan-

dard method, and were unable to find any cautionary notes in the particular AWPA standard that would explain the clearly false results. Our particular study involved depletion of arsenic, chromium, and copper from CCA-treated wood, a topic that has received much negative publicity lately. Thus, we felt that it

would be important to understand the reasons for the particular problem.

In brief, treated wood in soil contact undergoes complicated leaching, biodegradation, and chemical reactions that lower the effective biocide levels. The extent to which a particular biocide is depleted from treated wood is impor-

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**Table 1.**—Fe and Mn content of the soils used and in the CCA-treated stakelets exposed to the soils, and the percent CrO<sub>3</sub> leached as determined by either x-ray fluorescence (AWPA Method A9-01) or ICP (AWPA Method A21-00).

| Soil   | Metal content of soil |      | Metal in wood after leaching <sup>a</sup> |                    | Avg. CrO <sub>3</sub> leached. <sup>b</sup> |     |
|--------|-----------------------|------|-------------------------------------------|--------------------|---------------------------------------------|-----|
|        | Fe                    | Mn   | Fe                                        | Mn                 | (Asoma) x-ray                               | ICP |
|        | ----- (%) -----       |      |                                           |                    |                                             |     |
| FPL    | 1.61                  | 0.12 | 0.099 <sup>c</sup>                        | 0.061 <sup>c</sup> | -47.2                                       | 4.9 |
| MSU    | 4.34                  | 0.15 | 0.019                                     | 0.033              | -1.7                                        | 4.6 |
| Arch   | 1.66                  | 0.06 | 0.022                                     | 0.004              | 0.0                                         | 0.9 |
| MI     | 0.69                  | 0.01 | 0.033                                     | 0.004              | 5.8                                         | 3.1 |
| Osmose | 1.73                  | 0.06 | 0.009                                     | 0.006              | 6.2                                         | 4.6 |
| Water  | --                    | --   | 0.002                                     | 0.009              | 5.3                                         | 3.6 |

<sup>a</sup>The average Fe and Mn in the unleached samples was 0.004 and 0.012 percent, respectively.

<sup>b</sup>For the Madison soil, each leached value is the average of five samples; all other values are the average of three samples.

<sup>c</sup>An additional FPL sample was run by ICP, courtesy of Dr. J. Jellison at the Univ. of Maine, and had 0.082 and 0.052 percent Fe and Mn, respectively.

tant for predicting the long-term efficacy of wood treated with that biocide and determining potential environmental concerns. We recently conducted a laboratory leaching study (Crawford et al. 2002) using small samples of CCA-treated southern yellow pine (SYP) sapwood exposed to five different soils or water. For wood exposed to one of these soils, we noticed that the treated wood samples unexpectedly gained an average of 48 percent Cr, a result that was obviously inaccurate. We had previously observed this same interference (Wang et al. 1998), and suggested that some component in the soil interfered with measurement of Cr (CrO<sub>3</sub> basis) using a bench-top x-ray fluorescence instrument (AWPA Standard Method A9-01 2001) (AWPA 2001). Furthermore, this factor may have also affected data in other ground-contact CCA leaching studies.

The objective of this study was to determine what soil component(s) migrates into treated wood and interferes with Cr measurement when the wood is analyzed with a bench-top x-ray fluorescence instrument.

## Materials and methods

Stakelets measuring 14 mm square by 250 mm long were cut from five defect-free SYP (*Pinus* spp.) sapwood boards. The stakelets were equilibrated to a moisture content of approximately 8 percent before treatment with CCA-C to a target retention of 6.4 kg/m<sup>3</sup> (0.4 pcf) using a full-cell process (15 min. vacuum at 26 in. Hg then 150 psig pressure for 60 min.). After treatment, the stakelets were stored in plastic bags for 7 days at room temperature while the

CCA fixed, then the stakelets were unbagged and air-dried. A 100-mm-long section was then cut from each stakelet to determine the initial CCA retention prior to leaching.

Replicate stakelets were subjected to soil leaching at five different laboratories using small pots with drain holes that contained locally obtained soil at each of the five laboratories: USDA Forest Products Laboratory (FPL) soil from Wisconsin; Arch Wood Protection Inc. (Arch) soil from Georgia; Michigan State University (MI) soil; Osmose, Inc. (Osmose) soil from New York; and soil from Mississippi State University's Dorman Lake plot (MSU). In addition, one set of stakelets was leached in distilled water (water). At each laboratory, the soil was added to the pots and the hole at the bottom was plugged. Distilled water was then slowly added to excess and the water-saturated soil was left for 24 hours, then the excess water was drained by removing the rubber plug. After draining for 16 hours, the stakelets were inserted vertically into the pots. Additional water was added twice a week to maintain the original soil moisture content. After 12 weeks of exposure, the stakelets were removed from the pots, scrubbed, rinsed with distilled water, air-dried, then a 50-mm section was cut from each stakelet to determine the CCA content after leaching.

A 50-mm section from the initial (unleached) and leached sample from each stakelet were individually ground to 20 mesh, and each sample was analyzed three times using different ground wood each time. The three analyses were then averaged together to determine the individual CCA components

(Cr, Cu, and As; active oxide basis) by x-ray fluorescence (Asoma model 8620). Unfortunately, shortly after all samples were analyzed, this instrument ceased functioning. After analyzing the amount of each component leached, we found that the Cr content for stakelets exposed to the FPL soil gained an average of 48 percent Cr based on x-ray fluorescence. Therefore, further analyses on selected samples were conducted using inductively coupled plasma (ICP) emission spectrometry (AWPA Standard Method A21-00) (AWPA 2001). Five sets of matched (leached and unleached) samples were selected from stakelets exposed to the FPL soil, and three matched pairs were selected from the samples exposed to the other four soils or water.

To verify that a particular component would interfere with Cr determination, SYP sapwood was ground to 20 mesh then divided into three portions, with two of the portions placed into separate beakers. To one beaker of ground wood, 1 percent MnCl<sub>2</sub>·4H<sub>2</sub>O (salt wt./air-dry wood wt.) was added to give about 0.27 percent Mn; and to the second wood sample, 1.3 percent Fe<sub>2</sub>(SO<sub>4</sub>)<sub>3</sub>·H<sub>2</sub>O (about 0.36% Fe) was added. Relatively high levels were chosen since our intent was to simply determine if Fe and/or Mn interfered with Cr measurements using an energy dispersion x-ray fluorescence instrument. Sufficient distilled water was then added to the two beakers to make a thick paste of the ground wood and salt to ensure that the metallic salt was solubilized and the wet wood was then stirred so that the metal was dispersed throughout the wood meal, then the wet wood was dried at 45°C with frequent stirring until dry. The three samples were then run using an Asoma (model 111, courtesy of Dr. L. Jin at CSI, Inc.) and an Oxford (model 3000) bench-top energy dispersive x-ray fluorescence instrument, with each sample run at least twice and the results averaged.

## Results and discussion

### Metal analysis of the CCA-treated wood

ICP metal analysis of the leached CCA-samples showed that two minerals had migrated into the stakelets exposed to the FPL soil: Mn and Fe (Table 1). A significant increase in Fe, based on at least a three-fold Fe increase relative to the average Fe content of the unleached

**Table 2.** — Percent CrO<sub>3</sub> “content” measured in SYP ground wood using two energy dispersive x-ray fluorescence instruments. Each value is the average of at least two measurements. The amount of spiked metal is based on the metal wt./air-dry ground wood wt.

| Wood sample           | Percent CrO <sub>3</sub> |        |
|-----------------------|--------------------------|--------|
|                       | Asoma                    | Oxford |
|                       | ----- (%) -----          |        |
| Control               | -0.02                    | 0.07   |
| 0.36% Fe <sup>a</sup> | 0.73                     | 0.41   |
| 0.27% Mn              | 0.70                     | 0.51   |

<sup>a</sup> A CuO “content” of 0.05 percent was measured with the Fe-spiked sample using the Asoma instrument.

stakelets, was also found for stakelets exposed to three of the other four soils. In addition to the Mn increase observed for the FPL-exposed wood, an increase in Mn was also observed in stakelets exposed to one (MSU) of the other four soils. Fe and Mn are the only metals consistently present in the five soils at levels above 80 ppm (Crawford et al. 2002). The amounts of Fe and Mn present in each soil are given in **Table 1**. Essentially no Co, Ni, or Zn were detected in the stakelets by ICP. It is unlikely for a metal to diffuse into wood to give a concentration greater than that naturally present in a particular soil and, therefore, we conclude that only the metals Fe and/or Mn could possibly migrate into soil-contact wood at concentrations above trace levels. Consequently, we reasoned that Fe and/or Mn would be the most likely soil component to interfere with Cr determination.

The migration of Fe into the outer shell of untreated or treated wood in both laboratory and outdoor exposure has been previously reported (Ruddick and Kundzewicz 1991, Ruddick and Morris 1991, Ruddick 1992), with some of the articles suggesting that soil microflora may be involved. For treated stakes exposed outdoors for at least 1 year, the Fe content of the outer shell was reported to be highest (about 0.1 to 0.2%) for samples exposed at Westham Island, Canada, but Fe was also found in stakes exposed in other locations in Canada, the United Kingdom, and New Zealand. For our CCA-treated stakes exposed in a laboratory to five soils for 12 weeks, we found that the average Fe content of the entire stakelet (the outer shell was not separated prior to analysis) ranged from about 0.1 percent to 0.01 percent. However, for stakelets leached in distilled water for the same time period the Fe content was only 0.002 percent. By comparison, the Fe content of

the unleached CCA-treated stakelets was 0.004 percent.

No literature on the migration of Mn into CCA-treated wood was found, but migration of Mn into wood decayed by white- and brown-rot fungi is known (Blanchette 1984, Daniel et al. 1997, Jellison et al. 1997, Petric et al. 2002). Jellison (2002) has stated that they sometimes see Mn migrating into wood in laboratory decay tests, but the Mn migration is inconsistent and unpredictable. We observed Mn in stakelets exposed to two of the five soils; those two soils both had Mn contents above 0.1 percent. No Mn migration was observed into stakelets exposed to the other three soils that had Mn soil contents below 0.1 percent. The variable migration of Mn and Fe, both essential metals in the fungal decay process, raises interesting possibilities on explaining lab decay test variability and making lab test results more relevant to outdoor exposure.

### Fe and Mn interference with x-ray fluorescence

**Table 2** shows the average percent CrO<sub>3</sub> “content” in SYP wood samples that were untreated (control), or spiked with 0.36 percent Fe or 0.27 percent Mn, with the CrO<sub>3</sub> “retention” determined using two energy dispersive x-ray fluorescence instruments. Both Fe and Mn interfered with CrO<sub>3</sub> determination on both machines, but to different extents. Fe also interfered, to a “minor” degree, with CuO determination by the Asoma instrument.

Both of these instruments are bench-top energy dispersion spectrometers, as opposed to research-grade instruments that are wavelength dispersion instruments. Specifically, the latter instruments employ a crystal to separate the fluorescent radiation into the various wavelengths and, thus, the different bands from the various elements present

are separated prior to the detector (hence wavelength dispersion). By contrast, in an energy dispersion instrument, the fluorescence radiation is unseparated and the detector uses pulse height (energy) discrimination to differentiate radiation from the different elements present. This arrangement has several advantages, but a major drawback is that the resolution (ability to separate two different bands from adjacent elements) is as much as 50 times poorer as compared to wavelength dispersion spectrometers. Furthermore, energy dispersive instruments can only detect a limited number of elements, but wavelength dispersive instruments can detect multiple (and adjacent on the periodic chart) elements. Consequently, overlapping K spectral lines may occur with energy dispersion instruments, especially for elements that are adjacent on the periodic chart (Willard et al. 1981). Thus, an energy dispersion spectrometer is only recommended for analyzing samples that contain elements separated by at least several atomic numbers and in which only a limited number of elements are of interest. In examining **Table 2** and a periodic chart, it is apparent that Mn causes more interference than Fe, as predicted based on the atomic numbers of Fe, Mn, and Cr. The slight interference caused by Fe with the CuO measurement on the Asoma machine suggests that elements separated by three atomic numbers could interfere to a relatively minor extent with that particular instrument.

When examining the percent Cr leached based on x-ray fluorescence in stakelets exposed to the different soils (**Table 1**), it appears that samples exposed to the FPL soil gave the most unreasonable, and therefore likely inaccurate, Cr leaching data. This would be expected since those stakelets also gained the most Fe and Mn (**Table 1**). Stakelets exposed to the MSU soil also gained a fair amount of Mn and some Fe, and it appears that the percent Cr leaching data for stakelets exposed to the MSU soil may also be inaccurate. By contrast, the percent Cu leached, determined by ICP analysis for stakelets exposed to the FPL and MSU soils, is similar to the Cr leached from stakelets exposed to the other three soils and water. Consequently, this suggests that the leaching data based on ICP are more reasonable. Since stakelets exposed to four of the five soils gained Fe, and Mn also migrated into stakelets exposed to

two of the five soils, this problem could potentially occur in treated wood exposed to many soils.

The migration of Fe and/or Mn into decayed wood, and the interference of Fe and Mn with Cr using energy dispersive x-ray fluorescence (Wheeler 1987, 1988), have both been previously reported. However, no caution notes are given in AWP Standard Method A9-01 for this possibility. In quickly examining some leaching articles in refereed journals, we found two articles dealing with leaching of CCA-treated wood products where this factor may have affected the results. Thus, we suggest that AWP Standard Method A9-01 be modified to indicate this potential problem.

It is possible that wavelength dispersive instruments can minimize potential errors due to this effect. Inter-element correction for the interference error between As, Cr, and Cu is possible with energy dispersive instruments (Crawford and Steffes 1971); however, correcting for elements that are not typically present in treated wood, such as Fe and Mn, and which, therefore a bench-top instrument would not likely be able to detect, will be difficult. If investigators are aware of a potential problem it may be possible to use various hardware and software techniques to minimize the error caused by elements with similar energies (Hawthorne and

Gardner 1976, Goldstein et al. 1996), but the results will still have some uncertainty. Thus, it may be best to use other instruments when analyzing CCA-treated wood in soil-contact leaching studies.

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