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# Bioaccessibility of Mercury in Soils

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*The initial risk assessment for the East Fork Poplar Creek (EFPC) floodplain in Oak Ridge, Tennessee, a superfund site heavily contaminated with mercury, was based on a reference dose for mercuric chloride. Mercuric chloride, however, is a soluble mercury compound not expected to be present in the floodplain, which is frequently saturated with water. Previous investigations had suggested mercury in the EFPC floodplain was less soluble and therefore potentially less bioavailable than mercuric chloride, possibly making the results of the risk assessment unduly conservative. A bioaccessibility study, designed to measure the amount of mercury available for absorption in a child's digestive tract (the most critical risk pathway endpoint), was performed on 20 soils from the EFPC floodplain. The average bioaccessible mercury for the 20 soils was 5.3%, compared with 100% of the mercuric chloride subjected to the same conditions. The alteration of the procedure to more closely mimic conditions in the digestive tract did not significantly change the results. Therefore, the use of a reference dose for mercuric chloride at EFPC, and potentially at other mercury-contaminated sites, without incorporating a corresponding bioavailability adjustment factor may overestimate the risk posed by the site.*

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## INTRODUCTION

The floodplain of East Fork Poplar Creek (EFPC) in Oak Ridge, Tennessee, was heavily contaminated with mercury and other contaminants by historic releases from the Department of Energy Oak Ridge Y-12 Plant located at the headwaters (Widner *et al*., 1996). The affinity of mercury for the solid phase and the local hydrology led to the deposition of a significant fraction of the mercury in the floodplain soils, where concentrations of up to 3000 mg/kg were discovered in the early 1980s. In 1989, the site was placed on the National Priority List for remediation as a superfund site.

After the evaluation of a number of contaminant exposure pathways, the inadvertent ingestion of inorganic mercury in soil by children was established as the critical human health exposure pathway (methyl mercury was a minor fraction in soil and not a significant risk in the soil ingestion exposure pathway) (DOE, 1994). The calculated health risk due to soil ingestion is a function of several variables: soil metal concentration, soil ingestion rate, body weight, exposure frequency and duration, and the reference dose (RfD) for mercury (Kester *et al*., 1994). Exposure to noncarcinogenic contaminants, such as mercury, below the RfD (mg of metal per kg body weight per day) constitutes an acceptable risk, while exposure above the RfD constitutes an unacceptable risk. The RfD for mercury was established on the basis of the toxicity of mercuric chloride to animals (Schoof and Nielsen, 1997). However, mercuric chloride is a very soluble mercury species with a bioavailability (fraction of administered dose that reaches the biological system of interest, in this case a child's circulation system) estimated to be significantly greater than the bioavailability of soil-bound inorganic mercury.

Several investigations (Table 1) have suggested the mercury in EFPC soils may be less soluble and therefore potentially less bioavailable than mercuric chloride. Based on the results of a sequential extraction procedure, Revis *et al*. (1989) suggested that the mercury in EFPC soils had been converted predominantly to mercuric sulfide as the result of sulfate reduction in the floodplain soils. Barnett *et al*. (1995) showed that although the mercury speciation was not consistent among different sequential extraction procedures, the mercury in EFPC soils was resistant to all but the most aggressive extraction procedures. Subsequently, Harris *et al*. (1996) demonstrated a consistent association between elemental mercury and elemental sulfur in EFPC soils. Barnett *et al*. (1997) positively identified small crystals of metacinnabar (β-HgS(s)) and developed a reaction path model based on site mineralogy and soil water chemistry that was consistent with the formation of mercuric sulfide in flooded soils. The presence of mercuric sulfide in the soils is important in assessing the risk posed by the soils, because mercuric sulfide is orders of magnitude less soluble than mercuric chloride (Figure 1). Metals that do not dissolve in the digestive tract are not available to be absorbed into systemic circulation, that is, they are not bioavailable (Sheppard *et al*., 1995). The presence

**TABLE 1**
**Summary of Published Mercury Speciation Results for EFPC**

| Study | Primary Methodology | Conclusions |
|---|---|---|
| Revis et al. (1989) | Sequential extraction | Mercury had been converted predominantly (85%) to mercuric sulfide |
| Barnett et al. (1995) | Sequential extraction | Three different sequential extraction procedures produced inconsistent results. However, soil-bound mercury was resistant to all but the most aggressive extractants (e.g., >1 molar strong acid) |
| Harris et al. (1996) | Optical and electron microscopy | Observed consistent association between elemental mercury and elemental sulfur. |
| Barnett et al. (1997) | Transmission electron microscope with select area electron diffraction | Small crystals of metacinnabar (β-mercuric sulfide) positively identified. |

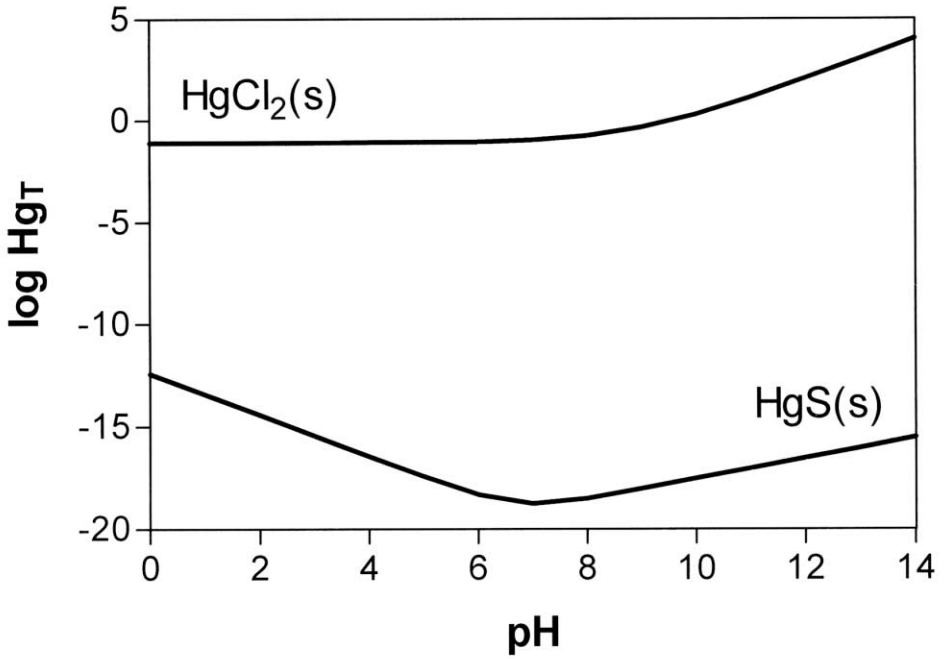


***FIGURE 1***

***Log total soluble mercury ($Hg_T$) in equilibrium with $HgCl_2$(s) and HgS (s, metacinnabar). Calculations were made using the geochemical speciation model MINTEQA2 (v4.00), assuming $4 \times 10^{-4}$ M $Cl^-$ and I = 0.01 M, which are typical conditions of surface soils at EFPC.***

of mercuric sulfide or other forms of mercury less soluble than mercuric chloride may lower the risk relative to the RfD based on mercuric chloride.

To investigate the potential effect of site-specific mercury speciation on bioavailability, a bioaccessibility study was conducted to measure the fraction of mercury in EFPC soils potentially available for absorption in the human digestive system. This study attempted to estimate the fraction of mercury in EFPC soils that will dissolve in the human digestive tract relative to mercuric chloride (i.e., the relative bioaccessibility). The study utilized an *in vitro* leaching procedure adapted from a protocol used in a risk assessment at another contaminated site (CDM, 1993), that was designed to mimic the conditions encountered in the human digestive tract (e.g., pH, residence time, solid to solution ratio, etc.). *In vitro* leaching procedures have become valuable tools in estimating the oral bioavailability of metals in soils (Ruby *et al*., 1993; Ruby *et al*., 1996). The fraction of metals dissolved in an *in vitro* leaching procedure is termed the bioaccessibility, which may be equated to the bioavailability by conservatively assuming that everything that is dissolved is taken up in systemic circulation (see Ruby *et al.* 1999) for a comprehensive discussion of the relationship between bioaccessibility and bioavailability). The study was conducted on a suite of soils from the floodplain

as well as some pure mercury compounds. The purpose of this article is to report the results of this study and discuss its potential impact on the remediation of EFPC and other mercury-contaminated sites.

## II. Experimental Methods

### A. Sample Collection and Processing

Soil samples were collected at two depths from ten sites (for a total of 20 samples) to represent a range of environmental conditions along the length of the floodplain. Surface samples were collected within 7.6 cm (3 in) of the surface to reflect the soils most likely to be inadvertently ingested by children. Deeper samples were collected in layers historically associated with the highest concentration of mercury in the floodplain. The sample designations, soil descriptions, and sample depths are shown in Table 2.

Samples were collected by channel sampling with a stainless steel spatula and spoon, composited by mixing in stainless steel bowls, placed in glass jars, transported back to the laboratory and refrigerated until processing. Mercury in the headspace of the sample containers was sampled with a Jerome (Arizona Instruments, Phoenix, Arizona) mercury vapor analyzer in the field. In the laboratory, samples were air dried in aluminum foil trays, lightly crushed with a clean mortar and pestle and sieved to 2 mm to remove rocks, roots, etc. The <2 mm material was disaggregated in a clean mortar and pestle and sieved to <180 μm. Subsamples of the <180 μm material were analyzed for total mercury by SW-846 Method 7471 *Mercury in Solid or Semisolid Waste* and total carbon and total sulfur with a LECO carbon/sulfur analyzer.

### B. Bioaccessibility

One-liter polypropylene containers were acid washed and rinsed with distilled, deionized water. A 0.74-g portion of each air-dried, <180 μm soil sample was added to 1 L of distilled, deionized water adjusted to pH 2.5 with hydrochloric acid in the containers. The samples were shaken continuously at room temperature (23°C), and the pH was rechecked after 10 min and again after 1 h. No pH readjustment was required for any of the samples at pH 2.5. After 4 h of leaching, the pH of each sample was measured and recorded, and the samples were allowed to settle. All samples had a final pH of 2.5 ± 0.2. After 25 min, 250 ml of the supernatant was poured into cleaned, disposable 0.2-μm filter units (Nalgene) and filtered. The filtrate was preserved with potassium dichromate in nitric acid prior to analysis for total mercury by SW-846 Method 7470 *Mercury in Liquid Waste*. This portion of the procedure simulated passage of soil through the stomach.

**TABLE 2**
**Sample Identification, Depths, and Description**

| Sample descriptor no.[a] | Depth (cm) | Description |
|---|---|---|
| 1-1 | 0-7.6 | Grayish-Brown, Medium Texture |
| 1-2 | 33-48 | Brownish-Gray, Medium Texture |
| 2-1 | 0-7.6 | Grayish-Brown, Medium Texture |
| 2-2 | 13-41 | Brownish-Gray, Medium Texture |
| 3-1 | 0-7.6 | Grayish-Brown, Medium Texture, Wetland |
| 3-2 | 7.6-23 | Dark Gray, Medium Texture |
| 4-1 | 0-7.6 | Dark Brown, Medium Texture |
| 4-2 | 25-51 | Dark Gray, Medium Texture |
| 5-1 | 0-7.6 | Brown, Fine Texture, Clay, Wetland |
| 5-2 | 25-35 | Dark Gray, Medium Texture, Clay |
| 6-1 | 0-7.6 | Dark Brown, Medium Texture |
| 6-2 | 25-41 | Dark Brownish-Gray, Medium Texture |
| 7-1 | 0-7.6 | Dark Brown, Medium Texture |
| 7-2 | 13-20 | Dark Gray, Medium Texture |
| 8-1 | 0-7.6 | Dark Brown, Medium Texture |
| 8-2 | 25-41 | Light Brown, Medium Texture |
| 9-1 | 0-7.6 | Dark Brown, Medium Texture |
| 9-2 | 20-30 | Dark Brown, Medium Texture |
| 10-1 | 0-7.6 | Dark Brown, Medium Texture |
| 10-2 | 41-81 | Reddish Brown, Fine Texture, Clay |

[a]Sample description numbers are keyed as follows: "Site-Sample Depth" with 1 for surface soils and 2 for deep soils (e.g., 9-1 represents the shallow sample from site 9). Site numbers increase downstream (i.e., with increasing distance from the contamination source).

The remaining 750 ml of suspension was combined with 250 ml of distilled, deionized water to restore the original solid to solution ratio, and the pH was adjusted to 6.5 with sodium hydroxide. The samples were shaken while the pH was rechecked and readjusted as necessary at 10 min and 1 h. After 4 hours, the sample pH was checked and recorded, and the samples were filtered as described above. There were some problems with pH drifting from 6.5 (particularly down) during the procedure. Of the 46 samples at pH 6.5, 25 had a final pH of 6.5 ± 0.2, an

additional fourteen had a final pH of 6.5 ± 0.5, and the remainder had a pH of 6.5 ± 1.0. This portion of the procedure simulated passage of soil through the small intestine. Two soil samples were processed in triplicate to measure the variability in the procedure.

In order to investigate the effects of more closely replicating the conditions of actual soil ingestion, the procedure was also repeated for a few samples at body temperature (37°C), with unprocessed field moist soil, and with 10 mg/l deoxycholic acid, a common constituent of the human digestive system. Pure mercuric chloride and two forms of mercuric sulfide, cinnabar and metacinnabar, were also processed as above. The mercuric chloride (Mallinckrodt) and cinnabar (EM Science) were reagent grade. The metacinnabar was synthesized in the laboratory and characterized by X-ray diffraction.

## III. Results and discussion

The results of total mercury, sulfur, and carbon analysis on the dry soil are shown in Table 3. Mercury concentrations ranged from 15 to 2630 mg/kg and, as expected, were higher for deeper samples in nine of the ten sites. The anomalous site (site 8) was located near the creek. Field observations indicated this site had been eroded recently, removing the surface soil and exposing the underlying, more highly contaminated soil at the surface.

As noted above, previous investigations have suggested that mercuric sulfide constitutes a significant fraction of the mercury in EFPC soils (Table 1). The results of the present study further support the association between mercury and sulfur in the soils of EFPC, which may influence mercury solubility and bioavailability. As shown in Figure 2, mercury was significantly correlated ($r = 0.84$, $p < 0.0001$) with sulfur in the 20 samples (as discussed below, this correlation was due predominately to the deeper samples). In 19 of the 20 samples, sufficient sulfur was present to bind all of the mercury as mercuric sulfide, with an average of almost seven times as much sulfur as mercury on a molar basis (Table 3). In one sample (10–2), the concentration of mercury exceeded the concentration of sulfur on a molar basis by approximately 20%, indicating that all the mercury in this sample cannot be mercuric sulfide. One other sample (1–2, Figure 2) clearly deviated from the mercury-sulfur relationship exhibited by the other samples. By removing this sample from the regression, the mercury-sulfur correlation improves significantly ($r = 0.92$, $p < 0.0001$) for the other 19 soils. This sample, the most upstream sample taken (i.e., closest to the source), was apparently geochemically different from the other samples, in that it contained the highest concentration of mercury and exhibited a significantly higher mercury bioaccessibility than the other samples (see below). In addition, this was the only sample among 20 that exhibited detectable mercury vapor in the headspace of the sample container. Carbon has also been shown to be strongly associated with mercury in the environ-

**TABLE 3**
**Mercury, Sulfur, and Carbon Concentrations in EFPC Soils**

| Sample no. | Hg (mg/kg) | S (mg/kg) | C (mg/kg) | S/Hg (mol/mol) |
|---|---|---|---|---|
| 1-1 | 260 | 150 | 65000 | 3.6 |
| 1-2 | 2630 | 683 | 44300 | 1.6 |
| 2-1 | 270 | 300 | 59000 | 7.0 |
| 2-2 | 1900 | 900 | 68000 | 3.0 |
| 3-1 | 230 | 350 | 93000 | 9.5 |
| 3-2 | 2100 | 1600 | 110000 | 4.8 |
| 4-1 | 85 | 140 | 40000 | 10.3 |
| 4-2 | 1300 | 650 | 81000 | 3.1 |
| 5-1 | 67 | 110 | 23000 | 10.3 |
| 5-2 | 2100 | 1700 | 120000 | 5.1 |
| 6-1 | 140 | 30 | 35000 | 1.3 |
| 6-2 | 1200 | 490 | 69000 | 2.6 |
| 7-1 | 230 | 150 | 33000 | 4.1 |
| 7-2 | 900 | 320 | 50000 | 2.2 |
| 8-1 | 480 | 200 | 30000 | 2.6 |
| 8-2 | 15 | 27 | 13600 | 10.9 |
| 9-1 | 55 | 120 | 25000 | 13.7 |
| 9-2 | 780 | 220 | 23000 | 1.8 |
| 10-1 | 28 | 150 | 38000 | 33.5 |
| 10-2 | 390 | 50 | 12000 | 0.8 |
| mean | 758 | 417 | 51600 | 6.6 |

ment (Kim *et al*., 1997). Overall, the correlation between mercury and carbon in EFPC soils is weak ($r = 0.59$, $p < 0.01$).

There was a significant difference between the association of mercury and sulfur in the surface samples compared with the samples taken at depth. As shown in Figure 3, total mercury was well correlated ($r = 0.95$, $p < 0.001$) with total sulfur in the deep samples. The correlation ($r = 0.53$, $p < 0.15$), however, was not as good in the surface samples (Figure 4), although the mercury bioaccessibility was lower in the surface samples as discussed below. In the preceding analysis, neither the sample that clearly deviated from the mercury-sulfur relationship (1–2) nor the sample from the area that had been eroded (site 8) was included. Several geochemical reasons for the better mercury-sulfur correlation at depth can be postulated. The formation and stability of mercuric sulfide is favored in reducing environments that may occur more favorably in the deeper soils. Alternatively, this may reflect the co-deposition of higher mercury concentrations and other sulfur-rich materials associated with the early operation of the Y-12 plant. Coal fragments and fly ash from the Y-12 plant are readily visible in the deeper soils (Harris *et al*., 1996).

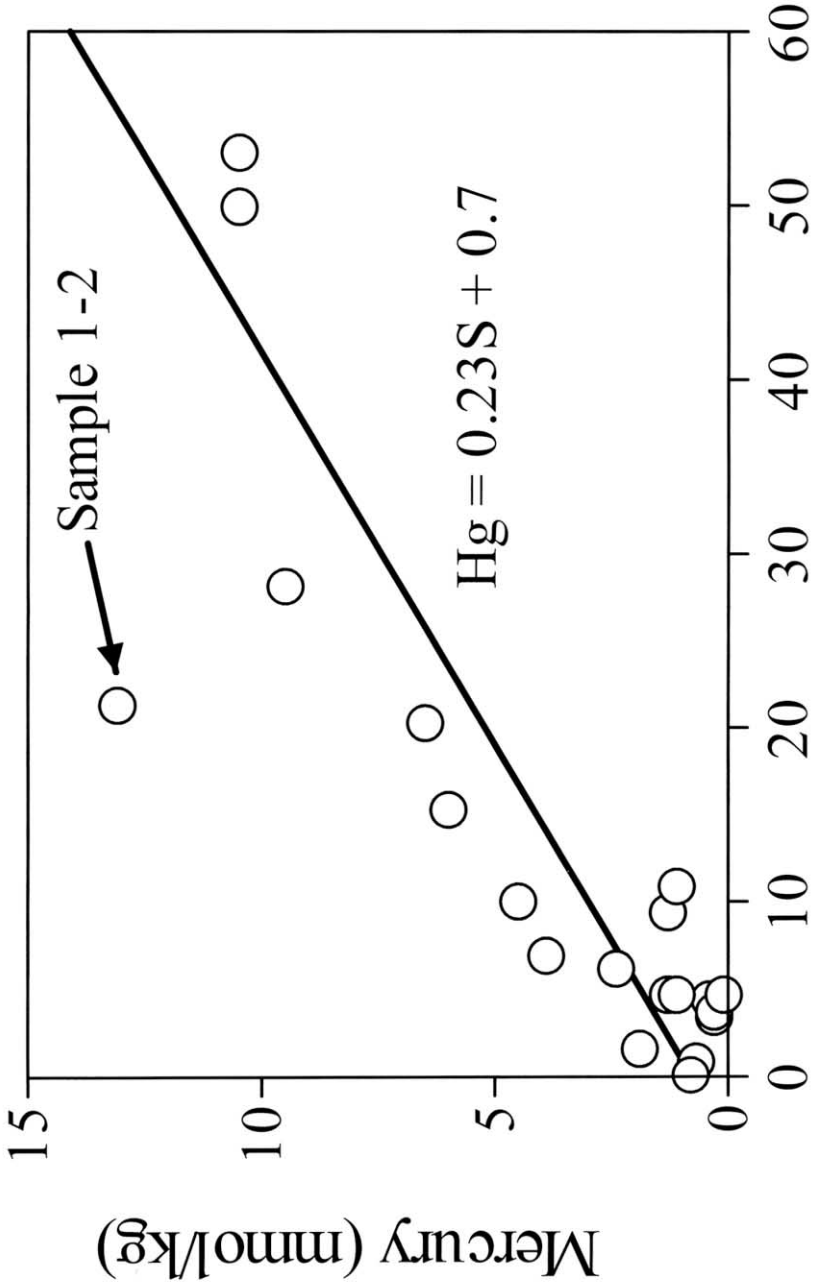


***FIGURE 2***

***Mercury vs. sulfur in EFPC soils.***

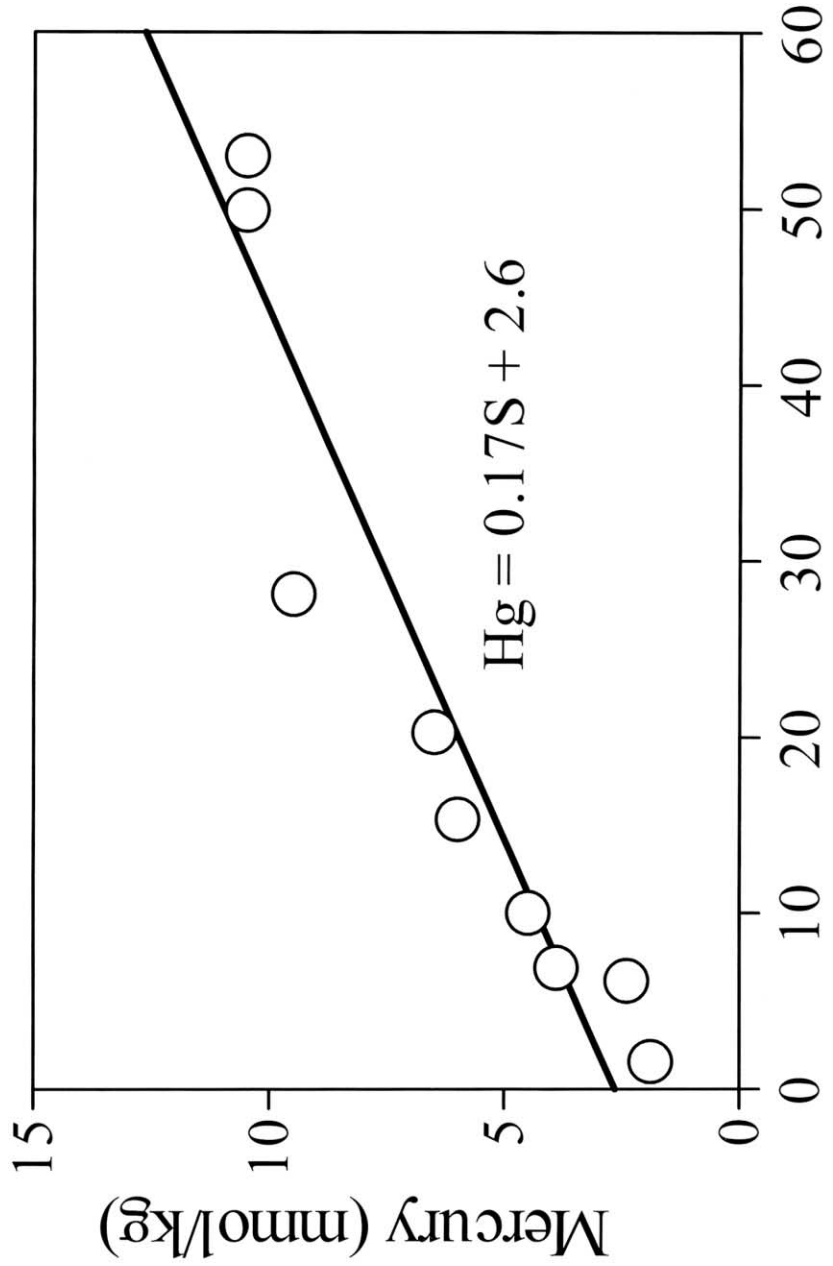


***FIGURE 3***

***Mercury vs. sulfur in deep soils.***

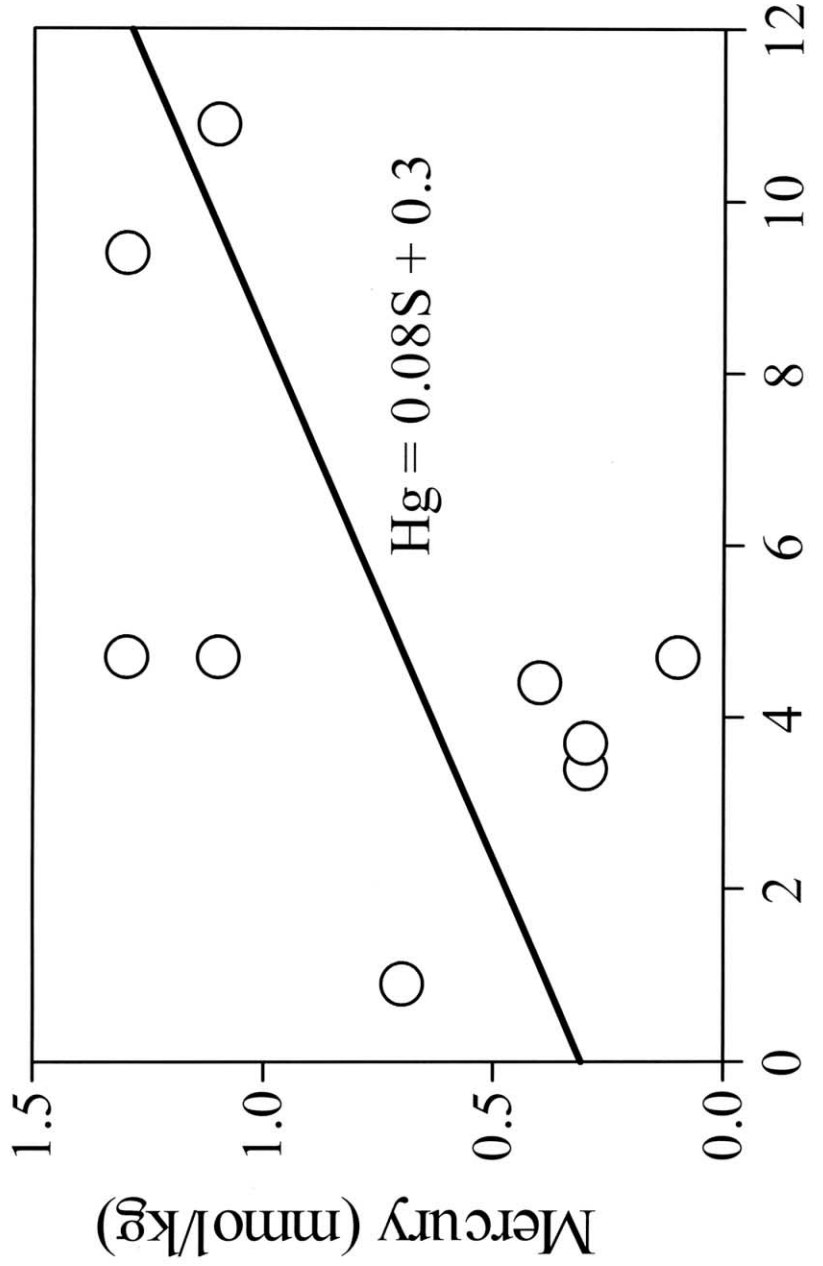


***FIGURE 4***

***Mercury vs. sulfur in surface soils.***

The results of the bioaccessibility study for the 20 soil samples are shown in Table 4 and graphically in Figure 5. The bioaccessibility at pH 6.5 is corrected for the soluble mercury lost from the sample when decanting the supernatant for filtration at pH 2.5. The total bioaccessible mercury (as a percentage) is conservatively estimated from the sum of the bioaccessible mercury at both pH values, because some of the mercury in the soil is undoubtedly bioaccessible at both pH values and therefore is counted twice in this conservative summation approach. Two of the soils were processed in triplicate yielding an average variability of $<\pm 1.0\%$ bioaccessibility. Recent research (Ruby *et al*., 1999) has suggested that the dissolution of soil-bound metals in the low-pH stomach environment is the limiting step in systemic uptake and bioavailability. The results in this *in vitro* study are consistent with Ruby's observation, as the bioaccessibility in the low-pH simulated stomach environment was almost twice the corresponding value in the neutral-pH-simulated intestinal environment (Table 4).

In 19 of the 20 samples, the bioaccessible mercury (as a percentage) was minimal at both pH 2.5 and 6.5. Total bioaccessible mercury in the 19 samples ranged from 0.3 to 14%, with an average of 3.2%. The maximum solution-phase mercury concentration was 77 μg/l. Less than 5% of the mercury was bioaccessible in 15 of the samples. For sample 1–2, the solution-phase mercury concentrations were 570 and 300 μg/l at pH 2.5 and 6.5, respectively, for a total of 46% bioaccessible mercury. The increased bioaccessibility of mercury in this sample relative to the other 19 is thought to reflect differences in the speciation of mercury in the sample, as this sample was an outlier with respect to the otherwise good correlation between total mercury and total sulfur (see above). Including this sample, the average bioaccessible mercury from the 20 samples was 5.3%.

The presence of mercuric sulfide or a mercury-sulfur association in the soils may be a reason for the low solubility and bioaccessibility of mercury in the EFPC soils, because the one sample that did not readily conform to the mercury-sulfur correlation was also the sample that had the highest bioaccessibility. However, the average bioaccessibility for the deep samples (3.6%) was higher than for the surface samples (1.6%), even though the deep samples exhibited a better mercury-sulfur correlation. This phenomenon may be indicative of the more water-soluble mercury forms being preferentially removed from the surface soils by water infiltration.

The procedure was also repeated for five samples at body temperature (37°C), for four field moist soils, and for two samples with 10 mg/l deoxycholic acid, a common constituent of the human digestive tract. These variations were selected to more realistically simulate uptake via soil ingestion and to facilitate comparisons between the above results and those obtained in conditions more representative of the digestive tract. The change in bioaccessibility for the samples (percent bioaccessible minus percent bioaccessible from dry soil at room temperature from Table 4) ranged from –7.7 to +1.8%. Using a paired t-test, these modifications to

**TABLE 4**
**Bioaccessibility of Mercury in EFPC Soils**

| Sample No. | Mercury concentration at pH 2.5 (μg/L) | Mercury concentration at pH 6.5 (μg/L) | Percent bioaccessible mercury at pH 2.5 | Percent bioaccessible mercury at pH 6.5 | Total percent bioaccessible mercury[a] |
|---|---|---|---|---|---|
| 1–1 | 0.70 | 1.0 | 0.4 | 0.5 | 0.9 |
| 1–2 | 570 | 300 | 29 | 17 | 46 |
| 2–1 | 0.80 | 0.80 | 0.4 | 0.4 | 0.8 |
| 2–2 | 77 | 20 | 5.5 | 1.4 | 6.9 |
| 3–1 | 0.20 | 1.8 | 0.1 | 1.1 | 1.2 |
| 3–2 | 30 | 11 | 1.9 | 0.7 | 2.6 |
| 4–1 | 0.20 | 0.40 | 0.3 | 0.6 | 1.0 |
| 4–2 | 73 | 14 | 7.6 | 1.5 | 9.1 |
| 5–1 | 1.6 | 1.1 | 3.2 | 2.2 | 5.5 |
| 5–2 | 26 | 8.2 | 1.7 | 0.5 | 2.2 |
| 6–1 | 0.10 | 0.20 | 0.1 | 0.2 | 0.3 |
| 6–2 | 11 | 4.9 | 1.2 | 0.6 | 1.7 |
| 7–1 | 1.8 | 2.6 | 1.1 | 1.5 | 2.6 |
| 7–2 | 13 | 3.2 | 2.0 | 0.5 | 2.4 |
| 8–1 | 2.4 | 1.5 | 0.7 | 0.4 | 1.1 |
| 8–2 | 1.1 | 0.50 | 9.7 | 4.5 | 14 |
| 9–1 | 0.20 | 0.20 | 0.5 | 0.5 | 1.0 |
| 9–2 | 14 | 5.8 | 2.4 | 1.0 | 3.4 |
| 10–1 | 0.03 | 0.20 | 0.1 | 1.0 | 1.1 |
| 10–2 | 6.3 | 1.9 | 2.2 | 0.7 | 2.8 |
| mean | 41.4 | 19.0 | 3.5 | 1.8 | 5.3 |

[a] Total percent bioaccessible mercury was obtained by summing the percent bioaccessible mercury at pH 2.5 and 6.5. Two of the soils were processed in triplicate yielding an average variability of <±1.0% bioaccessibility.

the *in vitro* procedure did not significantly ($p < 0.05$) increase the bioaccessibility of mercury from these soils.

Mercuric chloride and mercuric sulfide (cinnabar and metacinnabar) were also subjected to the *in vitro* leaching procedure. The entire mercuric chloride sample dissolved (i.e., was 100% bioaccessible), and the solution-phase mercury concentrations (540 and 450 mg/l) were much higher than for the soils, almost 1000 times higher than the highest soil solution-phase concentration. The solution-phase mercury concentrations were 0.05 and 0.5 μg/l in the metacinnabar sample and 97 μg/l and 42 μg/l in the cinnabar sample at pH 2.5 and 6.5, respectively. The cinnabar sample was reagent grade and may have contained other more soluble mercury phases (such as an oxidized surface coating) that resulted in higher solution-phase concentrations, whereas the metacinnabar had been precipitated recently and washed with distilled water. Differences in the particle size between the two materials may also have contributed to the difference in solubility as well.

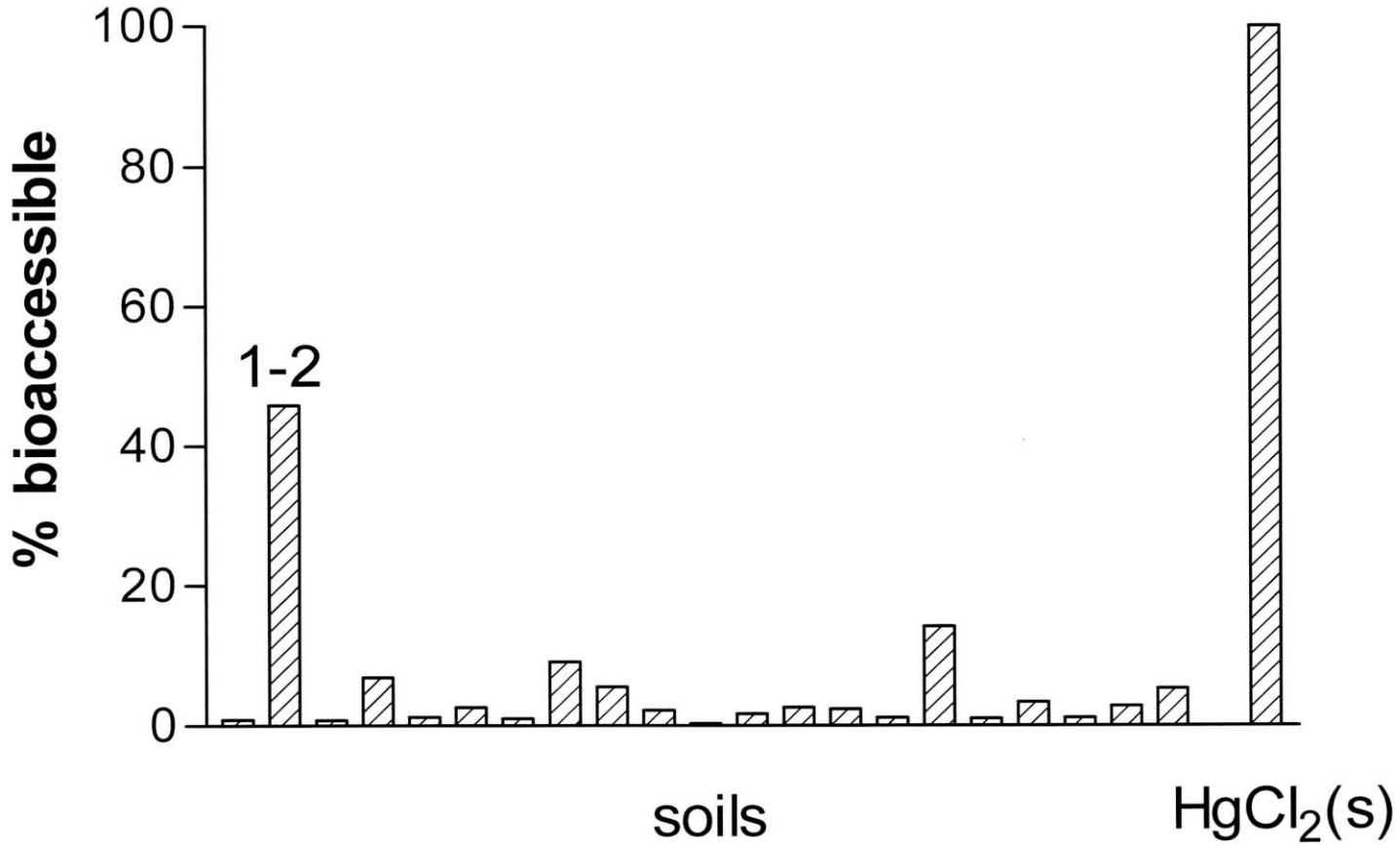


***FIGURE 5***

***Bioaccessibility of mercury in EFPC soils expressed as a percentage of total mercury in the solid phase. The bioaccessibility of the HgS(s) controls was too low to be visible on the figure.***

However, the bioaccessibility was less than 1% for both cinnabar and metacinnabar (this value is too low to be visible in Figure 5).

## IV. Summary and Conclusions

Twenty soil samples were collected from the EFPC floodplain to represent a range of biogeochemical environments and mercury contamination levels (15 to 2630 mg/kg). Total mercury was correlated with total sulfur in the soils, which is possibly indicative of the presence of mercuric sulfide in the soils, as has been suggested by previous investigations. The soils were subjected to an *in vitro* leaching procedure designed to simulate the human digestive system. For 1 of the 20 soils (1–2), 46% of total soil mercury was bioaccessible, while for the remainder of the soils <14% was bioaccessible. Only five soils had greater than 5% bioaccessible mercury, and the average bioaccessibility from the 20 soils was 5.3%. The procedure was repeated for several soils at body temperature, with deoxycholic acid, a common constituent of the digestive system, and on field moist soils. The changes in bioaccessibility were not significant.

Less than 1% of the mercuric sulfide samples, both cinnabar and metacinnabar, was bioaccessible. In contrast, the mercuric chloride sample was 100% bioaccessible, producing solution-phase concentrations almost 1000 times higher than the highest soil concentration. Although the *in vitro* procedure is a simple representation of a complex system (the human digestive system), the bioaccessibility and hence potentially the bioavailability of mercury in EFPC soils is substantially less than pure mercuric chloride. Therefore, the use of an RfD for mercuric chloride in assessing the risk posed by mercury-contaminated soils at EFPC, and possibly other mercury-contaminated sites, without incorporating a corresponding bioavailability adjustment factor may overstate the risk posed by the soils. As cleanup funds are finite, overestimating the risk at one site may divert needed cleanup funds from another site. These results clearly indicate the need to consider site-specific speciation and bioavailability in estimating the risk posed by mercury-contaminated soils.

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