

Addendum to the East Fork Poplar Creek – Sewer Line Beltway Remedial Investigation Report



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**Addendum to the East Fork Poplar Creek — Sewer Line Beltway
Remedial Investigation Report**

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ACRONYMS

AET	adverse effects threshold
ARAR	applicable or relevant and appropriate requirement
AWQC	ambient water quality criteria
BAF	bioaccumulation factor
BR	Bruner site
BRA	baseline risk assessment
CC	comparison concentration
CERCLA	Comprehensive Environmental Response, Compensation, and Liability Act
COC	contaminant of concern
DOE	U.S. Department of Energy
DQO	data quality objective
ECAO	Environmental Criteria and Assessment Office
EDS	energy dispersive spectrometer
EDTA	ethylenediametetraacetic acid
EFK	East Fork Kilometer
EFPC	East Fork Poplar Creek
EMSL	Environmental Monitoring Systems Laboratory
EP	equilibrium partitioning
EPA	U.S. Environmental Protection Agency
ERA	ecological risk assessment
FS	feasibility study
ICP-MS	inductivity coupled plasma-mass spectrometry
IT	International Technology Corporation
LOAEL	lowest observable adverse effects level
NAA	neutron activation analysis
NEPA	National Environmental Policy Act
NO	NOAA site
NOAA	National Oceanic and Atmospheric Administration
NOAEL	no observed adverse effects level
ORNL	Oak Ridge National Laboratory
PCB	polychlorinated biphenyl
PDF	probability density function
PP	Proposed Plan
QA	quality assurance
RAF	relative absorption factor
RAGS	<i>Risk Assessment Guidance for Superfund</i>
RCRA	Resource Conservation and Recovery Act
RfD	reference dose
RGO	remediation goal option
RI	remedial investigation
RTA	rotary thermal apparatus
SAED	selected area electron diffraction
SAIC	Science Applications International Corporation
SARA	Superfund Amendments and Reauthorization Act
SEM	scanning electron microscopy
SLB	Sewer Line Beltway
SOP	standard operating procedure

SQC	sediment quality criteria
TBC	to be considered
TCLP	toxicity characteristic leaching procedure
TDEC	Tennessee Department of Environment and Conservation
TEM	transmission electron microscopy
WC	White Oak Creek
XRD	X-ray diffraction
XRF	X-ray fluorescence

EXECUTIVE SUMMARY

This addendum to the *East Fork Poplar Creek - Sewer Line Beltway Remedial Investigation Report* (DOE 1994) fulfills several purposes in further defining and ensuring the completeness of the investigation and risk associated with the contaminants in the East Fork Poplar Creek (EFPC) floodplain. To verify that the EFPC remedial investigation (RI) addressed all potential contaminants of concern, the classified chemicals used by the Y-12 Plant and their potential for release into EFPC were assessed. Several studies were conducted to provide additional evidence of the chemical form of the mercury in the floodplain and to refine the available information concerning the transfer of mercury among the ecological receptors. This information was then used to develop a series of both human health and ecological remediation goal options (RGOs) for the risk managers to use in selecting the remediation level for the Record of Decision.

The purpose of the EFPC RI Report issued in January 1994 was to assess the nature and extent of the contamination within the boundaries of the 100-year floodplain of EFPC and to determine the risk to human health and the environment. Though the majority of the effort in the site characterization phase of the RI was spent determining the extent and distribution of mercury and other contaminants, specific studies were also performed to assess the form, or species, of mercury in the floodplain soils. These studies indicated that the mercury within the soil column may have been naturally altered to a mixture of compounds that differ in properties (such as solubility, bioavailability, mobility, toxicity, etc.) from mercuric chloride, which was the basis for the default assumptions that were incorporated into the baseline risk assessment. Determining the form of mercury allows environmental scientists to incorporate site-specific values into the risk assessment process when considering biological uptake and toxicity.

After the RI Report was issued, four mercury speciation studies were undertaken to provide additional evidence of the predominant chemical forms of mercury in the EFPC floodplain soils: (1) a sequential extraction study by EPA's Environmental Monitoring Systems Laboratory in Las Vegas; (2) a gastrointestinal simulation by the Environmental Sciences Division of the Oak Ridge National Laboratory; (3) a study to unequivocally identify mercuric sulfide (i.e., metacinnabar) in EFPC soil by the K-25 Materials Science Department; and (4) a thermal release study by International Technology (IT) Corporation.

Conclusions from these studies indicate that the mercury in EFPC is in a form that is not readily available for biological uptake and that the predominant forms are mercuric sulfide and metallic mercury. Evidence includes the co-location of mercury and sulfur in proportions that would be expected for mercuric sulfide, soil conditions that are favorable to the formation of mercuric sulfide, and thermal release properties that are representative of mercuric sulfide. The EPA Environmental Monitoring Systems Laboratory, using a mercury speciation protocol under development, indicated that metallic mercury is the major species present. Regardless of the actual form, the gastrointestinal simulation indicated that the solubility of the mercury compound(s), and hence the biological availability, was a very low percentage of the total mercury present. All of the studies support the conclusion that mercury is in one or more of the relatively insoluble forms.

Following EPA guidance and methods, an initial RGO of 50 (rounded down from 58) mg/kg (ppm) of mercury in soil was calculated on the basis of the site-specific exposure assumptions that children are the most sensitive receptor group and that ingestion and dermal contact are the exposure pathways of greatest significance. Originally, the EPA-recommended oral absorption

factor of 100% was used to calculate the RGO because an EPA-verified or accepted method to justify a reduced factor was not available. Thus, the relative bioavailabilities or absorption efficiencies of the various chemical forms of mercury in the floodplain soil were not considered in the RI. Both mercuric sulfide and metallic mercury are considerably less mobile and bioavailable than mercuric chloride, the toxicity value of which is used in the risk assessments to determine the RGO.

In parallel with the development of the RI Report, decisions were made at three mercury-contaminated sites in California that support the use of an efficiency factor to account for the difference in the bioavailability of the various forms of mercury in soils. This same approach, applied to EFPC with a 30% bioavailability factor, results in a calculated RGO of 180 mg/kg for the most sensitive receptor.

For the ecologically based RGOs, the speciation information and the results of additional field studies and literature research are used to develop a range of RGOs that can be used by the decision makers based on the level of protectiveness desired. One study, "Wetlands Study," provides data on the bioaccumulation factors from soil to an organism for use in the RGO development, and a second study, "Food Web Study," addresses the potential transfer of contaminants in the lower portions of the EFPC aquatic food web. A third study, "Sediment Chronic Toxicity," was conducted to help determine whether the sediment is a likely contributor to the contaminant impacts previously observed on fish and benthic community structures.

The additional data on bioaccumulation of mercury from EFPC soils and other soil/body burden relationships and the data derived from literature were integrated into an expanded ecological evaluation to develop protective RGOs at four different trophic levels under three distinct scenarios. The trophic groups are top predators, mid-level predators, first-level consumers, and vegetation. The scenarios range from upper-bound exposure, which is mathematically contrived to maximize exposure, to lower exposure, which uses less conservative assumptions based on data. Calculated soil RGOs, matrixed by scenarios and trophic groups, range from 1.6 mg/kg of mercury in soil for protection of the mid-level predators under the upper-level exposure scenario to > 440,000 mg/kg of mercury in soil for protection of plants in the lower exposure scenario. Model calculations showed that under reasonably conservative exposure conditions, mid-level predators were the most sensitive trophic group and, therefore, require the lowest soil mercury RGOs to protect them.

Proposed RGOs for total mercury that would be realistically protective of mid-level predators under each scenario would automatically also protect top predators, first-level terrestrial consumers, and plants. They are:

- Scenario 1 (upper-bound exposure): 3.3 mg/kg,
- Scenario 2 (intermediate exposure): 30 mg/kg,
- Food chain scenario (DOE 1994): 200 mg/kg, and
- Scenario 3 (lower exposure): 300 mg/kg.

These proposed RGOs will be evaluated further in the EFPC FS.

This addendum, in conjunction with Sect. 7 of the RI Report, provides the decision makers with ranges of human-health-based and ecologically derived RGOs. These RGOs are option values, all of which are protective by EPA definition, from which a risk manger can apply the nine CERCLA criteria to select the remediation level for the Record of Decision.

1. INTRODUCTION

1.1 INTRODUCTION

Lower East Fork Poplar Creek (EFPC), the associated floodplains, and the Sewer Line Beltway (SLB) have been directly and indirectly contaminated as a result of past releases of mercury from the Oak Ridge Reservation Y-12 Plant. In December 1989, the U.S. Environmental Protection Agency (EPA) placed the Oak Ridge Reservation, including EFPC, on the National Priorities List, thus requiring remediation under the Comprehensive Environmental Response, Compensation, and Liability Act (CERCLA) and the Superfund Amendments and Reauthorization Act (SARA) of 1986. In addition, because the remediation of EFPC may significantly affect the environment, the U. S. Department of Energy (DOE) is considering the potential environmental impacts by integrating the evaluation of National Environmental Policy Act (NEPA) values into the CERCLA process.

DOE's integrated approach results in the preparation of several major documents, including the Remedial Investigation (RI) report, the Feasibility Study (FS), and the Proposed Plan (PP). Following resolution of the comments on the D1 version, the D2 draft of the RI Report (DOE 1994) was issued to EPA and the Tennessee Department of Environment and Conservation (TDEC) in January 1994. This addendum to the RI Report, which supplements the information in that report, was developed to be responsive to suggestions by the regulatory reviewers and input from involved citizens requesting additional information.

1.2 PURPOSE

This addendum to the RI Report presents the results of additional studies that were performed to support and further delineate the recommended remediation goal options (RGOs) to be used for identifying the need for remedial action. These studies also included a review of classified chemicals utilized at the Y-12 facility to ensure that the list of chemicals investigated during the EFPC RI is complete and that there are no contaminants of concern (COCs) other than those previously identified.

The process of deriving an RGO for human health effects consists of establishing an acceptable target risk value for exposure to a contaminant and back-calculating the corresponding concentration in the environmental media under evaluation. Following EPA guidance and methods, an initial RGO of 50 (rounded down from 58) mg/kg (ppm) of mercury in soil was calculated based on the site-specific exposure assumptions that children are the most sensitive receptor group and that ingestion and dermal contact are the exposure pathways of greatest significance. A bioavailability factor of 100% was used to calculate the 50-mg/kg RGO because an EPA-verified or accepted method to justify a reduced factor was not available at the time the D2 draft of the RI Report was issued. The relative bioavailabilities or absorption efficiencies of the various chemical forms of mercury in the floodplain soil were not considered in the RI. The toxicity value for mercury that was used in the baseline risk assessment (BRA) to determine the RGO was based on exposure to mercuric chloride. Mercuric sulfide and metallic mercury, the predominant forms of mercury in the EFPC soils, are considerably less mobile and bioavailable than mercuric chloride.

In parallel with the development of the RI Report, regulatory decisions were made at three mercury-contaminated sites in California that support the use of an efficiency factor to account for the difference in the bioavailability of the various forms of mercury in soils (CDM 1993). Through this addendum, this same approach is now being recommended for calculating a revised RGO for identifying the need for remedial action on EFPC floodplain soil that is considered residential or agricultural land.

To provide better evidence of the predominant chemical forms of mercury in the EFPC floodplain soil and thus further justify the use of the proper absorption factor, several mercury speciation studies were conducted by EPA's Environmental Monitoring Systems Laboratory in Las Vegas, the Environmental Sciences Division of the Oak Ridge National Laboratory (ORNL), the K-25 Materials Science Department, and International Technology (IT) Corporation.

This addendum presents the results of these mercury speciation studies and provides the justification for the use of a bioavailability factor of 30% in the human health risk assessment. This adjustment would result in an alternate RGO of 180 mg/kg of mercury for the scenarios involving ingestion and dermal contact by a child. Using the 180-mg/kg RGO as an action level for residential and agricultural lands would significantly reduce the amount of contaminated floodplain soil that would be above the action level and, thus, require remediation.

In addition to the mercury speciation studies, three studies are being conducted to improve the understanding of the interactions of EFPC contaminants with ecological receptors. One study, "Wetlands Study," focuses on the unique conditions found in the EFPC wetlands and a second study, "Food Web Study," addresses the potential transfer of contaminants in the lower portions of the EFPC food web. Additionally, a "Sediment Chronic Toxicity Study" was performed to directly measure potential toxicological effects from the sediments.

1.3 ORGANIZATION

Section 2 of this addendum describes the technical basis and approach for the special studies undertaken and presents the results and conclusions. In Sect. 3, the conclusions drawn from each of the studies are used to derive new RGOs based on the human health risk assessment parameters for the most sensitive receptor. For the ecological risk assessment (ERA), the speciation information and the results of the wetlands and food web studies are used to develop a range of RGOs that can be used by the decision makers based on the level of protectiveness desired.

Section 3.3 of this addendum briefly discusses the risk management use of the ranges of RGOs derived from the information provided by the special studies.

2. SPECIAL STUDIES

This section describes the various special studies that were conducted in early 1994 to support both the human health and the ecological risk assessments. Section 2.1 describes a series of investigations performed to determine or further strengthen the weight of evidence that mercury in the EFPC floodplain is in a form that is neither readily mobile nor bioavailable. Section 2.2 describes the sampling effort and summarizes the data of a wetlands study, the results of which have been used to refine transfer coefficients for the ERA. Section 2.3 presents a food web study conducted by the Environmental Sciences Division at the K-25 Site. Section 2.4 describes an ongoing sediment chronic toxicity study. Each of these studies is presented in a summary manner, focusing on integration of the data and conclusions into both the human health and the ecological risk assessments. Each study will be published as an independent report that will more fully present the data and data analysis.

2.1 MERCURY SPECIATION

2.1.1 Introduction

The purpose of the EFPC RI Report is to assess the nature and extent of contamination within the boundaries of the 100-year floodplain of the creek and to determine the risk to human health and the environment. Though the majority of the effort in the site characterization phase of the RI was spent in determining the extent and distribution of mercury and other contaminants, specific studies were also performed to assess the form, or species, of the mercury in the floodplain soils. These studies indicate that the mercury within the soil column may have been naturally altered to a mixture of compounds that differ in properties (such as solubility, bioavailability, mobility, toxicity, etc.) from mercuric chloride, which was the basis of the default assumptions that were incorporated into the BRA. The study of a particular compound in trace quantities—especially one with unique properties such as mercury—and the determination of the relative proportions of each compound is not a straightforward or simple task. Much of the information about the form of mercury is derived from behavioral observations or empirical associations. Direct investigative techniques for submicron-sized particles are limited.

Determining the form of mercury allows environmental scientists to incorporate compound-specific reference values into the risk assessment process when considering biological uptake and toxicity. As an alternative to investigating the form of mercury, data were compiled on the solubility and bioavailability of mercury compounds in the EFPC soils. This line of investigation incorporates the site-specific properties of the soil medium without absolute determination of the mercury form.

This section of the addendum presents the approach to mercury speciation that was used during the RI and results from studies conducted since the RI Report was submitted in January 1994. Conclusions concerning the probable form of mercury are presented. These conclusions are incorporated into the risk assessments of Sect. 3 and then used in the development of site-specific RGOs.

2.1.2 Mercury Speciation Approaches

The methods used to characterize the forms of mercury in the EFPC soils include X-ray diffraction (XRD); optical microscopy and scanning and transmission electron microscopy (SEM/TEM); X-ray fluorescence (XRF); and sequential/selective chemical extraction. The level of confidence attributed to each technique ranges from unequivocal "fingerprinting" of the crystal structure to operational definitions that suggest that the mercury compound in question "behaves like" a pure reference compound. A brief discussion of each investigative method and the type of information that can be obtained from its use follows.

XRD. The most reliable technique for identifying a crystalline substance is XRD. A sample is subjected to a monochromatic X-ray beam, causing electrons in the path of the primary beam to emit X-rays, which are scattered in a characteristic manner by the unique lattice structure of the compound. Several conditions must exist for this method to be successful. The material must be in a crystalline or near-crystalline form. The compound must exist in sufficient quantity and the crystals must be of sufficient size to make the reflections distinguishable from background noise. Positive identification can be inhibited by coincident peaks of other compounds; therefore, secondary peaks must be employed for identification.

Optical microscopy, SEM, TEM. Electron microscopy provides evidence on the petrography, morphology, and chemistry of the soil. Combined with analytical capabilities, it can be used to analyze individual contaminant particles and ascertain elemental associations. Electron microscopy can also be used in conjunction with microdiffraction to identify crystalline materials.

XRF. XRF, used with SEM, provides quantitative and semiquantitative analyses of element composition and corresponding elemental associations.

Sequential/selective chemical extraction methods. Sequential/selective chemical extraction methods provide an operational definition of a compound by comparing the responses of compounds in soils to extractive solutions with the responses of reference materials to extractive solutions (see Table 2.1 for a matrix of solutions versus mercury forms used in EFPC extraction studies). The technique is usually calibrated by dosing uncontaminated soil with a pure compound and then observing the success of an extractive solution. This method can be complicated by compound interferences, nonuniform mixtures, or matrix interactions. Though this method of speciation constitutes the largest data set for the EFPC soils, it is subject to the most uncertainty of the above procedures.

The methods discussed in this section were used to provide as much information about the mercury form, species, and solubility as possible. No one method provides the absolute proof that mercury resides in a particular form throughout the 23 km (14.5 miles) of floodplain; however, in combination, the weight of evidence indicates that mercuric sulfide and metallic mercury are the most dominant species within the soils. It has been conclusively shown that the amounts of organic mercury compounds and soluble forms of mercury, such as mercuric chloride, are negligible and that their contributions to the total mercury toxicity are insignificant.

Table 2.1. Comparison of selective/sequential extraction schemes^a for mercury speciation in soil/sediment

Form extracted/recovered	Revis et al. 1989	Radian/SAIC 1992	EPA/EMSL 1994	Sakamoto et al. 1992	
Metallic mercury	5 d @ 150°C	30 min wet purging	1:3 HNO ₃	ND ^b	
Mercuric sulfide	Sodium sulfide (Na ₂ S) after 12 M HNO ₃	Sodium sulfide (Na ₂ S) after 12 M HNO ₃	HCl + HNO ₃ (aqua regia)	Acidic CuCl in 3% NaCl	
Methyl mercury	Toluene extract, gas chromatography	KOH/methanol extract, ethylation, CVAFS	ND	ND	
Mercuric oxide	12 M HNO ₃ digest	12 M HNO ₃ digest	0.2 M HNO ₃	0.05 M H ₂ SO ₄	
Mercurous oxide		30 min wet purging	ND	ND	
Mercuric chloride		Ethanol extract	0.01 M K ₂ SO ₄ + 0.01 M KCl from toluene	ND	ND
Mercurous chloride		Included with 12 M HNO ₃ digest	HCl + HNO ₃ (aqua regia)	ND	ND
Mercury amalgams			1:3 HNO ₃	ND	ND
Organic mercury			Toluene	0.01 M Na ₂ S ₂ O ₃ from chloroform	

^a Schemes are simplified here to conserve space. See reference for details.

^b ND means "Not Determined."

2.1.3 RI Report Studies

The following is a synopsis of the data presented in Sect. 3 of the RI Report:

Toxicity Characteristic Leaching Procedure (TCLP). Several samples were subjected to the TCLP, which simulates leaching in slightly acidic rainwater conditions. Though total mercury concentrations in the soil samples were in the 1000- to 2000-mg/kg range, no concentrations of mercury above the analytical detection limit (0.1 ppm) were extracted from EFPC soil.

Treatability Study. As part of the bench-scale treatability tests (Radian 1993) to select a suitable technique for treating the mercury-contaminated soils, extraction studies were performed using a variety of solutions. The list included distilled water, synthetic acid rain water, nitric acid, hydrochloric acid, hydrobromic acid, acetic acid, ethylenediametetraacetic acid (EDTA), citric acid, ammonium hydroxide, sodium hypochlorite, thiourea, and a proprietary reagent using potassium iodide (KI/I₂). Very little mercury is extracted with the above leaching agents, with the exception of unique compounds such as hydrobromic acid, sodium hypochlorite, or the potassium iodide solution, which are not indigenous to the natural environment.

Revis et al. 1989b. Revis demonstrated the effectiveness of sodium sulfide as a selective extractant for mercuric sulfide (see Table 2.1) after a 12-M nitric acid extraction of all other inorganic mercury forms and used a thermal treatment [150°C (302°F) for 5 d] to measure the elemental mercury content in separate portions of the soils. These measurements demonstrated that 3 to 8% of the mercury is in elemental form, 84 to 98% is in mercuric sulfide form, and 0.003 to 0.010% is methyl mercury (determined by direct extraction and gas chromatography).

Methyl mercury analyses by Brooks Rand Laboratory. Three samples were taken in the areas of highest mercury content in the EFPC floodplain and submitted to the Brooks Rand Laboratory for methyl mercury analysis by tetraethylborate derivitization and atomic fluorescence spectroscopy. Results ranged from 0.002 to 0.004% of total mercury and are commensurate with the Revis work. The overriding conclusion of the RI is that methyl mercury constitutes a minor fraction of total mercury and, although it may be significant for ecological exposures, it is not of concern to human health in the floodplain environment.

Optical microscopy and SEM. Twenty samples were obtained along the length of the floodplain and submitted for both optical microscopy and SEM. Soil cores were inspected under the optical mount for soil morphology, structure, and content. Fly ash and coal fragments were found to be more abundant in the mercury-rich samples and to be less abundant in those samples with less mercury. It is postulated that fly ash, coal fragments, and mercury are transported together and represent releases to the creek during the same time frame; however, no physical or chemical relationship could be established between the mercury and the ash material. Moreover, no genetic or characteristic differences were observed for the various samples over the length of the creek or in relation to the amount of mercury present (with the exception of the aforementioned correlation with fly ash).

SEM was employed to detect, image, and microanalyze the mercury-bearing matter in the soil samples. Backscatter electron images (dot maps indicating locations of elemental concentrations) displayed a strong association (co-location) between mercury and sulfur in all of

the samples. Additional microprobe work on a number of individual soil particles indicated a sulfur-to-mercury mole ratio in the 0.90 range, compared to a value of 0.98 for a cinnabar (mercuric sulfide) standard. The consistent similarity of the observed ratio to a mercuric sulfide standard would not be expected if only a physical association of elemental mercury and sulfur existed.

Current risk assessment dose calculations for mercury are based on mercuric chloride, a soluble form of mercury not expected to exist in the EFPC environment. The above data, gathered for the RI Report, indicate that mercury within the EFPC floodplain is in a relatively insoluble form and is probably complexed with sulfur in some form (probably mercuric sulfide).

2.1.4 Post-RI Report Studies

After the January 1994 draft of the RI Report was completed, several studies were performed to define the predominant form of mercury in EFPC floodplain soil. The following studies provide additional insight into the species and biological availability of the mercury in the EFPC floodplain. Inconsistencies between observed results and the assumptions incorporated into the development of RGOs indicated additional work was needed to fill a data gap. Discussions were held with researchers at ORNL and scientists at DOE's K-25 Site Materials Science Department and EPA's Environmental Monitoring Systems Laboratory in Las Vegas to seek more definitive methods to speciate the dominant form of mercury and/or to characterize its biological availability. The following is a summary of the results from those investigations. A separate report containing a complete discussion of the methods, results, and conclusions will be published for each study. These reports will be contained within the EFPC project file as part of the administrative record file.

Bioavailability study. A bioavailability study was conducted by Dr. Ralph Turner of the Environmental Sciences Division at ORNL to determine the fraction of mercury in EFPC soils that is available for absorption in the human digestive system, the most sensitive route of human exposure. The bioavailability study was designed to simulate the human digestive system and was adapted from another study, the Almaden Quicksilver County Park Risk Assessment, Santa Clara County, California (CDM 1993), which has undergone review by the State of California. The following is a condensation of Dr. Turner's report.

Two samples were obtained at each of 10 locations (Fig. 2.1) along the EFPC floodplain to represent the range of possible environments along the length of the creek. Locations were also selected to coincide with significant concentrations of mercury (> 50 mg/kg). At each location, samples were collected to represent the surface horizon and a subsurface soil horizon. The first sample was collected from 0 to 7.5 cm (0 to 3 in.) to provide evidence for the form of mercury that would most likely exist in an oxidizing environment and that would relate to a direct soil exposure pathway. The second sample was collected from a deeper stratum (see map for actual depths) that appeared to contain the highest mercury concentration. If the location was situated in an area where the water table was near the surface, the second soil sample was obtained below the water level.

In the laboratory, samples were air dried at room temperature [22 to 24°C (72 to 75°F)], lightly crushed with a mortar and pestle, and sieved to < 2 mm (0.08 in.) to remove rocks, roots, etc. The samples were then crushed to < 180 μm and subsampled for total mercury (SW-846

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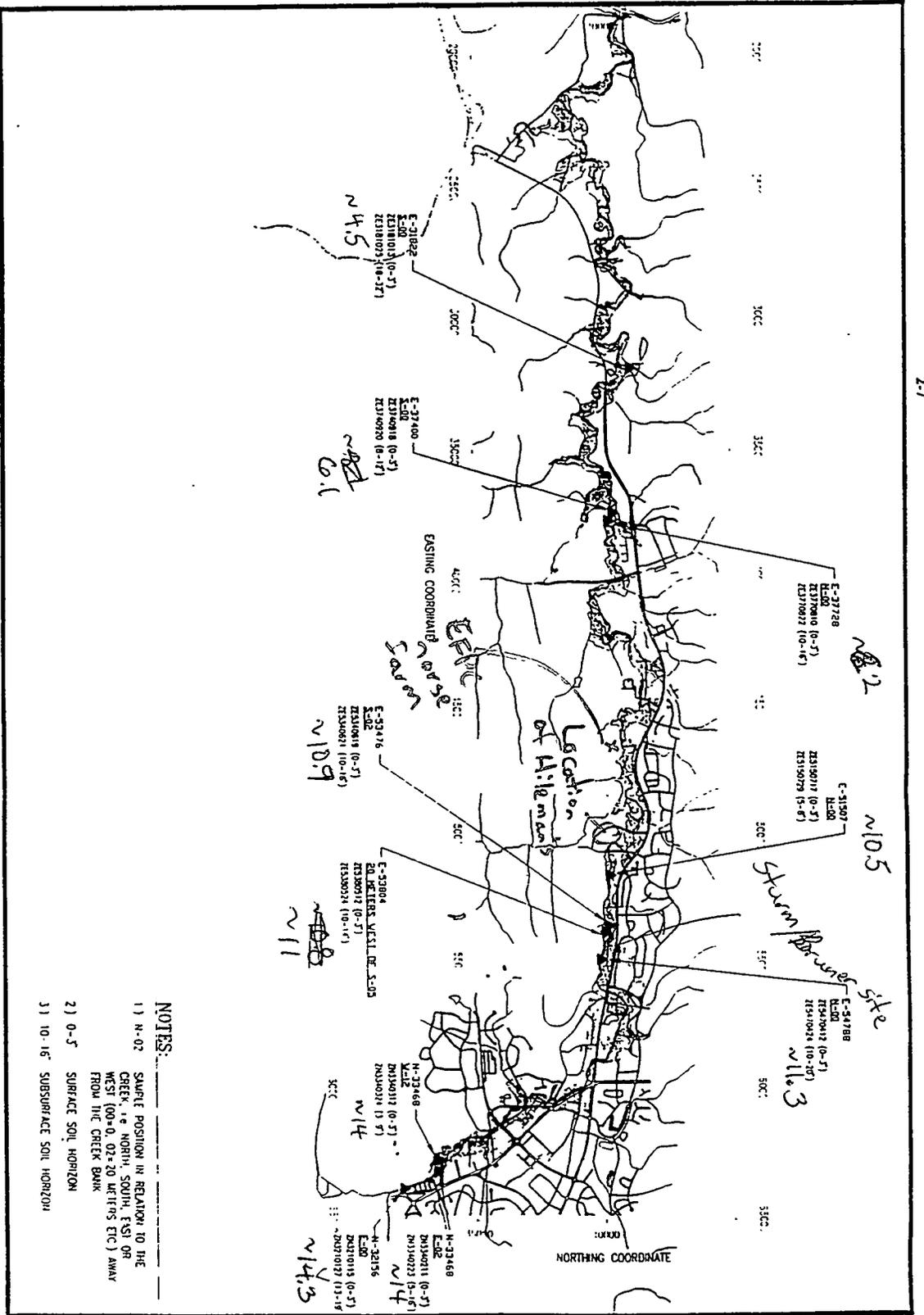


Fig. 2.1. Sample location for mercury speculation and solubility studies.

SAIC
Science Applications
International Corporation

**EAST FORK
POPLAR CREEK
OAK RIDGE, TENNESSEE**

SCALE 1" = 4000'

0 2000 4000 8000

OR ADJUT. GRID
TRUE NORTH

NOTE:

1) SAMPLE LOCATIONS RECEIVED FROM MERCURY SPECIATION LOG BOOK, JANUARY-FEBRUARY 1994 (SAC TRACKING #1331 930200 022)

REV.	DESCRIPTION	DATE

REV.	DESCRIPTION	DATE

SAIC
10100
10100
10100

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Method 7471), total carbon, and total sulfur. Aliquots of each soil sample were added to distilled, deionized water adjusted to pH 2.5 with 16 N hydrochloric acid. The samples were shaken and the pH was maintained for 4 h. After 4 h, the samples were allowed to settle and a portion of the supernatant was passed through a 0.20- μ m filter. The filtrate was preserved and submitted for analysis of total mercury.

The remaining soil-solution suspension was combined with distilled, deionized water to the original solid/solution ratio and the pH was adjusted to 6.5 with sodium hydroxide. Using the procedure described above, filtrate samples were taken after 4 h and submitted for mercury analysis. As a check of potential variables that might affect the results, the leaching procedure was repeated for samples such as: (1) as-received moist soil, (2) soil maintained at body temperature [37°C (98.6°F)] during leaching, and (3) soil with 10 mg/L deoxycholic acid-added (constituent of the human digestive system). Also tested as control standards were mercuric chloride and mercuric sulfide in both cinnabar and metacinnabar forms.

Mercury concentrations in these soil samples ranged from 15 to 2700 mg/kg and sulfur concentrations ranged from 26 to 1700 mg/kg. The predominant form of mercury is indicated from other studies to be mercuric sulfide. In 19 of 20 samples, sufficient sulfur was present to bind all of the mercury as mercuric sulfide, and mercury is significantly correlated with sulfur ($r=0.84$) in the 20 samples. By removing the sample with the maximum value (ZN3210127), the mercury-sulfur correlation becomes very strong ($r=0.92$). With the exception of the one sample, significant mercury was not extracted at either pH. Less than 5% of the mercury solubilized in 15 of the samples. Total soluble mercury for the 19 samples ranged from 0.3 to 14.2%, with an average of 3.2% (Table 2.2).

The remaining sample, apparently geochemically different from the other samples, leached significantly more mercury. Of the total mercury concentration in this sample (2700 mg/kg) 570 and 300 μ g/L were removed at pHs of 2.5 and 6.5, respectively, for a combined percent removal of 45.9%. Furthermore, this sample was unique among the 20 samples in displaying headspace mercury volatilization at room temperature. The sample was taken at the most upstream location immediately below the outfall of the Y-12 Plant. It is inferred, because of its proximity to the Y-12 Plant, that this sample may represent deposition of mercury that is not characteristic of the downstream locations. Two other sample locations 457 m (1500 ft) downstream of this site did not display similar leaching or sample headspace mercury vapor.

The change in percent solubility for samples leached at 37°C (98.6°F) (percent leached at 37°C minus percent leached at room temperature) ranged from -7.7 to 1.8% (Table 2.3). The change in percentage mercury leached for two samples with deoxycholic acid (percent leached with acid minus percent leached without) was 1.1 and -2.1% but the total percent of mercury leached from the two samples was only 2.1 and 1.3%. Leaching of as-received moist soil showed a wide range of percentage change, though the leachate concentrations were still relatively low. For example, the soil with the largest relative increase in leachate concentration (+426%) increased from 1.50 μ g/L to only 7.9 μ g/L, well within the range of leachate concentrations of the 19 dry soils. For both the cinnabar and metacinnabar control standards, the fraction of the sample dissolved was much less than 1%. The entire mercuric chloride samples dissolved and the leachate concentrations from these samples were almost 1000 times higher than the highest soil leachate concentration (540,000 versus 570 μ g/L).

Held at each pH for 4 hrs

Adj. to w/ hydrochloric acid

Soils added to deionized water

Adj. to w/ sodium hydroxide

Table 2.2. Leachate results for dry soils

Sample	Mercury (mg/kg)	pH 2.5		pH 6.5		% Soluble total
		Mercury (µg/L)	% Soluble	Mercury (µg/L)	% Soluble	
ZN3210115	260	0.70	0.4	1.00	0.5	0.9
ZN3210127	2,700	570.00	29.3	300.00	16.6	45.9
ZN3340211	270	0.80	0.4	0.80	0.4	0.8
ZN3340223	1900	77.00	5.5	20.00	1.4	6.9
ZN3340312	230	0.20	0.1	1.80	1.1	1.2
ZN3340324	2100	30.00	1.9	11.00	0.7	2.6
ZE5470412	85	0.20	0.3	0.40	0.6	0.9
ZE5470424	1300	73.00	7.6	14.00	1.5	9.1
ZE5380512	67	1.60	3.2	1.10	2.2	5.4
ZE5380524	2100	26.00	1.7	8.20	0.5	2.2
ZE5340619	140	0.10	0.1	0.20	0.2	0.3
ZE5340621	1200	10.50	1.2	4.90	0.6	1.8
ZE5150717	230	1.80	1.1	2.60	1.5	2.6
ZE5150729	900	13.00	2.0	3.20	0.5	2.5
ZE3770810	480	2.40	0.7	1.50	0.4	1.1
ZE3770822	15.3	1.10	9.7	0.50	4.5	14.2
Z43740918	55	0.20	0.5	0.20	0.5	1.0
ZE3740920	780	14.00	2.4	5.80	1.0	3.4
ZE3181013	28	0.03	0.1	0.20	1.0	1.1
ZE3181025	390	6.30	2.2	1.90	0.7	2.9

0.9 at 37°C
38.2 at 37°C

7.9 at 37°C

10.8 at 37°C

2.1 at 37°C
2.1 w/ stom. acid
1.9 w/ stom. acid

Table 2.3. Leachate results for field-moist soils; soils at body temperature; and soils with deoxycholic acid, mercuric chloride, and mercuric sulfide.

Sample	Mercury (mg/kg)	pH 2.5		pH 6.5		% Soluble total
		Mercury ($\mu\text{g/L}$)	% Soluble	Mercury ($\mu\text{g/L}$)	% Soluble	
ZN3210127-37 ^a Body Temp	2,630	580.00	29.0	170.00	9.2	38.2
ZN3210115-37 ^a	260	0.72	0.4	1.10	0.6	0.9
ZN3340223-37 ^a	1,900	97.00	6.9	14.00	1.0	7.9
ZE3740918-37 ^a	55	0.06	0.1	0.80	2.0	2.1
ZE5470424-37 ^a ↓	1,300	88.00	9.1	16.00	1.7	10.8
ZE5470424-W ^b	1,300	110.00		27.00		
ZE3740918-W ^b	55	0.10		0.87		
ZE3770810-W ^b	480	1.20		7.90		
ZE3740920-W ^b	780	7.80		13.00		
ZE3740918-C ^c	55	0.07	0.2	0.80	2.0	2.1
ZE3740920-C ^c	780	6.50	1.1	1.10	0.2	1.3
Mercuric chloride		540,000.00	98.8	450,000.00	109.3	100.0
Cinnabar		0.34	0.0	42.00	0.0	0.0
Metacinnabar		0.05	0.0	0.50	0.0	0.0

^a Conducted at 37°C. - Body temp

^b Field-moist soils. Percentage leached not calculated because mercury measurements were not made on bulk soils.

^c With 10 mg/L deoxycholic acid.

Conclusions from this study are based on site-specific data rather than information drawn from reference materials. Although the procedure is a simple representation of a complex system, the human digestive system, the solubility, and hence bioavailability, of mercury in EFPC soils is obviously substantially different than pure mercuric chloride. Consequently, incorporation of a bioavailability factor of 1 (i.e., 100%) in the human health risk assessment may be unduly conservative.

EPA's Environmental Monitoring Systems Laboratory speciation procedure. EPA's Environmental Monitoring Systems Laboratory in Las Vegas agreed to assist DOE in the EFPC speciation effort by applying a new method under development for the speciation of mercury compounds (Miller 1993). This procedure takes advantage of sequential/selective extraction of mercury, as does the Revis method, but uses different extractive solutions in its procedure (see Table 2.1). A major difference involves the determination of metallic mercury using acid extraction. Revis first extracted all of the inorganic mercury, except mercuric sulfide, with 12-M nitric acid and then employed sodium sulfide to extract mercuric sulfide. Metallic mercury was estimated by measuring the difference between unheated and heated [150°C (302°F), 5 d] total mercury content of separate soil aliquots. The Environmental Monitoring Systems Laboratory procedure (Fig. 2.2) groups its compounds into water soluble, acid soluble, metallic/amalgamated mercury, and mercuric sulfide. Water-soluble mercury represents the mercuric chloride fraction, and the acid-soluble mercury represents the mercuric oxide portion of the soil. This method uses only aqua regia (hydrochloric acid + nitric acid), instead of sodium sulfide, to extract the mercuric sulfide fraction.

The following paragraphs summarize a report by Dobb, Miller, and Cardenas (EPA 1994b). Splits of the 20 soil samples taken for the bioavailability study were supplied to the Environmental Monitoring Systems Laboratory for speciation work. The samples were stored on ice and shipped overnight to the Environmental Monitoring Systems Laboratory's contract laboratory, Lockheed Environmental Systems & Technologies Company, for analysis. Upon receipt, the samples were dried at 45 to 50°C (113 to 122°F) and weighed to determine moisture content. The samples were pulverized to pass a 60-mesh sieve (< 250 μ m) in a tungsten carbide-lined ball mill. A 2-g (0.07-oz.) aliquot of dried and pulverized EFPC soil was processed using the Environmental Monitoring Systems Laboratory extraction procedure. After performing the extraction procedure, XRF analysis showed a 98 to 99% extraction of mercury from samples that originally contained 2000 to 3000 mg/kg of mercury. Each extract in the process was analyzed for mercury by inductively coupled plasma - mass spectrometry (ICP-MS). Mercury concentrations for each step in the process determined by ICP-MS were summed and compared with total mercury determined by cold vapor atomic absorption spectroscopy. Percent relative standard deviations ranged from 1 to 27%, and 8 out of 20 samples had percent relative standard deviations > 15%. Replicate analyses performed on two samples showed relatively close correlation. Matrix spikes indicated recoveries ranging from 102 to 115%.

Results of this sequential extraction procedure are documented in Figs. 2.3 and 2.4. No organic mercury forms were detected by the Environmental Monitoring Systems Laboratory process; however, sample preparation (e.g., drying, grinding) may have affected the test. Analyses performed by the Brooks Rand laboratory (discussed in Sect. 3 of the RI Report) confirm that organic mercury constitutes < 0.01%. Water-soluble forms (mercuric chloride) were < 1%, and most were < 0.1 to 0.3%. The 0- to 7.5-cm (0- to 3-in.) interval samples had metallic/amalgamated mercury as the principal compound, and mercuric oxide increasing in the

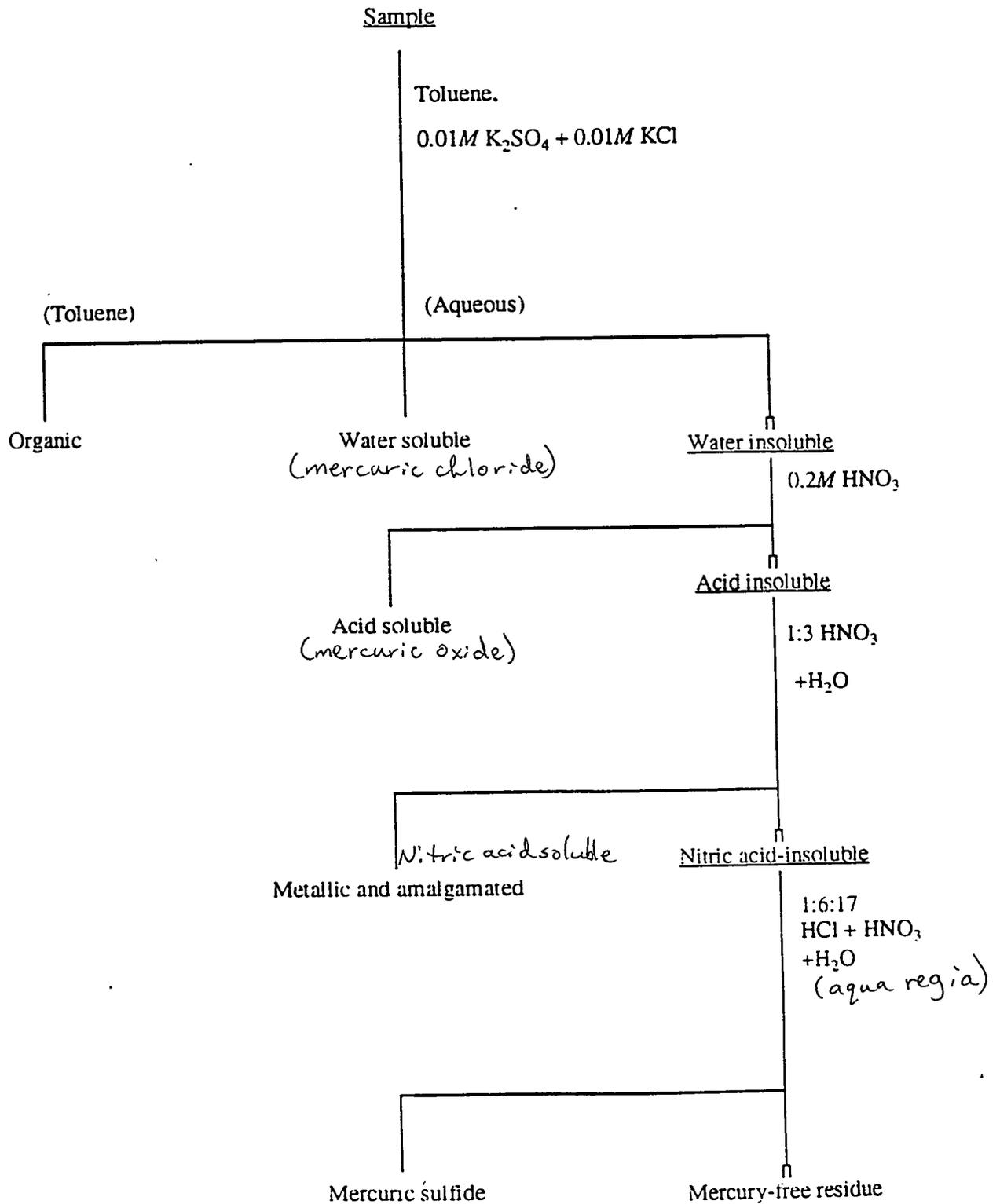


Fig. 2.2. Procedure for extracting and speciating mercury compounds in soil samples.
Note: a single vertical bar above an analyte, I, indicates a solution; a double vertical bar, II, indicates a solid.

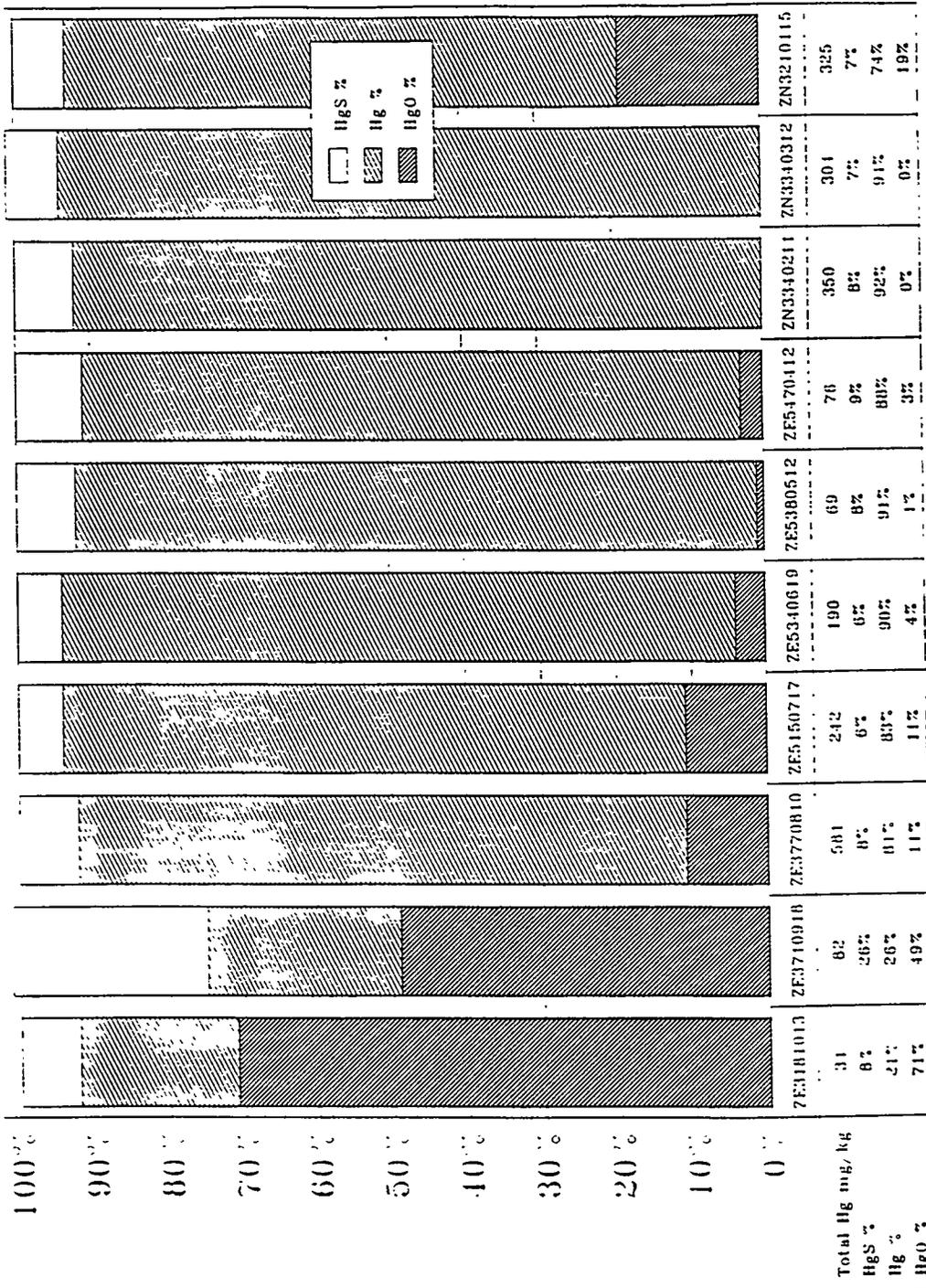


Fig. 2.3. Mercury speciation by the Environmental Monitoring Systems Laboratory extraction procedure of the surface interval (0 to 3 in.) of EFPC soils. The most upstream location is to the right.

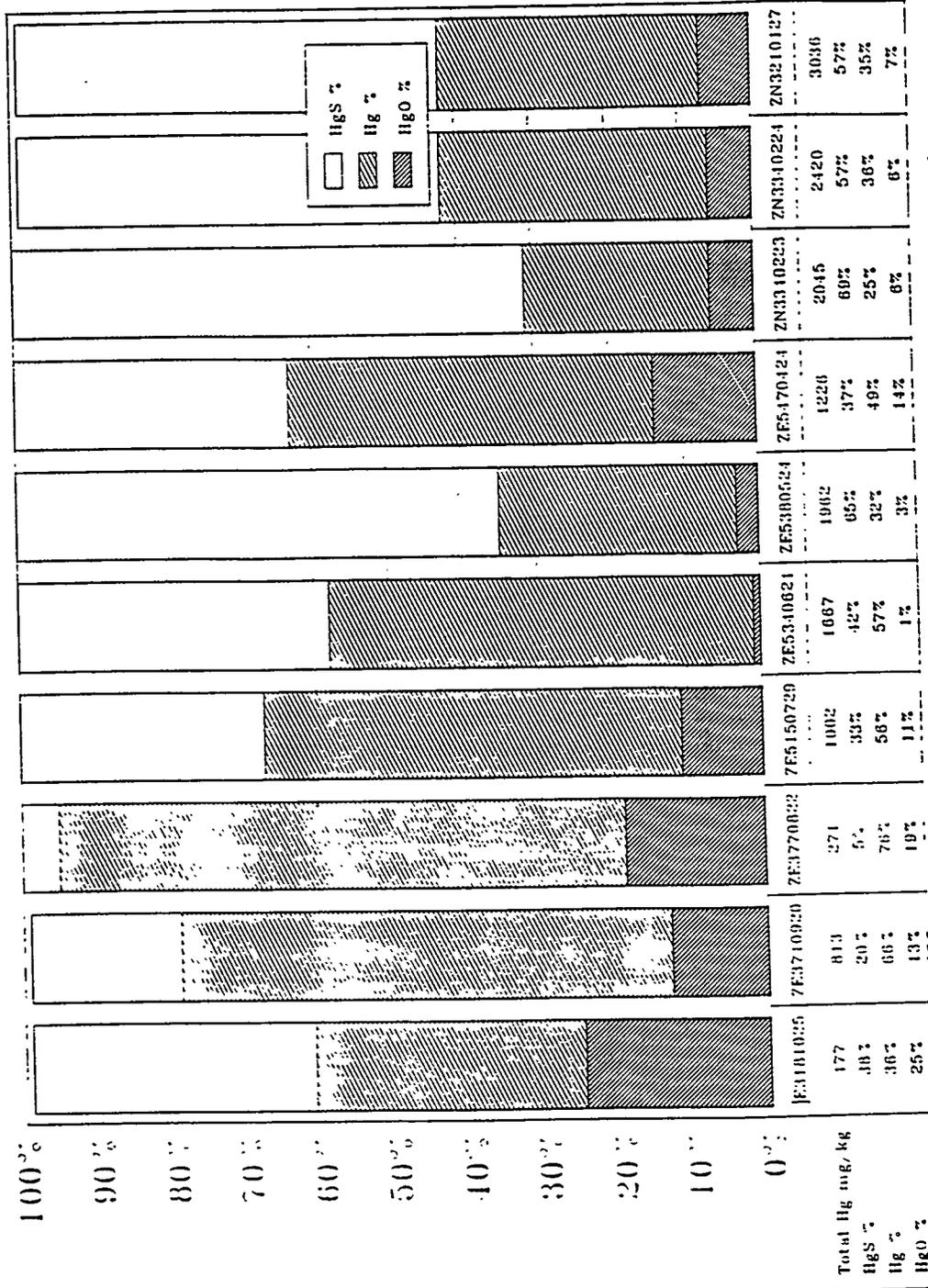


Fig. 2.4. Mercury speciation by the Environmental Monitoring Systems Laboratory extraction procedure of the deeper interval (8 to 16 in.) of EFPC soils. The most upstream location is to the right.

downstream samples. Mercuric sulfide was indicated to be < 10% in all but one of the samples from this interval. Samples from the deeper interval [- 20 to 40 cm (8 to 16 in.)] showed higher levels of mercuric sulfide, but metallic/ amalgamated mercury was still the dominant form. These results are discordant with other results. Additional laboratory work (Appendix A) and technical discussions between the Environmental Monitoring Systems Laboratory team and the EFPC team are ongoing to discern the reason.

Electron diffraction and XRD. The following is a summary of a study by the K-25 Site's Materials Science Department, which employed TEM and XRD to provide positive identification of mercuric sulfide in EFPC soils. XRD is a bulk analysis tool that requires sufficient concentrations of the compound in question; TEM can utilize low concentrations of the material. By adding selected area electron diffraction (SAED) to TEM, particles < 0.1 μm can be investigated. Mercury-enriched EFPC soil samples were characterized with a JEOL 2000FX transmission electron microscope. The microscope was equipped with an energy dispersive spectrometer (a type of XRF detector) for elemental analysis. This arrangement allowed for characterization of material by morphology, chemistry, and electron diffraction on small particles and groups of particles. An additional technique, dark field imaging, was used to identify the source of observed diffraction rings/spots. With dark field imaging, only the diffracted beams of electrons are used to observe the grain, and a correlation can be made between a diffraction pattern and an individual grain.

Mercury-enriched samples from a small number of highly contaminated sites consisting of soil particles < 2 μm in size were processed, placed on grids, and scanned for the presence of mercury and sulfur with a JEOL 840 SEM. Grid openings (~ 8000 μm square) that contained these elements were identified and used for the TEM. Because mercuric sulfide is relatively opaque to electron transmissions, the chemistry of each opaque grain was determined using the energy dispersive spectrometer (EDS). If the characteristic peaks of mercury and sulfur were observed, a photograph of the grain or grains was taken to show its morphology, and the SAED image photographed to document the diffraction pattern. Finally, a 100-s chemical analysis was performed to confirm the chemistry. If a mercuric sulfide grain was located on a clay grain, the grain would not be used because the clay SAED image can interfere with the unequivocal identification of metacinnabar. In many instances, the grains were associated with or near clay material, as would be expected in a natural soil. Most of the SAED images, therefore, have some component of clay diffractograms in them.

Thirty-seven analyses of grain areas are displayed in a ternary plot in Fig. 2.5. A ternary plot shows the percentage contribution of three end members. At its apices are the counts for sulfur ($\text{K}\alpha$) and mercury ($\text{M}\alpha$), lower left; iron ($\text{K}\alpha$), top; and mercury ($\text{L}\alpha$), lower right. The majority of the grains are located very close to the composition of the mercuric sulfide standard (asterisk symbols) but away from the mercuric oxide standard (triangle symbols). A small number of grain areas contain higher amounts of iron than most of the mercuric sulfide but these grains still display similar mercury-to-sulfur ratio.

Figure 2.6a is a TEM bright field image of a mercuric sulfide particle not associated with clays; Fig. 2.6b is a dark field image of the same area. The bright areas in Fig. 2.6b indicate the source of the diffraction rings and spots used for positive identification of mercuric sulfide in the SAED image (Fig. 2.6c). The grain areas are made up of many small individual mercuric sulfide grains (< 50 nanometer) composed of crystalline mercuric sulfide (as indicated by the

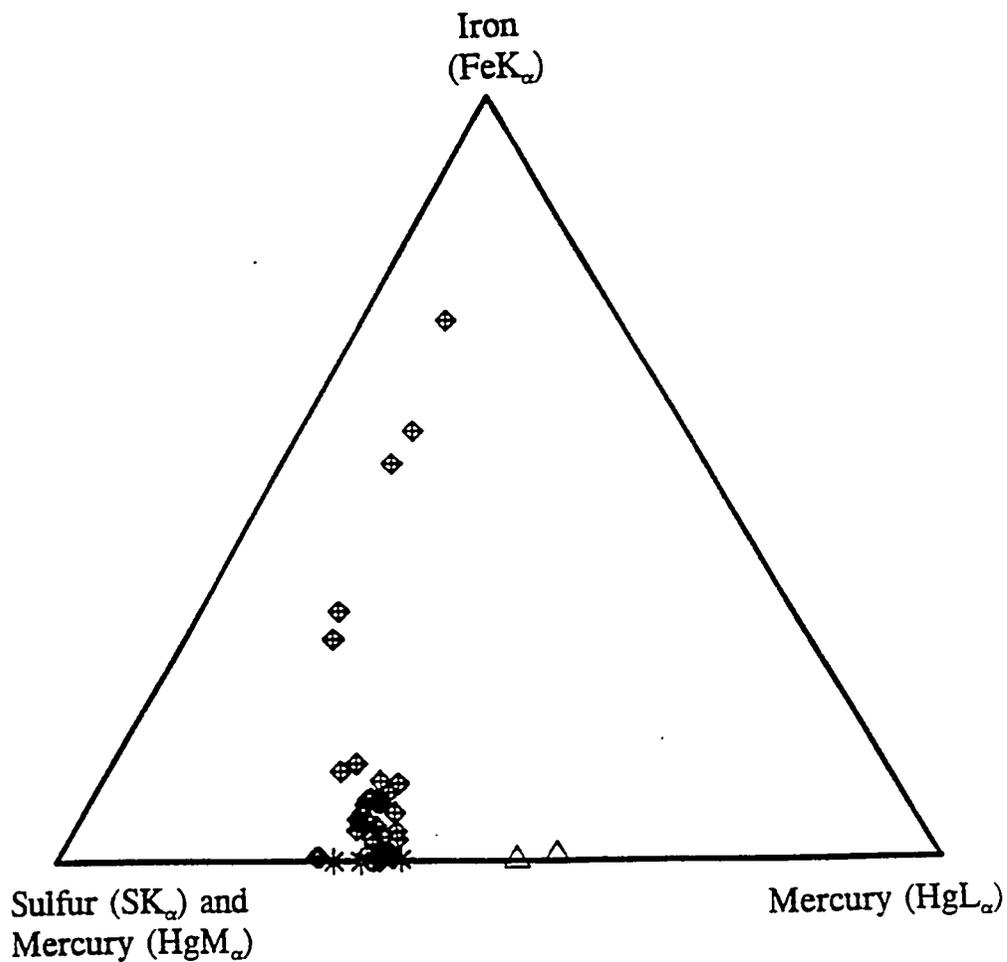


Fig. 2.5. Ternary plot of counts of SK_α and HgM_α, FeK_α, and HgL_α. The bulk of the mercuric sulfide grains (diamonds) plot near the location of the mercuric sulfide standards (asterisks) but they plot away from the mercuric oxide composition (triangles).



Fig. 2.6a. TEM bright field image of an area of mercuric sulfide. The bar is 100 nanometers long.

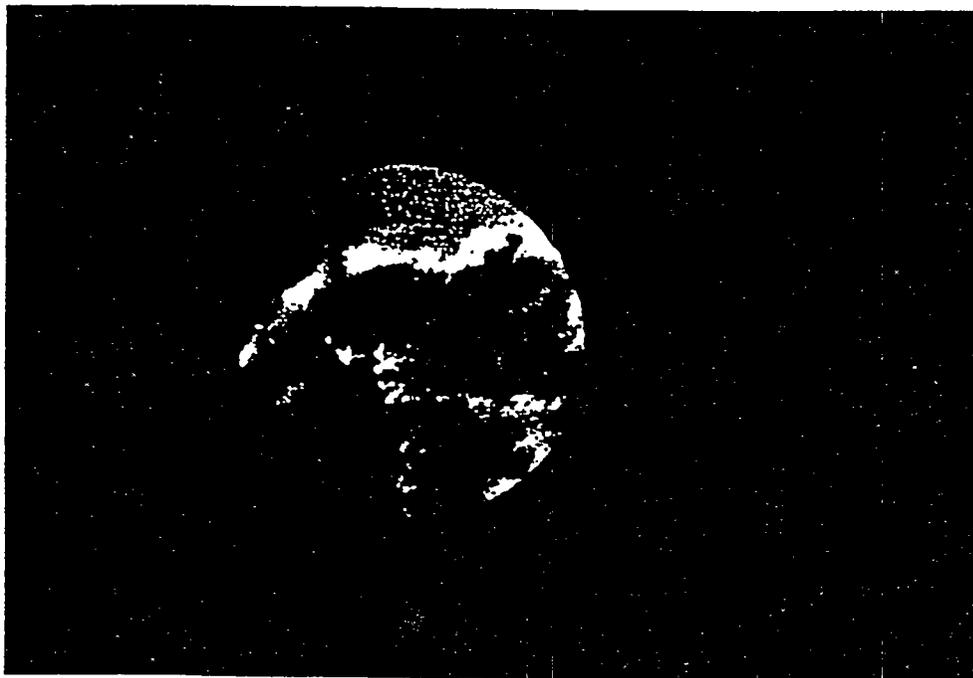


Fig. 2.6b. Dark field image of the mercuric sulfide area in Fig. 2.6a. Note that the bright areas indicate the source of the diffraction rings and spots in Fig. 2.6c. The grain area is really made up of many very small (< 50 nanometers) mercuric sulfide grains. The bar is 100 nanometers long.



Fig. 2.6c. SAED pattern of the grain area in Fig. 2.6a. There are multiple points on the diffraction rings indicating that the grain area is made up of many individual mercuric sulfide grains and less crystalline mercuric sulfide. The circle indicates where the diffracted beams have come from to form the dark field image of Fig. 2.6b.

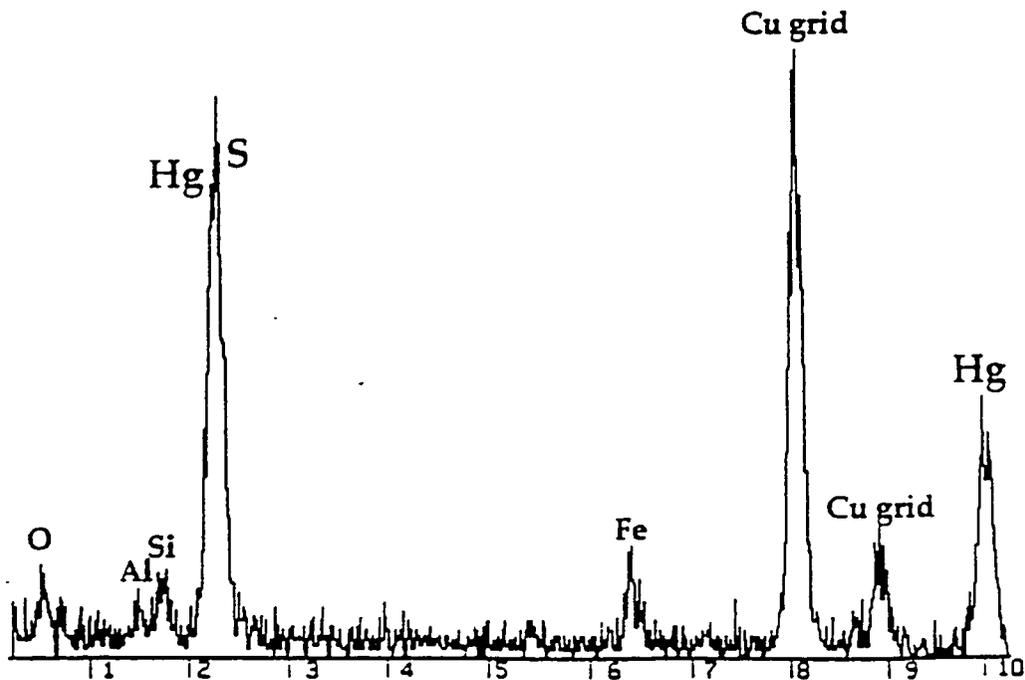


Fig. 2.6d. EDS spectra of the mercuric sulfide area in Fig. 2.6a. The spectra is dominated by the mercury (Hg) and sulfur (S) peaks with a minor amount of iron (Fe).

presence of diffuse rings). Figure 2.6d shows the EDS spectra of the mercuric sulfide area, which is dominated by mercury and sulfur with minor amounts of iron.

Prior to the TEM investigation, standard XRD was employed using a Phillips high-angle diffractometer. XRD analysis of as-received EFPC soils containing up to 3000 mg/kg of mercury failed to reveal any mercury compounds. Laboratory enrichment of EFPC soils resulted in two samples submitted for XRD analysis: (1) one consisting of particles under 2 μm containing 0.96 weight percent mercury and (2) one consisting of particles 2 to 5 μm in size containing 0.89 weight percent mercury. Figure 2.7 compares the XRD patterns for the above samples with the diffraction pattern for as-received soil and synthetic metacinnabar. Lines drawn through the maxima of the metacinnabar peaks at B and C highlight weak, broad peaks in the diffraction pattern of the mercury-enriched samples. The breadth of the peaks in the enriched samples reflects the very small crystal size seen in the TEM/SAED study. In contrast, these lines cut across flat regions of the as-received diffraction pattern. Though the less concentrated samples do not respond to bulk analysis by XRD, the presence of metacinnabar is confirmed by XRD in the enriched samples.

Though the above techniques cannot be applied to large numbers or volumes of samples within a reasonable time frame, they do supply unequivocal identification of mercuric sulfide in EFPC soils, which substantiates that geochemical conditions favorable to the formation of crystalline mercuric sulfide exist within the EFPC floodplain. This evidence, in combination with the similarity of petrographic, chemical, and morphological characteristics of the other samples, yields strong proof that analogous conditions exist throughout the floodplain environment.

Thermal desorption test. A final test was initiated, which might supply additional information about the dominant form of mercury in EFPC. The IT Corporation Process Development Laboratory in Knoxville was tasked to perform a thermal desorption test on EFPC soils and soils spiked with metallic and mercuric sulfide standards. The basis of the test was that metallic mercury volatilizes at a lower temperature than mercuric sulfide. The test was only recently completed, and the results reported here should be considered preliminary and subject to change. IT will issue a final report in the near future.

As-received EFPC background and mercury-spiked soils were placed in a rotary thermal apparatus (RTA), heated, and maintained at various temperatures for 30 min. An off-gas sampling system measured mercury content in the RTA's impinging air stream, and residual mercury concentrations were measured in the soil. Results for the EFPC and spiked soils are displayed in Fig. 2.8. Metallic mercury appears to show significant volatilization between 100 and 200°C (212 and 392°F); EFPC soil and soil spiked with mercuric sulfide only begin to show mercury releases at 200°C (the spiked metallic mercury soils were not heated above 200°C). Between 200 and 300°C (392 and 572°F), EFPC soils show higher mercury releases than the mercuric sulfide standard, but the results are well within the range of experimental and measurement error. The flattening of the metallic mercury curve is not understood and may be a consequence of the test method. This may result from the occlusion of metallic mercury in soils as a result of inadequate dispersion throughout the sample prior to the test. Overall, it can be said that the thermal release of mercury from EFPC soils better reflects the mercuric sulfide standard than the metallic mercury standard.

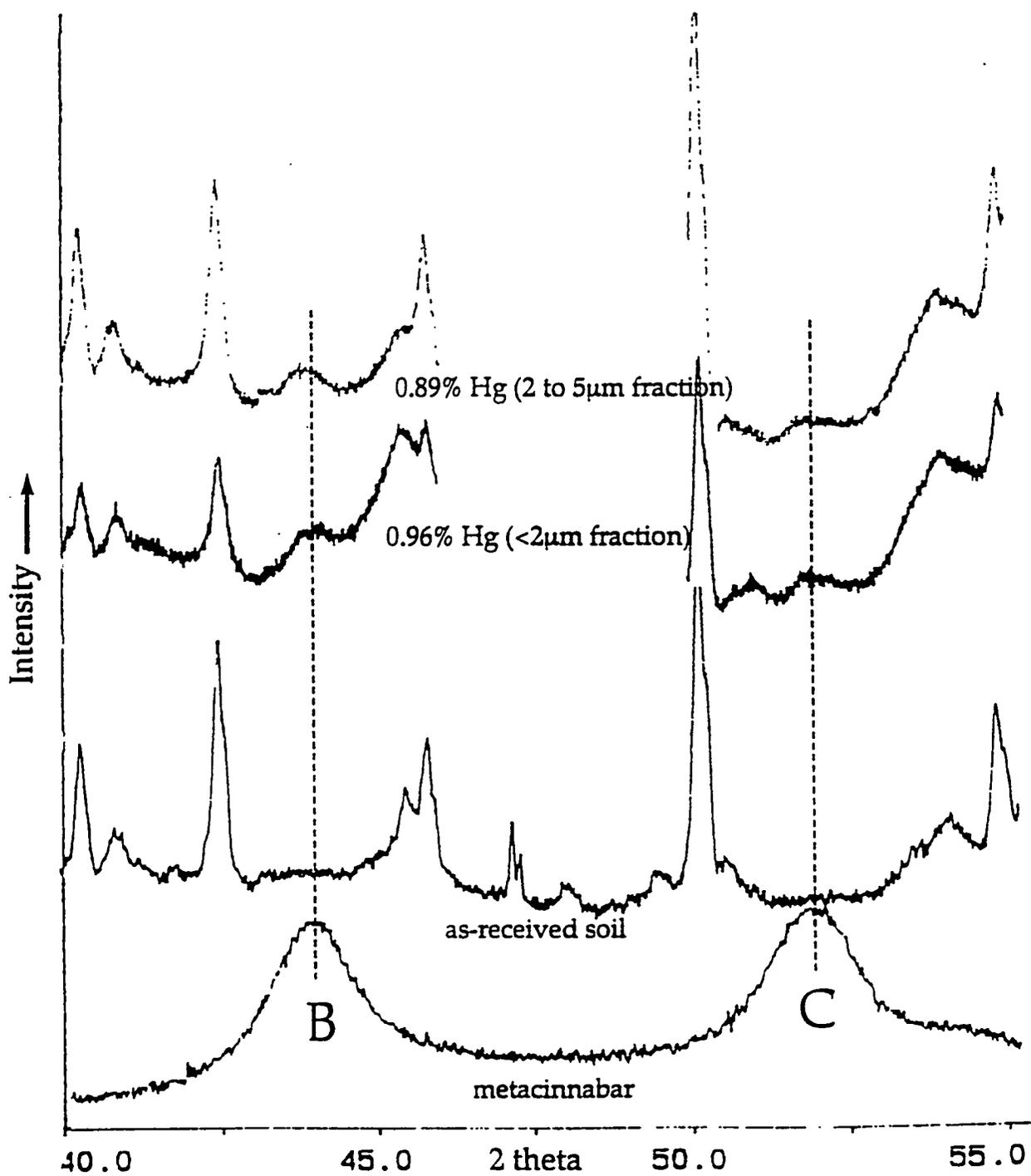


Fig. 2.7. Comparison of the X-ray diffraction patterns for mercury-enriched soil fractions with as-received soil and synthetic metacinnabar.

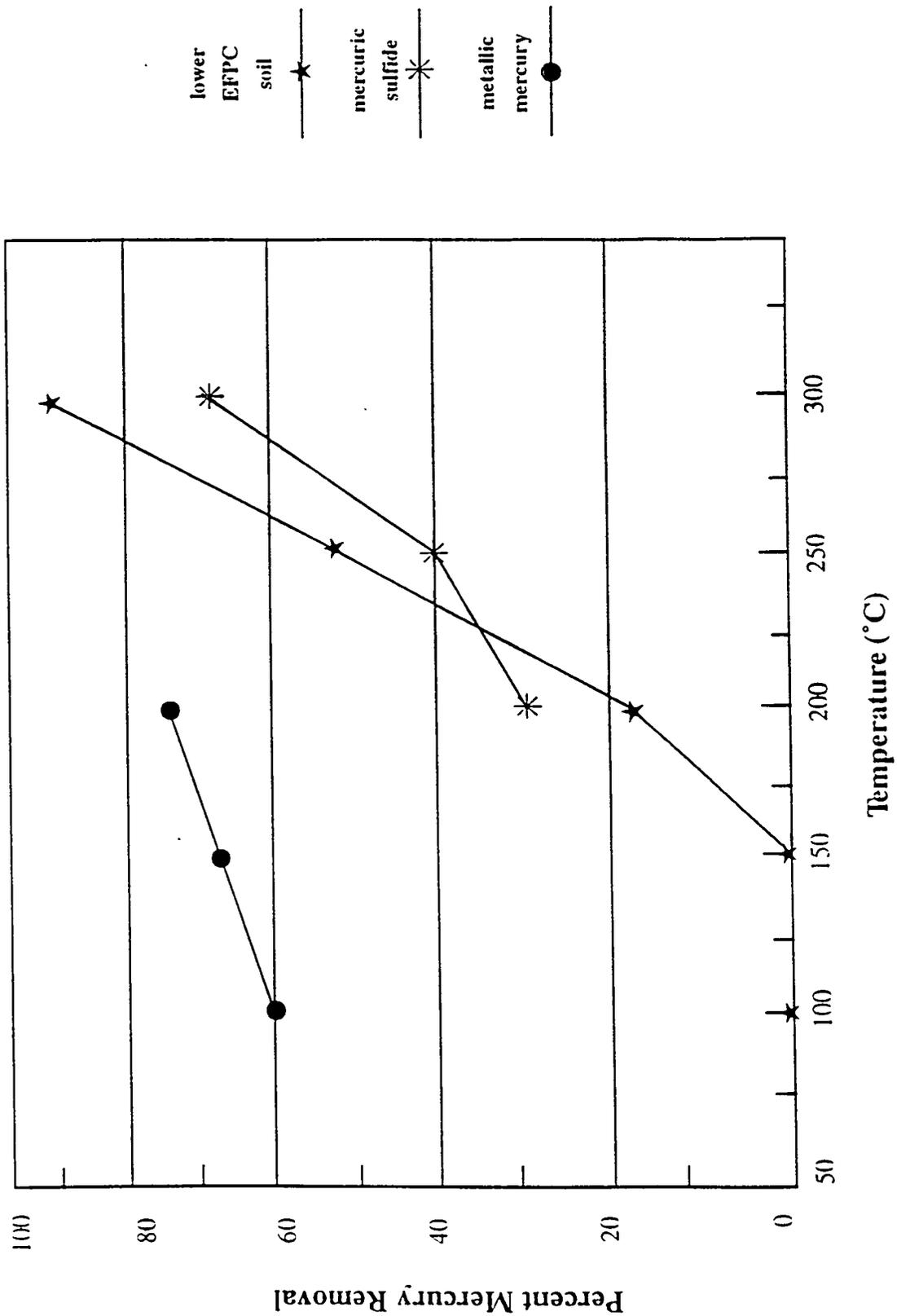


Fig. 2.8. Thermal desorption of mercury (Lower EFPC-mercury sulfide-metallic mercury).

2.1.5 Additional Work

Additional tests were conducted to resolve the disagreement between the Environmental Monitoring Systems Laboratory conclusions and the other body of speciation work. Three selective/sequential extraction schemes were applied to five soil samples from the EFPC floodplain. Included in this series were the Revis method, the Environmental Monitoring Systems Laboratory method, and a novel method described by Sakamoto et al. but not yet tested on previous EFPC soils (see Table 2.1 for a comparison of the methods). Four of the five soils used in this comparison were taken from the set of 20 used by Environmental Monitoring Systems Laboratory for their speciation work and by ORNL for the bioavailability study. The four soils were selected on the basis of: (1) the range of total and speciated mercury concentrations and (2) location and depth contrasts. The fifth soil was collected fresh from one of the locations previously sampled for the Environmental Monitoring Systems Laboratory and bioavailability work. The latter soil was selected mainly because it had exhibited independent evidence of high metallic mercury content. All of the soils were processed as-received in their naturally moist state to preclude any possible changes in speciation as a result of drying or pulverizing. In addition, the steps pertaining to organic mercury in each method were skipped because of time constraints, previously determined very low concentrations, and the apparent absence of any discordancy among methods for the organic fraction. To test the effectiveness of each extraction scheme in recovering mercuric sulfide, one of the five soils was also spiked with metacinnabar and included as a sixth soil in the series.

Because of the discordancy between the results of the Revis method and the Environmental Monitoring Systems Laboratory method regarding the relative predominance of elemental mercury in EFPC soils, all 20 samples employed in the Environmental Monitoring Systems Laboratory and bioavailability studies were tested for the presence of headspace mercury vapor at room temperature [22 to 24°C (72 to 75°F)] and 50°C (122°F). Furthermore, each soil was heated to 150°C (302°F) for 5 d following the approximate protocol used by Revis et al. (1989c) to measure the metallic mercury content of EFPC soils. The Revis protocol for elemental mercury was modified for mass balance purposes to allow measurement of both the evolved mercury (collected on iodated charcoal) and the mercury lost from the soil (before and after treatment). These thermal treatments were conducted in closed vessels under an air purge (125-cc volume vessel purged every 2 min).

Results of the additional work were only recently completed at the time of this addendum. Results of these methodological comparisons are provided in Appendix A.

2.1.6 Conclusions

Widely divergent methods have shown that mercuric sulfide and metallic mercury are the likely dominant forms of mercury in the EFPC floodplain soils. Unequivocal test methods have confirmed the presence of mercuric sulfide, and quantitative elemental analysis and electron microscopy demonstrate that sulfur and mercury are co-located in the correct proportions to form mercuric sulfide. The EPA Environmental Monitoring Systems Laboratory sequential extraction method indicated that metallic mercury may be the more abundant mercury species and that detectable quantities of mercuric oxide, or mercury forms that behave like mercuric oxide, are present (although subordinate to mercuric sulfide). More importantly, the evidence is in

agreement that concentrations of both methyl mercury and mercuric chloride constitute a minor fraction of the total mercury content in the EFPC soils.

The Revis and EPA Environmental Monitoring Systems Laboratory studies obtained discordant results on the relative abundance of metallic mercury to mercuric sulfide. At the time of this report, the cause of the discordancies has not been completely determined. Nonetheless, both the Revis and the EPA Environmental Monitoring Systems Laboratory results support the primary conclusion that the mercury form that occurs in the EFPC floodplain is not readily available for biological uptake.

Regardless of the actual form, the solubility of the mercury in the EFPC floodplain soils, and hence the biological availability, is low. A test specifically designed to mimic dissolution of mercury from EFPC soils in the human digestive tract reveals that only minimal mercury (average of 3%) is made available for uptake.

The conclusions of the special studies and the data are used in Sect. 3.1 to support the use and selection of a bioavailability factor for the development of human health RGOs.

2.2 WETLANDS

2.2.1 Introduction

The special field investigation for wetland soil, biota, and woody plants was conducted by Science Applications International Corporation (SAIC) to supplement the ERA for the Lower EFPC RI Report and the FS. The investigation addressed the need for additional data on the uptake of contaminants in EFPC wetland soils by wetland biota and the uptake of contaminants by trees. Wetlands were inventoried by the U.S. Army Corps of Engineers after the Phase Ib sampling plan was already approved. Hence, wetlands were sampled during Phase I of the RI only when sample points fell, by coincidence, within wetland boundaries. Because wetlands are sensitive ecological resources and because biological processes may differ in very hydric soils, additional data were required to assess the potential effects of contaminants present in the EFPC floodplain.

The objectives of the sampling and analysis of wetland soil, biota, and woody plants were (1) to determine the presence of mercury and methyl mercury in wetland soils and biota, (2) to refine estimates of the transfer of mercury and methyl mercury from soil to wetland biota, and (3) to determine whether the mercury content of trees would affect the options for disposal of trees removed from the EFPC floodplain during remediation. In the absence of adequate monitoring data, the transfer of contaminants from wetland soil to biota must be calculated from transfer factors. The use of published factors often produces extremely conservative upper-bound estimates that do not reflect the true potential for exposure or accumulation. Therefore, site-specific information is needed to provide better informed and more reasonable values for wetland soil-biota transfer factors, which will, in turn, provide information needed for the development and refinement of RGOs.

Data collected during the sampling and analysis of wetland soils and biota are used in an exposure assessment for EFPC floodplain ecosystems. These data are also used in the FS to

assess direct and indirect effects of proposed remedial actions on the environment. A separate final report detailing the wetlands study will be issued in the future.

2.2.2 Objectives of the Study

Data quality objectives (DQOs) were chosen to address data gaps remaining after the Phases Ia and Ib field investigations. DQOs for the sampling and analysis were developed following the steps recommended by EPA in *Ecological Assessment of Hazardous Waste Sites: A Field and Laboratory Reference* (EPA 1989a) and *Guidance for Data Usability in Risk Assessment* (EPA 1990). The DQO development process included identifying data uses and needs and refining the proposed data collection program to meet those needs. DQOs were specifically chosen to provide additional information for the ERA on the transfer of contaminants in wetlands from soils to biota and subsequently to their consumers and, in the case of woody plants, for choosing remedial and disposal options.

Mercury was identified as the major COC from the results of Phases Ia and Ib sampling and analysis. Methyl mercury was added as a COC because it can be converted from inorganic mercury, is readily bioavailable, and is highly toxic. The major goals of the proposed sampling and analysis were to determine mercury and methyl mercury concentrations in EFPC wetland soils, site-specific wetland soil-to-biota transfer factors for mercury and methyl mercury in EFPC wetland soils, and uptake and concentrations of mercury in woody plants on the EFPC floodplain.

Specific objectives of the sampling and analysis of soil, animals, and vegetation included determining:

- concentrations of total mercury in woody plants growing in EFPC floodplain soils;
- concentrations of total mercury in wetland soils;
- concentrations of total mercury in wetland foliage consumed by wetland animals;
- concentrations of total mercury in wetland biota exposed directly or indirectly to contaminants in wetland soils; and
- concentrations of methyl mercury in a small number of wetland soil and invertebrate samples.

These data are used to evaluate risks to biota in EFPC wetlands and to evaluate remedial actions that call for removal of wetland soil and vegetation, especially trees.

2.2.3 Methods

Sampling took place in September and October of 1993. All samples were collected using established technical procedures and sampling plans (LWA 1990, Radian 1992a and b). Each sampling point was referenced to the Phase Ib soil sampling transects. Sampling locations were selected that represented several orders of magnitude of measured mercury concentration in soil.

2.2.3.1 Tree cores

Tree cores were taken in both wetland and nonwetland areas with a range of soil mercury concentrations, as determined by Phase Ib sampling. The tree species chosen were those dominating the sample site in terms of woody biomass.

Tree cores were collected from 32 trees at 8 sampling locations in the EFPC floodplain (4 nonwetlands and 4 wetlands) and a reference site. Tree cores were extracted with a clean increment borer. The cores were immediately placed in individual polyethylene sample containers supplied by the lab and preserved in the field at 4°C (39°F). Tree core samples were frozen upon return from the field and samples were transported to the laboratory in a frozen state. The cores were analyzed for metals by neutron activation analysis (NAA) as a single sample data group with Level V quality assurance (QA) protocols.

2.2.3.2 Wetland soil

Soil and vegetation samples were taken from the same location to directly correlate mercury concentrations in the wetland soil and in the plant tissue. Soil samples were taken from seven wetlands in the EFPC floodplain that represent a range of contaminant levels and plant community types.

Forty-eight soil samples were planned to be collected from eight wetlands in the EFPC floodplain (Wetlands 3, 4, 5, 7, 8, 9, 14, and 17) (Fig. 2.9) and a reference site. Each sample was analyzed for metals by NAA. In addition, four samples each were collected from Wetlands 3, 4, 7, 8, and a reference site and analyzed for total mercury and methyl mercury. It was only possible to collect soil samples from five of the six planned sample locations in Wetland 5. No samples were collected from Wetland 9 because the site was inundated by 1 to 2 m (3 to 6 ft) of water as a result of recent beaver activity in that wetland.

Soil samples were collected to a maximum depth of 48 cm (18 in.) with a hand-operated, trier-type device. Soil samples were homogenized in a stainless steel bowl, according to TP-ESP-308-1. For NAA, ~50 g (1.7 oz) of sample were placed into a 125-mL polyethylene sample bottle, and for methyl mercury analysis a 125-mL glass jar with a teflon-sealed lid was filled with homogenized soil. All soil samples were immediately preserved at 4°C (39°F) and held at $4 \pm 2^\circ\text{C}$ ($39 \pm 2^\circ\text{F}$) until they were shipped to the laboratory. Level V QA protocols were followed for NAA; the equivalent of Level V QA protocols consistent with standard operating procedures (SOPs) of the analytical laboratory were followed for analyses of methyl mercury and total mercury.

2.2.3.3 Wetland vegetation

Plant foliage samples were paired with selected soil sampling locations in each of four wetlands (Wetlands 4, 7, 8, 14) and a reference site. Plant foliage and stems were harvested and packaged in the field. Leaves and stems were homogenized by shredding, and ~20 g (0.7 oz) were placed in a 125-mL polyethylene sample bottle. All samples were stored on ice in the field and frozen upon return from the field. All foliage samples were kept frozen and were transported

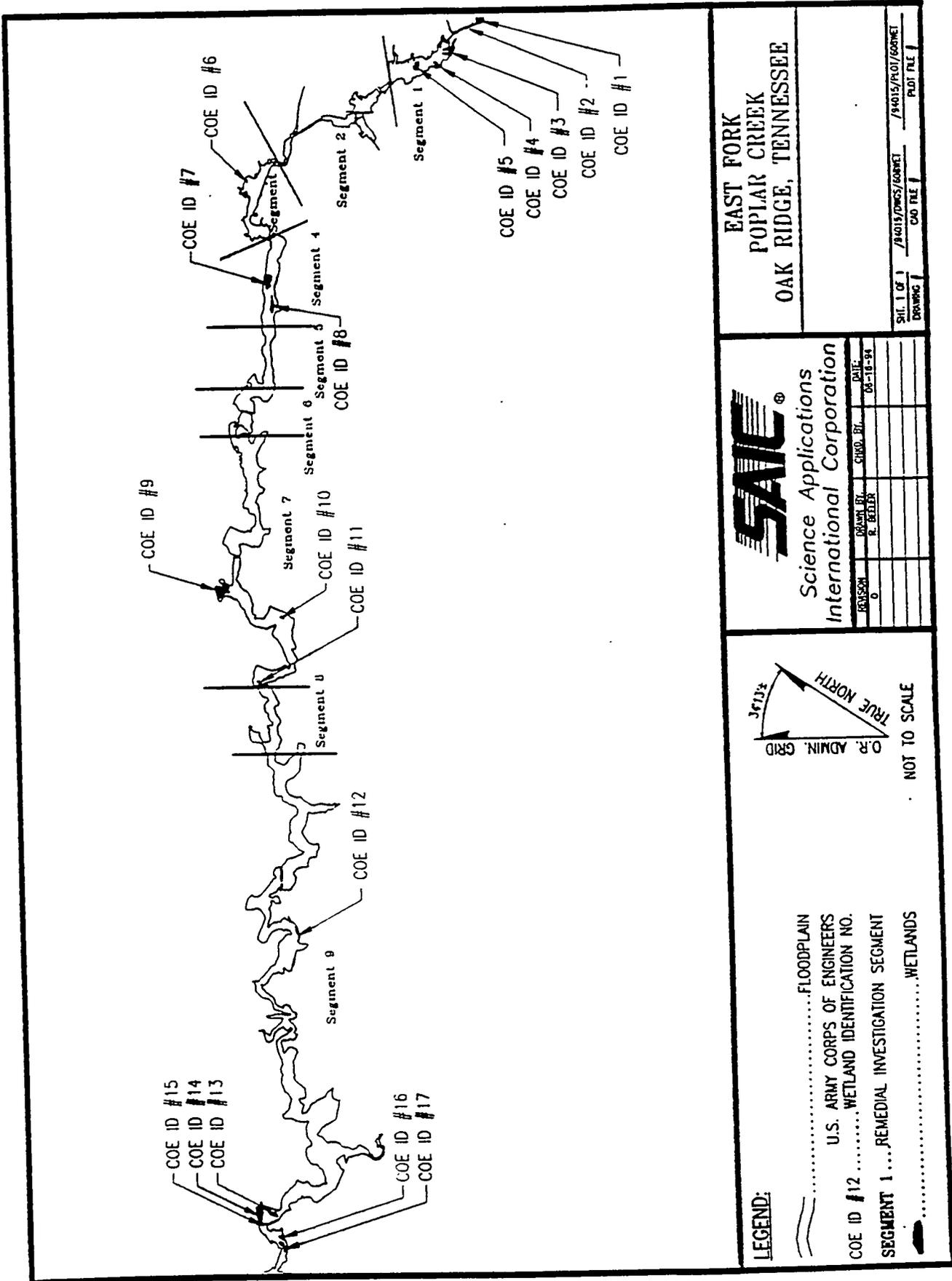


Fig. 2.9. EFPC 100-year floodplain and wetlands.

in that state to the laboratory. Vegetation samples were analyzed for metals by NAA as a single data group. Level V QA protocols were followed for NAA.

2.2.3.4 Wetland animals

Wetland animals were captured in Wetlands 3, 4, 7, 8, 14, and a reference site. The quantity and types of animals sampled varied from site to site but included crayfish, frogs, toads, shrews, and a salamander. Animals were harvested daily from pitfall traps using drift fences leading into the pits. Animals were packaged in the field in polyethylene bottles (for NAA) or wrapped in foil and sealed in Whirl-Pak™ bags (for methyl mercury analysis). All samples were stored on ice in the field and frozen in a freezer at the conclusion of the sampling trip. Samples were kept frozen with dry ice during transport to the laboratory. In a few cases, insufficient numbers of arthropod specimens were trapped and individuals were split longitudinally; half were analyzed for metals by NAA and half for mercury and methyl mercury.

2.2.4 Results and Discussion

2.2.4.1 Wetland soils

Table 2.4 shows mean, maximum, and minimum values for mercury and methyl mercury in soils from Wetlands 3, 4, 5, 7, 8, 14, 17, and the reference site.

Total mercury in soil was highest in Wetlands 3, 7, and 8 at the National Oceanic and Atmospheric Administration (NO) and Bruner (BR) sites. Generally, there was good agreement between mean values of total mercury as determined by the NAA and Brooks Rand procedures. However, the NAA values were usually higher than the Brooks Rand values, particularly at very high concentrations. This difference may be explained by methodology since NAA used the entire soil sample and Brooks Rand procedures used only a portion of a soil extract.

Methyl mercury concentrations were also highest in wetland soils at the NO and BR sites and were highest at sites with high total mercury values. Methyl mercury concentrations along EFPC accounted for between 0.004 (Wetland 8) and 0.02% (Wetland 7) of the mercury in the soil. The highest percentage, 2.3%, was at the reference site, where the total mercury content was very low. Even at the most contaminated sites, methyl mercury concentrations in soil did not exceed 0.114 mg/kg.

2.2.4.2 Wetland animals

Tables 2.5 and 2.6 show mean, maximum, and minimum values for mercury in amphibians and shrews from Wetlands 3, 4, 7, 8, 14, and the reference site. Table 2.7 shows mean, maximum, and minimum values for mercury and methyl mercury in crayfish from these same sites.

Amphibians. Generally, mercury content in amphibians appeared to be related to levels of mercury in soil. Mean mercury content in amphibians was highest (3.1 mg/kg) at Wetland 3 at the NO site where soil contamination is relatively high (up to 564 mg/kg) (Table 2.5). This wetland is the only site where three different types of amphibians were captured. In other wetlands with high levels of soil contamination (Wetlands 7 and 8), few or no amphibians were

Table 2.4. Mean, maximum, and minimum values of mercury and methyl mercury in selected soils of EFPC wetlands

Wetland	Mean	Maximum	Minimum
<i>Total mercury in soil - NAA (mg/kg)</i>			
3	143.6	564.1	0.6
4	97.3	45.0	0.06
5	31.3	67.7	6.8
7	191.2	398.4	39.3
8	559.5	1043.5	40.3
14	26.9	82.5	2.9
17	81.5	171.0	12.8
Reference	0.2	0.4	0.04
<i>Methyl mercury in soil (mg/g)</i>			
3	0.017	0.032	0.002
4	0.008	0.014	0.002
5	NS	NS	NS
7	0.041	0.114	0.01
8	0.02	0.035	0.003
14	NS	NS	NS
17	NS	NS	NS
Reference	0.005	0.005	0.005
<i>Total mercury in soil - Brooks Rand (mg/g)</i>			
3	138.9	353.0	1.2
4	80.6	299.0	0.3
5	NS	NS	NS
7	222.2	356.0	128.0
8	412.1	823.0	47.5
14	NS	NS	NS
17	NS	NS	NS
Reference	0.2	0.2	0.2

NS = Not sampled.

Table 2.5. Mean, maximum, and minimum total mercury values in amphibians from selected EFPC wetlands

Wetland	Mean (mg/kg)	Maximum (mg/kg)	Minimum (mg/kg)	Sample size
3	3.1	6.4	0.2	4
4	0.6	0.6	0.6	1
5	NS	NS	NS	NA
7	1.8	1.8	1.8	1
8	NC	NC	NC	NA
14	0.5	0.9	0.2	4
17	NS	NS	NS	NA
Reference	0.01	0.2	0.005	4

NA = Not applicable.

NC = Not captured.

NS = Not sampled.

Table 2.6. Mean, maximum, and minimum total mercury values in shrews from selected EFPC wetlands

Wetland	Mean (mg/kg)	Maximum (mg/kg)	Minimum (mg/kg)	Sample size
3	4.0	6.5	1.5	2
4	5.5	8.1	2.9	2
5	NS	NS	NS	NA
7	NC	NC	NC	NA
8	3.4	3.4	3.4	1
14	0.2	0.2	0.2	1
17	NS	NS	NS	NA
Reference	0.1	0.3	0.02	6

NA = Not applicable.

NC = Not captured.

NS = Not sampled.

Table 2.7. Mean, maximum, and minimum values of total mercury and methyl mercury in crayfish from selected EFPC wetlands

Wetland	Mean	Maximum	Minimum	Sample size
<i>Total mercury - NAA (mg/kg)</i>				
3	7.1	15.5	2.9	5
4	1.7	2.3	0.8	4
5	NS	NS	NS	NA
7	2.1	2.5	1.6	2
8	NC	NC	NC	NA
14	1.2	1.7	0.8	4
17	NS	NS	NS	NA
Reference	0.3	0.5	0.01	2
<i>Methyl mercury (mg/g)</i>				
3	0.5	0.7	0.4	4
4	0.5	0.9	0.3	4
5	NS	NS	NS	NA
7	0.5	0.6	0.4	2
8	NC	NC	NC	NA
14	0.2	0.4	0.2	4
17	NS	NS	NS	NA
Reference	0.03	0.03	0.03	2
<i>Total mercury - Brooks Rand (mg/g)</i>				
3	1.5	3.3	0.7	4
4	0.9	1.3	0.7	4
5	NS	NS	NS	NA
7	0.9	1.0	0.9	2
8	NC	NC	NC	NA
14	0.3	0.5	0.2	4
17	NS	NS	NS	NA
Reference	0.3	0.5	0.004	2

NA = Not applicable.

NS = Not sampled.

NC = Not captured.

captured. Contamination of soil or prey may be a factor influencing populations of amphibians at these sites, but other factors such as current and past land use may exert a greater influence. The time of year may also be a controlling factor because frogs are abundant at Wetlands 7 and 8 in the spring.

Small mammals. Mercury content in shrews was generally related to levels of soil contamination. Mean mercury content was highest at Wetlands 3, 4, and 8 (4.0 mg/kg, 5.5 mg/kg, and 3.4 mg/kg, respectively) where soil contamination can range as high as 450 mg/kg to > 1,000 mg/kg (Table 2.6). Shrews were noticeably more abundant at sites with little to no soil contamination (Wetland 14 and reference site). Apparent population trends could be attributable to many factors, including land use practices and contamination of soil or prey.

Crayfish. Mercury contamination in crayfish was highest (> 7 mg/kg) at Wetland 3 with intermediate to high levels of soil contamination (up to 564 mg/kg) (Table 2.7). Mercury in crayfish was very low (< 1 mg/kg) at the uncontaminated reference site and intermediate (1 to 2 mg/kg) at other EFPC wetlands (Table 2.7). This trend held true for both the NAA and Brooks Rand data. As was noted with the soil data, there was a noticeable difference in values reported by the two labs, sometimes for analyses of the same animal. For NAA results, mercury concentrations were as high as 15.6 mg/kg; the highest total mercury value reported by Brooks Rand was 3.3 mg/kg. At Wetland 8, where soil contamination is very high (> 1000 mg/kg), no crayfish were captured. There was little evidence that any crayfish were inhabiting this wetland. Contamination of soil or prey may be a factor influencing populations of crayfish at this site, but other factors such as current and past land use may exert a greater influence.

Methyl mercury in crayfish was generally related to total mercury content of crayfish. There was a trend for methyl mercury content to increase as body concentrations of total mercury increased. Methyl mercury made up a much greater percentage of total mercury in crayfish than in soil, indicating that crayfish are accumulating methyl mercury. Methyl mercury content of individual crayfish ranged from 6.5% in one animal at the reference site to 100% of total mercury in tissue. The high percentage of methyl mercury relative to total mercury occurred once at the reference site and once at Wetland 14 when analytical results for methyl mercury exceeded total mercury concentrations. This phenomenon only occurred at sites where both total and methyl mercury values were small. This occurred once at the reference site, where all values were very low (0.0301 mg/kg methyl mercury and 0.0037 mg/kg total mercury), and at Wetland 14, where contamination is very low. This phenomenon may indicate that the higher mercury content in crayfish at contaminated sites may be caused by large concentrations of inorganic forms of mercury that are in the intestines rather than actually incorporated into tissue.

2.2.4.3 Wetland vegetation

Table 2.8 shows mean, maximum, and minimum mercury values for plant foliage from Wetlands 4, 7, 8, 14, and the reference site.

Generally, mercury content in plant samples exhibited an insensitivity to mercury content of soils demonstrated previously by Van Winkle et al. (1984) and Gist (1987). Two samples at Wetland 4 had mercury values > 1 mg/kg, which greatly affected the mean value for this site. High mercury concentrations at Wetland 4 most likely resulted from surficial contamination from silt or soil on the foliage. Earlier work by Van Winkle et al. and Gist also demonstrated this

Table 2.8. Mean, maximum, and minimum mercury values for plant foliage from selected EFPC wetlands

Wetland	Mean (mg/kg)	Maximum (mg/kg)	Minimum (mg/kg)
3	NS	NS	NS
4	3.1	10.6	0.1
5	NS	NS	NS
7	0.1	0.3	0.04
8	0.1	0.1	0.06
14	0.1	0.2	0.06
17	NS	NS	NS
Reference	0.03	0.03	0.03

NS = Not sampled.

phenomenon. Samples were not washed in order to evaluate realistically the transfer of soil contaminants to herbivores.

2.2.4.4 Tree cores

Table 2.9 contains mean, maximum, and minimum mercury values for tree cores collected from several nonwetland and wetland sites in the EFPC floodplain and the reference site.

In all cases, mercury values in trees were very low. The highest reported mercury value was 0.9454 mg/kg for a sweet gum in the nonwetland portion of the NO site (Transect N33468). The low concentrations of mercury in wood should not result in any particular restrictions for the use or disposal options should the trees be removed during remediation. On nonwetland sites, mercury content in wood increased as levels of soil mercury content increased. On wetland sites, this relationship was not displayed and no clear pattern was evident. Perhaps some process or condition in wetland soils suppresses the uptake of mercury by trees.

2.2.5 Summary

Samples of soil, animals, plants, and trees were collected in several wetlands in the EFPC floodplain to provide additional information about the nature and behavior of contaminants in wetlands soils and biota for ecological risk assessment. The information was also used to evaluate factors affecting use and disposal of trees in the floodplain.

Table 2.9. Mean, maximum, and minimum values of mercury in trees from selected nonwetland and wetland sites in the EFPC floodplain

Wetland	Mean	Maximum	Minimum
<i>Mercury in trees in nonwetland sites (mg/g)</i>			
N33468	0.38	0.95	0.09
E53476	0.20	0.28	0.12
E53804	0.1	0.02	0.17
E37728	0.04	0.06	0.005
E31822	0.03	0.04	0.02
<i>Mercury in trees in wetland sites (mg/g)</i>			
3	0.21	0.60	0.01
4	0.38	0.87	0.05
7	0.12	0.18	0.05
8	0.010	0.12	0.08
Reference	0.01	0.01	0.001

2.2.5.1 Wetland Soils

- Total mercury in soil was highest in Wetlands 3, 7, and 8 at the NO and BR sites.
- Methyl mercury concentrations were highest in wetland soils at the NO and BR sites and were highest at sites with high total mercury values.
- Methyl mercury concentrations accounted for between 0.004% and 2.3% of the total mercury content in soil. At the most contaminated sites, methyl mercury concentrations in soil never exceeded 0.114 mg/kg.

2.2.5.2 Wetland animals

Amphibians

- Generally, mercury content in amphibians increased as soil concentrations increased. Mean mercury content in amphibians was highest (3.1 mg/kg) at Wetland 3 at the NO site where soil contamination is relatively high (up to 564 mg/kg). This wetland is the only site where three different types of amphibians were captured.
- In other wetlands with high levels of soil contamination (Wetlands 7 and 8) very few or no amphibians were captured.

- Contamination of soil or prey may be a factor influencing populations of amphibians at these sites, but other factors such as current and past land use or seasonal influences may exert greater control.

Small mammals

- Mercury content in shrews was generally related to levels of soil contamination. Mean mercury content was highest at wetlands where soil contamination is high.
- Shrews were noticeably more abundant at sites with little to no soil contamination. Apparent population trends could be attributable to many factors, including land use practices, contamination of soil or prey, or seasonal influences.

Crayfish

- Mercury contamination in crayfish (Table 2.7) was highest (> 7 mg/kg) at Wetland 3 with intermediate to high levels of soil contamination (up to 564 mg/kg).
- Mercury in crayfish was very low (< 1 mg/kg) at the uncontaminated reference site and intermediate (1 to 2 mg/kg) at other EFPC wetlands.
- Maximum mercury concentration reported was 15.5 mg/kg (NAA) at Wetland 3.
- At Wetland 8 where soil contamination is very high (> 1000 mg/kg), no crayfish were captured and there was little evidence that crayfish were inhabiting this wetland. Contamination of soil or prey may be a factor influencing populations of crayfish at this site, but other factors such as current and past land use may exert a greater influence.
- Methyl mercury in crayfish generally increased as total mercury content of crayfish increased.
- Methyl mercury made up a much greater percentage of total mercury in crayfish than in soil, indicating that crayfish are accumulating methyl mercury. Methyl mercury made up between 6.5% of total mercury in individual crayfish at the reference site and 100% at Wetlands 3 and 14. This phenomenon only occurred at sites where both total and methyl mercury values were small. This phenomenon may indicate that the higher mercury content in crayfish at contaminated sites may be caused by large concentrations of inorganic forms of mercury that are in the intestines rather than actually incorporated into tissue.

2.2.5.3 Wetland plants

- Mercury contents in plant foliage samples exhibited an insensitivity to mercury content of soils demonstrated previously by Van Winkle et al. (1984) and Gist (1987).
- High mercury concentrations in foliage most likely resulted from surficial contamination from silt or soil on the foliage.

2.2.5.4 Trees

- In all cases, mercury values in trees were very low. The low concentrations of mercury in wood should not result in any particular restrictions for the use of trees as lumber or mulch or on disposal options should the trees be removed during remediation.
- On nonwetland sites, mercury content in wood increased as levels of soil mercury content increased.
- On wetland sites, this relationship was not displayed, and no clear pattern was evident.

The wetland study yielded valuable data for the development of soil RGOs. Measurements of mercury concentrations in soil and in nearby trees and animals showed what the quantitative relationships are of soil, plants, and animals. These quantitative relationships were expressed as bioaccumulation factors, which were used in the food ingestion equations to derive the soil RGO shown in Sect. 3.2.

2.3 FOOD WEB

2.3.1 Introduction

In the RI Report (DOE 1994), it was reported that the common stoneroller minnows (*Camptostoma anomalum*) had much higher body burdens of mercury than redbreast sunfish (*Lepomis auritus*) or crayfish, and that body burdens decreased downstream of the Y-12 Plant. The food habits of the common stoneroller minnow are different from most fish: these minnows are specialized grazers of periphyton (algae and other microbes attached to rocks). The specialized feeding habit and relatively high body burdens of mercury in common stoneroller minnows suggest the possibility that periphyton may be an important link between contaminants in water/sediments and higher trophic levels in EFPC. This study investigated the link between contaminants in periphyton and contaminants in common stoneroller minnows and other grazers in upper EFPC with a series of related tasks that focused on current concentrations of contaminants in periphyton and grazers and examined the potential transfer of these contaminants in the lower portions of the food web. This work was performed by Walter Hill and Art Stewart at ORNL. More detailed knowledge of the pathways of contaminants into and through these food webs will help to more clearly define effective remedial action strategies, especially for sediment.

2.3.2 Methods

2.3.2.1 Mercury levels in periphyton

Periphyton was collected at three sites in EFPC, plus one location at the Hinds Creek reference site at the Rosenbalm Road bridge. Periphyton collections were made during 1 week in September 1993. The EFPC sites were located at East Fork Kilometer (EFK) 24.4 (above Lake Reality), EFK 23.4 (just downstream from Lake Reality), and EFK 18.4. Three periphyton samples were obtained at each site by brushing periphyton from 5 to 14 large rocks into a stainless steel pan. Stream water was used to rinse periphyton off of the rocks. The resulting slurry was centrifuged at 1500 rpm for 30 to 60 min in a refrigerated centrifuge. The periphyton

pellet was subdivided into portions for analysis of mercury, polychlorinated biphenyls (PCBs)/pesticides, lipids, and dry mass.

Two water samples were also collected at each site during the periphyton sampling. The water samples were returned to the laboratory where they were filtered through Whatman GFC filters. Additional water samples were collected on March 7, 1994, to differentiate dissolved mercury from particle-associated mercury at EFK 24.4 and EFK 23.4. One sample from each site was filtered through a GFC filter, while another sample was left unfiltered.

2.3.2.2 Mercury levels in fish

Common stonerollers were collected by electrofishing and seining from the same sites in EFPC and Hinds Creek that were used for periphyton sampling. Striped shiners (*Luxilus chrysocephalus*) were also collected at EFK 24.4 and EFK 23.4, during September 15 through 21, 1993. Composite samples of ten fish each, except for one stoneroller sample from EFK 24.4 that only had four fish, were homogenized with dry ice. Aliquots of the frozen powder fish tissue were shipped in Teflon containers to laboratories for mercury and PCB/pesticide analysis, as well as lipid and dry mass analysis.

2.3.2.3 Mercury levels in grazing snails (field study)

This experiment was not completed because high stream flows washed away the study organisms during the study. Since no results were obtained, this experiment will not be discussed further.

2.3.2.4 Trophic transfer experiment--periphyton to snails (laboratory study)

Two species of grazing snails (*Physella* sp. and *Elimia* sp.) were collected from White Oak Creek (WC) upstream from ORNL operations (approximately WCK 6.2 for *Physella*, and from WCK 6.8 for *Elimia*) on June 30, 1993. Experimental units consisted of 1-mm mesh cages containing either a group of 50 *Physella* or 100 *Elimia* (weighed en mass) in a flow-through water bath containing 11 cm (4.4 in.) of water kept at 25°C (77°F). The experiment lasted 39 d (July 11 to August 19, 1993). The food treatments consisted of periphyton on rocks collected either from EFK 23.4 (contaminated) or from ponds behind Building 1504 at ORNL (uncontaminated). Thus, four treatment combinations were used in the experiment (*Physella* with EFK 23.4 periphyton, *Physella* with 1504 Pond periphyton, and *Elimia* with the two different periphyton sources). Four replicates were conducted for each treatment combination. Two to five rocks were added to each cage to ensure sufficient food for the snails, and were replaced with fresh rocks every 2 to 5 d. On each day that the rocks were replaced in the cages, periphyton from two additional rocks was collected and composited for subsequent analysis of mercury. At the end of the experiment, the snails in each cage were collected and weighed en mass to estimate growth. The individuals from each of the four replicates of the four treatment combinations were combined, frozen, and later analyzed for methyl mercury and total mercury.

2.3.2.5 Mercury analyses

Methyl mercury and inorganic mercury analyses were performed by Brooks Rand, Ltd., in Seattle, Washington.

2.3.3 Results

2.3.3.1 Mercury in water

Significant site-to-site differences existed in both total and dissolved mercury in EFPC water. Total dissolved mercury was an order of magnitude higher at EFK 24.4 than at either EFK 23.4 or EFK 18.4 (Table 2.10). In contrast, dissolved methyl mercury increased slightly with distance downstream: EFK 18.4 concentrations were almost twice those of EFK 24.4 or EFK 23.4. Previously reported concentrations of total mercury in the water at EFK 23.4 (e.g., Loar 1992, Hinzman 1993) were many times higher than those observed in our initial sampling, prompting resampling. Samples collected the second time were split into filtered and unfiltered subsamples. Total mercury in the unfiltered sample from EFK 23.4 was close to expected levels (Table 2.11). The substantially lower concentration of total mercury in the filtered sample indicated that most of the mercury was particle associated and explained why initial samples (which were all filtered) had unexpectedly low concentrations at this site. A considerable portion of total mercury was particle-bound at EFK 24.4, but not nearly as much as at EFK 23.4, indicating that Lake Reality converts dissolved total mercury to particulate total mercury. A substantial portion of methyl mercury was also particle-associated at EFK 23.4, but not as large a proportion as was total mercury. Mercury concentrations at Hinds Creek were very low, as expected (Table 2.10).

2.3.3.2 Mercury in periphyton

The concentration ($\mu\text{g/g}$ dry mass) of total mercury in periphyton was quite high and decreased significantly with distance downstream in EFPC (Table 2.10). Total mercury in periphyton per unit rock area also decreased significantly with distance downstream in EFPC. Total mercury per unit dry mass was 4 to 5 times higher in periphyton than in common stonerollers at all EFPC sites. Methyl mercury was a very small proportion ($<1\%$) of total mercury in all of the EFPC samples and did not differ significantly between sites in EFPC, either on a concentration (ng/dry mass) or on an areal (ng/cm^2) basis. However, the proportion of methyl mercury increased substantially with distance downstream, from 0.15% at EFK 24.4 to 0.37% at EFK 18.4.

2.3.3.3 Mercury in fish

Total mercury concentrations in EFPC common stonerollers were relatively high, averaging over 3.4 and 1.3 $\mu\text{g/g}$ wet mass at the two most upstream sites (Table 2.10). These concentrations are approximately twice those found in axial muscle tissue of redbreast sunfish collected at EFK 24.8 and EFK 23.4 in May of 1993 (G. Southworth, unpublished data). However, the concentration of total mercury in common stonerollers sampled by SAIC (DOE 1994) in Lower EFPC were several times greater than the concentrations found in the current study. Total mercury concentrations in EFPC common stonerollers decreased substantially with distance downstream (Table 2.10). Decreases in total mercury in EFPC fish downstream of the Y-12 Plant has been well documented (e.g., Elwood et al. 1988, Southworth and Peterson 1993, DOE 1994).

Table 2.10. Mercury in water, periphyton, and fish from Upper EFPC and Hinds Creek

Medium	Units	EPK 24.4	EPK 23.4	EPK 18.4	Hinds Creek	F
<i>Total mercury</i>						
Water	ng/L	730 ± 40 (A)	57 ± 4 (B)	65 ± 6 (B)	3.3 ± 0.5 (C)	493***
Periphyton	µg/g dry mass	50.9 ± 26.9 (A)	19.9 ± 6.9 (B)	6.05 ± 1.81 (B)	0.07 ± 0.02 (C)	46.3***
	ng/cm ²	78.1 ± 44.5 (A)	30.6 ± 9.9 (AB)	11.1 ± 7.8 (B)	.59 ± 0.22 (C)	18.8***
Common stonerollers	µg/g wet mass	3.40 ± .49 (A)	1.27 ± 0.14 (B)	0.43 ± 0.03 (B)	0.045 ± 0.004 (D)	258***
	µg/g dry mass	11.18 ± 1.95 (A)	4.28 ± 1.95 (B)	1.59 ± 0.14 (C)	0.18 ± 0.02 (D)	184***
Shiners	µg/g wet mass	2.09 ± 0.08 (A)	0.58 ± 0.07 (B)	—	—	124***
	µg/g dry mass	8.87 ± 0.61 (A)	2.34 ± 0.19 (B)	—	—	155***
<i>Methyl mercury</i>						
Water	ng/L	0.104 ± 0.008 (B)	0.118 ± 0.014 (B)	0.195 ± 0.015 (A)	<0.003 (C)	558***
Periphyton	ng/g dry mass	57.5 ± 21.1 (A)	27.1 ± 6.3 (A)	20.5 ± 3.8 (A)	5.04 ± 0.18 (B)	11.8**
	ng/cm ²	0.086 ± 0.035	0.042 ± 0.010	0.039 ± 0.003	0.042 ± 0.005	0.55 ^m
Common stonerollers	ng/g wet mass	49.4 ± 7.9 (B)	118.0 ± 6.4 (A)	90.9 ± 6.6 (A)	19.4 ± 1.6 (C)	56.7***
	ng/g dry mass	159.9 ± 23.3 (B)	398.6 ± 23.8 (A)	332.8 ± 20.7	78.6 ± 7.51 (C)	54.6***
Shiners	ng/g wet mass	231.7 ± 18.2	277.7 ± 13.9	—	—	0.02 ^m
	ng/g dry mass	976.5 ± 70.7	931.2 ± 65.6	—	—	0.22 ^m
<i>% Methyl mercury</i>						
Water	% of total mercury	0.014 ± 0.0002 (C)	0.210 ± 0.039 (A)	0.300 ± 0.006 (A)	<0.09	59.3***
Periphyton	% of total mercury	0.15 ± 0.05 (B)	0.23 ± 0.15 (B)	0.37 ± 0.07 (B)	8.17 ± 1.57 (A)	48.0***
Common stonerollers	% of total mercury	1.57 ± 0.45 (D)	9.49 ± 0.85 (C)	21.38 ± 2.91 (B)	43.98 ± 4.78 (A)	62.5***
Shiners	% of total mercury	11.13 ± 1.12 (A)	40.28 ± 4.63	—	—	47.3**

Means ± SE (n = 3) and multiple comparison results are listed. Means were compared with Fisher's protected least significant difference (PLSD) multiple comparison procedure; means with the same letter are not significantly different ($\alpha = .05$). Analysis of variance (ANOVA) F tested for overall differences between sites; ns = not statistically significant ($\alpha = .05$). Fisher's PLSD was not performed when the overall ANOVA F was not significant.

Table 2.11. Mercury in filtered and unfiltered water samples, collected March 7, 1994

Analyte	EFK 24.4		EFK 23.4	
	Unfiltered	Filtered	Unfiltered	Filtered
Total mercury (ng/L)	813	440	857	127
Methyl mercury (ng/L)	0.014	0.073	0.253	0.135

Methyl mercury concentrations in EFPC common stonerollers were low, averaging $<0.12 \mu\text{g}$ wet mass at all sites (Table 2.10). In contrast to total mercury, methyl mercury concentrations for common stonerollers in EFPC were lowest at EFK 24.4. Stonerollers from EFK 23.4 had the highest mean value for methyl mercury, but the difference between EFK 23.4 and EFK 18.4 was not statistically significant. The proportion of methyl mercury to total mercury increased substantially with distance downstream, rising from 1.6% at EFK 24.4 to 9.5% at EFK 23.4 to 21% at EFK 18.4.

Striped shiners from upstream EFPC also had elevated total mercury concentrations, although the concentrations were not quite as high as those in the common stonerollers (Table 2.10). Like the total mercury in the common stonerollers, however, concentrations were significantly higher at EFK 24.4.

Methyl mercury concentrations in shiners were substantially higher than those in common stonerollers: concentrations in shiners were ~5 times higher at EFK 24.4 and 2 times higher at EFK 23.4 than common stoneroller concentrations at these sites. There were no significant differences between methyl mercury concentrations in shiners at EFK 24.4 and EFK 23.4. However, the proportion of methyl mercury to total mercury was substantially higher at the downstream site (40%) than at the upstream site (11%). The proportion of methyl mercury was many times higher in shiners than in common stonerollers at both EFK 24.4 and EFK 23.4.

2.3.3.4 Trophic transfer experiment - periphyton to snails

In this experiment, snails were used as representative invertebrate grazers, and their exposure to mercury occurred by way of their food: exposure via water was minimal, as was intended. Both species of snails grew and accumulated mercury from both types of periphyton during the 39-d experiment (Table 2.12). EFPC periphyton was a better source of inorganic mercury than pond periphyton, as concentrations were considerably higher in both species that were given the EFPC diet. Both species also appeared to accumulate more methyl mercury from the EFPC diet, though the effect of diet was not quite as strong as it was for inorganic mercury. By the end of the experiment, both snail species were enriched with methyl mercury, relative to the proportion of methyl mercury in the periphyton they consumed. However, the concentrations of methyl mercury in *Elimia* and *Physella* at the end of the experiment were only 44 to 54% as great as the concentration of methyl mercury in pond periphyton (wet-mass comparisons in both cases), and only 6.3 to 8.2% as great as the concentration of methyl mercury in EFPC periphyton. The concentration of inorganic mercury in the snails was much less than that in the periphyton.

Water is clearly the medium by which contaminants are introduced and transported in EFPC. However, direct uptake of dissolved mercury and other compounds from water is only one path by which fish in EFPC can be contaminated. Mercury and other contaminants can also accumulate in fish by means of trophic transfer. This study was initiated to explore the potential for trophic transfer of contaminants from periphyton to higher trophic levels, and was stimulated in large part by levels reported in the RI Report, unusually high levels of contaminants found in common stonerollers (DOE 1994). The results in the food web study demonstrate that periphyton is a potentially important source of mercury for fish and other aquatic consumers in EFPC: total mercury concentrations were very high in periphyton, and grazers accumulated mercury in the absence of contaminated water when they were provided with contaminated periphyton.

Table 2.12. Mercury concentrations in periphyton and snails from the laboratory grazing experiment

Receptor	Methyl mercury	Total mercury	Methyl mercury	Mean growth
	(ng/g wet weight)	(ug/g wet weight)	(% total mercury)	(mg/snail \pm SE)
EFPC periphyton	91.7 \pm 2.4	49,177 \pm 2,253	0.19	—
Pond periphyton	8.1 \pm 5.5	542.0 \pm 277	1.49	—
<i>Elimia</i> (pond diet)	4.4	50.1	8.78	15.98 \pm 1.48
<i>Elimia</i> (EFPC diet)	5.8	94.4	6.14	19.81 \pm 1.86
<i>Physella</i> (pond diet)	3.6	91.0	3.96	36.84 \pm 5.15
<i>Physella</i> (EFPC diet)	7.5	265.5	2.82	36.94 \pm 5.00

Although the results of this study implicate periphyton as an important contributor to high levels of inorganic mercury in common stonerollers, they do not exclude water from being an additional direct source of mercury. Because of the relatively high concentrations of dissolved mercury in upper EFPC, fish could accumulate significant amounts of inorganic mercury directly from water contact. However, Southworth et al. (1994) found that redbreast sunfish in upper EFPC (EFK 24.8, EFK 23.4) had little inorganic mercury, suggesting that direct uptake is not important.

2.3.4 Summary

Four significant results of this study were:

1. Periphyton contained very high concentrations of total mercury, demonstrating its potential as a significant source of contamination to higher trophic levels, such as snails and fish.
2. Mercury speciation analyses showed that although common stoneroller minnows contained high levels of total mercury, most of it was in the inorganic form, which has different toxicological and bioaccumulation potential than does organic (methyl) mercury. The

proportion of organic mercury in water, periphyton, common stonerollers, and striped shiners increased slightly with distance downstream from the Y-12 Plant.

3. Common stonerollers (herbivores) had lower concentrations of organic mercury than striped shiners (omnivores). Muscle tissue of redbreast sunfish (presumed carnivores) from upper EFPC above Lake Reality (Southworth et al. 1994) had higher methyl mercury concentrations than striped shiners. The feeding niche of fish probably influences the form of mercury as well as its concentration in their tissues.
4. Periphyton by itself can be an important source of mercury body burdens, as indicated by a laboratory experiment with grazing snails. The specific proportion of common stoneroller body burdens that can be attributed to a periphyton diet requires more measurements.

Periphyton, fish, and grazing snails—all ecological components in EFPC—exhibited presence of methyl mercury and total mercury. Also, significant site-to-site differences existed in the water. Concentrations of total mercury were higher above Lake Reality than below Lake Reality. For methyl mercury, this trend was the opposite for some ecological components. The relationships of water to plants to consumer will provide quantitative knowledge on which to base better RGOs.

2.4 SEDIMENT CHRONIC TOXICITY

The ERA for Lower EFPC presented evidence of contaminant impacts on fish and benthic community structures. Body burdens of several contaminants [most noticeably mercury and the PCB Aroclor 1260] in fish and benthic macroinvertebrates from most of the six sampling sites in Lower EFPC exceeded the levels obtained from a presumably uncontaminated reference site (Hinds Creek). Furthermore, the body burdens of mercury in fish and benthic macroinvertebrates exceeded levels that were reported to cause direct toxicological hazards to these organisms, as well as to their predators. However, no sediment toxicity tests were conducted during the EFPC RI. Subsequently, sediment toxicity tests were performed to help clarify whether the observed impacts on fish and benthic community structures were the result of toxicological effects from the sediments or were the effects of water-borne contaminants or nontoxicological stressors.

This special study used a phased approach for determining sediment chronic toxicity. Phase I consisted of a screening study to establish the extent of toxicity among several sediment samples collected by SAIC from Lower EFPC and one reference site in Hinds Creek, near Oak Ridge, Tennessee. Sediments were collected from four sites that were used during the ERA sampling, including the three closest downstream from the Y-12 Plant. The three sites closest to the Y-12 Plant had the greatest impacts to aquatic biota during the field surveys of the ERA (DOE 1994). An additional sediment sample was collected from a location where the mercury concentrations were among the highest observed in Lower EFPC. One field duplicate was also collected. Sediment elutriates were used in 7-d tests with *Ceriodaphnia dubia*; mortality and number of offspring were the test endpoints. Because no toxicity was observed during the Phase I tests with 100% elutriate, the Phase II definitive tests for concentration-response information were not required.

This study provides direct measurement of the potential sediment toxicity and additionally provides support to DOE's recommendation to defer remedial action on the sediments until after remediation is completed on the floodplain soils and further reductions in releases to Upper EFPC.

2.5 CLASSIFIED CHEMICALS REVIEW

Since the mid-1950s, EFPC and its floodplain have been exposed to releases from the Y-12 Plant, a plant that has been actively engaged in the development and manufacture of classified materials. Subsequent to the review of the D2 draft of the RI Report, TDEC requested verification that the EFPC RI addresses all potential COCs, including any classified chemicals. A review of classified chemicals utilized at the Y-12 facility was performed. The scope of this review included a comprehensive assessment of chemicals employed, processed involved, and controls imposed, which provides assurance that the classified chemicals used at the Y-12 Plant either were not a source of contamination to the creek or were encompassed by the EFPC RI.

The review of classified chemicals at the Y-12 Plant considered both current and historical processes and uses and is documented in the classified report *Oak Ridge Y-12 Site Remedial Investigation Comprehensive Environmental Response, Compensation, and Liability Act (CERCLA) Classified Information Review*. Included with this report is a comprehensive elemental analysis of selected EFPC samples, which provides information on elemental composition relative to natural elemental levels. An unclassified summary of the report is provided in Appendix B.

Assessment of Y-12 Plant classified chemicals has shown that these classified chemicals were sampled as part of the EFPC RI, were controlled through processes that precluded release, were utilized in limited quantities, or present no toxicity concern. Comprehensive elemental analysis of selected soils indicated no elevated elemental concentrations beyond those previously identified as COCs by the EFPC RI.

3. DEVELOPMENT OF ALTERNATIVE RGOs

This section presents alternative RGOs for contaminants in environmental media of EFPC. These RGOs are derived based on an evaluation of risks to human health and ecological receptors and incorporate new information that has become available since the D2 draft of the RI Report (DOE 1994) was issued in January 1994. A full discussion of the development of RGOs and the methods for deriving these numbers is provided in Sect. 7 of the RI Report, Remediation Goal Options for EFPC. This addendum extends the previous work. The discussion in this addendum is limited to mercury.

3.1 RGOs FOR THE PROTECTION OF HUMAN HEALTH

The EFPC Risk Assessment Team derived a risk-based RGO for mercury in floodplain soil (See Sect. 7 of the RI Report). This RGO was developed to protect the most sensitive receptors (i.e., children) following long-term, inadvertent ingestion exposure and dermal contact with soil containing mercury. Consistent with the BRA, the derivation of the RGO assumed that mercury in floodplain soils was present in a highly toxic and mobile form (i.e., mercuric chloride). Based on the weight of evidence, however, it was hypothesized in the RI Report that less soluble and less toxic mercury species predominate. As discussed in Sect. 2.1 of this addendum, recent results of additional speciation and leaching/availability studies support the original hypothesis that less mobile and less bioavailable forms of mercury predominate in EFPC floodplain soils.

Given this new information, an additional RGO for mercury in soil for protection of human health has been derived based on the presence of mercuric sulfide and metallic mercury. EPA recognizes that development of alternate RGOs is a part of the RI/FS process that will occur as new supporting information becomes available. This section of the RI addendum provides the rationale and supporting material and presents the derivation of an additional RGO for mercury in soils. Note that at this point in the RI process, all RGOs are open for consideration. The final selection of remediation levels for mercury in EFPC soils will not occur until the FS is complete and the Record of Decision is prepared.

The new RGO for mercury (i.e., alternate value) derived in this section is presented as a conservative, risk-based, deterministic point estimate based on methods recommended by EPA. In addition to the point estimate, the EFPC Risk Assessment Team has conducted a quantitative uncertainty analysis to examine the uncertainty surrounding this additional RGO and the assumptions that form the basis of this estimate.

3.1.1 Overview of Absorption, Bioavailability, and Exposure Estimates

Bioavailability and absorption of mercury in soil directly influence exposure potential. Greater exposure potential will result in higher projected risk estimates and an associated lower value for the remediation goal (i.e., the higher the risk, the smaller the quantity of contaminant that is acceptable in soil). It is important at this point to review the concepts of absorption and bioavailability as they relate to human exposure to mercury species in soil.

Exposure estimates may be based on administered or absorbed dose. EPA defines *administered dose* as the mass of a substance that the receptor comes in contact with at an exchange boundary (e.g., gastrointestinal tract) per unit body weight per unit time (i.e., mg/kg-day). Alternatively, *absorbed dose* is the quantity of chemical crossing the exchange boundary following contact. Absorbed dose is expressed as mass absorbed into the body (e.g., into the blood stream) per unit body weight per unit time (i.e., mg/kg-day). Administered dose is referred to by EPA as "exposure intake" (not dose) and is not considered a true measure of the quantity of chemical experienced by the receptor at the target organ or target tissue (i.e., site of toxic action). Absorbed dose is considered by EPA to be a true dose estimate and may be used to quantify chemical concentration at the site of toxic action.

Absorbed dose is calculated from estimates of intake and is modified through application of a factor for *absorption efficiency*. Note, however, that only a fraction of the total contaminant concentration measured in soil is released from the soil matrix to the gastrointestinal environment and is available for absorption. The concept of *bioavailability* is important in this regard. Bioavailability is a function of both the compound-specific physical/chemical properties and the properties of the soil matrix itself. When soil is inadvertently ingested, not all of the contaminants in the ingested soil are available to be absorbed across the gut lining. In turn, only a percentage of the amount that is available within the gastrointestinal tract will be absorbed across the biological membrane. Absorption efficiency and bioavailability will differ as a function of the mercury species under evaluation.

To summarize, at least two important steps must be considered in understanding absorbed dose: (1) bioavailability of the chemical from the soil matrix and (2) chemical-specific absorption efficiency across the biological membrane. This is somewhat simplified, however, and true estimates of tissue or target organ dose would need to consider the pharmacokinetics and pharmacodynamics of the subject chemical. In addition to uptake or transport across the biological membrane, distribution, metabolism, and excretion are also important. However, for the purposes of this discussion, it is enough to understand that by not incorporating these considerations for the less mobile mercury species, the BRA for EFPC is likely to have overestimated intake/dose of contaminants from floodplain soils.

In *Risk Assessment Guidance for Superfund (RAGS)* (EPA 1989b), none of the recommended exposure equations incorporate a factor for absorption efficiency (or bioavailability), except the dermal contact pathway (EPA includes a factor for chemical-specific dermal permeability). EPA headquarters, by not specifying an efficiency factor in equations for other exposure pathways, is functionally assigning a value of 1.0 (or 100%) as the absorption efficiency.

The EFPC Risk Assessment Team began outlining the approach and methods for human health risk assessment for EFPC almost 2 years ago. The team prepared and distributed a formal methods document for review by EPA, DOE, the State of Tennessee, and ORNL before the risk assessment was initiated. In addition, the EFPC Risk Assessment Team gave a series of briefings regarding the proposed approach. At that time, the team raised the issue of the use of absorption or bioavailability factors in the EFPC risk assessment. Following a review of the literature and discussions with EPA Region IV, the team decided that such factors would only be used for the dermal contact pathway. EPA Region IV provided the EFPC Risk Assessment Team with default absorption factors for the dermal pathway. A default absorption factor of 1.0 was recommended by EPA Region IV for use for all other pathways (ingestion and inhalation). The decision to use

a default value of 1.0 was based in part on the lack of EPA-verified or accepted absorption or availability factors for the ingestion pathway.

Use of an oral bioavailability factor of 1.0 for chemicals in soils results in a conservative estimate of dose. A chemical that may be 90 to 100% available for uptake and absorption from drinking water may exhibit only a fraction of this availability from soil. This is the case for many metals in soil. In *RAGS* (EPA 1989b, Appendix A), EPA notes that some metals tend to be poorly absorbed (<5%) from the gastrointestinal tract. EPA indicates that a relatively conservative assumption for bioavailability and oral absorption of metals in the absence of appropriate information would be 5%.

3.1.2 Review of Oral Absorption and Bioavailability of Mercury Species

3.1.2.1 Literature review: oral absorption of mercury species

Published literature was reviewed to examine differences in the oral absorption of mercury for various mercury compounds. Although epidemiological, occupational, and clinical studies were reviewed, this discussion is largely drawn from experimental studies in animals.

Mercury absorption from the gastrointestinal tract is a complex process (Suzuki et al. 1990). The underlying pharmacokinetics of mercury absorption and distribution for the oral route indicate that aqueous solubility, ionic charge, nature of the matrix (e.g., food, soil), pH of the gut, and presence of complexing agents modify the absorption of mercury. The literature review focused mainly on the less soluble mercury species found in EFPC soils (i.e., mercuric sulfide, metallic mercury, and mercurous mercury) and indicates that four critical factors affect intestinal absorption: (1) the species of mercury, (2) the distribution of mercury, (3) the age of the receptor, and (4) the condition of the intestinal epithelium.

The first factor that affects the rate and extent of absorption from the gastrointestinal tract is the mercury species. Differences in the rates of absorption are the result of the ease with which less soluble mercury species convert to more soluble forms, resulting in increased rates of absorption. In general, metallic mercury, mercuric sulfide, and mercury-selenium complex are relatively less toxic forms of mercury for oral exposure than mercuric mercury and organic mercury. Metallic mercury is characterized by low aqueous solubility, greater lipophilicity, and an inert chargeless state. For these reasons, metallic mercury is less bioavailable and, consequently, less toxic by the oral route.

Table 3.1 summarizes the relative absorption of different forms of mercury (as a percent of the administered dose) reported in the literature for the oral route.

A review of the reported values for the absorption of mercury compounds indicates that absorption of mercury from the gastrointestinal tract is highly dependent on the form of mercury. For example, absorption from the gastrointestinal tract could range from 0.01% for metallic mercury to 80% for methyl mercury. Oral absorption of methyl mercury is high; up to 80% of the ingested dose was absorbed by this route in both humans and experimental animals. Other soluble compounds, such as mercuric chloride and mercuric nitrate, are generally absorbed at high levels (up to 79%) compared to less soluble species such as mercuric sulfide and mercuric acetate. Feeding studies in experimental animals indicated that, on average, only 0.5% of the

Table 3.1. Relative percent absorption of mercury compounds^a

Mercury compound	Percent absorbed by the oral route
Metallic mercury	0.01
Mercurous mercury	
Mercurous chloride	2
Mercuric mercury	0.03 to 79 ^b
Mercuric acetate	20
Mercuric chloride	2 to 79
Mercuric nitrate	15
Mercuric sulfide	0.03 to 2
Cinnabar	0.7
Methyl mercury	50 to 80

^a Based on evidence from experimental animals and humans.

^b 79% of the dose was retained 6 d after administration to the suckling rats. However, the literature appears to reflect a consensus for an average absorbed dose of 10% for mercuric mercury.

administered doses of pure mercuric sulfide (cinnabar) and soil samples containing mercuric sulfide was absorbed.

Experimental studies with animals, human volunteers, and occupational workers indicated that a negligible amount of metallic mercury is absorbed from the gastrointestinal tract. Although conversion of metallic mercury to organic forms in the gastrointestinal tract may result in increased absorption of mercury, there is no evidence of biotransformation of metallic mercury to organic species (particularly methyl mercury) in higher mammals, including humans.

Oxidation of metallic mercury to ionic species requires the participation of an enzyme called catalase, which, in the presence of hydrogen peroxide, converts metallic mercury to mercuric mercury. Conversion of metallic mercury to ionic forms is of minor significance for absorption by the oral route because this reaction occurs predominantly in the blood and not in the gut. Mercuric sulfide was shown to be poorly absorbed from the gastrointestinal tract. The percent absorbed ranged from 0.03 to 2% of the administered dose in experimental studies (Revis et al. 1990). Percent absorbed in the Revis study was measured in comparison with quantities excreted. The percent of mercury absorbed from cinnabar was reported to be up to 0.7% of the administered dose.

The second critical factor affecting absorption estimates is the manner in which mercury is distributed and retained in the body. Resecretion of mercury from the bile into the gastrointestinal tract is not accounted for in studies of oral absorption of mercury. This could

lead to an underestimation of the absorbed doses for less soluble (or more fat-soluble) mercury. Mercury is resecreted into the gastrointestinal tract by means of the bile secretions and then excreted through the feces. This is the primary mode of excretion of mercury. Some of the early ingestion studies with metallic mercury do not seem to have considered biliary resecretion in the calculation of metallic mercury absorbed from the gastrointestinal tract. This might result in an underestimation of absorption from the gastrointestinal tract. Some researchers are skeptical about feeding studies reporting low absorption of 0.01% based on only two sets of measurements (i.e., administered dose and fecal excretion) to estimate mercury retention in the body.

The third critical factor affecting absorption estimate is age-specific differences in the absorption of mercury from the gastrointestinal tract. In particular, increased absorption among the young has been reported. A recent report by Kargacin and Kostial (1990) on the retention of orally administered mercury (mercuric chloride) indicates that suckling rats retained as much as 80% of the administered dose, whereas older rats retained only 1% of the administered dose 6 d after the last day of administration.

There is some corroborating evidence that indicates suckling animals retain higher levels of mercury than adults (Jugo et al. 1975, Kostial et al. 1989). Researchers have implicated age-specific features such as immaturity of the kidneys and bile transport, differences in the binding affinities, and contents of metal carrier proteins as plausible reasons for the increased retention of mercury in the younger animals. Although these results are based on studies of mercuric chloride, the fate of mercuric sulfide and metallic mercury may be similar in younger age groups.

The fourth critical factor affecting the absorption estimates is the condition of the intestinal epithelium. Stripping of the epithelial cells of the intestinal lumen containing bound mercury may alter the mass balance calculations for the administered dose versus fecal excretion of mercury. Mercury retention (or elimination) from the gastrointestinal tract does not consider the effect of mercury binding to the lumen of the intestine. Stripping of the lumen will result in the release of bound mercury to the gastrointestinal tract and, consequently, in the feces. Epithelial stripping is a normal process that may confound measurements of excreted mercury. The effect depends on variations in the number of epithelial cells shed into the feces. Oral intubation studies interpreting mercury absorption based on administered dose and mercury recovered from the feces do not adequately account for the contribution of mercury from the stripping of the lumen. Moreover, it is not clear if the lumen-bound form is metallic or ionic mercury.

3.1.2.2 Recent studies: EPA Region IX and State of California

EPA regional offices have acknowledged that relative absorption factors (RAF) or bioavailability factors may be appropriately used if a chemical in the soil matrix is believed to be less available than the chemical present in solvent or water. EPA Region I defines the RAF as ". . . the ratio of the estimated absorption factor for the site-specific medium and route of exposure to the known or estimated absorption factor from the laboratory study from the which the cancer potency factor or the reference dose was derived." EPA Region I notes that use of this factor allows the risk assessor to make appropriate adjustments to dose estimates if the efficiency of absorption is known or expected to differ because of physiological, matrix, or vehicle effects. Note that the Region I RAF incorporates consideration of both bioavailability and absorption efficiency.

The EFPC Risk Assessment Team became aware of two waste sites under EPA Region IX jurisdiction at which mercury is the principal COC: Sulfur Bank and Carson River (*Preliminary Draft, Human Health Risk Assessment/Remedial Investigation Report, Carson River Mercury Site*, EPA, Region IX, San Francisco, California, April 1994; EPA 1994a). Mining was conducted at these sites and mercuric sulfide is one of the principal contaminants under investigation. The EFPC Risk Assessment Team contacted EPA Region IX to learn more regarding the Region's approach to risk assessment for mercury. EPA Region IX noted that the Agency had not derived alternate reference doses (RfDs) for different mercury species, but had adopted absorption factors for use in dose estimation.

EPA Region IX indicated that mercuric sulfide is the predominant form of mercury at the sites. Understanding that the EPA RfD for mercury is based on administration of mercuric chloride in test animals, and that the sulfide is much less mobile than the chloride species, EPA Region IX chose to use a factor to reflect the relative difference in absorption between the chloride and the sulfide forms. The decision to use the relative absorption factor was supported by the results of analysis of blood samples taken from residents living in the vicinity of the contaminated sites. EPA compared measured concentrations of mercury in blood with reference or background levels. They found no statistically significant difference and concluded that mercury exposure was being limited by the mobility of the sulfide species.

EPA Region IX had requested that the EPA Environmental Criteria and Assessment Office (ECAO) conduct a literature review of absorption factors for mercury species. The ECAO review identified an absorption factor of 15% for mercuric chloride via the oral route. Furthermore, ECAO indicated that absorption of mercuric sulfide by means of the oral route is 1/30th to 1/80th that of the chloride. EPA Region IX decided to use a conservative factor of 20% (1/5th) relative absorption of the sulfide versus the chloride. Based on this information, EPA Region IX adopted a relative absorption factor of 3.0% for use in estimating exposure of human receptors to mercuric sulfide at the Sulfur Bank and Carson River sites ($15\% \times 0.20 = 3.0\%$).

Another recent example of the use of availability factors in risk assessment of exposure to mercury in soils is the Almaden Quicksilver County Park site in California. Almaden Quicksilver was the site of mercury mining for more than 100 years and is extensively contaminated with cinnabar. The State of California, Department of Health Services has oversight responsibility for the RI/FS of the facility. Mercuric sulfide is the predominant COC. In this BRA, an availability factor of 0.3 (30%) was used for the soil ingestion pathway to reflect the differences in bioavailability between the sulfide and chloride species of mercury.

In the studies discussed above, neither EPA Region IX nor the State of California adjusted the RfD value for mercury in association with use of an oral absorption factor. (Note that EPA specifies the need for comparability in toxicity and exposure estimates and both must be expressed either as absorbed or administered dose). In this regard, the "absorption factors" for mercury species used by EPA Region IX and the State of California might better be considered "bioavailability factors" that reflect the relative mobility of mercuric sulfide versus mercuric chloride from the soil matrix.

3.1.3 Selection of Bioavailability Factor for Mercury in EFPC Soils

In the BRA, the bioavailability factor for mercury in EFPC soils was set at 1.0 for the ingestion exposure route. As previously noted, this conservatively assumed that the bioavailability of mercury in EFPC soils was equivalent to that of mercuric chloride. Note that mercuric chloride is the mercury species that is the basis of the chronic oral RfD recommended by EPA for use in human health risk assessment. However, the available analytical data indicate that less mobile, less bioavailable mercury species predominate in EFPC soils. The weight of evidence points to mercuric sulfide and metallic mercury as the predominant forms.

On the basis of the available scientific data and the work conducted under authorization of EPA Region IX and the State of California, the EFPC Risk Assessment Team has selected a conservative bioavailability factor of 30% (0.3) for mercuric sulfide. Metallic mercury is considerably less mobile and bioavailable via the oral route than the sulfide species, and 30% is appropriate. The combined bioavailability of metallic mercury and mercuric sulfide from soil (oral route) is projected to be <30%. This conclusion is supported by the results of the solubility/leaching studies conducted by ORNL using EFPC soils (See Sect. 2.1 of this addendum).

3.1.4 Derivation of an Additional RGO for Mercury

RGOs were presented in the EFPC RI Report, addressing both human health effects (i.e., children/adult, residential/open land use, SLB worker) and ecological effects (i.e., various receptors in the food web). As previously noted, EPA recognizes that revision of RGOs is a part of the RI/FS process that will occur as new supporting information becomes available (EPA 1991). The new RGO presented here is a refinement arising from an improved understanding of mercury speciation and behavior in EFPC soil.

For human health assessment, the most important RGO is the one that will protect the most sensitive receptors (resident children) from adverse noncancer effects related to exposures to EFPC soils. The RGO is the concentration in soil below which the hazard index is likely to remain <1.0 over extended periods of time. Equation 1 was used to derive the RGOs for human health that are presented in the EFPC RI Report, and the same equation may be used to derive the revised RGO for resident children (as well as RGOs for less sensitive receptors).

$$RGO_{soil} = \frac{THQ \times BW \times AT \times RfD}{EF \times ED \times (CR_I \times B_I + CR_D \times ABS_D)} \quad (1)$$

where

- RGO = remediation goal option for mercury in soils (mg/kg),
- THQ = target hazard quotient (unitless),
- BW = body weight (kg),
- AT = averaging time (days),
- RfD = reference dose for mercury [mg/(kg-day)],
- EF = exposure frequency (days/year),
- ED = exposure duration (years),

CR_I	=	contact rate for ingestion exposure to soil (mg/day),
CR_D	=	contact rate for dermal contact with soil (mg/day),
B_I	=	oral bioavailability factor for mercury (unitless),
ABS_D	=	percutaneous absorption factor for dermal contact with mercury.

RGOs developed from Equation 1 account for both oral ingestion and dermal contact with EFPC soil. The change in the RGOs is directly related to the revised bioavailability factor for oral ingestion, noted in Equation 1 as B_I . In the EFPC RI Report this value was set equal to 1.0. This assumes that the mercury in EFPC soils is as bioavailable as mercuric chloride, upon which the RfD for mercury is based. As noted in Sect. 3.1.3, the additional RGOs are based on a bioavailability factor (B_I) that is 30% of the bioavailability of mercuric chloride, so the revised B_I for EFPC soil is 0.3.

The newly derived RGO for resident children is 180 mg of mercury/kg of soil for residential and agricultural land use scenarios. The previously derived RGO (RI Report, Sect. 7) was 58 mg of mercury/kg of soil and was rounded down to 50 mg/kg. The new RGO is based on consideration of the reduced mobility and bioavailability (B_I) of mercury species in EFPC soils. No other factors or variables in Equation 1 have been changed. Note that the value of 180 mg of mercury/kg of soil remains protective and is an effective target concentration for human contact with EFPC soil. As derived, the value of 180 is based on a target hazard quotient of 1.0 and consideration of reduced bioavailability of mercury species in EFPC soils. Therefore, potential exposure of children to concentrations below 180 mg/kg will result in a hazard index < 1.0 (i.e., within the target range established by EPA).

3.1.5 Quantitative Uncertainty Analysis of RGO

The uncertainty analysis presented in the EFPC BRA included a quantitative assessment of the sources of uncertainty in the input parameters and the relative influences on the results of risk assessment. In a similar manner, this section examines uncertainty in the derivation of the RGO for mercury in EFPC soils. The approach used incorporates consideration of the uncertainty surrounding estimates of bioavailability of mercury for the ingestion pathway.

In Sect. 3.1.4, the RGO was presented as a single number but should be viewed as an estimate that spans a range of possible values. Monte Carlo simulation was used to explore the uncertainty surrounding this value. Monte Carlo techniques were used to propagate the uncertainty in each exposure variable in Equation 1 and to create an output distribution (i.e., the RGO) that may be statistically evaluated. This analysis assists in evaluating the degree of "protection" or conservatism built into the value of 180 mg/kg of mercury in soil.

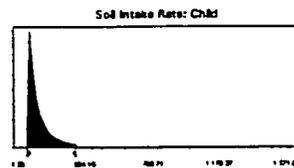
Monte Carlo simulation requires the development of a probability density function (PDF) for each uncertain variable. PDFs have been developed for the majority of the variables needed in deriving the RGO. These were presented in the BRA. A summary of the PDFs used in this evaluation is provided in Fig. 3.1. (See Sect. 5.5 of the RI Report for a more detailed discussion of the development of these distributions).

A new PDF had to be developed for bioavailability of mercury from EFPC soils. This distribution was developed using the experimental bioavailability data generated by ORNL (Sect. 2.1). As discussed previously, ORNL conducted a leaching/solubility study using EFPC

PDF for soil intake rate

Lognormal distribution with parameters:

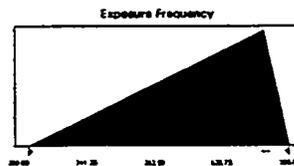
Mean	96.66
Standard Deviation	160.38



PDF for exposure frequency

Triangular distribution with parameters:

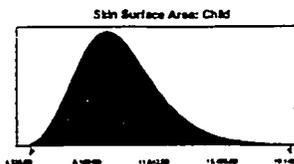
Minimum	200.00
Most Likely	350.00
Maximum	365.00



PDF for skin surface area - child

Lognormal distribution with parameters:

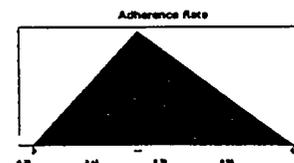
Mean	9,593.11
Standard Deviation	2,335.90



PDF for adherence factor

Triangular distribution with parameters:

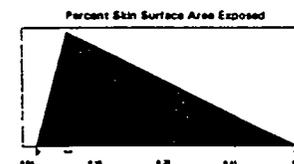
Minimum	0.20
Most Likely	0.60
Maximum	1.20



PDF for skin surface area exposed

Triangular distribution with parameters:

Minimum	0.04
Most Likely	0.10
Maximum	0.53



PDF for body weight

Lognormal distribution with parameters:

Mean	26.52
Standard Deviation	9.28

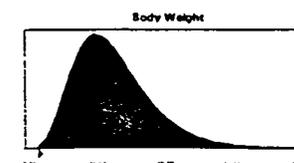


Fig. 3.1. Probability density functions: exposure assumptions.

soil to simulate the bioavailability of mercury in the gastrointestinal tract. The bioavailability factor of 30% used to calculate the RGO of 180 mg/kg (point estimate) may be evaluated in light of the results of the ORNL study.

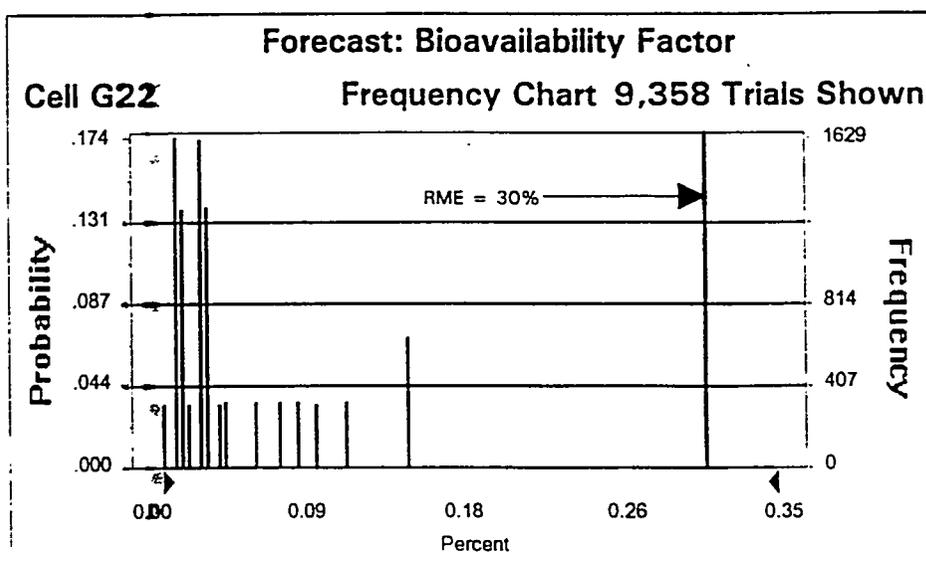
The results of the ORNL bioavailability study indicated that solubilities (percent mercury extraction from EFPC soils) are generally < 10%. Values ranged from 0.3 to 45.9%. These data were used to develop a PDF for bioavailability of mercury, which was then used in the Monte Carlo simulation. To determine the shape and appropriate characteristics of the distribution (e.g., mean and standard deviation), a probability plot of the data was prepared and examined. The data did not clearly fit a normal distribution, and were transformed to a log_e scale, plotted, and examined for goodness-of-fit. The data also did not approximate a lognormal distribution. A "custom" distribution was then developed using the actual ORNL data.

The custom distribution was developed using Crystal Ball[®] Version 3.01 for Microsoft[®] Excel (Decisioneering 1993). All of the solubilities were entered with an equal probability of occurrence. The resulting PDF was statistically evaluated and used to determine the percentile value associated with the point estimate of 30% used in Equation 1. The point estimate of 30% was plotted on the PDF for bioavailability (Fig. 3.2) and was found to fall above the 90th percentile. This supports the results of the literature survey and the work of EPA Region IX and the State of California indicating that 30% bioavailability is a conservative (and protective) estimate for mercuric sulfide and metallic mercury in EFPC soils.

Once the PDFs for each exposure variable had been generated and evaluated, Monte Carlo simulation was used to derive a probabilistic estimate of the RGO for mercury. (Note that no PDF was developed for the target hazard quotient; it was treated as a point estimate). The simulation consisted of 10,000 samples from each PDF and recalculation of the RGO. The 10,000 results were saved and aggregated as an output distribution. This output distribution for the RGO (Fig. 3.3) is depicted in the form of a reverse cumulative distribution. Figure 3.3 also presents the statistics and corresponding deciles of the forecast. As shown, 180 mg/kg of mercury in soil is the 98th percentile of the output distribution. In other words, given the uncertainty in the input variables, there is a 98% probability that the RGO is actually > 180 mg/kg. Conversely, the likelihood that the selected RGO is not sufficiently conservative (i.e., has been overestimated) is only 2%.

As a final step, a sensitivity analysis was conducted to examine the influence of each uncertain variable (in Equation 1) on the RGO estimate. Crystal Ball[®] was used to compute the Spearman rank correlation coefficient between each uncertain input variable and the projected RGO estimate. The results of the sensitivity analysis are depicted in Fig. 3.4. The size of each bar is proportional to the measured rank correlation or influence of that variable on the magnitude of the RGO estimate. As illustrated, the bioavailability factor has the greatest influence on the RGO, followed by the other exposure variables (depicted in descending order of influence). The sign of the measured rank correlation coefficient (positive or negative) indicates the effect on the output forecast (RGO). For example, the negative correlation coefficients indicate that an increase in the magnitude of a given variable is associated with a corresponding decrease in the output estimate. This is evident in the decrease in the bioavailability factor for mercury from 100 to 30% and the resultant change in RGO values from 50 mg/kg to 180 mg/kg of mercury in soil.

Statistics:	<u>Value</u>
Trials	10000
Mean	0.06
Median (approx.)	0.02
Mode (approx.)	0.01
Standard Deviation	0.10
Variance	0.01
Skewness	2.90
Kurtosis	10.76
Coeff. of Variability	1.63
Range Minimum	0.00
Range Maximum	0.46
Range Width	0.46
Mean Std. Error	0.00

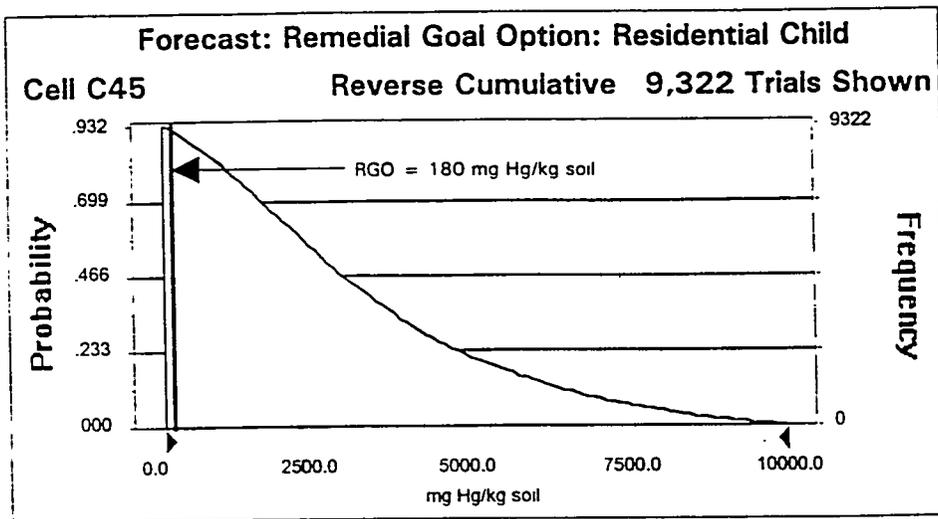


Percentiles:

<u>Percentile</u>	<u>Percent (approx.)</u>
0%	0.00
10%	0.01
20%	0.01
30%	0.01
40%	0.02
50%	0.02
60%	0.03
70%	0.04
80%	0.08
90%	0.14
100%	0.46

Fig. 3.2. Probability density functions: bioavailability of mercury in EFPC soils.

Statistics:	Value
Trials	10000
Mean	4128.1
Median (approx.)	3083.9
Mode (approx.)	1559.2
Standard Deviation	3837.1
Variance	14723666.2
Skewness	2.67
Kurtosis	15.41
Coeff. of Variability	0.93
Range Minimum	52.9
Range Maximum	43091.5
Range Width	43038.7
Mean Std. Error	38.37



Percentiles:

Percentile	mg Hg/kg soil (approx.)
100% 99.88%	58 mg Hg/kg soil
90% 98.70%	180 mg Hg/kg soil
80%	1384.3
70%	1934.9
60%	2470.5
50%	3083.9
40%	3811.4
30%	4726.8
20%	6091.9
10%	8544.0
0%	43091.5

Fig. 3.3. Probability distribution: RGO for mercury in EFPC soil.

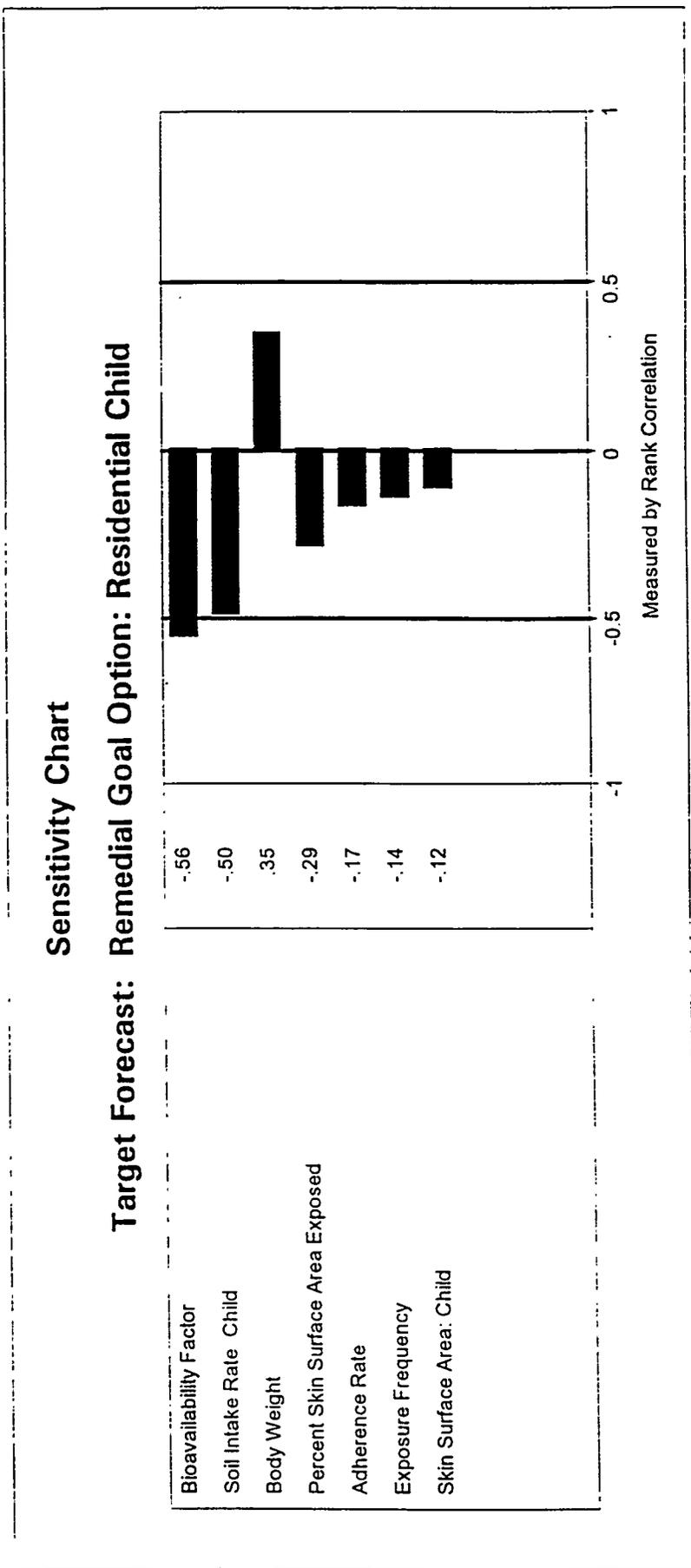


Fig. 3.4. Sensitivity analysis results.

3.1.6 Human Health Remediation Goal Option

The results of sampling and analysis indicate that the less soluble and less toxic mercury species predominate in EFPC soils. Recent results of additional speciation and leaching/availability studies using EFPC soils contribute to the weight of evidence that less mobile and bioavailable forms of mercury predominate. The weight of evidence points to mercuric sulfide and metallic mercury as the primary forms.

EPA recognizes that revision, or development of alternate RGOs is a normal part of the RI/FS process and will occur as new supporting information becomes available. In the BRA, the bioavailability factor for mercury in EFPC soils was set at 1.0 for the ingestion exposure route. In using a factor of 1.0, it was assumed that the bioavailability of mercury in EFPC soils was equivalent to that of mercuric chloride. (Note that mercuric chloride is the mercury species that is the basis of the chronic oral RfD recommended by EPA for use in human health risk assessment). In this addendum, the RGO for mercury in soil for protection of human health has been recalculated. This recalculation is based on inadvertent ingestion and dermal exposure of children to mercuric sulfide and metallic mercury in soil.

Based on the available scientific data and results of work conducted under authorization of EPA Region IX and the State of California, the EFPC Risk Assessment Team has selected a conservative bioavailability factor of 30% (0.3) for mercuric sulfide. Metallic mercury is considerably less mobile and bioavailable via the oral route than the sulfide species, and 30% is appropriate. The combined bioavailability of metallic mercury and mercuric sulfide from soil (oral route) is projected to be <30%. This conclusion is supported by the results of the solubility/leaching studies conducted by ORNL using EFPC soils.

A new RGO of 180 mg of mercury per kg of soil has been calculated using a bioavailability factor of 30%. This RGO is approximately three times greater than the RGO of 50 mg/kg of mercury in soil derived in the D2 draft of the RI Report. Both RGOs (along with those derived in the RI Report, Sect. 7) will be presented for consideration in the feasibility study. The new RGO of 180 mg/kg remains protective (i.e., due to consideration of reduced bioavailability) for human contact with EFPC soil for residential and agricultural land use scenarios. As derived, the value of 180 mg/kg is based on a target hazard quotient of 1.0. Therefore, potential exposure of children to concentrations below 180 mg/kg will result in a hazard index < 1.0 (i.e., within the target range established by EPA). The change in bioavailability from 100 to 30% is applicable to the development of other human health RGOs for other land uses (e.g., the 331 mg/kg soil for commercial, DOE-owned, and other land uses would become 938 mg/kg).

3.2 DERIVATION OF ALTERNATIVE ECOLOGICALLY BASED RGOs FOR MERCURY

3.2.1 Introduction

Potential transport pathways and exposure routes for contaminants, especially mercury in EFPC and the EFPC floodplain, were described in the EFPC RI Report (DOE 1994). They are shown schematically in Figs. 6.38 (Y-12 Plant contaminants) and 6.39 (EFPC floodplain contaminants) in the RI Report. These figures indicate that some transport pathways and some

exposure routes are considered more important than others for exposure to ecological receptors. Exposure may occur by ingestion of or dermal contact with soil, inhalation of vapors from soil, ingestion of or direct uptake from water from contaminated seeps or surface water from EFPC, or ingestion of contaminated food. Exposures through contaminated physical media may be reduced by remediation of the media. RGOs are to be established that will ensure that residual contaminant levels will be protective of ecological resources.

Biota in the EFPC floodplain are exposed to these contaminants in five media sources—air, surface water, groundwater, instream sediments, and soils. These media are considered separately in the discussion of RGOs in the RI Report and this addendum. Biota are a source of exposure through the food web, but it is assumed that biota cannot be remediated. Remedial goals for biota depend ultimately on uptake from abiotic media. Therefore, separate RGOs for biota are not derived in this addendum.

The following section summarizes the RGOs for air, surface water, and groundwater. A range of RGOs for sediment follows. A range of soil RGOs under three scenarios is followed by a brief discussion of uncertainties. The section concludes with a summary.

3.2.2 Air, Surface Water, and Groundwater RGOs

As explained in the RI Report, air is not considered a major pathway of ecological exposure to contaminants in EFPC or the EFPC floodplain. Therefore, RGOs for air are not proposed. However, exposures of biota to airborne contaminants in or near the ground are considered in the derivation of RGOs for soil in Sect. 7.3.6.2 of the RI Report and again in this addendum.

Surface water has been shown to be a major pathway transporting dissolved and particulate contaminants to aquatic biota in EFPC, either directly or through the food chain. The RI Report discussion of surface water RGOs focused on applicable or relevant and appropriate requirements (ARARs) and to-be-considered (TBC) guidance, protection of EFPC biota from contaminant toxicity, and protection of predators from contaminant toxicity. An evaluation of RGOs calculated for surface water and the methods used to derive them is presented in Table 7.9 of the RI Report. Comparing ARARs to risk-based RGOs shows that the ambient water quality criteria (AWQC) for mercury are protective of biota in the EFPC environment. All of the four proposed surface water RGOs for mercury are below the contract-required analytical detection limit of 1 $\mu\text{g/L}$. Bioconcentration results in accumulation of mercury species in biota above detectable limits even when mercury is below concentration levels detectable in water, and the concentration in water can be estimated from the observed body burdens in aquatic biota. Therefore, attainment of surface water RGOs must be measured by methods more sensitive than Contract Laboratory Program methods or by continued monitoring of aquatic biota.

No remedial goals based on ecological risk are being proposed for groundwater. Deep groundwater is not considered a major exposure pathway for ecological receptors. Because of the lateral migration of groundwater from the EFPC floodplain to the creek or from the creek to the floodplain under dry conditions, shallow groundwater was evaluated as a potential pathway to terrestrial insects and worms by dermal contact and ingestion, and to plants by root uptake (Fig. 6.39 in the RI Report). Furthermore, most mercury in groundwater is particle bound and not dissolved. However, shallow groundwater is transient, and contaminants found there are presumed to come either by leaching from EFPC floodplain soils, by infiltration of EFPC surface

water, or from sources outside the EFPC floodplain. Treatability studies have shown that the concentration of mercury in a water leachate of EFPC floodplain soils was ~0.08% of the concentration in soil (Radian 1993). This means that the mobility of soil mercury in groundwater is minor. In addition, cleanup of groundwater would not remediate the sources of contaminants to the groundwater and would not be an effective remedy. Therefore, no ecologically based remedial goals are being proposed for shallow groundwater.

In conclusion, ecologically based RGOs for air and surface water are presented in the RI Report and no alternatives are provided in this addendum.

3.2.3 Sediment RGOs

Instream sediments may be an important source of ecological exposure to contaminants released from the Y-12 Plant or from the EFPC floodplain (Figs. 6.38 and 6.39 in the RI Report). Benthic invertebrates (e.g., stoneflies and snails) live in and on the sediment and associated substrates and are exposed by dermal absorption and ingestion. Crayfish and common stonerollers may be exposed by incidental ingestion of sediment during feeding. Sediment may also be the source of exposure to other levels of the aquatic food chain. Guideline values for sediment concentrations have been proposed by NOAA. They are: low effects range, 0.15 mg/kg; median effects range, 1.3 mg/kg; and overall apparent effects threshold, 1.0 mg/kg. These values are not ARARs but are TBC guidance intended to identify sediments for which further study may be necessary.

A number of methods have been proposed for the assessment of sediment toxicity (Adams et al. 1992). They include the equilibrium partitioning (EP) method, the adverse effects threshold (AET) method, and other effects-based methods. These methods were discussed in the RI Report. The EP method is used to derive sediment quality criteria (SQC) based on the toxicological properties of the sediment or on considerations of further transport pathways and exposure routes. This method is restated below because it was used to develop additional RGOs for sediment.

3.2.3.1 Partitioning methods

The EP method assumes that the most important exposure to sediment contaminants is via pore water and that contaminant concentrations in pore water and in the contiguous particulate or solid phase come to a chemical equilibrium. Therefore, the concentration of contaminant in one phase can be predicted if the concentration in the other phase and the equilibrium coefficient are known. However, partition coefficients for ions and polar compounds depend on properties of the sediment and cannot be predicted for any given site. In addition, the EP method assumes that pore water is in equilibrium with sediment, so it cannot be applied under non-equilibrium conditions, such as those that occur when the pore water of coarse sediment exchanges rapidly with surface water. It may be particularly difficult to achieve equilibrium with mercury in pore water because of the formation, destruction, and biological assimilation of methyl mercury. Therefore, EP may not formally apply to conditions at EFPC.

In the following RGO derivation, it is not assumed that mercury species are in steady-state. Instead, we assume that mercury species in sediment, pore water, and surface water attain steady-state conditions. That is, they are present at ratios that remain constant. In the derivation, we

use K_D values to represent the steady-state ratio rather than the equilibrium ratio. Site-specific K_D values for inorganic mercury and methyl mercury in EFPC sediments and their pore water were obtained as part of the mesocosm study by Turner et al. (DOE 1994, Appendix Q). This study was designed to mimic flow rates and sediment conditions at locations in EFPC where sediment is deposited, so the K_D values should conservatively represent steady-state conditions in other portions of the creek.

The K_D values used were 7.1×10^5 L/kg for inorganic mercury and 2.7×10^4 L/kg for methyl mercury. Toxicity thresholds used for this determination in the RI Report were the lowest values reported by Eisler (1987). They were $0.3 \mu\text{g}$ inorganic mercury/L for toxicity to larval rainbow trout (*Oncorhynchus mykiss*) and $1 \mu\text{g}$ methyl mercury/L for toxicity to *Daphnia magna*.

The equation used in the RI Report for deriving the SQC is:

$$SQC = CC \times 0.001 \text{ mg}/\mu\text{g} \times K_D \quad (2)$$

Therefore, the SQC for inorganic mercury is:

$$SQC = 0.3 \mu\text{g}/\text{L} \times 1 \times 10^{-3} \text{ mg}/\mu\text{g} \times 7.1 \times 10^5 \text{ L}/\text{kg} = 213 \text{ mg}/\text{kg} \quad (3)$$

This RGO was rounded to 210 (Table 3.2) and is the one published in the RI Report (DOE 1994).

Table 3.2. Endpoint, evaluation method, and potential RGO for sediment mercury in EFPC from the previously published RI Report

Endpoint	Method	RGO (mg/kg sediment)	Remarks
Larval trout toxicity	Partitioning	210	System not currently at equilibrium

3.2.3.2 Sediment-water partitioning and alternative sediment RGOs

The EP equation used in the RI Report to generate the 210 mg/kg sediment RGO was expanded to accommodate new information. These expanded equations and associated exposure conditions resulting in additional RGOs (Table 3.3) are presented in this section of the addendum.

Equations describing the relationships among concentrations of mercury species in water, sediment, and tissue are:

$$CW_{\text{MeHg}} = SQC_{\text{MeHg}} / K_{D,\text{MeHg}} \quad (4)$$

$$CW_{\text{Inorg}} = SQC_{\text{Inorg}} / K_{D,\text{Inorg}} \quad (5)$$

$$F_{\text{MeHg}} = \text{Sed}_{\text{MeHg}} / \text{Sed}_{\text{Total}} \quad (6)$$

$$Hg_{\text{Tissue}} = CW \times BCF \quad (7)$$

Table 3.3. EFPC sediment RGOs (mg of total mercury/kg) and assumptions

Scenario	Endpoint	Method	RGO* (mg/kg)	Assumptions	
				Remarks	Degree of conservatism
1	Toxicity to piscivorous birds (0.1 mg MeHg/kg diet)	Partitioning, food chain	0.03	Sediment is the sole source of mercury to fish. All sediment mercury is methylated, pore water is in steady-state with sediment, overlying creek water is same as pore water.	Very high
2	Toxicity to piscivorous birds (0.1 mg MeHg/kg diet)	Partitioning, food chain	0.9	Sediment is the sole source of mercury to fish. All sediment mercury is methylated, pore water is in equilibrium with sediment, overlying creek water is not the same with pore water.	Very high
3	Toxicity to piscivorous birds (0.1 mg MeHg/kg diet, 28.9 mg Inorg. Hg/kg diet)	Partitioning, food chain	120	Sediment is the sole source of mercury to fish. Methyl mercury in sediment is in equilibrium with total mercury, pore water is in steady-state with sediment, overlying creek water is same as pore water.	High
4	Toxicity to piscivorous birds (0.1 mg MeHg/kg diet, 28.9 mg Inorg. Hg/kg diet)	Partitioning, food chain	3200	Sediment is the sole source of mercury to fish. Methyl mercury in sediment is in equilibrium with total mercury, pore water is in equilibrium with sediment, overlying creek water is not the same with pore water.	Moderate
5	Toxicity to piscivorous mammals (0.11 mg MeHg/kg diet)	Partitioning, food chain	0.04	Sediment is the sole source of mercury to fish. All sediment mercury is methylated, pore water is in steady-state with sediment, overlying creek water is same as pore water.	Very high

Table 3.3 (continued)

Scenario		Endpoint	Method	RGO ^a (mg/kg)	Assumptions Remarks	Degree of conservatism
6	Toxicity to piscivorous mammals (0.11 mg MeHg/kg diet)	Partitioning, food chain	1.0	Sediment is the sole source of mercury to fish. All sediment mercury is methylated, pore water is in equilibrium with sediment, overlying creek water is not the same with pore water.	Very high	
7	Toxicity to piscivorous mammals (0.11 mg MeHg/kg diet, 57 mg Inorg. Hg/kg diet)	Partitioning, food chain	130	Sediment is the sole source of mercury to fish. Methyl mercury in sediment is in equilibrium with total mercury, pore water is in steady-state with sediment, overlying creek water is same as pore water.	High	
8	Toxicity to piscivorous mammals (0.11 mg MeHg/kg diet, 57 mg Inorg. Hg/kg diet)	Partitioning, food chain	3600	Sediment is the sole source of mercury to fish. Methyl mercury in sediment is in equilibrium with total mercury, pore water is in equilibrium with sediment, overlying creek water is not the same with pore water.	Moderate	
9	Marketability of fish (max 1 mg MeHg/kg flesh)	Partitioning	0.3	Sediment is the sole source of mercury to fish. All sediment mercury is methylated, pore water is in steady-state with sediment, overlying creek water is same as pore water. Surface water concentration = AWQC of 0.012 µg/L.	Very high	
10	Marketability of fish (max 1 mg MeHg/kg flesh)	Partitioning	10.6	Sediment is the sole source of mercury to fish. All sediment mercury is methylated, pore water is in steady-state with sediment and has a K_p of 8.85×10^3 , overlying creek water is same as pore water. Surface water concentration = AWQC of 0.012 µg/L.	Very high	

Table 3.3 (continued)

Scenario	Endpoint	Method	RGO ^a (mg/kg)	Assumptions	
				Remarks	Degree of conservatism
11	Marketability of fish (max 1 mg Total Hg/ kg flesh)	Partitioning	162	Sediment is the sole source of mercury to fish. Methyl mercury in sediment is in equilibrium with total mercury, pore water is in steady-state with sediment, overlying creek water is same as pore water. Surface water concentration = AWQC of 0.012 µg/L.	High
12	Marketability of fish (max 1 mg MeHg/kg flesh)	Partitioning	1100	Sediment Methyl mercury is the sole source of Methyl mercury to fish. Methyl mercury in sediment is in equilibrium with total mercury, pore water is in steady-state with sediment, overlying creek water is same as pore water. Surface water concentration = AWQC of 0.012 µg/L.	Moderate
13	Toxicity to fish (0.03 µg MeHg/L, 0.03 µg Inorg. Hg/L)	Partitioning	21	Sediment is the sole source of mercury to fish. Methyl mercury in sediment is in equilibrium with total mercury, pore water is in steady-state with sediment, overlying creek water is same as pore water.	Very high
14	Toxicity to fish (0.23 µg MeHg/L, 0.23 µg Inorg. Hg/L)	Partitioning	163	Sediment is the sole source of mercury to fish. Methyl mercury in sediment is in equilibrium with total mercury, pore water is in steady-state with sediment, overlying creek water is same as pore water.	High
15	Toxicity to aquatic biota (1.0 µg MeHg/L, 0.3 µg Inorg. Hg/L)	Partitioning	213 ^d	Sediment is the sole source of mercury to fish. Methyl mercury in sediment is in equilibrium with total mercury, pore water is in steady-state with sediment, overlying creek water is same as pore water.	High
16	Toxicity to fish (0.23 µg MeHg/L, 0.87 µg Inorg. Hg/L)	Partitioning	620	Sediment is the sole source of mercury to fish. Methyl mercury in sediment is in steady-state with total mercury, pore water is in equilibrium with sediment, overlying creek water is same as pore water.	High

Table 3.3 (continued)

Scenario	Endpoint	Method	RGO ^a (mg/kg)	Assumptions	
				Remarks	Degree of conservatism
17	Toxicity to fish (0.23 µg MeHg/L)	Partitioning	175	Sediment is the sole source of mercury to fish. All sediment mercury is methylated, pore water is in equilibrium with sediment, overlying creek water is not the same with pore water.	High
18	Toxicity to fish (0.23 µg MeHg/L, 0.87 µg Inorg. Hg/L)	Partitioning	3600	Sediment is the sole source of mercury to fish. Methyl mercury in sediment is in equilibrium with total mercury, pore water is in equilibrium with sediment, overlying creek water is not the same with pore water.	Moderate
19	Toxicity to benthic biota (0.87 µg MeHg/L)	Partitioning	24	Sediment is the sole source of mercury to benthic biota. All mercury is methylated, pore water is in steady-state with sediment.	High
20	Toxicity to benthic biota (0.87 µg/L)	Partitioning	620	Sediment is the sole source of mercury to benthic biota. Methyl mercury in sediment is in steady-state with total mercury, pore water is in equilibrium with sediment.	Moderate

^a RGOs given in terms of total mercury in sediment.

^b MeHg = methyl mercury, Inorg. = inorganic

^c Logarithmic mean of K_p values for total mercury reported in Appendix Q of the RI Report.

^d The number in this cell is the value presented in the RI report.

where

CW_{MeHg}	=	concentration of methyl mercury in pore water or surface water (mg/L),
SQC_{MeHg}	=	maximum allowable concentration of methyl mercury in sediment (mg/kg),
$K_{D,MeHg}$	=	sediment-to-water partitioning coefficient for methyl mercury (L/kg),
CW_{Inorg}	=	concentration of inorganic mercury in pore water or surface water (mg/L),
SQC_{Inorg}	=	maximum allowable concentration of inorganic mercury in sediment (mg/kg),
$K_{D,Inorg}$	=	sediment-to-water partitioning coefficient for inorganic mercury (L/kg),
F_{MeHg}	=	fraction of total sediment mercury as methyl mercury,
Sed_{MeHg}	=	observed concentration of methyl mercury in sediment (mg/kg),
Sed_{Total}	=	observed concentration of total mercury in sediment (mg/kg),
Hg_{Tissue}	=	mercury species concentration in tissue (mg/kg),
BCF	=	bioconcentration factor of mercury species (L/kg) in exposed organism.

In the derivation of SQC, a comparison concentration (CC_{MeHg} or CC_{Inorg}) is used to represent the endpoint for the derivation. CC is the concentration of mercury species in water, sediment, or tissue, depending on the endpoint. Independent derivations of SQC for mercury species are derived in parallel.

Calculations of direct exposure are described by the following equations:

$$CC_{MeHg} = SQC_{Sed,Tot} \times \frac{F_{MeHg}}{K_{D,MeHg}} \quad (8)$$

and

$$CC_{Inorg} = SQC_{Sed,Tot} \times \frac{F_{Inorg}}{K_{D,Inorg}} \quad (9)$$

Therefore, the sediment RGOs for toxicity by direct exposure are given by:

$$SQC_{Tot} = CC_{MeHg} \times \frac{K_{D,MeHg}}{F_{MeHg}} \quad (10)$$

and

$$SQC_{Tot} = CC_{Inorg} \times \frac{K_{D,Inorg}}{F_{Inorg}} \quad (11)$$

Calculations of exposure for bioaccumulation of inorganic and methyl mercury species are described by:

$$Bodyburden_{MeHg} = SQC_{Sed,Tot} \times \frac{F_{MeHg} \times BCF_{MeHg}}{K_{D,MeHg}} \quad (12)$$

and

$$Bodyburden_{Inorg} = SQC_{Sed,Tot} \times \frac{F_{Inorg} \times BCF_{Inorg}}{K_{D,Inorg}} \quad (13)$$

where BCF refers to the dietary items of the predator. Therefore, the sediment RGOs for food chain exposure to inorganic and methyl mercury species are given by:

$$SQC_{Tot} = CC_{MeHg} \times \frac{K_{D,MeHg}}{F_{MeHg} \times BCF_{MeHg}} \quad (14)$$

and

$$SQC_{Tot} = CC_{Inorg} \times \frac{K_{D,Inorg}}{F_{Inorg} \times BCF_{Inorg}} \quad (15)$$

A number of assumptions were made in deriving the alternative sediment RGOs. These assumptions led to various parameter values used in the equations. In each case, it was assumed that sediment is the sole source of mercury to biota by various routes. The other assumptions and their effect on parameters were:

- mercury in EFPC sediments may be entirely methylated ($F_{MeHg} = 1$), or the concentration of methyl mercury can be at a steady state with total mercury at the fraction observed in the mesocosm study ($F_{MeHg} = 2.86 \times 10^{-4}$);
- mercury in pore water is at a steady state with mercury in sediment ($K_{D,MeHg} = 2.7 \times 10^4$ and $K_{D,Inorg} = 7.1 \times 10^5$);
- the concentrations of mercury species in surface water may be the same as in pore water or mercury in surface water may be at a steady state with sediment at the fraction observed in the mesocosm study ($K_{D,MeHg} = 7.6 \times 10^5$ and $K_{D,Inorg} = 4.1 \times 10^6$); and
- toxicity endpoints vary, depending on the organisms chosen (range of CCs or benchmark values).

The parameter values for the different combinations modeled are listed in Table 3.4. When the values were used in the equations presented above, the resulting RGOs varied widely. They are presented in Table 3.3 as RGOs for total mercury in sediment. In some scenarios, separate RGOs were calculated for methyl mercury and inorganic mercury endpoints; in the scenario cells, the lower RGO and endpoint were reported.

More specifically, the 20 scenarios treat the following:

- toxicity to fish predators (i.e., birds and mammals) (8 scenarios) with sediment RGOs from the very conservative 0.03 to 3600 mg/kg;
- marketability of fish (4 scenarios) with sediment RGOs ranging from the very conservative 0.3 to 1100 mg/kg;
- toxicity to fish/aquatic biota (6 scenarios) with sediment RGOs of 21 to 3600 mg/kg;
- toxicity to benthic macroinvertebrates (2 scenarios) with sediment RGOs of 24 to 620 mg/kg.

Table 3.4. Parameters for sediment RGOs

Scenario	MeHg benchmark	Inorg Hg benchmark	$K_{D(\text{MeHg})}$	$K_{D(\text{Inorg})}$	FMe	BCF_{MeHg}	$\text{BCF}_{\text{Inorg}}$
1	0.1 mg/kg diet	—	2.7×10^4	—	1.0	8.2×10^4	—
2	0.1 mg/kg diet	—	7.6×10^5	—	1.0	8.2×10^4	—
3	0.1 mg/kg diet	28.9 mg/kg diet	2.7×10^4	7.1×10^5	2.86×10^{-4}	8.2×10^4	5.0×10^3
4	0.1 mg/kg diet	28.9 mg/kg diet	7.6×10^5	4.1×10^6	2.86×10^{-4}	8.2×10^4	5.0×10^3
5	0.11 mg/kg diet	—	2.7×10^4	—	1.0	8.2×10^4	—
6	0.11 mg/kg diet	—	7.6×10^5	—	1.0	8.2×10^4	—
7	0.11 mg/kg diet	57 mg/kg diet	2.7×10^4	7.1×10^5	2.86×10^{-4}	8.2×10^4	5.0×10^3
8	0.11 mg/kg diet	57 mg/kg diet	7.6×10^5	4.1×10^6	2.86×10^{-4}	8.2×10^4	5.0×10^3
9	1.0 mg/kg flesh	—	2.7×10^4	—	1.0	8.2×10^4	—
10	1.0 mg/kg flesh	1.0 mg/kg flesh	8.8×10^5	—	—	8.2×10^4	—
11	1.0 mg/kg flesh	1.0 mg/kg flesh	2.7×10^4	7.1×10^5	2.86×10^{-4}	8.2×10^4	5.0×10^3
12	1.0 mg/kg flesh	—	2.7×10^4	—	2.86×10^{-4}	8.2×10^4	—
13	0.03 $\mu\text{g/L}$	—	2.7×10^4	—	1.0	—	—
14	0.23 $\mu\text{g/L}$	—	2.7×10^4	—	1.0	—	—
15	1.0 $\mu\text{g/L}$	0.3 $\mu\text{g/L}$	2.7×10^4	7.1×10^5	1.0	—	—
16	0.23 $\mu\text{g/L}$	0.87 $\mu\text{g/L}$	2.7×10^4	7.1×10^5	2.86×10^{-4}	—	—
17	0.23 $\mu\text{g/L}$	—	7.6×10^5	—	1.0	—	—
18	0.23 $\mu\text{g/L}$	0.87 $\mu\text{g/L}$	7.6×10^5	4.1×10^6	2.86×10^{-4}	—	—
19	0.87 $\mu\text{g/L}$	—	2.7×10^4	—	1.0	—	—
20	0.87 $\mu\text{g/L}$	0.87 $\mu\text{g/L}$	2.7×10^4	7.1×10^5	2.86×10^{-4}	—	—

Inorg Hg = inorganic mercury
 MeHg = methyl mercury

Thus, there is a wide range of RGOs—0.03 to 3600 mg/kg—depending on which assumptions one adopts. The lowest values in each scenario are associated with the assumption of surface water having the same mercury concentration as pore water and pore water being in steady-state with sediment. These assumptions are evaluated below.

3.2.3.3 Summary of ecologically based RGOs for sediment

The potential RGO for sediment of 210 mg/kg from the RI Report is listed in Table 3.2. This was based on a larval trout toxicity endpoint. Table 3.3 provides additional RGOs based on additional endpoints. The most conservative scenarios in this addendum include the assumption that most surface water contaminants were at the same concentration as in sediment pore water (described by the K_p for pore water). This is not likely to be true of fine, deep sediments that prevent rapid water exchange. These assumptions gave a range of RGOs for sediment from 0.03 to 1100 mg/kg. If it is assumed that the steady-state ratio of mercury species in surface water to mercury species in sediment is reflected by the results of the mesocosm study (DOE 1994, Appendix Q), sediment RGOs range from 0.9 to 3600 mg/kg, depending on endpoints and other assumptions. Because of the wide range of calculated RGOs (which results from the wide range of assumptions) all available site-specific data on sediment and pore-water toxicity should be included in the final evaluation of sediment RGOs.

Exposure to contaminants in sediment is assumed to result from transport of contaminants into water trapped in interstitial pores of the sediment; thus, the nature of the pore water is very important in determining exposure. Fine-grained sediments, which may be found in pools and other areas with low flow rates, have more pores than coarse-grained sediments. Pore water in fine sediments also exchanges with surface water more slowly than pore water in coarse sediments, so pore water contaminant concentrations can build up to higher levels in fine sediments. EFPC sediments are mostly coarse because the high flow rate of the creek removes the fine material. The concentration of mercury in pore water in coarse sediments is more likely to be similar to that in surface water and lower than if pore water were in equilibrium with sediment.

Surface water, which receives mercury loading from the Y-12 Plant and runoff from EFPC floodplain, is currently the major source of mercury contamination to aquatic biota. The average mercury level in the sediment composite representing Site 1 was 18 mg/kg (Fig. 6.43 in the RI Report). At this site, the observed mercury concentration in surface water was 0.54 $\mu\text{g/L}$, whereas the calculated equilibrium concentration would be $\sim 18,000 \mu\text{g/kg} / 7.1 \times 10^5 \text{ L/kg} = 0.025 \mu\text{g/L}$, lower than the observed value by a factor of ~ 20 . This implies that sediment could not supply the observed concentration of mercury. A sediment toxicity study discussed in Sect. 2.4 showed no toxicity; therefore, risks from instream sediments should be evaluated after the source of mercury to EFPC surface water and EFPC floodplain soils have been remediated.

3.2.4 Soil RGOs

Terrestrial animals were shown to have accumulated concentrations of mercury exceeding guidelines for protection from toxicity and for protection of predators (Sect. 6.4.1.1 of the RI Report). Soil is the potential source of exposure by direct ingestion and inhalation and indirectly through the food chain. These pathways were discussed in the RI Report. The equation for calculating exposure by ingestion is restated because it was used in the computations of additional soil RGOs.

3.2.4.1 Soil ingestion

Exposure by ingestion of contaminated soil is calculated by modifying the standard formula for calculating the hazard quotient (EPA 1989b):

$$EQ = (C_{\text{soil}} \times 10^{-3} \text{ kg/g} \times SI \times FI \times ABS) / (CD \times BW \times 10^{-3} \text{ kg/g}), \text{ and} \quad (16)$$

$$C_{\text{soil}} = (EQ \times CD \times BW \times 10^{-3}) / (SI \times 10^{-3} \times FI \times ABS) \quad (17)$$

where

C_{soil}	=	contaminant concentration in soil (mg contaminant/kg soil),
EQ	=	exposure quotient = 1,
CD	=	comparison dose (mg contaminant/kg body weight/day),
BW	=	body weight (kg),
SI	=	soil intake (g soil/day),
FI	=	fraction of soil from contaminated area (g contaminated soil/g soil ingested),
ABS	=	fraction of ingested dose absorbed (g contaminant absorbed/g contaminant ingested).

Justification and comments on variables:

EQ: The target exposure quotient is always 1. Assuming other parameters are known reliably, a higher value would not be protective, and lower values would be overly protective.

CD: The comparison dose is the toxicological benchmark to which the organism is to be protected. It should preferably be a No Observed Adverse Effects Level (NOAEL), Lowest Observable Adverse Effects Level (LOAEL), or similar measure of effect.

BW: Body weight of shrews is typically ~8 to 20 g, whereas body weight of mice is ~25 to 40 g. Variability in body weight is likely to be compensated by a similar variability in soil ingestion.

SI: Incidental ingestion of soil by small mammals is likely to be variable, depending on feeding habits. Birds may ingest soil intentionally for grit to help grind their food. For this calculation, a range of 1 to 5% body weight per day was used in the RI Report (Sect. 6.2.2.1). In this addendum, additional data on percent soil in the diet (EPA 1993) are used as well because comparison dose is in terms of contaminant concentration in the diet.

FI: It was assumed in the RI that the home range of the subject animal is restricted to the contaminated area of the EFPC floodplain (FI = 1). That assumption is probably reasonable for mice and shrews. Scenarios are presented here, as well as in the RI Report, in which the home range includes areas outside the floodplain.

ABS: The absorption factor may depend on both the contaminant and the medium in which the contaminant is contained. Typically, the absorption factor of organic chemicals is assumed to be 1, whereas it is usually lower for inorganic chemicals. If the medium used

to determine the comparison dose is the same as the exposure medium, no correction for absorption should be made. Toxicological studies of inorganic chemicals may be based on absorption of 20% or less of the administered dose (EPA 1989b). Feeding studies have shown that absorption of mercury by laboratory mice from contaminated soil taken from the EFPC floodplain was < 10% (Revis et al. 1989a). However, for the calculation of RGOs, a conservative value of ABS = 1 was used in the RI Report. In this addendum, it is assumed that the absorption factor from soil may vary, but absorption of mercury, especially methyl mercury, from the ingested prey tissue is always 1 (WHO 1990).

Evaluation of mercury ingestion with soil follows:

A dietary concentration of 100 to 200 mg of mercury/kg/d caused histological damage to rat kidney, whereas no damage was observed in mink fed 10 mg/kg/d (Table 6.42 in the RI Report). Revis et al. (1989a) reported a NOAEL of 13.7 mg/kg for mice fed soil-bound mercury. For this derivation, the range of these numbers, 13.7 to 100 mg/kg/d, will be used as values for CD.

Calculation of an RGO, with the values listed above:

$$\begin{aligned} C_{\text{soil}} &= [1 \times (13.7 \text{ to } 100) \times 25 \times 10^{-3}] / [(0.01 \text{ to } 0.05) \times 25] \times 10^{-3} \times 1 \times 1 \quad (18) \\ &= 274 \text{ to } 10,000 \text{ mg/kg.} \end{aligned}$$

Because mercury concentrations above 1600 mg/kg were observed in surface soils, it is concluded in the RI that the soil ingestion pathway may be of major significance for mercury exposure of small mammals. The RGO for soil mercury based on soil ingestion was thus 274 mg/kg in the RI Report and is shown on Table 3.5 in this addendum.

3.2.4.2 Inhalation

Animals living close to or in the ground may be exposed to volatile chemicals in the soil. RGOs for these chemicals in soil are addressed as soil RGOs because cleanup of soil would be required to reduce any deleterious inhalation exposures.

The calculated value of C_{soil} for mercury in the RI Report was 1000 to 7475 mg/kg, depending on the values of the chronic RfD used (Table 3.5). The value of C_{soil} assumed that all soil mercury is in the firmly bound ionic form. Because the majority of the mercury is actually ionic or bound in a nonvolatile form, the lower RGO of 1000 mg/kg for inhalation of vapors is probably adequately conservative.

3.2.4.3 Protection of mid-level predators in the EFPC floodplain from toxicity via the food chain

Mid-level predators are those organisms feeding on insects, earthworms, and other herbivores and being eaten by top predators (e.g., hawks, owls, and foxes). Wrens and shrews are mid-level predators found in the EFPC floodplain. Small mammals were shown to have body burdens of some contaminants above concentrations considered to be potentially toxic. The major route of contaminant accumulation is probably the food chain. Contaminants are expected to enter the food chain of these terrestrial biota by uptake from soil into plants, earthworms, and insects, as well as by the ingestion and possibly inhalation pathways described in Sects. 7.3.6.1

Table 3.5. Endpoints, evaluation methods, and potential RGOs for surface soil in the EFPC floodplain from the previously published RI Report

Endpoint	Method	RGO (mg/kg soil)	Remarks
Incidental ingestion of soil with histological damage to rat kidney	Soil ingestion equation	274 to 10,000	Based on highly conservative estimates of ingestion
Inhalation of vapors from soil	Inhalation model	1,000 to 7,475	Based on nonvolatile mercury; elemental fraction is low
Food chain, protection from toxicity to rodents	Food ingestion equation	230 to 1,670	Assumes proportional bioaccumulation in food chain
Food chain, protection of predators	Food ingestion equation	230	Allows for mix of diet, range of predators

Table summarized from RI Report (DOE 1994).

and 7.3.6.2 of the RI Report. Because elevated body burdens were observed in shrews and wrens, but generally not in mice and voles (which are first-group consumers), it appears that a diet of soil-dwelling arthropods and worms is a likely source for bioaccumulation of contaminants.

In a study of mercury accumulation from soil by earthworms, a bioaccumulation factor (BAF) of 0.34 mg/kg of worm tissue mercury per mg/kg of soil mercury was calculated (EPA 1985a). This value was expressed as dry weight of worm tissue and must be converted to a fresh weight basis to be comparable to other data. The water content of earthworms has been reported to range from 70 to 95% (Minnich 1977). Using the median water content of 82.5%, a fresh-weight basis BAF was calculated:

$$\begin{aligned} \text{BAF} &= 0.34 \text{ mg/kg dry weight (mg/kg soil)}^{-1} \times 0.175 \text{ dry weight/fresh weight} \\ &= 0.06 \text{ mg/kg fresh weight (mg/kg soil)}^{-1}. \end{aligned} \quad (19)$$

The target daily dietary intake range for protection of small mammals from toxicity to mercury is 13.7 (Revis et al. 1989a) to 100 mg/kg (Table 6.42 in the RI Report). Using the BAF for earthworms,

$$\begin{aligned} C_{\text{soil}} &= 13.7 \text{ to } 100 \text{ mg/kg} / 0.06 \text{ mg/kg (mg/kg soil)}^{-1} \\ &= 228 \text{ to } 1670 \text{ mg/kg soil.} \end{aligned} \quad (20)$$

The lower value reflects a no-effect level, whereas the higher value represents reported damage to organs of the receptor. Therefore, these values represent a range below which there is no concern and above which there is a threat to mid-level predators. On the basis of this calculation, the proposed soil RGO for protection of predators of earthworms (i.e., small mammals and birds)

from toxicity of mercury was 230 mg/kg, which was rounded downward to 200 in the RI Report and is presented again in Table 3.5 of this addendum. The food ingestion approach is utilized with additional endpoints and technical assumptions to produce additional RGOs to protect mid-level predators.

3.2.4.4 Protection of higher predators from contaminant toxicity via the food chain

Biomagnification increases the body burdens of predators over those of their prey. For example, mercury was not detected in four of the six floodplain samples of terrestrial insects but had become magnified in wrens (average 3.5 mg/kg) and shrews (average 4.9 mg/kg). Mid-level predators, especially wrens and shrews, are prey to higher predators. RGOs must protect predators from biomagnification to toxic levels as a result of eating contaminated prey. The calculated RGOs would provide this protection.

Soil RGOs for the protection of wrens, shrews, and other mid-level predators from mercury in the food chain were presented in Sect. 7.3.6.3 of the RI Report. An RGO of 230 mg/kg (rounded to 200) was indicated based on the protection of mid-level predators (i.e., small mammals whose diet is 100% contaminated earthworms). The observed ratios of dietary exposure to criteria for toxicological effects for mercury were 8.8 in shrews and 6.9 in wrens (Table 6.84 in the RI Report). However, the highest calculated dietary exposure quotient for top predators was 1.4 in owls (Table 6.84 in the RI Report). The feeding ranges of top predators and the typical dietary mix (Sect. 6.4.1.1 in the RI Report) are included in these derivations. Thus, reduction of mercury concentrations in soil to levels that are protective of shrews and wrens should adequately protect top predators as well because the average BAF of their prey (0.036) is less than the ratio of the top predator's comparison dose to that of their prey ($CD_{top\ pred}/CD_{prey} \geq 0.25$). Therefore, the RGO for protection of top predators from mercury in the food chain in the RI Report is 230 mg/kg soil, which was rounded downward to 200. This and other RGOs published in the RI Report are shown in Table 3.5. Additional RGOs are provided in this addendum.

3.2.4.5 Assumptions for upper-bound, intermediate, and lower-exposure scenarios involving food chain biomagnification of mercury

Additional data on bioaccumulation of mercury from EFPC soils and other soil/body burden relationships have become available from the wetlands study described in this addendum (Sect. 2.2). Additional effects data were available through literature searches. Also, there has been more available time to gather and organize information about three scenarios:

- upper-bound exposure (Scenario 1) -- Home ranges of predators and prey are mathematically compressed to assure maximum contact. Further, all prey is contaminated at a high measured concentration and all subsequent exposure parameters are set at 100% (e.g., methyl mercury is 100% of total mercury, 100% of ingested mercury is absorbed).
- intermediate exposure (Scenario 2) -- Many parameters are intermediate between upper-bound and the lower exposure scenarios.
- lower exposure (Scenario 3) -- Home ranges of predators are allowed to overlap as they do in nature with a fraction of top predator foraging time and space on the floodplain. The

predators eat a realistic mix of contaminated prey with different BAFs, and some exposure parameters are based on measured and technical common-sense values.

Scenarios 1 and 3 span the range from most mathematically contrived (upper-bound exposure) to less conservative estimate (lower exposure). Each scenario is calculated for four trophic groups comprising indicator organisms (Fig. 3.5) as follows:

- top predators (e.g., hawks, owls, and foxes);
- mid-level predators (e.g., wrens and shrews);
- first group consumers (e.g., mice, insects, crayfish, and earthworms); and
- plants (e.g., grasses and trees).

Table 3.6 shows the scenarios and indicator organism/trophic groups as a matrix. In the cells of the matrix, RGOs are presented for each trophic group/scenario conformation. The assumptions are stated inside the matrix. For example, the assumptions that govern the derivation of the RGO for each top predator are provided. Likewise, each of the four trophic groups and three scenarios (or twelve situations) has its own assumptions. Toxicological effects endpoints of mercury, methyl mercury, and mercuric sulfide are presented in Table 3.7. Other data and assumptions set the coefficients in the food ingestion equations; they are published in Table 3.8. Bioaccumulation factors are provided in Table 3.9.

Exposure by ingestion of contaminated prey may be calculated by modifying the standard formula for calculating the hazard quotient (EPA 1989b):

$$EQ = (C_{\text{diet}} \times 10^{-3} \text{ kg/g} \times DI \times FI \times ABS)/(CD \times BW \times 10^{-3} \text{ kg/g}) \quad (21)$$

and

$$C_{\text{diet}} = C_{\text{soil}} \sum p_i \text{ BAF}_i, \quad (22)$$

rearranged to

$$C_{\text{soil}} = (EQ \times CD \times BW \times 10^{-3})/(DI \times 10^{-3} \times FI \times ABS \times \sum p_i \text{ BAF}_i) \quad (23)$$

where

C_{soil}	=	contaminant concentration in soil (mg contaminant/kg soil),
C_{diet}	=	contaminant concentrations in diet (mg contaminant/kg diet),
EQ	=	exposure quotient = 1,
CD	=	comparison dose (mg contaminant/kg body weight/day),
BW	=	body weight,
DI	=	dietary intake (g/day),
FI	=	fraction of diet and/or soil from contaminated area,
ABS	=	fraction of ingested dose absorbed,
BAF_i	=	bioaccumulation factor of dietary component i,
p_i	=	fraction of diet of type i.

Justification and comments on C_{soil} , EQ, CD, BW, FI, and ABS were given in Sect. 3.2.4.1. Justification and comments on the remaining variables follow:



Fig. 3.5. Food web relationships of terrestrial biota sampled or modeled for EFPC ERA and RGOs.

Table 3.6. EFPC soil RGOs (C_{soil} ; mg of total mercury/kg soil) and assumptions

Indicator organism	Assessment endpoint (CD)	Scenario 1 Upper-bound exposure	Scenario 2 Intermediate exposure	Scenario 3 Lower exposure
Top predators	mg MeHg ^a /kg diet ^b	100% diet from floodplain (FI) 100% diet contaminated shrews; 100% absorption, methyl mercury (ABS); 0.04 = shrew BAF; 100% methyl mercury in prey (D_{Me})	100% diet from floodplain see Table 3.8 for diet %; 100% absorption of methyl mercury; see Table 3.9 for BAFs; 10% methyl mercury in prey	% diet from floodplain varies ^c see Table 3.8 for diet %; 100% absorption of methyl mercury; see Table 3.9 for BAFs; 10% methyl mercury in prey
owl	0.1	3	94	2337
hawk	0.1	3	105	3500
fox	1.1	31	1102	12,247
Mid-level predators	mg MeHg/kg diet	100% diet from floodplain; 100% of diet earthworms ^d ; 100% absorption of mercury; see Table 3.9 for BAFs; 100% methyl mercury in prey	100% diet from floodplain; see Table 3.8 for diet; 100% absorption of mercury; see Table 3.9 for BAFs; 40% methyl mercury in prey	100% diet from floodplain; see Table 3.8 for diet; 100% absorption of mercury; see Table 3.9 for BAFs; 10, 4, and 1% methyl mercury in prey
wren	0.1 ^b	1.6	15	61 153 612
wren	0.2 ^c	3.3	30	122 306 1225
shrew	0.4 ^f	7	38	152 381 1525
shrew	1.1 ^b	18	105	419 1048 4193

Table 3.6 (continued)

Indicator organism	Assessment endpoint (CD)	Scenario 1 Upper-bound exposure	Scenario 2 Intermediate exposure	Scenario 3 Lower exposure
First-level Consumers	Miscellaneous (Inorg. mercury)	100% diet from floodplain; 100% soil ingestion (SI); 100% mercury absorbed from soil; I = worm BAF; 1.0 m ³ /d inhalation rate; pore water in equil. with soil; 8.8E04 = K _p inorg. mercury ^l	100% diet from floodplain; % soil ingestion varies ^g ; 50% mercury absorbed from soil; 0.06 = worm BAF ^h ; 0.5 m ³ /d inhalation rate; pore water in equil. with soil; 4.0E05 = K _p inorg. mercury	100% diet from floodplain; % soil ingestion varies ^g ; 10% mercury absorbed from soil; 0.06 = worm BAF ^h ; 0.026 m ³ /d inhalation rate ⁱ ; pore water in equil. with soil; 7.1E05 = K _p inorg. mercury ^k
earthworm	body burden 80 mg/kg worm ^b	80	2667	13,333
shrew	soil ingestion 87.7 Hg ^{g,e,r}	87.7	8770	87,700
mice	soil-vapor inhalation 13.7 mg/kg/d	500	1000 ⁱ	19,000
mice	soil ingestion 90.4 mg/kg diet ^m	90.4	18,080	301,333
crayfish	pore water LC ₅₀ of 0.2 mg HgCl ₂ /L ⁿ	17	80	142
amphibian	pore water LC ₅₀ of 1.3 mg Inorg. mercury L ^o	114	520	923
Plants	Soil-Pore water Concentration ^p (mg Hg/L)	pore water in equil. with soil; 8.8E04 = K _p inorg. mercury ⁱ ; 100% indicated form of mercury	pore water in equil. with soil; 4.0E05 = K _p inorg. mercury; 1.25% pore water methyl mercury ^k	pore water in equil. with soil; 7.1E05 = K _p inorg. mercury ^k ; 1.25% pore water methyl mercury ^k
Coniferous Evergreen [O ₂ /CO ₂]	0.002 MeHg	176	64,000	113,600

Table 3.6 (continued)

Indicator organism	Assessment endpoint (CD)	Scenario 1 Upper-bound exposure	Scenario 2 Intermediate exposure	Scenario 3 Lower exposure
Coniferous Evergreen [chl a]	0.02 MeHg	1760	640,000	NF ^q
Coniferous Evergreen [chl a]	0.02 HgCl ₂ ^a	1760	8101	14,379
Grass [root/shoot]	5 HgCl ₂ ^a	440,000	NF ^q	NF ^q

^a MeHg = methyl mercury, Inorg. = inorganic, HgS = mercuric sulfide; HgCl₂ = mercuric chloride.

^b Eisler (1987), mercury toxicity to wildlife

^c For owl 4.0%; for hawk 3.0%, for fox 9.0%

^d Earthworms have highest BAF of potential wren and shrew prey items (0.06).

^e Scheuhammer (1988), methyl mercury toxicity to finches.

^f Opresko et al. (1993), wildlife benchmarks.

^g For earthworms 100%; for mice 1.0% for Scenario 2, 0.3% for Scenario 3 (Beyer et al. 1991); for shrews 2.0% and 1.0%.

^h EPA (1985b), earthworm BAF.

ⁱ EPA (1993), estimated using extrapolation equation.

^j DOE (1994), EFPC Treatability Study, soil washing study results.

^k Appendix Q (DOE 1994), EFPC mercury availability study.

^l Lower value in range of RGOs based on inhalation in RI (DOE 1994).

^m Revis et al. (1989a), EFPC mouse soil-ingestion study results.

ⁿ Heit and Fingerman (1977), mercury toxicity for crayfish, *Procambrus clarki*.

^o Birge et al. (1979), mercury toxicity for amphibian larvae.

^p Suter et al. (1993), phytotoxicity data.

^q NF = Not feasible because maximum possible pore water concentration is less than assessment endpoint, given indicated K_D and percent methyl mercury.

Table 3.7. Toxicity benchmarks for terrestrial organisms

Organism	Benchmark level	Source of data	Remarks
Owl, hawk	0.1 mg MeHg/kg diet ^a	Eisler 1987	Based on Heinz 1979. LOAEL for behavior abnormalities in mallards (reproductive effects not observed)
Fox	1.1 mg MeHg/kg diet	Eisler 1987	Based on Kucera 1983, toxic effects in mink
Wren	0.1 mg MeHg/kg diet	Eisler 1987	Based on Heinz 1979. LOAEL for behavior abnormalities in mallards (reproductive effects not observed)
Wren	0.2 mg MeHg/kg diet	Scheuhammer 1988	Estimated LOAEL for reproduction based on toxicity to adult finches
Shrew	0.4 mg MeHg/kg diet	Opresko et al. 1993	Based on NOAEL for reproduction in rats
Shrew	1.1 mg MeHg/kg diet	Eisler 1987	Based on Kucera 1983, toxic effects in mink
Shrew	87.7 mg HgS/kg diet	Opresko et al. 1993	Based on NOAEL for behavior, reproduction, and nephrotoxicity in mice (Revis et al. 1989a)
Earthworm	Body burden 80 mg MeHg/kg	Eisler 1987	Reduced regeneration of segments
Mouse	Inhalation of 13.7 mg HgS/kg/d	Opresko et al. 1993	Based on NOAEL for behavior, reproduction, and nephrotoxicity in mice (Revis et al. 1989a)
Mouse	Ingestion of 90 mg HgS/kg/d	Opresko et al. 1993	Based on NOAEL for behavior, reproduction, and nephrotoxicity in mice (Revis et al. 1989a)
Crayfish	Pore water concentration 0.2 $\mu\text{g Hg}^{++}/\text{L}$	Heit and Fingerman 1977	Lowest 3-d LC_{50} for <i>Procambrus clarki</i>
Amphibian	Pore water concentration 1.3 $\mu\text{g Hg}^{++}/\text{L}$	Birge et al. 1979	Lowest 3-d LC_{50} for embryo/larvae
Tree	Pore water concentration 0.002 mg MeHg/L	Suter et al. 1993	Respiration by coniferous evergreens
Tree	Pore water concentration 0.02 mg MeHg/L	Suter et al. 1993	Chlorophyll a synthesis by coniferous evergreens
Tree	Pore water concentration 0.02 mg Hg^{++}/L	Suter et al. 1993	Chlorophyll a synthesis by coniferous evergreens
Grass	Pore water concentration 5 mg Hg^{++}/L	Suter et al. 1993	Root/shoot growth by grass

^a Concentrations in diet are on a fresh weight basis.

Table 3.8. Composition of predators' diets

Scenario	Predator	Dietary Items									
		Plants	Crayfish	Amphibians	Wrens	Shrews	Mice	Earthworms	Insects		
1	Hawk	0	0	0	0	1	0	0	0	0	
1	Owl	0	0	0	0	1	0	0	0	0	
1	Fox	0	0	0	0	1	0	0	0	0	
1	Wren	0	0	0	0	0	0	0	0	1	
1	Shrew	0	0	0	0	0	0	1	0	0	
2	Hawk	0	0	0.3	0.1	0.06	0.54	0	0	0	
2	Owl	0	0.15	0.1	0.15	0.04	0.36	0	0	0.2	
2	Fox	0.02	0.1	0.15	0.05	0.05	0.5	0.05	0.08	0	
2	Wren	0.05	0	0	0	0	0	0.15	0.8	0	
2	Shrew	0	0	0.1	0	0	0.1	0.4	0.4	0	
3	Hawk	0	0	0.3	0.1	0.06	0.54	0	0	0	
3	Owl	0	0.15	0.1	0.15	0.04	0.36	0	0	0.2	
3	Fox	0.02	0.1	0.15	0.05	0.05	0.5	0.05	0.08	0	
3	Wren	0.05	0	0	0	0	0	0.15	0.8	0	
3	Shrew	0	0	0.1	0	0	0.1	0.4	0.4	0	

Table 3.9. Bioaccumulation factors for prey taxa^a

Organism	BAF	Source of data	Remarks
Crayfish	0.0091	EFPC wetlands study	4 data points, $r^2 = 0.9$
Amphibian	0.012	EFPC wetlands study	5 data points, $r^2 = 0.6$
Shrew	0.036	EFPC wetlands study	5 data points, $r^2 = 0.7$
Wren	0.036	Assumption	Assumed to be same as shrew because observed body burdens (RI Report, Sect. 6.2.3.2) were similar.
Mouse	0.0003	Revis et al. 1989a, Melby and Altman 1976	Calculated from uptake into kidney; assumes kidney weight is 1% of whole body and half of body mercury is in kidney.
Earthworm	0.06	Assumption	Used in RI Report, Sect. 7.3.6.3 (DOE 1994).
Insect	0.006	Talmage and Walton 1993	Calculated from range of data.
Plant	0.0025	Talmage and Walton 1993	Calculated from range of data.

^a BAF = total mercury in body/total mercury in soil

DI: Comparison doses are in terms of diet, so dietary intake parameter is not needed.

BAF_i: Bioaccumulation factors (Table 3.9) for dietary component i are based on published values or were calculated from observed soil concentrations and animal body burdens from EFPC studies, especially the EFPC wetlands study (Sect. 2.2). Body burden is assumed to be proportional to soil contaminant concentration.

p_i: The compositions of predators' diets are presented in Table 3.8.

When calculating RGO concentrations of total mercury in soil based on the exposure of top predators and mid-level predators, whose comparison doses are specified in terms of methyl mercury, the equation must be modified slightly. The BAF for each prey item must be multiplied by the fraction of total mercury in the prey tissue that is methyl mercury (D_{me}). That is,

$$C_{soil} = (EQ \times CD \times BW \times 10^{-3}) / (DI \times 10^{-3} \times FI \times ABS \times \sum p_i BAF_i D_{Me, i}) \quad (24)$$

Additionally, if the benchmark used for CD is the concentration of contaminant in the diet (CD in units of mg contaminant/kg diet), equation 24 simplifies to

$$C_{soil} = (EQ \times CD) / (FI \times ABS \times \sum p_i BAF_i D_{Me, i}) \quad (25)$$

This form was used in the calculation presented in Table 3.7. The fraction of total tissue mercury in prey items of top predators is conservatively assumed in Scenarios 2 and 3 to be 0.1, except for crayfish, whose measured D_{Me} is 0.4. Comparison doses (e.g., toxicological endpoints for predators) are for methyl mercury only; thus assuring that the neurotoxicity of methyl mercury is recognized.

The most conservative soil RGOs for mercury of 3 to 31 mg/kg are associated with protection of the top predators under the upper-bound exposure scenario. For the lower exposure scenario, protection of top predators is assured by a soil RGO of 3500 mg/kg. The intermediate exposure scenario ranges from 94 to 1100 mg/kg.

Soil RGOs that protect mid-level predators, such as wrens and shrews, are the lowest at 1.6 to 18 mg/kg total mercury for the upper-bound exposure scenario. Under the lower exposure scenario, soil RGOs of 60 to 1050 mg/kg total mercury (at 10 and 4% methyl mercury in the prey) would protect this trophic group. The middle scenario provides intermediate RGOs.

First-level consumers (e.g., mice, crayfish, insects, and earthworms) exhibit RGOs of 17 to 500 mg/kg for the upper-bound exposure assumption and 142 to ~300,000 mg/kg for the lower exposure scenario. The middle scenario shows intermediate RGOs.

RGOs for protection of plants range from 176 to 440,000 mg/kg (upper-bound) and from ~14,000 mg/kg to even higher levels (lower exposure).

The soil RGOs given in Tables 3.5 and 3.6 are soil concentrations of total mercury that are expected to protect ecological receptors from an adverse effect. The receptors requiring the lowest RGOs in the lower exposure scenario (Scenario 3) of Table 3.6 are mid-level predators represented by shrews and wrens exposed to methyl mercury in their predominately earthworm and insect diet (Table 3.8).

Because of the structure of the food-chain exposure equations, RGOs based on food-chain exposures are inversely proportional to the fraction of total mercury in the diet that is methylated. In the following comparisons, a value of 4% is assumed for terrestrial biota (see Sect. 3.2.4.6). The toxicity endpoint used to derive the RGOs for these species were a NOAEL for the shrew, 0.4 mg/kg of methyl mercury diet based on laboratory exposures to rats (Opresko et al. 1993), a LOAEL for wrens of 0.2 mg/kg of methyl mercury in the diet based on effects in finches (Scheuhammer 1988) and a LOAEL for wrens, 0.1 mg/kg of methyl mercury diet based on behavioral effects in mallards (Eisler 1987) (Table 3.7). These are the lowest toxicity endpoints available for these two species. These RGOs imply that if all soil on the EFPC floodplain had a concentration of mercury less than the 153 mg/kg (Table 3.6), virtually every individual shrew and wren would be protected from any adverse toxicological effects under the lower-exposure scenario.

The soil RGOs derived from these different toxicological endpoints (Table 3.7) may need to be evaluated in the FS on the basis of whether they protect individuals or populations. Some adverse effects (e.g., behavioral effects) may not reduce the probability of an individual organism surviving or successfully reproducing. Except when the individuals are protected by law (e.g., the Endangered Species Act) populations may be a more appropriate assessment endpoint for ecological risk assessments (Suter 1993). From this perspective, the LOAELs of 0.2 and 0.4 mg

methyl mercury/kg diet for wrens and shrews, respectively, may be more appropriate than the NOAEL of 0.1 mg methyl mercury/kg diet for wrens.

3.2.4.6 Uncertainty

The development of RGOs has many uncertainties. These uncertainties are associated, to varying degrees, with every variable of every equation. For example, toxicological endpoints in both the sediment-water partitioning and the food chain equations were from laboratory dose-response bioassays; it is known that there may be measurement errors in both the dose and the effect.

There are fewer than 10 variables for each type of RGO, sediment and soil (Table 3.10). Thus, there are boundaries to the assumptions and measurement or modeled values that contribute to the derivation of the RGOs and the uncertainty associated with each RGO. In every case, the EFPC Risk Assessment Team has sought to upgrade assumptions with modeled values and to upgrade modeled values with measurements. For example, we gathered published data on the amount of soil eaten by various ecological receptors to replace our earlier assumptions. Despite these upgrades, there is some uncertainty remaining about certain variables, which has yet to be quantified.

In acknowledgement of this uncertainty, the EFPC Risk Assessment Team has considered a range of assumptions in the three scenarios. By considering multiple scenarios involving a range of values for any given parameter, the sensitivity of RGOs to variables can be observed and the RGOs derived from different scenarios can be evaluated. The range of assumptions is bounded by Scenario 1, or the upper-bound exposure, and Scenario 3, or the lower exposure. The former is highly unlikely because it makes unreasonable assumptions about the feeding ranges of top predators, the diets of top and mid-level predators, and the fraction of mercury in terrestrial biota that is methylated. By contrast, the lower exposure scenario is based on published data and relevant site-specific measurements (Table 3.10).

There is uncertainty about two factors that would allow development of soil RGOs that protect populations rather than individuals. These are: (1) the distribution of mid-level predators such as wrens and shrews on the EFPC floodplain relative to the mercury concentrations in soil and (2) the level of mortality or decrease in reproduction that can be experienced by a population without unacceptable consequences to the local population. The actual distribution of wrens and shrews and the distribution of surface soil mercury concentrations on the floodplain determine what proportion of those populations are exposed to a given mercury concentration. For example, the EFPC surface soil data show that >90% of the floodplain is already below RGOs protective of individual wrens and individual shrews (61 and 153 mg/kg). So, if one assumes that shrews and wrens are uniformly distributed over the floodplain, then >90% of the individual wrens and shrews experience soil mercury concentration \leq 61 mg/kg. Further study would be required to determine what level of mortality wren and shrew populations on EFPC could suffer without serious and measurable ecological consequences.

There is uncertainty about the concentration of methyl mercury in terrestrial biota. In aquatic biota, methyl mercury comprises a much higher fraction of total mercury than is likely in terrestrial systems (EPA 1985c). Mercury is methylated by bacteria in anaerobic sediment and in the slime coat and intestines of fish (EPA 1985c), but much less methylation occurs in

Table 3.10. Evaluation of soil RGO parameters for Scenario 3

Parameter	Value	Confidence	Comments
% diet from floodplain (FI)	3-9, 100	High	Values for top predators (3 to 9%) from published literature (DOE 1994); small sizes and behaviors of mid-level predators makes 100% most probable and conservative.
Diet composition (p _i)	See Table 3.8	Intermediate	Diets for predators based on professional judgement.
% MeHg ^a absorption (ABS)	10, 100	High	Absorption from soil (10%) based on published data (Revis et al. 1989a); 100% absorption from tissue reasonable and conservative.
Bioaccumulation factors (BAFs)	See Table 3.9	High	Shrew, crayfish, amphibian, and wren BAFs based on EFPC measurements; earthworm, mouse, plant, and insect BAFs based on published data (EPA 1985a, Revis et al. 1989a, Talmage and Walton 1993).
% MeHg in prey (D _{Me})	1-10	Intermediate	Scant published evidence for terrestrial predators feeding on terrestrial prey; published values below 10% (i.e., 1 to 4%) (Hildebrand et al. 1980).
% soil ingestion (SI)	0.3, 1, 100	High	Values based on published data for small mammals (EPA 1993).
Soil-vapor inhalation rate (IR _{air})	0.026 m ³ /d	Intermediate	Value based on allometric equations for small mammals (EPA 1993).
Soil-pore water partition coefficient (K _D)	7.1E05 L/kg	Intermediate	Value based on sediment-pore water partition coefficient observed in EFPC mesocosm study (DOE 1994).
% MeHg in soil pore water	1.25	Intermediate	Value based on ratio of methyl mercury to inorganic mercury in sediment pore water observed in EFPC mesocosm study (DOE 1994).

^a MeHg = methyl mercury

terrestrial soils (Porvari et al. 1992; Schuster 1991). We have assumed (DOE 1994) that 100% of mercury in aquatic biota is methylated. Terrestrial crayfish, whose habitat is mainly water, were evaluated in the wetland study (Sect. 2.2.4.2). The total mercury content of individuals from contaminated areas ranged from 20 to 100% methyl mercury.

Methyl mercury concentrations in soil may not be linearly related to total soil mercury concentrations. For example, in the wetland study, the concentration of methyl mercury in crayfish appeared to saturate as soil concentration increased, so the fraction of methyl mercury was higher at low total soil mercury concentrations. A range of 1 to 4% methyl mercury was observed in sparrows exposed to elevated mercury concentrations at Almaden, Spain (Hildebrand et al. 1980). Mice at Almaden, whose total mercury content was not above background, had up to 20% methyl mercury, but no data were available for mice whose total body burdens were elevated. Therefore, 4% may be a reasonable upper limit for the methyl mercury fraction in terrestrial mid-level predators. Hildebrand et al. (1980) reported that the concentration of total mercury in sparrows varied seasonally, whereas the concentration of methyl mercury did not. Because methyl mercury concentrations in organisms exposed to contaminated soil may not be proportional to the soil concentration, the assumption that a BAF for total mercury and an assumed fraction of methyl mercury can be used to calculate methyl mercury body burdens from soil mercury content is likely to be highly conservative at high soil mercury concentrations.

3.2.4.7 Summary and evaluation of soil RGOs

In the lower exposure scenario (Scenario 3), top predators who have large home ranges are protected at soil RGOs of 2300 mg/kg and above. It is the mid-level predators (shrews and wrens) who have small home ranges that show the highest risk because they both live in the floodplain and ingest organisms that also live in the floodplain. The potential RGOs for soil that were published in the RI Report are listed in Table 3.5; the lowest, 230 mg/kg, was rounded down to 200 mg/kg. Additional RGOs for three scenarios and four trophic groups are provided in Table 3.6 with many being less and many being more than 200 mg/kg. Proposed RGOs that would be realistically protective of mid-level predators under each scenario would automatically also protect top predators, first-level terrestrial consumers, and plants. They are:

- Scenario 1 (upper-bound exposure): 3.3 mg/kg,
- Scenario 2 (intermediate exposure): 30 mg/kg,
- Food chain scenario (DOE 1994): 200 mg/kg, and
- Scenario 3 (lower exposure): 300 mg/kg.

These proposed RGOs will be evaluated further in the EFPC FS.

3.3 RGOs FOR HUMAN HEALTH AND ECOLOGICAL PROTECTION

RGOs for human health and for ecological protection are based on different exposure pathways, exposure concentrations, and receptor populations. As a result, the human health and the ecological RGOs are likely to be different for each environmental medium considered. Although the most important ecological exposures are to methyl mercury, RGOs were calculated in terms of total soil mercury, so ecologically based and human health RGOs are comparable. On the basis of the derivations of risk presented in Sect. 7 of the RI Report and the revisions

resulting from the special studies of this addendum, the EFPC Risk Assessment Team has provided the decision makers with a range of human-health-based RGOs for mercury in soils for the remedial unit land uses and with ecologically based RGOs for various scenarios and trophic levels. These RGOs are option values, all of which are protective by EPA definition, from which a risk manager can apply the nine CERCLA criteria to select the remediation level for the Record of Decision.

4. REFERENCES

- Adams, W.J., R.A. Kimerle, and J.W. Barnett, Jr. 1992. "Sediment Quality and Aquatic Life Assessment," *Environ. Sci. Technol.*, 26(10):1864-1875.
- Beyer, N., E. Conner, and S. Gerould. 1991. *Survey of Soil Ingestion by Wildlife*. Report on work funded by U.S. Environmental Protection Agency and supervised by Ruth Miller, OPPE.
- Birge, W.J., J.A. Black, A.G. Westerman, and J.E. Hudson. 1979. "The Effect of Mercury on Reproduction of Fish and Amphibians," Pages 629-655. *The Biogeochemistry of Mercury in the Environment*, J.O. Nriagu (ed.). Eisevier/North-Holland Biomedical Press, New York.
- CDM (Camp, Dresser, & McKee, Inc.). 1993. *Risk Assessment: Almaden Quicksilver County Park, Vol. I - Text*, Prepared for Santa Clara County Parks and Recreation Department, Los Gatos, California, May 29 (Revised September 2, 1992).
- Decisioneering, Inc. 1993. User manual for Crystal Ball[®] Version 3.0, Boulder, Colorado.
- DOE (U.S. Department of Energy). 1994. *East Fork Poplar Creek/Sewer Line Beltway Remedial Investigation Report*, DOE/OR/02-1119&D2, Oak Ridge, Tennessee.
- Eisler (U.S. Fish and Wildlife Service). 1987. *Mercury Hazards to Fish, Wildlife, and Invertebrates: A Synoptic Review*. Biological Report 85(1.10), Fish and Wildlife Service, U.S. Department of the Interior, Patuxent, Maryland.
- Elwood, J.W., R.R. Turner, R.B. Cook, and M.A. Bogle. 1988. "Behavior and Fish Uptake of Mercury in a Contaminated Stream," *Proceedings, 6th International Conference on Heavy Metals in the Environment*. New Orleans, Louisiana, September 15-18, 1987. CEP Consultants Ltd., Edinburgh, United Kingdom.
- EPA (U.S. Environmental Protection Agency). 1985a. *Environmental Profiles and Hazard Indices for Constituents of Municipal Sludge: Mercury*. Office of Water Regulations and Standards, U.S. EPA, Washington, D.C.
- EPA. 1985b. *Environmental Profiles and Hazard Indices for Constituents of Municipal Sludge: Cadmium*, Office of Water Regulations and Standards, U.S. EPA, Washington, D.C.
- EPA. 1985c. *Ambient Water Quality Criteria for Mercury—1984*. EPA/440/5-84-026. Office of Water Regulations and Standards, U.S. EPA, Washington, D.C.
- EPA. 1989a. *Ecological Assessment of Hazardous Waste Sites: A Field and Laboratory Reference*, EPA/600/3-89-013. U.S. EPA, Corvallis, Oregon.
- EPA. 1989b. *Risk Assessment Guidance for Superfund: Volume I - Human Health Evaluation Manual (Part A)*, EPA/540/1-89/002, U.S. Environmental Protection Agency, Office of Solid Waste and Emergency and Remedial Response.

- EPA. 1990. *Guidance for Data Usability in Risk Assessment*, EPA/540/G-90/008, U.S. Environmental Protection Agency, Office of Solid Waste and Emergency and Remedial Response.
- EPA. 1991. *Risk Assessment Guidance for Superfund: Human Health Evaluation Manual (Part B)*, U.S. Environmental Protection Agency, Office of Solid Waste and Emergency and Remedial Response. OSWER Directive 9285.7-01B.
- EPA. 1993. *Wildlife Exposure Factors Handbook*, EPA/600/R-93/187A,B. U.S. Environmental Protection Agency, Office of Research and Development.
- EPA. 1994a. *Baseline Public Health Evaluation, Sulphur Bank Mercury Mine Superfund Site, Clear Lake, California*, EPA, Region IX, January 24.
- EPA. 1994b. *Determination of Mercury, with Speciation, in Poplar Creek Soil Samples*. Prepared by D. Dobb, E. Miller, and D. Cardenas of Lockheed Environmental Systems & Technologies Company, Las Vegas, Nevada, and K. Brown of Technology Support Center, Environmental Monitoring Systems Laboratory, Environmental Protection Agency, Las Vegas, Nevada, March.
- Gist, C. 1987. *Soil Contaminant Uptake by Plants in the Terrestrial Food Chain in the Floodplain of East Fork Poplar Creek*, Oak Ridge Associated Universities, Oak Ridge, Tennessee.
- Haakanson, L., T. Andersson, and A. Nilsson. 1990. "Mercury in Fish in Swedish Lakes - Linkages to Domestic and European Sources of Emission." *Water Air Soil Pollut.*, 50:171-191.
- Heinz, G.H. 1979. "Methyl Mercury: Reproductive and Behavioral Effects on Three Generations of Mallard Ducks." *J. Wild. Manage.*, 43:394-401.
- Heit, M., and M. Fingerman. 1977. "The Influence of Size, Sex and Temperature on the Toxicity of Mercury to Two Species of Crayfishes." *Bull. Environ. Contam. Toxicol.*, 18:572-580.
- Hildebrand, S., J. Huckabee, F. Diaz, S. Janzen, J. Solomon, and K. Kumar. 1980. *Distribution of Mercury in the Environment at Almaden, Spain*. ORNL/TM-7446, Oak Ridge, Tennessee.
- Hinzman, R.L., ed. 1993. *Second Report on the Oak Ridge Y-12 Plant Biological Monitoring and Abatement Program for East Fork Poplar Creek*, Y/TS-888, Oak Ridge National Laboratory, Oak Ridge, Tennessee.
- Jugo, S., T. Maljkovic, and K. Kostial. 1975. "The Effect of Chelating Agents on Lead Excretion in Rats in Relation to Age." *Environ. Res.*, 10:271-279.

- Kargacin, B. and K. Kostial. 1990. "Methods for Decreasing ^{203}Hg Retention in Relation to Age and Route of Exposure." *Advances in Mercury Toxicology* (T. Suzuki, N. Imura, and T.W. Clarkson, eds.), Rochester Series on Environmental Toxicity, Plenum Press, New York.
- Kostial, K., B. Kargacin, and M. Landeka. 1989. "Efficiency of Chelation Therapy in Relation to Age," *Proceedings of the Third International Congress on Trace Elements in Health and Disease*, Adana, Turkey.
- Kucera, E. 1983. "Mink and Otter as Indicators of Mercury in Manitoba Waters," *Canad. J. Zool.*, 61:2250-2256.
- Landa, E.R. 1978. "The Retention of Metallic Mercury Vapor by Soils," *Geochimica et Cosmochimica Acta*, 42:1407-1411.
- Loar, J.M., ed. 1992. *First Report on the Oak Ridge Y-12 Plant Biological Monitoring and Abatement Program for East Fork Poplar Creek, Y/TS-886*, Oak Ridge National Laboratory, Oak Ridge, Tennessee.
- LWA (Lee Wan & Associates). 1990. *Environmental Restoration Program, Technical Support Contractor, Quality Assurance Technical Procedures Manual*, DOE/OR-933 and LWA/90-008, Oak Ridge, Tennessee.
- Melby, E.C., Jr. and N. H. Altman, eds. 1976. *Handbook of Laboratory Animal Science*, Vol. III, CRC Press, Cleveland, Ohio.
- Miller, E.L. 1993. *Speciation of Mercury in Soil*, Environmental Monitoring Systems Laboratory, Office of Research and Development, U.S. Environmental Protection Agency, Las Vegas, Nevada.
- Minnich, J. 1977. *The Earthworm Book*, Rodale Press, Emmaus, Pennsylvania. 382 pp.
- Nagy, K.A. 1987. "Field Metabolic Rate and Food Requirement Scaling in Mammals and Birds," *Ecol. Monogr.*, 57:111-128.
- Opresko, D.M., B.E. Sample, and G.W. Suter. 1993. *Toxicological Benchmarks for Wildlife*, ES/ER/TM-86, Oak Ridge National Laboratory, Oak Ridge, Tennessee.
- Porvari, P., M. Verta, and T. Matilainen. 1992. "Mercury Methylation and Demethylation in Soil," *Proceedings of the International Conference on Mercury as a Global Pollutant*, Monterrey, California.
- Radian (Radian Corporation). 1992a. *Phase Ib Sampling and Analysis Plan for Soil, Sediment, and Water*, DOE/OR-983 and OKR/91-051, Oak Ridge, Tennessee.
- Radian. 1992b. *Phase Ib Sampling and Analysis Plan Addendum for Ecological Risk Assessment*, DOE/OR-1021D0 and 92-225-161-25, Oak Ridge, Tennessee.

- Radian. 1993. *Treatability Study Report for Mercury in East Fork Poplar Creek, Oak Ridge, Tennessee*, DOE/OR/02-1221&D1, September.
- Revis, N., G. Holdsworth, G. Bingham, A. King, and J. Elmore. 1989a. *An Assessment of Health Risk Associated with Mercury in Soil and Sediment from East Fork Poplar Creek, Oak Ridge, Tennessee*, Oak Ridge Research Institute, Final report, pp. 1-58.
- Revis, N.W., T.R. Osborne, G. Holdsworth, and C. Hadden. 1989b. "Distribution of Mercury Species in Soil from a Mercury-Contaminated Site," *Water Air Soil Pollut.*, 45:105-113.
- Revis, N.W., T.R. Osborne, D. Sedgley, and A. King. 1989c. "Quantitative Method for Determining the Concentration of Mercury (II) Sulfide in Soils and Sediments," *Analyst*, 114:823-825.
- Revis, N.W., T.R. Osborne, G. Holdsworth, and C. Hadden. 1990. "Mercury in Soil: A Method for Assessing Acceptable Limits," *Arch. Environ. Contam. Toxicol.*, 19:221-226.
- Sakamoto, H., T. Tomiyasu, and N. Yonehara. 1992. "Differential Determination of Organic Mercury, Mercury (II) Oxide, and Mercury (II) Sulfide in Sediments by Cold Vapor Atomic Absorption Spectrometry," *Analytical Sciences*, 8:35-39, February.
- Scheuhammer, A.M. 1988. "Chronic Dietary Toxicity of Methylmercury in the Zebra Finch, *Poephila Guttata*," *Bull. Environ. Contam. Toxicol.*, 40: 123-130.
- Schuster, E. 1991. "The Behavior of Mercury in the Soil with Special Emphasis on Complexation and Adsorption Processes — a Review of the Literature," *Water Air Soil Pollut.*, 56: 667-680.
- Southworth, G.R., R.R. Turner, M.J. Peterson, and M.A. Bogle. 1994. "Speciation of Mercury in Stream Fish Exposed to High Concentrations of Dissolved Inorganic Mercury," manuscript submitted to *Water Air Soil Pollut.*
- Suter, G.W. 1993. *Ecological Risk Assessment*, Lewis Publishers, Chelsea, Michigan. pp. 238.
- Suter, G.W., M.E. Will, and C. Evans. 1993. *Toxicological Benchmarks for Screening Potential Contaminants of Concern for Effects on Terrestrial Plants*, ES/ER/TM-85. Oak Ridge National Laboratory, Oak Ridge, Tennessee.
- Suzuki, T., N. Imura, and T.W. Clarkson. 1990. *Advances in Mercury Toxicology*. Rochester Series on Environmental Toxicity, Plenum Press, New York.
- Talmage, S. and B. Walton. 1993. "Food Chain Transfer and Potential Renal Toxicity of Mercury to Small Mammals at a Contaminated Terrestrial Field Site," *Ecotoxicology*, 2:243-256.
- Van Winkle, W., R.W. Counts, J.G. Dorsey, J.W. Elwood, V.W. Lowe, Jr., R. McElhaney, S.D. Schlotzhauer, F.G. Taylor, Jr., and R.R. Turner. 1984. *Mercury Contamination in*

East Fork Poplar Creek and Bear Creek. ORNL/TM-8894, Oak Ridge National Laboratory, Oak Ridge, Tennessee.

Willett, K.L., R.R. Turner and J.J. Beauchamp. 1992. "Effect of Chemical Form of Mercury on the Performance of Dosed Soils in Standard Leaching Tests: EP and TCLP," *Hazardous Waste & Hazardous Materials*, 9:275-288.

World Health Organization. 1990. *Environmental Health Criteria 101. Methylmercury*. World Health Organization, Geneva, 144 pp.

APPENDIX A
- DRAFT REPORT:
COMPARISON OF MERCURY SPECIATION METHODS

COMPARISON OF MERCURY SPECIATION METHODS

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INTRODUCTION

The floodplain of East Fork Poplar Creek (EFPC) in Oak Ridge, Tennessee, is contaminated with mercury from historical releases from the U.S. Department of Energy Y-12 Plant located in the headwaters. The creek and its floodplain are currently being investigated as a Superfund site. Selection of appropriate remedial actions will depend in part on information concerning the speciation, or chemical form of mercury, in the floodplain soils. The history of studies of the speciation of mercury in these soils has been reviewed in detail elsewhere (Sect. 2.1 of this addendum). Revis et al. (1989a,b), in one of the earliest attempts to characterize the forms of mercury in EFPC soils, developed a sequential extraction procedure for mercury in soils. The results of applying this extraction procedure to EFPC soils with a range of total mercury concentrations indicated that mercuric sulfide was the predominant mercury form in these soils, accounting for 63 to 100% of the mercury in the soil. Evidence to support Revis' work has been provided by the results from a variety of electron and X-ray beam techniques [scanning electron microscopy (SEM), X-ray diffraction (XRD), transmission electron microscopy (TEM)/selected area electron diffraction (SAED)] applied to EFPC soil as discussed in Sect. 2.1.

Recently, a new sequential extraction procedure (Miller 1993), developed for the Environmental Protection Agency (EPA) at the Environmental Monitoring Systems Laboratory (EMSL) in Las Vegas, Nevada, was used to characterize a suite of 20 soils from EFPC (results discussed in Sect. 2.1). The soils were not the same soils analyzed by Revis et al. Although mercuric sulfide was suggested by the EMSL results to be a significant species in some soils, metallic mercury or mercury amalgams were suggested as the predominant forms in the soils tested (EPA 1994).

To resolve the discordance between the Revis and EMSL results, a study was initiated in late April 1994 to perform both the Revis and EMSL extraction procedures on the same set of EFPC soils. An additional sequential extraction procedure (Sakamoto et al. 1992), never before used for EFPC soil, was also included in this comparison. Finally, estimates of the presence and relative fraction of metallic mercury in EFPC soils were made using sample headspace measurements and losses of mercury from the soils due to thermal treatment.

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² Managed for the U.S. Department of Energy by Martin Marietta Energy Systems, Inc. under contract DE-AC05-84OR21400.

METHODS

A subset of the soil samples collected in January 1994 and used for the EMSL extraction study were used for the present comparison. The samples were collected from a variety of locations within the EFPC floodplain, homogenized in stainless steel bowls, and refrigerated in the naturally moist state at ORNL in sealed containers until use. Four soils (ZN5470424, ZE3340211, ZN3181013, ZN5150729) were selected from the original group, and a fifth soil (ZN3210127) from the original location and depth in the floodplain was resampled on April 24, 1994. The fresh sample exhibited a very similar total mercury concentration (2400 mg/kg) to the earlier sample (2700 mg/kg) from the same location. In the discussion and tables that follow, the soils are identified by reference only to the last three digits of the sample identifier as underlined above.

Small (≤ 100 g) subsamples of each soil were removed and further homogenized. One portion (~ 3 g) of each soil was air dried to determine percent moisture, ground, and submitted for mercury analysis by EPA Method 7471 (SW-846). Aliquots of each moist soil were sequentially extracted in 50-mL centrifuge tubes in accordance with the methods outlined in each of the three procedures (some slight deviations are discussed below). Triplicate aliquots were run for sample 729 for each procedure to quantify the reproducibility of results. In addition, metacinnabar, the form of mercuric sulfide identified unequivocally in EFPC soil by TEM/SAED (Sect. 2.1), was spiked into the soil with the lowest total mercury concentration (013) to measure recovery of a known mercury species of interest. The metacinnabar was precipitated in the laboratory and submitted for XRD verification of crystal form. The supernatant from each extraction was preserved with 17.5 mL of 0.7% potassium dichromate in 1:1 nitric acid and diluted to ~ 250 mL prior to analysis for total mercury by EPA Method 7470 (SW-846). Process blanks were carried through each procedure and analyzed for total mercury. The residual soil left after the last extraction step was also recovered, dried, weighed, ground, and submitted for total mercury analysis by EPA Method 7471 (SW-846). National Institute for Standards and Technology SRM 2710, Montana Soil (certified mercury value = 32.6 ± 1.8 mg/kg) was submitted blind to the analytical laboratory as a check on accuracy. All mercury analyses were performed by the Y-12 Plant Laboratory.

There were a few deviations between the sequential extraction protocols, as described by their respective authors, and the manner in which they were carried out by us. All extraction protocols were run using field-moist soils in contrast to the EMSL specification of dried and pulverized soils. However, all results were corrected to a dry weight basis. Revis et al. used field-moist soils and Sakamoto et al. did not clearly specify whether samples were first dried or not. Drying (especially at 45 to 50°C) and machine pulverizing the soils, as was done by EMSL, was thought by us to potentially alter mercury speciation. Ten-gram portions, as opposed to 20-g portions, of soil for the EMSL procedure were used to avoid overflow problems due to sample foaming noted in a trial run with 20 g in the 50-mL centrifuge tubes. Solid/solution and solid/extractant ratios were, however, maintained at their specified values. The supernatants from each of the centrifuged extracts were filtered using 0.2- or 0.4- μ m pore size filters to avoid any possible transfer of soil into the extracts (some soils produced a floating fraction after extraction and centrifugation). Finally, the determination of "organic" mercury in each procedure was deleted because both the Revis et al. and EMSL results, as well as other data, have not indicated that organic mercury constitutes a significant fraction in the EFPC soils (typically $< 0.1\%$ of total mercury).

Revis et al. (1989a,b) estimated the fraction of metallic mercury in EFPC soils by the loss of mercury from soils heated to 150°C for 5 d. Landa (1978), using Montana soils exposed to mercury vapor, had shown previously that metallic mercury "sorbed" to soils is quantitatively volatilized between 100 to 200°C over a period of several days. Revis et al. (1989a,b) recovered 100% of metallic mercury dosed into soils and held at 150°C for 5 d. We applied the Revis et al. method of estimating the fraction of metallic mercury to all 20 EFPC soil samples previously characterized by the EMSL speciation protocol. One-gram aliquots (moist weight) were air dried and placed in 125-mL glass reagent bottles fitted with gas-purging closures. The outlet side of each closure was fitted with an iodated charcoal mercury sorbent tube (MSA Part No. 459003). After placing the bottles in an oven, the inlet side of each closure was connected to a mercury-free air supply (60 cc/min) using silicone tubing. The oven was brought to temperature (150 ± 5°C) and held for 3 d. After 3 d the oven and air flow were turned off long enough to change the charcoal tubes and then restarted for an additional 2 d of thermal treatment. After cooling, the soil in each bottle was recovered for total mercury analysis by EPA Method 7471 (SW-846). The charcoal sorbent were analyzed by a modified version of Method 7471.

In addition to applying the Revis et al. protocol for metallic mercury, we also measured mercury vapor in the headspace of 1-L glass jars containing 1.0 gram aliquots of air-dried and ground soils from the same group of 20 EFPC soils characterized by EMSL and used in the bioavailability study (Sect. 2.1). Soils were equilibrated for 24 h prior to headspace mercury vapor measurements using a Jerome Model 431-X Gold Film Mercury Analyzer (Arizona Instruments Inc, Tempe, Arizona). The highest of three successive 10-second (125 cc of headspace air) measurements was recorded. Measurements were conducted at room temperature (23°C) and 50°C.

RESULTS AND DISCUSSION

Sakamoto Protocol

Results for the protocol developed by Sakamoto et al. (1992) are summarized in Table A.1. Mercury and material balances for this protocol were relatively good (mean mercury recovery of 98%) with the possible exception of that for Soil 013 (70%). The total mercury value for this soil, obtained by analysis of the aliquot used for moisture determination, may be unrepresentative. Earlier analyses of mercury in this soil by both us and EMSL gave values between 28 and 34 mg/kg, or 66 to 81% of the value (42 mg/kg) shown in Table A.1. Using the lower value to calculate mercury balance would yield much better overall recovery.

Virtually no mercury was extracted from the soils by the 0.05 molar sulfuric acid solution intended by developers of this protocol to extract mercuric oxide. The cuprous chloride solution, intended as a selective extractant for mercuric sulfide, extracted significant fractions (63 to 112%) of the soil mercury for all samples except for the sample dosed with metacinnabar (which released only ~24% of its mercury into this extractant).

Revis Protocol

Considerable difficulty was experienced in analyzing the sodium sulfide extracts from this procedure. The entire procedure was carried out twice for the study soils without resolving the

Table A.1. Results of application of Sakamoto et al. (1992) mercury speciation protocol to EFPC soils

Soil sample	mercuric oxide 0.05 M H ₂ SO ₄			mercuric sulfide CuCl in 1 M HCl			Residue			Hg recovery %
	Total Hg mg/kg	Solution Hg mg/L	Percent total Hg	Solution Hg mg/L	Percent total Hg	Weight g	Residue Hg mg/kg	Percent total Hg		
013	42	0.0002	0.04	0.36	66	3.55	1.8	4.2	70	
127	2400	0.0071	0.0007	19	63	3.49	750	30	93	
211	270	0.0002	0.006	3.4	105	3.21	34	12	117	
424	1300	0.0013	0.009	12	83	3.25	180	14	98	
729-1	840	0.0002	0.002	11	112	3.34	86	10	122	
729-2	840	0.0002	0.002	8.6	89	3.10	72	7.9	97	
729 Mean			0.002		100			9.1	110	
Total Mean			0.011		84			14	98	
HgS Spike	4540	0.0002	0.000	14	24	3.60	3000	65	89	

difficulty. Acidification of the sodium sulfide extracts caused elemental sulfur to precipitate in the extracts. The presence of elemental sulfur in turn caused low recovery of the mercury. Partial results for the protocol are summarized in Table A.2. Although the results are incomplete, sufficient results are available to conclude that substantially more mercury (average of 54% with range from 19 to 99%) was released from the soils by 12 M nitric acid than expected (~15%) based on the findings of Revis et al. (1989a). The relatively low residue fractions (mean of 4.2%) for most of the soils, and the metacinnabar-spiked soil (mean of 1.5%), suggest that the bulk of the unaccounted for mercury should have been in the sodium sulfide extracts that could not be analyzed. Assuming reasonable mass balance, the sodium sulfide extracts should have accounted for 1 to 76% of total mercury. Contrary to expectation based on results from Revis et al. (1989a.b), the concentrated nitric acid extracted ~12 and 31% of the metacinnabar in the duplicate spiked soils.

EMSL Protocol

Results for the protocol developed by EMSL (Miller 1994) are summarized in Table A.3. Overall mass balance was reasonably good with the same tendency noted by EPA (1994) for the sum of the fractions to exceed 100%. The notable exception to this trend is Soil 013 which indicated only 65% mercury recovery. As noted for the Sakamoto results, the total mercury value (42 mg/kg) used to calculate the species fractions may be unrepresentative (and too high) of the soil actually extracted. Mercury remaining in the residual soils after the last sequential extraction was low, accounting for from 2 to 7% of the total soil mercury and indicating relatively complete extraction of all the mercury from the soils by the complete sequence.

The potassium sulfate/chloride solution extracted ^(organic & HgCl₂) almost no mercury (<0.1%) from the soils. The dilute nitric acid extracted an average of ^(mercuric oxide) ~6% of soil mercury, with Soil 127 exhibiting the maximum fraction (22%) for this extractant. Metacinnabar was essentially insoluble in both the potassium sulfate/chloride and dilute nitric acid solutions.

The 4 M nitric acid solution was particularly effective in extracting mercury ^(metallic & amalgamated) (average of 72%) from all the soils, including from the soil spiked with metacinnabar (45%). EMSL attributed the mercury extracted by this solution to metallic or amalgamated mercury. The average fraction of soil mercury extracted by aqua regia was 30%, with a range from 6 to 46%. Compared to the Sakamoto and Revis protocols, the EMSL protocol was the most destructive of the soil, with ~40% of the soil mass lost in the overall extraction compared with ~10 to 15% in the Revis protocol. sample 013
spiked

Discussion of Extraction Results

Although all three mercury speciation protocols underwent some form of validation by the respective authors, it is clear that the extractants are not as selective in removing a given form of mercury as implied by the original publications describing each protocol. Sakamoto et al. (1992) did not propose a selective extractant for metallic/amalgamated mercury, and the effectiveness of the cuprous chloride in removing metallic mercury was not evaluated by the original authors or by us. Nonetheless, the cuprous chloride solution was notably ineffective (only 24%) in removing the very form of mercury claimed by the protocol developers to be extracted with this reagent. The EMSL protocol suffered the opposite problem: the extractant targeted at metallic/amalgamated mercury actually extracted almost one half (45%) of the

Table A.2. Partial results of application of Revis et al. (1989b) mercury speciation protocol to EFPC soils (First run/Second run)

Soil sample	12 M HNO ₃		Saturated Na ₂ S		Residue			Percent mercury recovery ^b	
	Total Hg mg/kg	Solution Hg mg/L	Percent total Hg	Solution Hg mg/L	Percent total Hg	Weight g	Residue Hg mg/kg		Percent total Hg
013	42/29	0.068/0.073	64/99	— ^a	— ^a	0.84/0.65	1.0/0.5	2.7/1.6	66/101
127	2400/2300	2.5/3.0	41/52	— ^a	— ^a	0.97/73	74/80	4.2/3.6	46/56
211	270/270	0.57/0.64	88/96	— ^a	— ^a	0.81/0.62	5.0/5.3	2.2/1.8	91/98
424	1300/1100	0.56/0.52	19/21	— ^a	— ^a	0.86/0.61	52/35	5.4/3.1	26/24
729-1	840/810	0.58/0.58	30/31	— ^a	— ^a	0.93/0.65	105/10	17/1.2	48/32
729-2	840/810	0.60/0.57	31/30	— ^a	— ^a	0.94/0.59	140/16	23/1.7	55/32
729-3	840/810	0.57/0.64	29/33	— ^a	— ^a	0.90/0.62	52/13	8.3/1.5	38/35
729 Mean			30/31	— ^a	— ^a			16/1.5	47/33
Total Mean			48/60	— ^a	— ^a			6.1/2.3	55/62
HgS Spike	3340/1240	1.0	12/31	— ^a	— ^a	0.84/0.65	52/12	2.1/0.9	14/32

^a Results rejected because of low recovery of mercury after elemental sulfur precipitated in samples.^b Based on recovery by 12 M HNO₃ and in residue only.

Table A.3. Results of application of EMSL mercury speciation protocol to EFPC soils

Soil sample	Total Hg mg/kg	mercuric chloride 0.01 M K ₂ SO ₄ /KCl			mercuric oxide 0.2 M HNO ₃			amalgamated 4 M HNO ₃			mercuric sulfate Aqua Regia			Residue			Percent mercury recovery
		Solution Hg mg/L	Percent total Hg	Solution Hg mg/L	Percent total Hg	Solution Hg mg/L	Percent total Hg	Solution Hg mg/L	Percent total Hg	Solution Hg mg/L	Percent total Hg	Weight g	Residue Hg mg/kg	Percent total Hg			
013	42	0.00004	0.004	0.0003	0.03	0.62	58	0.065	6.1	6.45	0.81	1.7	66				
127	2400	0.01	0.017	13	22	22	36	24	41	6.63	190	7.3	106				
211	270	0.0002	0.003	0.0026	0.04	6.2	95	0.47	7.5	5.70	6.2	1.9	105				
424	1300	0.0013	0.004	1.6	5.5	20	68	13	46	5.73	100	6.9	126				
729-1	840	0.0008	0.004	0.33	1.7	16	81	5.0	26	5.69	35	3.5	112				
729-2	840	0.0005	0.003	0.40	2.0	21	104	4.8	25	6.22	35	3.9	135				
729-3	840	0.0005	0.003	0.37	1.9	24	120	5.1	27	6.16	39	4.3	153				
729 Mean			0.003		1.9		102		26			3.9	133				
Total Mean			0.006		5.8		72		25			4.3	107				
HgS Spike	1530	0.00003	0.0001	0.0006	0.002	18	45	32	84	6.51	84	4.9	134				



mercury in a metacinnabar-spiked soil. Both the EMSL and Revis protocols under-predicted the amount of mercuric sulfide in the metacinnabar-spike soil. The results for the protocol (Revis) which was used originally to suggest that mercury occurred predominantly in the sulfide form clearly contradict the original findings (average of 85% mercuric sulfide). One unpublished report (Revis et al. 1989c) to DOE by the Revis group does show results obtained using 12 *M* nitric acid applied to 21 soils and sediments from EFPC ranging in total mercury concentration from 2.0 to 1800 mg/kg. For this group of soils the percent of total mercury which was soluble in the nitric acid ranged from 12 to 92%, with an average of 43%. This range and average agrees much better with the results obtained here using the Revis protocol.

Because we employed a subset of essentially the same soils used by EMSL in their recent characterization (EPA 1994) of mercury speciation, it is instructive to compare these interlaboratory (EMSL versus ORNL) results (Table A.4). As noted in the Methods section, we employed naturally moist soils instead of dried and ground soils to avoid any possibility of changing the in situ speciation of mercury in the soils. We might expect drying and grinding to improve recovery of some forms of mercury in some extractants by virtue of the greater surface area exposed to leaching. On the other hand, dry grinding can cause reactions and phase changes among otherwise unreactive components (e.g., metallic mercury and elemental sulfur). One reference in a handbook of preparative chemistry notes that metacinnabar can be converted to cinnabar by grinding, and we have produced metacinnabar by gentle grinding of a mixture of elemental sulfur and metallic mercury.

With some notable exceptions, the results given in Table A.4 are remarkably similar in many cases (e.g., Soils 127 and 424) and within the uncertainty expected given the differences in sample processing prior to extraction. No consistent laboratory bias appears to be present even where significant differences exist between laboratories (e.g., results for 0.2 *M* nitric acid). We experienced considerable difficulty achieving and maintaining the target pH value specified by EMSL for the 0.2 *M* nitric acid, which may explain the large discrepancies between laboratories in these results. EFPC soils are known to have considerable acid neutralizing capacity. Even anticipating this issue, it was still a challenge to maintain pH during the heating portion of this step. We contend that "adsorbed" mercury, rather than mercuric oxide, is being removed during this step and thus solution pH is critical to control within close limits.

Thermal Release and Sample Headspace Measurements

Results of thermal treatment to release metallic mercury in accordance with the method of Revis et al. (1989b) are given in Table A.5 and compared with EMSL results for metallic/amalgamated mercury in Fig. A.1. In most cases, but not all, the EMSL results are higher than the Revis results. The two negative percentages probably result from sample inhomogeneity due to using the total mercury analyses for air-dried and ground soils as the basis for the initial concentration. There is no correlation between the EMSL extraction results and the thermal release results. The results based on mercury trapped on the charcoal tubes show 5 and 24% soil losses, respectively, for the two samples which yielded negative recoveries. Unfortunately, either method (thermal or chemical) of estimating this mercury fraction could be in error. Estimates based on thermal release could be low due to presence of mercury amalgams or high due to thermal degradation of non-elemental forms. The charcoal tubes which collected mercury being released from the soils on thermal treatment days 4 and 5 typically contained only ~10% of the total mercury volatilized, indicating that most of the volatilization occurred in the

Table A.4. Comparison of results of EMSL mercury speciation protocol conducted at EMSL and at ORNL^a

Soil sample	Total Hg mg/kg ^b	Organic/mercuric chloride 0.01 M K ₂ SO ₄ /KCl		mercuric oxide 0.2 M HNO ₃		metallic & amalgamated 4 M HNO ₃		mercuric sulfide Aqua Regia	
		EMSL %	ORNL %	EMSL %	ORNL %	EMSL %	ORNL %	EMSL %	ORNL %
013	28/42	0.1	<0.1	71	<0.1	21	58	7.7	6.1
127	2700/2400	0.3	<0.1	7.1	22	35	36	57	41
211	270/270	<0.1	<0.1	<0.1	<0.1	92	95	8.4	7.5
424	1300/1300	0.1	<0.1	14	5.5	49	68	37	46
729	900/840	0.1	<0.1	11	1.9	56	102	33	26

^a Soils were from same sampling event (1/31/94), except for Sample 127 which was resampled (4/24/94) for ORNL effort. Expressed as percent (dry weight basis) of total mercury soluble in each extracting solution. EMSL used pulverized dry soil while ORNL used soil in naturally moist state.

^b First value is for dry ground aliquot from "Bioavailability Study"; second value from dry ground aliquot for "% moisture."

EMSL% ORNL%
 29 ~~28~~7 64%
 92 77
 100.4 102.5
 86 114
 89 128
 (Total "insoluble")

Table A.5. Results of thermal treatment of EFPC soils and sample headspace measurements, including results from EMSL for metallic/amalgamated mercury

Soil sample	Total Hg mg/kg	150°C Total Hg mg/kg	150°C Percent volatilized ^a	EMSL percent metallic ^b	23°C Headspace mg/m ³	50°C Headspace mg/m ³
ZN3210115	260	200	23/21	74	<0.001	<0.001
ZN3210127	2700	1300	52/40	35	0.152	0.806
ZN3340211	270	240	11/13	92	<0.001	<0.001
ZN3340223	1900	1600	16/4.0	25	0.005	0.069
ZN3340312	230	160	30/19	94	<0.001	<0.001
ZN3340324	2100	1800	14/10	36	<0.001	<0.001
ZE5470412	85	32	62/53	88	<0.001	<0.001
ZE5470424	1300	1200	8/5.5	49	<0.001	<0.001
ZE5380512	67	32	52/37	91	<0.001	<0.001
ZE5380524	2100	1400	33/4.3	32	<0.001	<0.001
ZE5340619	140	61	56/47	90	<0.001	<0.001
ZE5340621	1200	1600	-33/5.2	57	<0.001	<0.001
ZE5150717	230	66	71/52	83	<0.001	<0.001
ZE5150729	900	700	22/8.3	56	<0.001	<0.001
ZE3770810	480	420	13/8.4	81	<0.001	<0.001
ZE3770822	15	19	-27/24	76	<0.001	<0.001
ZE3740918	55	19	65/60	26	<0.001	<0.001
ZE3740920	780	560	28/19	66	<0.001	<0.001
ZE3181013	28	15	46/36	21	<0.001	<0.001
ZE3181025	180	180	54/16	36	<0.001	<0.001

^a First value is based on loss from soil; second value is based on mercury trapped on charcoal.

^b EPA (1994).

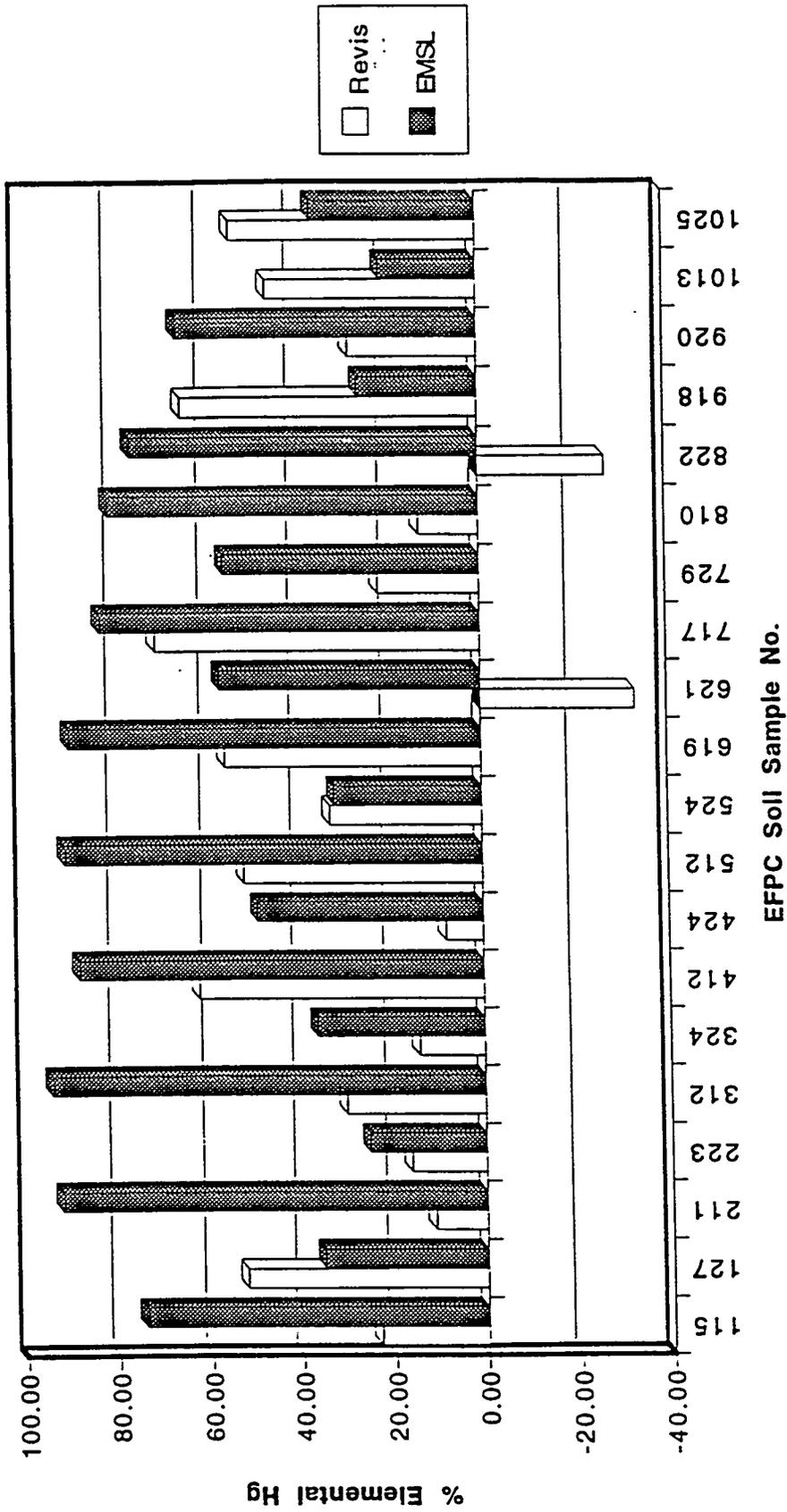


Fig. 1. Comparison of estimates of elemental mercury fractions in EFPC soils using thermal treatment (Revis) and chemical extraction (EMSL).

first 3 d. The notable exceptions to this pattern included soils 621, 729, 810, 822, 920, and 1025, which typically showed 30 to 40% of the total release occurring in treatment days 4 and 5. The latter pattern is suggestive of slow conversion of the mercury in these soils to a volatile form. Results from the Pilot Thermal Desorption work performed by IT Corporation and several literature citations suggest that metacinnabar does not begin thermal decomposition until temperatures above 200°C are reached. As discussed above, the EMSL extractant targeted at metallic/ amalgamated mercury extracted a substantial fraction (45%) of mercury in the soil spiked with metacinnabar, the form of mercury identified unequivocally as being present in EFPC soils.

Sample headspace measurements of mercury vapor can reveal the presence of metallic mercury in soil if sufficient metallic mercury is present to overcome the natural sorptive capacity of the soil. Landa (1978) suggested that soil organic matter plays a key role in binding metallic mercury vapor in soils. Willett et al. (1992) observed that sample headspace mercury vapor concentration increased as the quantity of metallic mercury dosed into a soil (2.08% organic carbon) increased from 100 to 1000 to 10000 mg/kg. Thus, while the absence of detectable mercury vapor in soil sample headspace does not preclude presence of metallic mercury in the soil, detection of mercury vapor in the headspace is unambiguous evidence of presence in the soil. Of the 20 soils tested for headspace vapor only two showed detectable concentrations at room temperature and 50°C (Table A.5). These soils represented two of the four soils with the highest total mercury concentrations (0.2% or more total mercury). Paradoxically, neither of these soils display atypical percentages of metallic mercury as measured thermally (Revis) or by extraction (EMSL).

CONCLUSIONS

The results of this comparison of three mercury speciation protocols challenge the notion that selective/sequential chemical extractions can provide unambiguous identification and quantification of mercury forms in soil. There was insufficient concordance among results from the methods to support any general statement about the fraction of any given mercury species in the soil. The authors of all three methods have reported that samples spiked with the target pure mercury compounds were recovered quantitatively by the individual procedures. However, such calibration does not mean that the target mercury forms are unequivocally present in study soils, only that mercury forms which seem to behave like the target form are present. Thus, mercuric oxide and mercury adsorbed to soil minerals and organic matter may both extract in 0.2 *M* acid, but the true nature of indigenous soil mercury cannot presently be discriminated. Similarly, hot 4 *M* nitric acid is likely to extract both metallic mercury and mercury incorporated into mineral and organic matter in soils. The intercomparison results do support the hypothesis that mercury in the EFPC floodplain soils is generally insoluble in all but the most harsh chemical extractants. Metallic mercury is definitely present in some soils but resists volatilization unless heated to temperatures (> 50°C) well beyond the range expected to occur on the EFPC floodplain.

REFERENCES

- EPA. 1994. *Determination of Mercury, with Speciation, in Poplar Creek Soil Samples*. Prepared by D. Dobb, E. Miller, and D. Cardenas of Lockheed Environmental Systems & Technologies Company, Las Vegas, Nevada. and K. Brown of Technology Support Center, Environmental Monitoring Systems Laboratory, Environmental Protection Agency, Las Vegas, Nevada, March.
- Landa, E.R. 1978. The retention of metallic mercury vapor by soils. *Geochimica et Cosmochimica Acta*, 42:1407-1411.
- Miller, E.L. 1993. Speciation of mercury in soil. EPA Environmental Monitoring Systems Laboratory, Las Vegas, Nevada.
- Revis, N.W., T.R. Osborne, G. Holdsworth and C. Hadden. 1989a. Distribution of mercury species in soil from a mercury-contaminated site. *Water Air Soil Pollut.*, 45:105-113.
- Revis, N.W., T.R. Osborne, D. Sedgley, and A. King. 1989b. Quantitative method for determining the concentration of mercury (II) sulphide in soils and sediments. *Analyst*, 114:823-825.
- Revis, N.W., G. Holdsworth, G. Bingham, A. King and J. Elmore. 1989c. An assessment of health risk associated with mercury in soil and sediment from East Fork Poplar Creek, Oak Ridge, Tennessee. Revised Final Report. Prepared by Oak Ridge Research Institute, 113 Union Valley Road, Oak Ridge, Tennessee. April.
- Sakamoto, H., T. Tomiyasu, and N. Yonehara. 1992. Differential determination of organic mercury, mercury (II) oxide and mercury (II) sulfide in sediments by cold vapor atomic absorption spectrometry. *Analytical Sciences*, 8:35-39.
- Willet, K.L., R.R. Turner, and J.J. Beauchamp. 1992. Effect of chemical form of mercury on the performance of dosed soils in standard leaching tests: EP and TCLP. *Hazardous Waste & Hazardous Materials*, 9:275-288.

APPENDIX B

SUMMARY OF

OAK RIDGE Y-12 SITE REMEDIAL INVESTIGATION

COMPREHENSIVE ENVIRONMENTAL RESPONSE,

COMPENSATION, AND LIABILITY ACT (CERCLA)

CLASSIFIED INFORMATION REVIEW (U)

**This appendix is an Unclassified Nonsensitive version of Y/DK-1040,
which was originally issued in June 1994 as Secret Restricted Data.**

**SUMMARY OF OAK RIDGE Y-12 SITE REMEDIAL INVESTIGATION
COMPREHENSIVE ENVIRONMENTAL RESPONSE,
COMPENSATION, AND LIABILITY ACT (CERCLA)
CLASSIFIED INFORMATION REVIEW (U)**

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**SUMMARY OF
OAK RIDGE Y-12 SITE REMEDIAL INVESTIGATION
COMPREHENSIVE ENVIRONMENTAL RESPONSE,
COMPENSATION, AND LIABILITY ACT (CERCLA)
CLASSIFIED INFORMATION REVIEW (U)**

East Fork Poplar Creek (EFPC) and its floodplain have been exposed to releases from the Y-12 Plant since the mid-1950s. The Y-12 Plant has been actively engaged in the development and manufacture of classified materials throughout its history. This review of classified chemicals utilized at the Y-12 facility allowed a comprehensive assessment of chemicals employed, processes involved, and controls imposed, which provides assurance that the classified chemicals used at the Y-12 Plant either were not a source of contamination to the creek or were encompassed by the EFPC remedial investigation (RI).

The *Y-12 Plant Production Material Classification Guide*, Section 3, Appendix, Materials List "U" was reviewed in relation to the EFPC RI. It has been determined that all chemicals found in this listing have been considered and there are no contaminants of concern (COCs) for the EFPC RI other than those previously identified.

The review of classified chemicals at the Y-12 Plant considered both current and historical processes and uses and is documented in the classified report *Oak Ridge Y-12 Site Remedial Investigation Comprehensive Environmental Response, Compensation, and Liability Act (CERCLA) Classified Information Review (Y/DK-1040)*. Included with this report is a comprehensive elemental analysis of selected EFPC samples, which provides information on elemental composition relative to natural elemental levels.

B.1 CHEMICAL REVIEW

Each Y-12 Plant classified chemical was evaluated relative to the analytical methodologies employed to generate EFPC RI data. When the analytical methods were appropriate for the chemical form or its potential degradation products, no further evaluation was required. When the EFPC RI analytical methods employed were ineffective for specific chemicals or their forms, additional investigation of the chemical followed.

Additional investigation of each chemical encompassed two primary avenues, quantity and process. The relative magnitude of classified chemical usage at the Y-12 Plant was assessed and placed in context with on-site control systems. These systems covered: (1) Y-12 Industrial Hygiene assessment, including carcinogenicity evaluation and reproductive/developmental toxicity for mammalian species; (2) Y-12 Plant accountability control through Precious Metals Inventory Control and Nuclear Material Control & Accountability; and (3) Y-12 Physical Security Safeguards control. The processes involved in the use of the chemicals were assessed for the following:

- location relative to the EFPC study area and potential contribution to it;
- operational handling and manipulation controls;

- administrative personnel exposure and health controls; and
- environmental controls (air emission, waste, and waste water containment).

Processes were evaluated through interviews with Y-12 Plant personnel knowledgeable of the processes and historical uses of the chemicals. Specific processes were investigated by on-site inspections of actual work areas and environmental controls.

Through this review, it has been determined that chemicals found on the Y-12 Plant's Classified listing do not present additional concerns for the areas of the EFPC RI. The chemicals on the Y-12 Plant Classified listing:

- have been determined as part of the RI,
- are related to controlled processes that preclude release,
- were utilized in limited quantities and present no toxicity concern,
- were held under strict control programs, or
- are included in the following comprehensive elemental analysis of selected soils.

B.2 COMPREHENSIVE ELEMENTAL ANALYSIS OF SELECTED SOILS FROM EAST FORK POPLAR CREEK

Three soil samples from highly mercury contaminated areas of the EFPC floodplain in Oak Ridge, Tennessee, were submitted to the Y-12 Plant Laboratory for analysis. These samples represent primary depositional areas of EFPC and would be indicative of worst-case chemical contamination. The soils that exhibited the highest mercury concentrations (2700, 2100, and 1300 $\mu\text{g/g}$) of the 20 soils collected during a January sampling event were selected for analysis. Samples included material from depths of 25 to 40 cm (10 to 16 in.) at the Clark Property, Bruner Site (E-53476 S-00); 32.5 to 47.5 cm (13 to 19 in.) at the DOE Property (N-32156 E-00); and 7.5 to 22.5 cm (3 to 9 in.) at Wetland 3, Monday Property (N-33468 W-12). The soils were collected on January 29, 1994, by Oak Ridge National Laboratory and Science Applications International Corporation (SAIC) staff as part of a mercury speciation and bioavailability study. Results of these studies, including further documentation of sampling locations and methods, are given in the main text of this *Addendum to the East Fork Poplar Creek - Sewer Line Beltway Remedial Investigation Report*.

Determinations of 66 elements in these samples is presented in the *Oak Ridge Y-12 Site Remedial Investigation Comprehensive Environmental Response, Compensation, and Liability Act (CERCLA) Classified Information Review (Y/DK-1040)*. Analysis employed spark source optical spectroscopy and inductively-coupled plasma emission spectroscopy. Where applicable, these data have been compared to the Oak Ridge, Environmental Restoration Background Soils Characterization elemental ranges. Additional comparison was made to National Institute of Standards and Technology Reference Material 8406, soil from the Big Creek floodplain near Norris Lake, LaFollette, Tennessee. With few exceptions, the elemental concentrations are consistent with the background level ranges. In those cases in which the samples exhibited concentrations higher than the background range, the elements had been characterized in more detail during the actual EFPC RI or were within a factor of five of the range.

B.3 CONCLUSION

Assessment of Y-12 Plant classified chemicals has ascertained that these chemicals were determined as part of the EFPC RI, were controlled through processes that precluded release, were utilized in limited quantities, or present no toxicity concern. Comprehensive elemental analysis of selected soils indicated no elevated elemental concentrations beyond those previously identified as COCs by the EFPC RI.