ABSTRACT

The objectives of this study were to investigate the current status of mercury distribution, speciation and bioavailability in the floodplain soils of Lower East Fork Poplar Creek (LEFPC) after decades of US Department of Energy’s remediation. Historically as part of its national security mission, the U.S. Department of Energy’s Y-12 National Security Facility in Oak Ridge, TN, USA acquired a significant fraction of the world’s supply of elemental mercury. During the 1950s and 1960s, a large amount of elemental mercury escaped confinement and is still present in the watershed surrounding the Y-12 facility. A series of remediation efforts have been deployed in the watersheds around the Oak Ridge site during the following years. The sampling fields were located in a floodplain of LEFPC of Oak Ridge, TN, USA. A series of surface soils (10-20 cm) were sampled from both wooded areas and wetland/grass land. Two 8x8 m fields were selected in the woodland. Five profiles each consisting of three layers were randomly taken from each field. The three layers were the surface layer at 0-10cm, subsurface layer at 50-60 cm, and bottom layer at 100-110 cm. Soil in both wood and wetland areas was well developed with a clear B horizon. The present study clearly shows that the total mercury in floodplain soils of LEFPC significantly decreased after the series of remediation. However, the average total mercury level of all soil samples collected are in the range of 50-80 mg/kg, still significantly above toxic level (> 5mg/kg). Furthermore, contrary to conventional believing, the major mercury form in current soils of this particular area of floodplain of LEFPC is mainly in non-cinnabar mercury bound in clay minerals (after decades of remediation). The floodplains can act both as a medium-term sink and as long-term sources. Native North American earthworms (Diplocardia spp.) and adjacent soils were taken from each spot in each field. Our results show strong linear relationships between mercury concentrations in earthworms (both mature and immature groups) and non-cinnabar mercury form, while cinnabar mercury is less bioavailable to native earthworms. Earthworms may be used as a potential mercury ecological bio-indicator (bio-marker) for demonstrating mercury bioavailability and ecotoxicity in the ecosystem. The long-term stability, mobility and bioavailability of mercury contaminants in these floodplains still needs to be monitored continuously and closely.

INTRODUCTION

Mercury, a naturally occurring trace element in the earth’s crust, has proven to be a potent neurotoxin. Mercury is released into the environment in considerable amounts by anthropogenic activities, such as combustion of coal, mining and processing; and it has been transported globally and eventually deposited by wet and dry processes into the pedosphere [1-4]. The global mercury production since the beginning of the industrial revolution has been estimated at
0.64 million metric tons [4]. Nriagu and Pacyna [2] reported that the annual anthropogenic input of mercury into the environment is as high as 6x10⁶ kg/yr. About 741 x 10⁶ kg mercury from both anthropogenic input and natural sources has been released into the atmosphere, 118 x 10⁶ kg released in water and 806 x 10⁶ kg released into soils [1]. As of 2008, 27 states of the US have statewide advisories for mercury in freshwater lakes and/or rivers. Thirteen states have statewide advisories for mercury in their coastal waters and one state has a statewide advisory for mercury in marine fish [5]. The total number of advisories for mercury increased from 3,080 in 2006 to 3,361 in 2008 [5].

The Y-12 National Security Facility near the city of Oak Ridge, Tennessee, USA is a manufacturing and developmental engineering facility that formerly produced components for various nuclear weapons systems. Mercury has been identified as a key contaminant in soil, sediment, surface water, groundwater, buildings, drains, and sumps in the Y-12 watershed [6,7]. The source of the mercury is from elemental mercury used during the 1950s and early 1960s for the manufacture of nuclear weapons. Mercury was used to capture enriched lithium by separating the lithium isotopes. The estimates of the total mercury released to the environment range from about 75 to 150 metric tons [8,9]. Most mercury has been accumulated in the upper 3 m of floodplain soils and the sediments of a 24 km-long reach of the East Fork Poplar Creek (EFPC). Lower East Fork Poplar Creek (LEFPC) flows north from the Y-12 plant, off-site into the city of Oak Ridge through a gap in Pine Ridge. Lower EFPC flows through residential and business sections of Oak Ridge to join Poplar Creek, which flows into the Clinch River. The concentrations of mercury in the Upper EFPC watershed (soil) ranged from 0.01 to 7700 mg/kg [10]. Mercury has been detected at higher than background levels in sediments of the Clinch River and the Tennessee River near Chattanooga, some 190 km downstream of Oak Ridge [9].

A series of remediation efforts have been employed in the Oak Ridge watersheds. These include central pollution control facility, source collection, elimination of untreated discharges, central and east end mercury treatment systems, relining of sanitary and storm sewers, permanent bypass of Lake Reality (a concrete-lined catch basin located on Y-12 plants), dechlorination of cooling water discharges, and bank stabilization project [11]. The U.S. Department of Energy has removed highly mercury contaminated floodplain soil at several locations along the creek where mercury concentrations were higher than 400 mg/kg [9,12]. Remediation field activities with excavation began in 1996. All floodplain soils with mercury above this level have been removed [9,12]. All these remediation efforts have significantly reduced mercury concentrations in water of Upper EFPC from 1.6-1.8 µg/L in 1988 to 0.3-0.5 µg/L in 2003-2004 [11]. Mercury speciation in UEFPC floodplain soil strongly controls solubility, mobility, and bioavailability of mercury in both terrestrial and aquatic ecosystems and downstream mercury concentrations. Floodplain soils can act both as a medium-term sink and long-term mercury source. Our previous study was to mimic the initial stage of transformation and redistribution of mercury (as nitrate mercury and other forms), which actually occurred in contaminated field soils (floodplain) in Oak Ridge [7]. It is essential to assess the current status of mercury concentrations, speciation, distribution and its ecological bioavailability in floodplain soils after this series of remediation efforts.

The objectives of the present study were to investigate the current status of mercury distribution, speciation and bioavailability in the floodplain soils of East Fork Poplar Creek after decades of US Department of Energy’s remediation efforts. This report may confirm the long-term effectiveness of the remediation, especially after excavation of highly contaminated floodplain soils.

**NOMENCLATURE**

**AmoFe** amorphous iron oxides  
**BF** bioaccumulation factor  
**CEC** cation exchange capacity  
**CryFe** crystalline iron oxides  
**CVAAS** cold vapor atomic absorption spectrometry  
**EDTA** ethylenediaminetetraacetic acid  
**EFPC** East Fork Popular Creek  
**ERO** easily reducible oxides  
**EXC** exchangeable mercury  
**HgS** mercury sulfide  
**ICET** Institute for Clean Energy Technology  
**ICP-AES** inductively coupled plasma atomic emission spectrometry  
**ICP-MS** inductively coupled plasma mass spectrometry  
**LEFPC** Lower East Fork Popular Creek  
**OM** organic matter  
**RES** residual non-cinnabar mercury  
**SSD** selective sequential dissolution  
**TOT<sub>HNO<sub>3</sub></sub>** total non-cinnabar mercury  
**USDOE** U.S. Department of Energy  
**USEPA** U.S. Environmental Protection Agency  

**MATERIALS AND METHODS**

**Location of Sampling Field**

The sampling site was located in a floodplain field of LEFPC of Oak Ridge, TN, USA (Fig. 1). A series of surface soils (0-20 cm) were sampled from both wooded area and wetland/grassland. Two 8x8 m fields were selected in the woodland. Five profiles consisting of three layers were randomly taken from each field. The three layers were the surface (0-10cm), subsurface (50-60 cm), and bottom layer (100-110 cm). Soil in both wooded and wetland areas was well developed with a clear B horizon. Fresh field samples were
stored in a refrigerator for mercury level and speciation analyses.

![Image](image_url)

**Figure 1.** Location of field sampling.

**Soil Characterization and Earthworm Sampling**

The soil at the study site is Armuchee soil (clayey, mixed, thermic Ochreptic Hapludults). This is a moderately deep soil with a clayey subsoil. Armuchee soils are formed in residuum of shale and river alluvia.

Soils were also characterized by soil pH, total organic carbon, iron and manganese oxide and cation exchange capacity (CEC). Soil pH was measured by pH electrodes in 1:1 water extracts and CEC was determined by the NH₄Cl-KNO₃ method [13]. Organic matter was measured by Total C/N/S Analyzer (Perkin-Elmer) and free Fe (Mn/Al/Si) oxides were analyzed by the citrate-bicarbonate-dithionite method [13].

Native North American earthworms (Diplocardia spp.) and immediate surrounding soils were taken from each spot in the fields. The earthworms were divided into two groups: immature and mature groups, based on a distinct swelling clitellum. Sexually mature earthworms are those with full clitellate adults. Earthworms were depurified over wet filter papers for 48 hours to purge their gut contents. Earthworms were dried in oven at 70 °C for 10 hours before mercury analyses.

**Mercury Analyses**

All soils were analyzed for total mercury and mercury speciation with fresh samples. Soil non-cinnabar and cinnabar mercury were sequentially extracted with 4M HNO₃ at 80 °C for 16 hours and HCl:HNO₃:H₂O at 95 °C for 20 min with a repeat (1:6:7, EPA method) [7,14,15]. Earthworm samples were digested with concentrated HNO₃ and H₂O₂ on a hot plate [16,17]. The digested solutions were filtered and then analyzed for Hg using inductively coupled plasma-atomic emission spectrometry (ICP-AES), inductively coupled mass spectrometry (ICP-MS), and cold vapor atomic absorption spectrometry (CVAAS).

Mercury in soils was assumed to be present in six operationally defined solid-phase fractions, which are obtained by selective sequential dissolution (SSD). The protocol employed in this study was developed based on the procedures by Tessier et al. [18], Shuman [19], and Han et al. [20]. Compared to the traditional sequential dissolution extraction procedures by Tessier et al. [18] and Biester and Scholz [21], we added one more fraction at the end aimed at extraction of cinnabar HgS form: HCl:HNO₃:H₂O extractable fraction [22]. The residual fraction (RES) with 4M HNO₃ before the cinnabar fraction may extract mercury remaining from all previous steps (except for HgS) due to incomplete extraction, such as humin-bound mercury. The modified sequential dissolution extraction procedure clearly distinguishes mercury in the cinnabar HgS form (by HCl:HNO₃:H₂O, 1:6:7) from humic/humin binding Hg in the RES fraction.

**NH₄OAc-extractable mercury.** This fraction includes soluble plus exchangeable mercury (EXC). Twenty-five mL of a 1 M ammonium acetate solution (pH adjusted to 7.0 with NH₄OH) were added to 1.1 g of air-dried soil (equivalent to 1 g of oven-dried soil) in a 50-mL Teflon centrifuge tube. The mixture was shaken for 30 min at 25°C and then centrifuged. The supernatant was decanted and filtered through a 0.45-μm filter. The soil residue was kept for the next analysis/dissolution step. The same centrifugation-decantation steps were used after each of the following extractions.

**NH₄OH-HCl-extractable mercury.** This fraction mainly targets mercury bound to easily reducible oxides, such as Mn oxides (ERO) [19]. Twenty-five mL of a 0.1 M NH₄OH-HCl + 0.01 M HCl solution (pH 2) were added to the soil residue and shaken for 30 min. This acid might attack some organic matter, resulting in underestimating the organically bound metal. However after extraction of the exchangeable fraction, this attack is less serious.

**H₂O₂-oxidizable Mercury.** This fraction mainly targets mercury bound to organic matter (OM) [18,20] as well as Hg⁰ and to some extent HgS [21]. Three mL of 0.01 M HNO₃ and 5 mL of 30% H₂O₂ were added to the soil residue. The mixture was digested in a water-bath at 80 °C for 2 hrs. An additional 2 mL of H₂O₂ were added and the mixture was heated for one hour. Fifteen mLs of a 1 M ammonium acetate solution were then added and the sample agitated for 10 min.

**Oxalate-extractable Mercury.** This fraction extracts mercury bound to amorphous iron oxides (AmoFe). Twenty-five mL of a 0.2 M oxalate buffer solution (0.2 M (NH₄)₂C₂O₄–0.2 M H₂C₂O₄ at pH 3.25) were added to the soil residue and the sample shaken in the dark for 4 hours [19].

**Hot NH₄OH-HCl and HOAc-extractable Mercury.** This fraction extracts mercury bound to crystalline iron oxides (CryFe). Twenty-five mL of 0.04 M NH₄OH-HCl in a 25% acetic acid solution were added to the soil residue and the sample digested in a water bath at 97-100 °C for 3 hours.

**HNO₃-extractable mercury.** 4M HNO₃ extracts the residual non-cinnabar mercury (RES) from the incomplete extraction of previous fractions (mostly from the organically bound mercury, such as humin-bound mercury) as well as Hg⁰.
[21]. Twenty-five mL of 4 M HNO₃ were added to the residue or soil and the sample was transferred to a glass digestion tube. Digestion was conducted in a water bath at 80 °C for 16 hours [14,20]. The same procedure was used to determine total non-cinnabar mercury (TOT_Hg_NO3).

Cinnabar mercury (Hg₅S). Four mL of a mixture of HCl:HNO₃:H₂O (1:6:7) were added to the residue soil and digested in water bath at 95 °C for 20 min. The extraction is repeated twice [23].

RESULTS AND DISCUSSION

Spatial and Soil Profile Distribution of Total Hg

The total mercury concentrations in floodplain surface soils (0-20 cm) East Fork Poplar Creek (EFPC) of Oak Ridge, TN were in the range of 28 to 201 mg/kg with an average of 62.5 mg/kg ±37.6 mk/kg (Table 1). Concentrations of total mercury at both depths of soil profiles around 50-60 cm and 100-110 cm ranged from 0.4 to 239 mg/kg and averaged 64-82 mg/kg. There are larger variations in the total mercury in subsurface and deep subsurface soils. The total mercury was distributed among soil profiles irregularly (Fig. 2). Some profiles had much higher mercury in surface soils, some profiles had higher mercury concentrations in the middle layer around 50-60 cm, while other profiles had the highest mercury in the deep down soil profiles.

The total mercury was strongly affected by topography and land use. Spatially the total mercury concentrations were higher in wetlands (with depressions) than in soils of woodland (Fig. 3). Wetlands usually had lower elevation with woodlands. Wetland along East Fork Poplar Creek was overflown by surface/runoff water after storms and from the creek. Wetland was flourished with dense grasses. On the other hand, woodland had relatively high elevation with less dense grasses. Wetland/grassland surface soils had an average of 62.5 ± 34 mg/kg total mercury, while woodland surface soils had 40 ± 9.6 mg/kg total mercury. Woodland soils had less variation (CV%: 24%) than those in wetland/grassland (CV%: 54.4%).

On the other hand, surface creek bank soils had similar total mercury (47.5 - 58.1 mg/kg) with an average 52.3 ± 5.3 mg/kg (Table 1). However, middle layer of the bank soil (20-40 cm) had 61 mg/kg total mercury. Mercury concentrations decreased to 18.1-53.9 mg/kg (average: 41.1 ± 20 mg/kg) in the deep layer around 50-60 cm. The creek sediment (around 100-120 cm in depth) contained total mercury 74.2 mg/kg.

There is not any significant correlation between total mercury and soil physicochemical properties (CEC, total C, iron oxide, manganese oxide, pH, etc.). The surface soils had 2.45 ± 0.29%, 0.11 ± 0.02%, 3.7 ± 1.7% iron oxide, manganese and organic carbon as well as 18.5 ± 7.73 cmol/kg, respectively. Basically, the soils down the soil profiles had less iron oxide, CEC, and less organic carbon contents, but similar Mn contents (Table 2). Soils from banks of the creek had relatively less iron oxide, CEC and organic carbon in the surface bank soils. This phenomenon on soil-property-independent-distribution of the total mercury and irregular distribution along soil profiles may be explained by a history of a series of remediation activities, including digging and filling. In the past decades, US Department of Energy has excavated all floodplain soils along the East Pork Poplar Creek with total mercury > 400 mg/kg[9,12] and filled with guest clean soils. The present analyses confirmed the effect of cleaning-up and remediation efforts, which indeed lowered the total mercury well below the DOE target, 400 mg/kg. As indicated by this study, the total mercury concentrations in the all soil samples investigated in the present study were well below that target.

Table 1. Concentrations of cinnabar mercury, non-cinnabar mercury and total mercury in floodplain field samples of Oak Ridge, Tennessee, USA. Uncertainty is one standard deviation. Range is minimum and maximum values.

<table>
<thead>
<tr>
<th>Soil Type</th>
<th>Depth (cm)</th>
<th>Noncinnabar-Hg (mg/kg)</th>
<th>Cinnabar-Hg (mg/kg)</th>
<th>Total Hg (mg/kg)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Wood/grass</td>
<td>0-20</td>
<td>55.5 ± 34.0 (27.8 – 196.7)</td>
<td>6.0 ± 15.2 (0.3 - 68.4)</td>
<td>61.5 ± 37.6 (28.1 – 201.0)</td>
</tr>
<tr>
<td>Wood/grass</td>
<td>50-60</td>
<td>73.2 ± 59.5 (0.3 – 196.7)</td>
<td>12.7 ± 20.9 (0.3 – 76.1)</td>
<td>82.5 ± 68.1 (0.6 – 239.2)</td>
</tr>
<tr>
<td>Wood/grass</td>
<td>100-110</td>
<td>58.6 ± 68.9 (0.1 – 196.7)</td>
<td>11.5 ± 18.2 (0.2 – 76.1)</td>
<td>67.4 ± 76.7 (0.4 – 239.2)</td>
</tr>
<tr>
<td>Bank</td>
<td>0-20</td>
<td>51.4 ± 4.7 (47.0 – 56.3)</td>
<td>1.0 ± 0.7 (0.5 – 1.7)</td>
<td>52.3 ± 5.3 (47.5 – 58.1)</td>
</tr>
<tr>
<td>Bank</td>
<td>20-40</td>
<td>60.1</td>
<td>0.8</td>
<td>61.0</td>
</tr>
<tr>
<td>Bank</td>
<td>50-60</td>
<td>23.2 ± 26.9 (0.5 – 52.9)</td>
<td>17.9 ± 28.5 (1.0 – 50.8)</td>
<td>41.1 ± 20.0 (18.1 – 53.9)</td>
</tr>
<tr>
<td>Bank</td>
<td>100-110</td>
<td>72.5</td>
<td>1.7</td>
<td>74.2</td>
</tr>
</tbody>
</table>

Figure 2. Mercury distribution along soil profiles in the woodland.
Cinnabar and Non-Cinnabar Mercury and Mercury Speciation in Floodplain Soils

We firstly divided the total mercury into non-cinnabar and cinnabar form. Non-cinnabar mercury was the major form (93%) of mercury in the floodplain surface soils (55.5 ± 34 mg/kg non-cinnabar mercury) (Table 3). Cinnabar mercury was 7% (6.0±15.2 mg/kg) of the total mercury. In addition, wetland/grassland soils contained 51.6 ±19.5 mg/kg non-cinnabar mercury and 10.9 ±25.4 mg/kg cinnabar mercury, respectively. Woodland soils had 39.4±9.4 mg/kg and 0.6±0.2 mg/kg for non-cinnabar and cinnabar mercury, respectively (Fig. 4). In the deeper soil profiles, non-cinnabar mercury decreased with depth (surface: 93%, middle subsurface: 82% and deep subsurface: 63.8%), while cinnabar mercury increased with depth (Fig. 5).

On the other hand, creek bank soils had a higher percentage of non-cinnabar mercury and less cinnabar mercury than floodplain soils (Table 3). Surface creek bank soils contained 98.2±1.05% non-cinnabar mercury while cinnabar form was 1.77 ± 1.05%. Bank soils at depths of 20-40 cm and sediment (100-120 cm) had a similar percentage of mercury distribution between cinnabar (1.37±2.29%) and non-cinnabar mercury (97.7-96.6%), However the bank soil had a significantly higher percentage of cinnabar mercury (37%).

Table 3. Concentrations (expressed as percentages) of cinnabar mercury and noncinnabar mercury for the same samples as in Table 1. Uncertainty is one standard deviation. Range is minimum and maximum values.

<table>
<thead>
<tr>
<th>Soil Type</th>
<th>Depth (cm)</th>
<th>Noncinnabar-Hg (%)</th>
<th>Cinnabar-Hg (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Wood/grass</td>
<td>0-20</td>
<td>92.9 ± 13.1 (45.4 – 99.0)</td>
<td>7.1 ± 13.1 (1.0 – 54.6)</td>
</tr>
<tr>
<td></td>
<td>50-60</td>
<td>82.2 ± 22.8 (13.1 – 99.0)</td>
<td>14.4 ± 16.7 (1.0 – 54.6)</td>
</tr>
<tr>
<td></td>
<td>100-110</td>
<td>63.8 ± 33.6 (1.3 – 99.0)</td>
<td>30.8 ± 30.0 (1.0 – 98.7)</td>
</tr>
<tr>
<td>Bank</td>
<td>0-20</td>
<td>98.2 ± 1.1 (97.0 – 98.9)</td>
<td>1.8 ± 1.1 (1.1 – 3.0)</td>
</tr>
<tr>
<td></td>
<td>20-40</td>
<td>98.6 ± 0.6</td>
<td>1.4</td>
</tr>
<tr>
<td></td>
<td>50-60</td>
<td>63.0 ± 53.9 (1.0 – 98.2)</td>
<td>37.0 ± 53.9 (1.8 – 99.0)</td>
</tr>
<tr>
<td></td>
<td>100-110</td>
<td>97.7 ± 2.3</td>
<td>2.3</td>
</tr>
</tbody>
</table>

It is clearly demonstrated by the present study that the total mercury in floodplain soils of EFPC decreased after a series of remediation, especially excavation of the highly contaminated soils/sediments along the creek. The concentrations of mercury in Upper EFPC watershed soil were earlier reported to range from 0.01 to 7700 mg/kg [10]. Some sediment cores contained 460 mg/kg mercury at depths of 80-84 cm [24]. Mercury has been detected at higher than background levels in sediments of the Clinch River and the Tennessee River near Chattanooga, some 190 km (118 miles) downstream of Oak Ridge [9]. Another recent study by Pant and Allen [25] indicated the total mercury in floodplain soils (54 samples) along EFPC at Oak Ridge ranged from 0.11 to 103.3 mg/kg with a mean of 24.3 mg/kg. All these imply the overall effectiveness of DOE remediation efforts that achieved the cleaning up targets.

**Table 2.** Some soil physicochemical properties in surface, subsurface and bank soils. Uncertainties are one standard deviation.

<table>
<thead>
<tr>
<th>Soil Type</th>
<th>Land Use</th>
<th>Depth (cm)</th>
<th>Fe(II) (%)</th>
<th>Mn (%)</th>
<th>CEC (cmol/kg)</th>
<th>C (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Surface</td>
<td>Grassland</td>
<td>0-20</td>
<td>2.45 ±0.29</td>
<td>0.11 ±0.02</td>
<td>18.50 ±7.73</td>
<td>4.44 ±0.93</td>
</tr>
<tr>
<td>Surface</td>
<td>Woodland</td>
<td>0-20</td>
<td>2.20 ±0.86</td>
<td>0.10 ±0.04</td>
<td>18.86 ±9.80</td>
<td>4.07 ±1.73</td>
</tr>
<tr>
<td>Bank</td>
<td>0-20</td>
<td>1.99 ±0.26</td>
<td>0.09 ±0.01</td>
<td>13.31 ±7.36</td>
<td>2.09 ±0.97</td>
<td></td>
</tr>
<tr>
<td>Bank</td>
<td>20-40</td>
<td>2.35 ±0.10</td>
<td>0.10 ±0.04</td>
<td>8.56 ±0.26</td>
<td>2.84 ±0.48</td>
<td></td>
</tr>
<tr>
<td>Bank</td>
<td>50-60</td>
<td>2.91 ±0.07</td>
<td>0.08 ±0.01</td>
<td>6.96 ±0.24</td>
<td>1.29 ±0.48</td>
<td></td>
</tr>
<tr>
<td>Bank</td>
<td>100-110</td>
<td>2.50 ±0.14</td>
<td>0.14 ±0.04</td>
<td>7.30 ±0.24</td>
<td>2.78 ±0.48</td>
<td></td>
</tr>
<tr>
<td>Soil Profile</td>
<td>Woodland</td>
<td>0-10</td>
<td>2.85 ±0.89</td>
<td>0.11 ±0.04</td>
<td>12.33 ±5.12</td>
<td>3.10 ±1.24</td>
</tr>
<tr>
<td>Soil Profile</td>
<td>Woodland</td>
<td>50-60</td>
<td>2.15 ±0.59</td>
<td>0.08 ±0.03</td>
<td>11.33 ±4.47</td>
<td>1.34 ±0.84</td>
</tr>
<tr>
<td>Soil Profile</td>
<td>Woodland</td>
<td>100-110</td>
<td>2.79 ±0.30</td>
<td>0.08 ±0.05</td>
<td>10.20 ±3.33</td>
<td>2.48 ±2.54</td>
</tr>
</tbody>
</table>

**Figure 3.** Spatial distribution of the total Hg in a floodplain field (wetland/grassland had higher mercury concentrations than woodland) (X, Y: in meter).
Figure 4. Concentrations of total mercury, cinnabar-mercury and non-cinnabar mercury in the surface soils (0-20 cm) of floodplain fields under wetland/grassland and woodland uses.

Figure 5. Soil profile distribution of cinnabar-Hg and non-cinnabar Hg in a floodplain field (averages with standard deviation).

Furthermore, non-cinnabar mercury in the solid-phase components was divided into operationally defined six fractions (exchangeable, easily reducible oxide bound, organic matter bound, amorphous iron oxide bound, crystalline iron oxide bound, and non-cinnabar residual forms). In general, a majority of non-cinnabar mercury was residual mercury bound with clay minerals (91 - 99.8%), followed by organic matter bound and crystalline iron oxide bound (Figs. 6-8). Mercury in the exchangeable and easily oxide bound fractions was the lowest with most below the detection limit.

In the surface soils of woodlands, non-cinnabar mercury was mainly in a clay mineral-bound residual fraction (92% ± 7.0%), followed by the organic matter-bound fraction (3.77% ± 3.06%) and crystalline iron oxide-bound fraction (2.72% ± 3.87%) (Fig. 6). Mercury in the amorphous iron oxide-bound, easily reducible oxide-bound, and the exchangeable fractions was 0.81 ± 2.27%, 0.18 ± 0.68%, and 0.40 ± 1.49%, respectively. Compared to woodland soil, surface soils in the wetland/grassland had higher mercury concentrations in the organic matter-bound fraction (7.53 ± 4.29%) and lower in non-cinnabar bound residual fraction (90.97 ± 5.42%) (Fig. 6).

On the other hand, bank surface and subsurface soils contained slightly higher non-cinnabar clay mineral-bound residual fraction (88-100%), followed by organic bound fraction and amorphous and crystalline iron oxide-bound fractions (Fig. 7).

Compared to surface soils, subsurface soils (both middle layers around 50-60 cm and the bottom layer around 100-110 cm) from the woodland had higher mercury concentrations in the non-cinnabar clay mineral-bound residual fraction (>97.5%), less mercury in the organic matter fraction (0.12%), crystalline iron oxide-bound, amorphous iron oxide-bound, easily reducible oxide and exchangeable fractions (Fig. 8). Mercury in exchangeable and easily oxide reducible oxide-bound fractions was below the detection limit.
Mercury can occur as various species (e.g., HgS, Hg(II), methyl-Hg, Hg(O)), but the predominant form of mercury in the floodplain soils of the region was previously reported to be mercuric sulfide (cinnabar and meta-cinnabar forms) [26,27]. Barnett et al. [27] used three different sequential extraction speciation schemes and found that mercury at the site was predominantly relatively insoluble mercuric sulfide or metallic Hg. They further confirmed the presence of meta-cinnabar, a form of mercuric sulfide, in site soils using X-ray and electron beam studies; this confirmed the first known evidence of authigenic mercuric sulfide formation in floodplain soils. Han et al. [7] simulated the solubility and initial distribution/transformation of mercury in solid-phase components in floodplain soils freshly spiked with various forms of mercury. They found that mercury in floodplain soils freshly spiked with soluble mercury chloride and nitrate was dominated by the organic matter bound fraction, while mercury in soils spiked with mercury sulfide was dominated by the cinnabar form.

However, the present study indicates that the major mercury in the floodplain soils of EFPC after decades of remediation is mainly in non-cinnabar mercury bound in clay minerals. This form is not as stable as the cinnabar form, but very stable and less bioavailable than other solid-phase mercury components as discussed earlier. Liu et al. [28] reported that some floodplain soils from EFPC of Oak Ridge were dominated by the organic matter bound mercury fraction (50%). They further reported that the redoximorphic concentration component had higher Hg concentrations than the redoximorphic depletion component in the soil and Hg retained in the redoximorphic concentrations was less volatile and labile than Hg in the redoximorphic depletions possibly due to the strong binding affinity of Fe/Mn oxides and organic matter to Hg. As indicated by the present study, mercury bound in both iron oxide and organic matter fractions, which are more sensitive to environmental changes such as redox changes than other solid phase compounds, play an important role in controlling mercury solubility and bioavailability in the floodplain ecosystem.

Bioavailability of Mercury in Floodplain Soils to Native Earthworms

The total mercury in earthworms was in the range of 30-120 and 14-89 mg/kg for the mature and immature groups, respectively (Fig. 9). The average mercury concentrations in both mature and immature groups were 68 ± 33 and 39 ± 29 mg/kg, respectively. Concentrations of mercury in earthworms in contaminated floodplain soils of East Fork Poplar Creek were significantly higher than those in grassland where there is no mercury contamination (1.97± 0.46 mg/kg).
Figure 9. Concentrations and bioaccumulation factors of mercury in both mature and immature earthworms grown in contaminated floodplain field soils from Oak Ridge.

The bioaccumulation factors (BF) (ratios of concentrations of mercury in earthworm to those in soil) of mercury in the mature group ranged from 0.47 to 1.75 with an average of 1.0 ± 0.49 (Fig. 9). However in the immature group of earthworm, BF factors were from 0.32 to 1.11 and averaged 0.64 ± 0.36. This indicates that mercury has been accumulated in the mature group and mature earthworms had almost double BF as the immature group. Burton et al. [29] reported bioaccumulation factors for inorganic matter in earthworms were 0.6 to 3.3 and were usually < 1, but BFs for monomethylmercury ranged from 175 to 249. This may imply that most mercury in soils of floodplain of Oak Ridge site may be mainly inorganic mercury with limited amount of monomethylmercury.

Further we examined the contribution of mercury species in solid phases to bioavailability of mercury in earthworms (Fig. 10). We first divided total inorganic mercury into cinnabar form and non-cinnabar form. A strong linear relationship was found between mercury concentrations in earthworms (both mature and immature groups) and those in non-cinnabar mercury while no correlations between cinnabar mercury and mercury in earthworm were found (Fig. 10). This clearly indicates that 4M HNO₃ extractable non-cinnabar mercury posed higher bioavailability of mercury to earthworms than the stable cinnabar form in floodplain soils. It is interesting that no correlation between mercury concentrations in earthworm and mercury concentrations in solid phase components was found.

However, our previous study indicated that mercury sulfide in contaminated floodplain soils of Oak Ridge was still to some extent bioavailable to plants [22]. The increase of bioavailability of soil mercury sulfide after multiple seasons of planting may contribute to the recent increase of mercury levels in water of the Lower East Fork Popular Creek (LEFPC) of Oak Ridge. We found that after three seasons of planting, soil mercury sulfide is more easily dissolved by both 4 M and 12 M nitric acid than is pure mercury sulfide reagent as indicated by their dissolution kinetics. Mercury release by EDTA from HgS-contaminated soil increased with time of reaction and soil mercury level. This chelating chemical increases the solubility of mercury in HgS-contaminated Oak Ridge soil.

Figure 10. Relationship between concentrations of mercury in earthworms (both mature and immature) and non-cinnabar (with 4M HNO₃) and cinnabar mercury (with HCl:HNO₃:H₂O, 1:6:7) in surface floodplain soils from Oak Ridge, Tennessee, USA.

Earthworms play an important role in carbon recycling and maintenance of soil fertility and texture through decomposing organic residuals and mechanical mixing. They are essential to maintain good physical soil characteristics and balance soil aeration, water permeability, and mineral turnover. In addition, earthworms are key components in natural food chains, providing a food source for many small mammals and important food sources for small birds. The present study indicates that the native earthworms grown in the field mercury contaminated floodplain soils is a better estimate of mercury bioavailability and bioaccumulation in risk assessment than using freshly spiked contaminated soils as reported in the literature [29].

SUMMARY

The present study clearly shows that the total mercury in floodplain soils of EFPC significantly decreased after a series of remediation, especially after excavation of the highly contaminated soils/sediments along the creek. The major mercury in the current floodplain soils of EFPC decades after remediation is mainly in non-cinnabar mercury bound in clay minerals. This form is not so stable as cinnabar form, but less bioavailable than other solid-phase components. The results also show linear relationships between mercury concentrations...
in earthworms (both mature and immature groups) and non-
cinnabar mercury form, which is less bioavailable to
earthworms. Native earthworms may be used as a potential
ercury ecological bio-indicator (bio-marker) for
demonstrating mercury bioavailability and ecotoxicity. Long-
term monitoring mercury bioavailability and speciation in
floodplain soils is of importance since these soils act as both a
medium-term sink and a long-term source to downstream
mercury. The long-term stability, mobility and bioavailability of
mercury contaminants in these floodplains still needs to be
monitored continuously and closely.

ACKNOWLEDGMENTS

We wish to thank Michael Parsons (ICET) for sampling
assistance. This research is supported by U.S. Department of
Energy’s Office of Environmental Management through
Cooperative Agreement DE-FC01-06EW-07040.

REFERENCES

1. J.O. NRIAGU, “Global inventory of natural and
anthropogenic emissions of trace metals to the
assessment of worldwide contamination of the air,
water and soils with trace metals,” Nature 333, 134-
139 (1988).
3. J.M. BEWERS, P.J. BARRY, and D.J.
MACGREGOR, “Distribution and cycling of
cadmium in the environment,” In J.O. Nriagu and J.B.
Sprague (eds), Cadmium in the aquatic environment
4. F.X. HAN, A. BANIN, Y. SU, D.L. MONTS, M.J.
PLODINEC, W.L. KINGERY, and G.B. TRIPLETT,
“Industrial age anthropogenic inputs of heavy metals
into the pedosphere,” Naturwissenschaften 89, 497-
504 (2002).
5. USEPA, “National Listing of Fish Advisories.
General Fact Sheet: 2008 National Listing.”
html#listing (2008).
6. USDOE, Report on the Remedial Investigation of the
Upper East Fork Popular Creek Characterization
Area at the Oak Ridge Y-12 Plant, Oak Ridge,
Tennessee, Volume I, DOE/OR/01-1641/V1&D2, pp.
3-10 to 3-106.
http://newweb.ead.anl.gov/techcon/Projects/mercury/
7. F.X. HAN, Y. SU, D.L. MONTS, C.A. WAGGONER,
and M.J. PLODINEC, “Binding, Distribution, and
Plant Uptake of Mercury in a Soil from Oak Ridge,
Tennessee, USA,” Science of the Total Environment
368, 753-768 (2006).
8. R.R. TURNER, C.R. OLSSEN, and W.J. WILCOX,
JR., “Environmental fate of Hg and 137-Cs
discharged from Oak Ridge facilities,” In: Hemphill
DD, editor. Trace Substances in the Environment
(Elsevier/North-Holland Biomed. Press, New York,
1985).
9. USEPA, “National Priorities List for Uncontrolled
Hazardous Waste Sites,” Federal Register 54 (223),
10. E. PHILIPS, “Upper East Fork Poplar Creek
Watershed,” US Department of Energy Mercury
of Ecological Recovery,” US Department of Energy
Mercury Workshop, Oak Ridge, TN, November,
2004.
12. US DEPARTMENT OF HEALTH AND HUMAN
SERVICES, Public Health Assessment, Y-12
Uranium |Release, Oak Ridge Reservation (USDOE),
Oak Ridge, Anderson County, Tennessee,
http://www.atsdr.cdc.gov/hac/PHA/oakridgey12/oak_t
13. D.L. SPARKS, Methods of Soil Analysis, Part 3,
Chemical Methods (American Society of Agronomy,
metal chemistry in arid-zone field soils amended with
sewage sludge: I. Fractionation of Ni, Cu, Zn, Cd,
and Pb in solid phases,” Soil Science Society of
transformations and redistribution of potentially toxic
heavy metals in arid-zone soils. I: Under saturated
conditions,” Water, Air & Soil Pollution 94, 399-
423 (1997).
16. M.L. JACKSON, Soil Chemical Analysis (Prentice
17. F.X. HAN, B.B.M. SRIDHAR, D.L. MONTS, and Y.
SU, “Phytoavailability and toxicity of trivalent and
hexavalent chromium to Brassica juncea L. Czern.,”
18. A. TESSIER, P.G.C. CAMPELL, and M. BISSON,
“Sequential extraction procedure for the speciation of
particulate trace metals,” Analytical Chemistry 51,
19. L.M. SHUMAN, “Separating soil iron- and
manganese-oxide fractions for microelement
analysis,” Soil Science Society of America Journal
46, 1099-1102 (1982).
20. F.X. HAN, A. BANIN, W.L. KINGERLY, G.B.
TRIPLETT, L.X. ZHOU, S.J. ZHENG, and W.X.
DING, “New approach to studies of redistribution of
heavy metals in soils,” Advances in Environmental


26. NCEDR Workshop on Decision-Making Related to the Clean-up of Mercury Contamination at Lower East Fork Poplar Creek, Oak Ridge, TN, August 14, 1996.

