

## CHARACTERIZATION OF MERCURY FORMS IN CONTAMINATED FLOODPLAIN SOILS

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MAY 01 1996

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**Abstract.** The chemical form or speciation of mercury in the floodplain soils of the East Fork Poplar Creek in Oak Ridge, Tennessee, a site contaminated from past industrial activity, was investigated. The speciation of mercury in the soils is an important factor in controlling the fate and effect of mercury at the site and in assessing human health and ecological risk. Application of three different sequential extraction schemes indicated the mercury at the site was predominantly relatively insoluble mercuric sulfide or metallic mercury, though the relative proportions of each did not agree well between procedures. Application of x-ray and electron beam studies to site soils confirmed the presence of metacinnabar, a form of mercuric sulfide, the first known evidence of authigenic mercuric sulfide formation in soils.

### 1. Introduction

During the 1950s, approximately one hundred metric tons of mercury were discharged from the U. S. Department of Energy facilities in Oak Ridge, Tennessee to East Fork Poplar Creek (EFPC). Much of the mercury has remained trapped in the floodplain soils which are currently being investigated under U.S. Superfund legislation. The chemical form or speciation of mercury in the soils is a controlling factor in the fate and effect of mercury at the site and influences the site risk assessment and required remedial actions.

A sequential extraction methodology for the speciation of mercury in soils (method 1) indicated the mercury in the floodplain soils was almost entirely inorganic, of which approximately 85% was mercuric sulfide (Revis, et al, 1989 a,b). Since several investigators have shown mercuric sulfide is a relatively insoluble and non-bioavailable form of mercury (Fagerstrom and Jernelov, 1971; Gillespie and Scott, 1971; Engler and Patrick, 1975; Rogers, 1979; Willett, et al, 1992), the study was considered significant in terms of the fate and effect of mercury at the site. Subsequently, X-ray fluorescence (XRF) dot maps obtained from a scanning electron microscope (SEM) examination of twenty soils revealed a consistent elemental association between mercury and sulfur (Harris, et al, in press).

To support the characterization effort, another sequential extraction methodology in development for characterization of mercury in soils was applied to twenty floodplain soils (method 2) (Miller, 1993). The results of this analysis indicated that although mercuric sulfide was a significant form, elemental mercury (or mercury amalgams) was the predominant form of mercury in the floodplain (Dobb, et al, 1994).

Although the speciation results from two different sequential extraction methodologies did not agree, the analysis were not performed on the same soils. In order to resolve the discordance, the two previously utilized sequential extraction methodologies as well as a third method (method 3) (Sakamoto, et al, 1992) were each tested on five soils. In addition, supplemental x-ray and electron beam studies were initiated to further characterize the form of mercury in the floodplain.

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## 2. Methods

Soil samples were collected from the floodplain, composited in stainless steel bowls and refrigerated in the laboratory in sealed containers until use. Small (<100 g) subsamples of five soils were taken and further homogenized. One portion (approximately 3 g) of each soil was air dried to determine percent moisture, ground and analyzed for mercury by SW-846 Method 7470. The remaining portions of moist soil were sequentially extracted in 50 ml centrifuge tubes similar to the methods outlined in each of the three procedures. The determination of organic mercury in each analysis was omitted because the results of all studies have consistently indicated organic mercury is an insignificant fraction in EFPC soils. The supernatant from each extraction was preserved with 17.5 ml 0.7% potassium dichromate in 1:1 nitric acid, and diluted to approximately 250 ml prior to analysis for total mercury by SW-846 Method 7471. In addition, one soil was spiked with metacinnabar, the form of mercuric sulfide identified in EFPC soils as discussed below.

For the x-ray and electron beam studies, one of the most mercury-contaminated soils was selected because of the relatively high minimum detectable concentrations of some of the methods (i.e. nominally 1% for x-ray diffraction). Further enhancements of mercury concentration were achieved by particle size separation by differential sedimentation/centrifugation. Soils were characterized by a JEOL 2000FX transmission electron microscope (TEM) with select area electron diffraction (SAED) using an accelerating voltage of 100 KV and a beam current of 15  $\mu$ A and a Phillips high angle diffractometer with a graphite crystal monochromator using  $\text{CuK}\alpha$  ( $\lambda=1.5418$  angstroms) radiation operated at 40 KV and 40  $\mu$ A.

## 3. Results and Discussion

The concentration of mercury in the five soils ranged from 42 - 2400  $\mu\text{g/g}$ . The results of the sequential extraction studies are shown in Figure 1. The percentage of metallic mercury detected in each of the soils by methods 1 and 2 are not in agreement (method 3 did not have a determination for metallic mercury). The average percentage of metallic mercury in the soils by method 1 was 28% compared to 72% by method 2 and differences within individual soils were even more pronounced. The percentage of mercuric sulfide detected by the three procedures also did not agree. For the five natural soils, method 1 detected an average of 46% mercuric sulfide compared to 25% for method 2 and 65% for method 3. For all five soils, the percentage of mercuric sulfide detected was highest for method 3 followed by method 1 and then method 2. The recoveries of the metacinnabar spike were 87% for method 1, 84% for method 2 and only 24% for method 3. The relative fraction of mercuric sulfide determined by method 1 (46%) did not agree with earlier results from the same procedure (85%).

A series of X-ray/electron beam studies were initiated to further refine the mercury speciation at the site. Mercury-rich soil fractions with a concentration of 0.89% (<2  $\mu\text{m}$ ) and 0.96% (2 - 5  $\mu\text{m}$ ) were obtained by particle size separation from a 2670  $\mu\text{g/g}$  soil and further analyzed by SEM energy dispersive spectroscopy (EDS) and wavelength dispersive spectroscopy (WDS), x-ray diffraction (XRD) and TEM with SAED. EDS/WDS of numerous mercury-rich soil particles showed consistent stoichiometric relationships between soil mercury and mercuric sulfide standards, particularly metacinnabar. TEM with SAED confirmed the presence of sub-micron crystals of metacinnabar, often in close association with the clay matrix (Stevenson, et al, 1994). As shown in Figure 2, the

XRD patterns of the enriched soil fractions have peaks indicative of metacinnabar. The relatively small, broad peaks are caused by the sub-micron crystallite size and concentrations of mercury near the nominal detection limit, but are pronounced when compared to the as-received soil.

**Fig. 1. Comparison of speciation from different sequential extraction procedures for metallic mercury (left) and mercuric sulfide (right)**

**Fig. 2. Comparison of XRD patterns for mercury rich size fractions with as-received soil and with synthetic metacinnabar.**

The results of the three sequential extraction studies concurred the mercury at the site consists primarily of inorganic metallic mercury and mercuric sulfide, though the relative percentages of each did not agree between methodologies. There is supporting evidence of mercuric sulfide from x-ray/electron beam studies, including unequivocal identification of crystalline mercuric sulfide (metacinnabar) by TEM with SAED and XRD. In addition, there has been no optical or x-ray/electron beam evidence of metallic mercury. Nonetheless, x-ray/electron beam studies have been limited to a few soils making extrapolation of the results for validation of the sequential extraction schemes problematic. In addition, method 2 is still under development and the developers are aware of the discordancies between the sequential extraction methodologies and are attempting to determine the causes and find a resolution. In the interim, the use of sequential extraction procedures alone for the speciation of mercury in soils is considered problematic.

#### 4. Conclusions

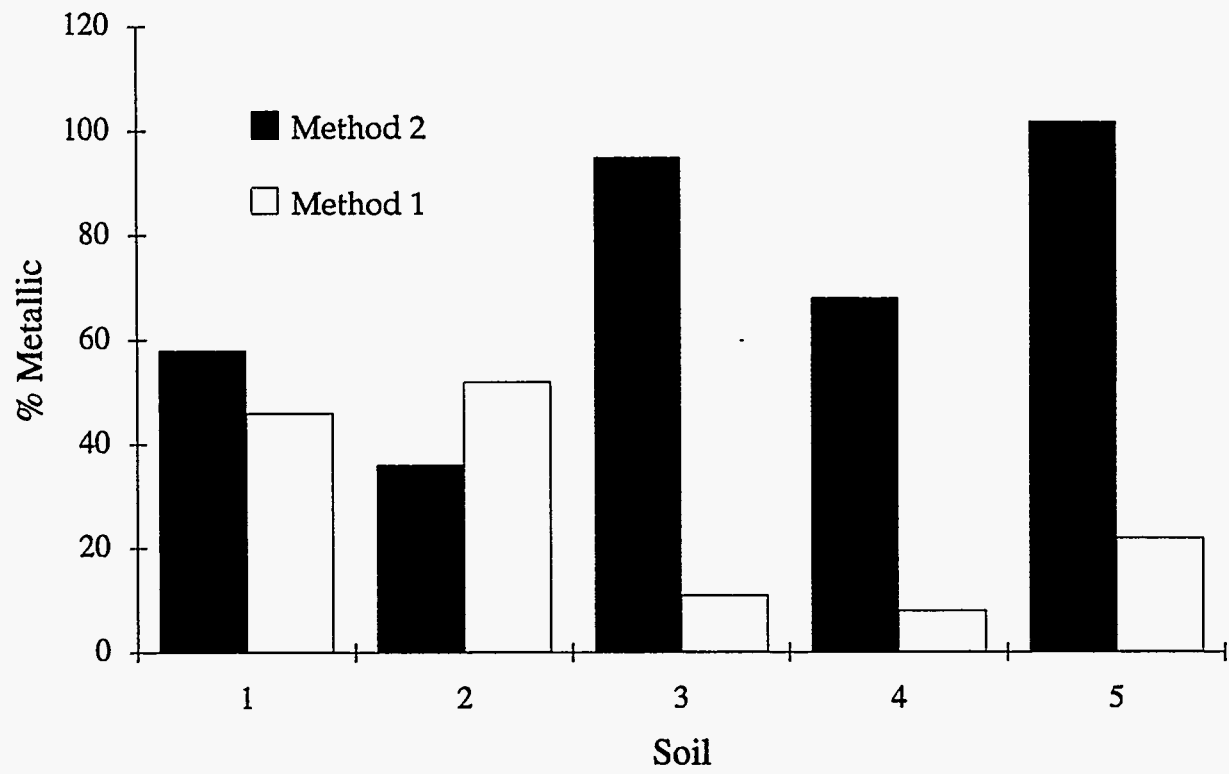
From sequential extraction procedures, mercury in EFPC soils exists in relatively insoluble and non-bioavailable elemental or sulfide forms. The proposed sequential extraction procedures for individual mercury species did not agree well in site soils. The presence of sub-micron, crystalline mercuric sulfide (metacinnabar) in soils was confirmed by TEM with SAED and XRD. This is the first known evidence of the formation of authigenic mercuric sulfide in soils.

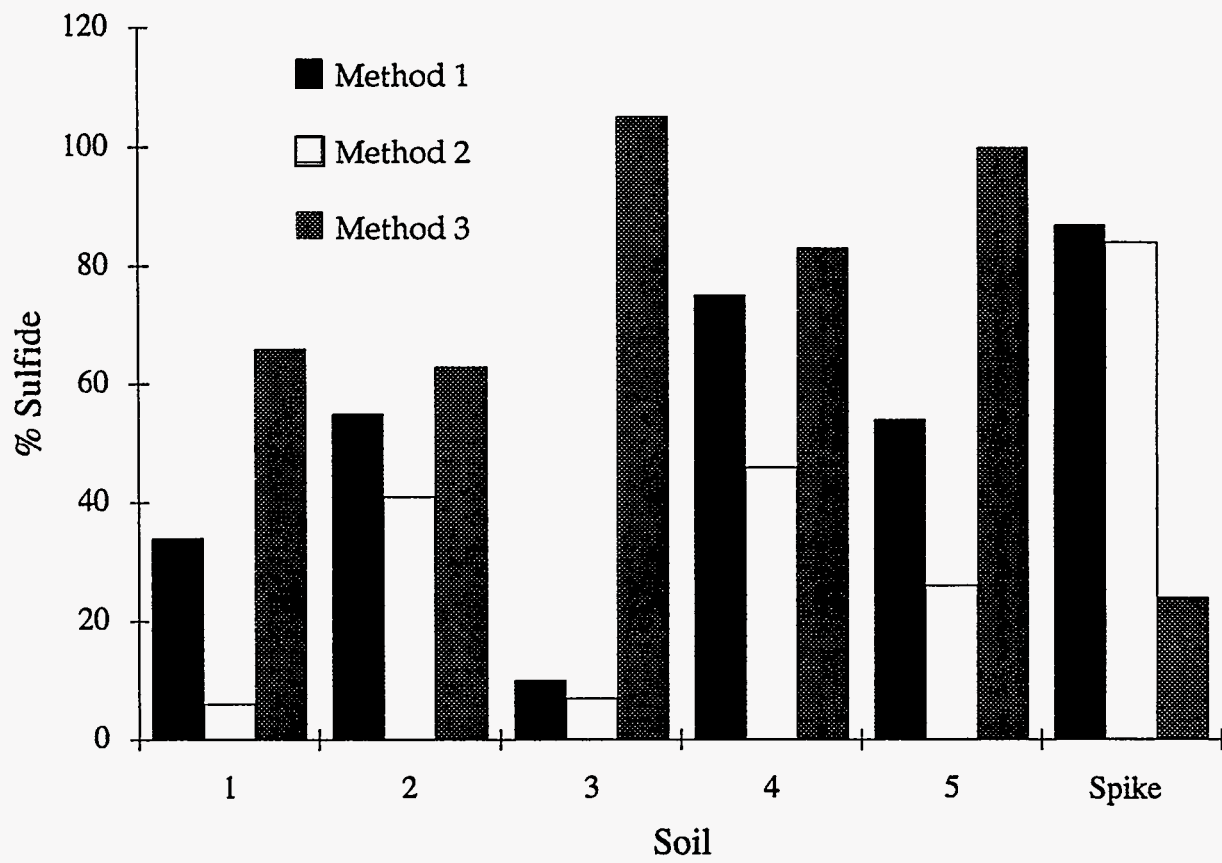
#### Acknowledgments

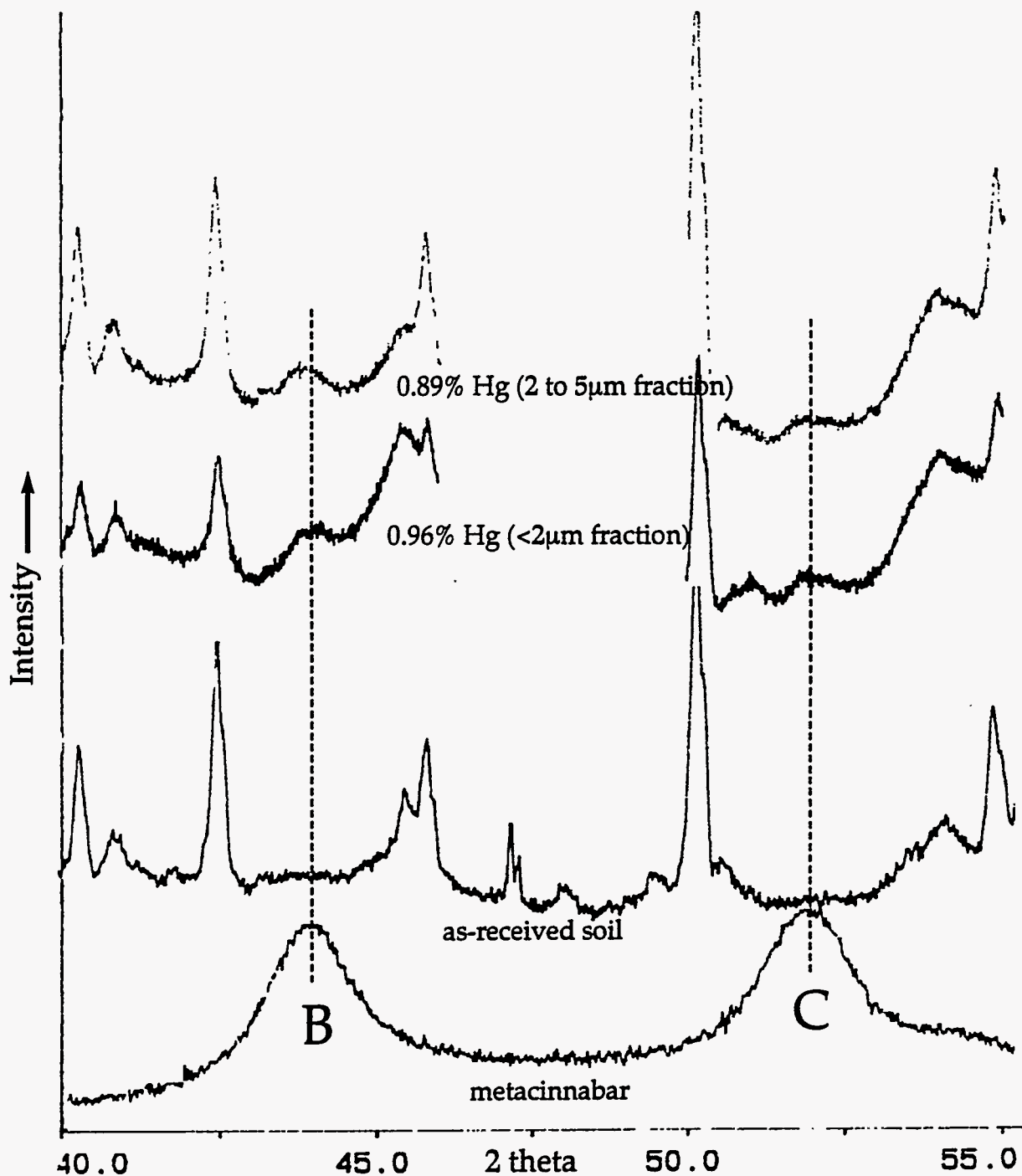
This research was sponsored by the U. S. Department of Energy's Environmental Restoration Division. Oak Ridge National Laboratory and K25 are managed for the U. S. DOE under contract DE-AC05-84OR21400 with Martin Marietta Energy Systems, Inc.

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