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Mercury characterization in soil collected nearby the Department of Energy Oak Ridge reservation

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FLORIDA INTERNATIONAL UNIVERSITY

Miami, Florida

MERCURY CHARACTERIZATION IN SOIL COLLECTED NEARBY THE
DEPARTMENT OF ENERGY OAK RIDGE RESERVATION

A thesis submitted in partial fulfillment of the
requirements for the degree of

MASTER OF SCIENCE

in

CHEMISTRY

by

Julio Cesar Cabrera

2009

To: Dean Kenneth Furton
College of Arts and Sciences

This thesis, written by Julio Cesar Cabrera, and entitled Mercury Characterization in Soil Collected Nearby the Department of Energy Oak Ridge Reservation, having been approved in respect to style and intellectual content, is referred to you for judgment.

We have read this thesis and recommend that it be approved.

Konstantinos Kavallieratos

Rudolf Jaffe

Yong Cai, Major Professor

Date of Defense: March 6, 2009

The thesis of Julio Cesar Cabrera is approved.

Dean Kenneth Furton
College of Arts and Sciences

Dean George Walker
University Graduate School

Florida International University, 2009

DEDICATION

To my family, for all their unconditional love and support and to the memory of my
father.

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I thank my major Professor Dr. Yong Cai, for his guidance, for his suggestions through my graduate studies and for the financial support through a research assistantship. I also owe gratitude to Guangliang Liu for his help in and outside the lab. I would also like to thank to Marshall Allen for his support in throughout the project.

I would like to thank Dr. Rudolf Jaffe and Dr. Konstantinos Kavallieratos for their support and understanding.

ABSTRACT OF THE THESIS

MERCURY CHARACTERIZATION IN SOIL COLLECTED NEARBY THE
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by

Julio Cesar Cabrera

Florida International University, 2009

Miami, Florida

Professor Yong Cai, Major Professor

Total mercury (Hg) concentration provides insufficient information to understand Hg behavior in Hg-contaminated soil systems and to seek potential remediation technologies, because the distribution, mobility, bioavailability, and toxicity of Hg are dependent on Hg forms present in soils. The phase association of Hg in soil is investigated to evaluate potential environmental risk through combination of total Hg determination, soil fractionation, and speciation analysis of Hg in a Hg-contaminated DOE site. Besides total Hg concentration analysis, sequential extraction procedures and thermal desorption techniques were employed to study Hg binding forms in soils in this study. Total mercury concentrations ranging from less than 100 ng/g to more than 30,000 ng/g were detected. The highest form of mercury present in the soil is organically-bound mercury, followed by elemental mercury, and mercury sulfide. Bioavailable and mobile mercury is minimal.

TABLE OF CONTENTS

CHAPTER		PAGE
Chapter 1	Introduction.....	1
1.1	Mercury contamination in the environment.....	1
1.2	Sources of mercury in the environment.....	5
1.3	Biogeochemical cycling of mercury	7
1.4	Mercury in soil.....	10
1.5	Mercury problems in Oak Ridge Reservation	12
1.6	Research Objectives.....	13
Chapter 2	Mercury speciation in Oak Ridge Reservation soil	14
2.1	Introduction.....	14
2.2	Experimental.....	17
2.2.1	Soil sample collection.....	17
2.2.2	Fractionation of soil sample.....	17
2.2.3	Reagents and instrumentation.....	19
2.2.4	Determination of Hg in fractionated samples	20
2.2.5	Thermal desorption experiments.....	20
2.2.6	Sequential extraction procedure.....	21
2.3	Results and Discussion	24
2.3.1	Soil characterization.....	24
2.3.2	Hg in the redoximorphic depletions and redoximorphic concentrations with different particle sizes.....	25
2.3.3	Thermal desorption experiments.....	27
2.3.4	Sequential extraction.....	31
2.3.5	Environmental implications.....	34
2.4	Conclusions.....	35
Chapter 3	Analysis of mercury species in samples from ORR	37
3.1	Introduction.....	37
3.2	Experimental.....	38
3.2.1	Instrumentation	38
3.2.2	Chemicals and Reagents	38
3.2.3	Sampling site selection	40
3.3	Procedure	41
3.3.1	Total mercury in soil and sediment.....	41
3.3.2	Total mercury in water.....	41
3.3.3	Methylmercury in soil and sediment.....	43
3.4	Results and Discussion	44
3.4.1	Initial evaluation of total mercury concentrations in ORR area	44
3.4.2	Survey of the mercury problem in the ORR area	46
3.4.3	Methylmercury in ORR soil and sediment	48
3.5	Conclusions.....	52

Chapter 4	Conclusions.....	53
Chapter 5	Future Work.....	55
	REFERENCES	56

LIST OF TABLES

TABLE	PAGE
Table 2.1	Extractants and Hg fractions used in the sequential extraction procedure.....21
Table 2.2	Content of major elements and organic carbon in fractionated subsamples.....25
Table 2.3	Hg concentrations in the redoximorphic depletions and redoximorphic concentration from the ORR soil sample with different particle size.....26
Table 2.4	Concentrations of different Hg species in different fractions of the ORR soil and SRM NIST 8406 by using sequential extraction procedure.....32
Table 3.1	Total mercury concentrations in ORR samples during initial sampling event.....46
Table 3.2	Mercury concentrations in the selected soil, sediment, and water samples collected from Oak Ridge LEFPC mercury-contaminates samples.....47
Table 3.3	Methylmercury concentrations in ORR soil and sediment samples.....50

LIST OF FIGURES

FIGURE	PAGE
Figure 1.1	The mercury cycle. Sources and fate. Hgp refers to mercury in the particulate.....8
Figure 1.2	Diagram summarizing the biogeochemical cycling of mercury in aquatic environments. M ^a = methylation (oxidative); D ^b = demethylation (bacterial reduction)10
Figure 2.1	Redoximorphic depletions (gray color) and redoximorphic concentrations (brown color) in Y-12 soil sample.....18
Figure 2.2	A scheme showing the sequential extraction procedure used in this study.....22
Figure 2.3	Hg concentration in the ORR soil sample and SRM NIST 8406 after thermal desorption treatments.....29
Figure 2.4	Distribution of Hg in the freeze-dried subsamples from the ORR soil sample and the SRM NIST8406 using sequential extraction.....33
Figure 3.1	Sampling points along the LEFPC.....40
Figure 3.2	Distribution of MeHg in soil and sediment along the EFPC.....51
Figure 3.3	Distribution of Thg in soil and sediment along the EFPC.....52

LIST OF ABBREVIATIONS

ABBREVIATION	MEANING
Å	armstrong
AAS	atomic absorption spectrometry
CVAFS	cold vapor atomic fluorescence
DOE	Department of Energy
EFPC	East Fork Poplar Creek
EPA	Enviromental Protection Agency
Hg	mercury
Hg ⁽⁰⁾	elemental mercury
HgCl ₂	mercury chloride
HgS	mercury sulfide
ICPMS	Inductively Coupled Mass Spectrometry
LEFPC	Lower East Fork Poplar Creek
MeHg	Methyl mercury
MMHg	monomethyl mercury
NIST	National Institute of Standards and Technology
ORR	Oak Ridge Reservation
ppt	parts per trillion

ABBREVIATION

MEANING

SEP	sequential extraction procedure
SRM	Standard Reference Material
THg	Total mercury

Chapter 1 Introduction

1.1 Mercury contamination in the environment.

Mercury is a liquid metal at ambient temperatures and pressures. It forms salts in two ionic states: mercury (I) and mercury (II). Mercury (II) salts are much more common in the environment, and if soluble in water are bioavailable and considered toxic. Mercury also forms organometallic compounds, many of which have industrial and agricultural uses. Elementary mercury gives rise to a vapor that is only slightly soluble in water, but is problematic because of easy transport in the atmosphere. The most common form of mercury is insoluble mercury (II) sulfide (naturally occurring cinnabar) which is less bioavailable than other forms. (Nriagu, 1993, 1994; Pirrone, 2001; Renneberg and Dudas, 2001). In contrast to many other metal/metalloid contaminants, mercury displays a complex environmental speciation behavior. Widespread, detectable environmental mercury species include divalent mercury (Hg^{2+}), elemental mercury (Hg^0) and monomethylmercury (CH_3Hg^+) (Akagi, 2000; Schroeder, 1989). Less frequently encountered compounds include dimethylmercury (Mason, 1994), monovalent mercury (Hg_2^{2+} , a species that disproportionates via the following reaction: $\text{Hg}_2^{2+} \rightarrow \text{Hg}^{2+} + \text{Hg}$ (Pehkonen, 1989). More recently, detectable quantities of ethylmercury compounds (e.g., $\text{C}_2\text{H}_5\text{Hg}^+$, $\text{C}_2\text{H}_5\text{HgC}_2\text{H}_5$, etc.) have been reported in environmental media (Cai, 1997; Hintelmann et al., 1995; Holmes and Lean, 2006; Siciliano et al., 2003).

Elemental mercury is known to be globally transported before it is deposited on soil or water (Pilgrim et al., 2001). Mercury contamination has long been recognized as a problem for both humans and ecosystems. Mercury is considered by the United States Environmental Protection Agency (EPA) to be a highly dangerous element because

methylated mercury is accumulative and persistent in the environment and biota. Since mercury does not degrade once it is released to the environment it will always be present in one form or another (U.S.E.P.A., 2000). Mercury in natural waters is mostly in the form of inorganic species; however, its biological toxic effects are primarily due to methylmercury (Agency for Toxic Substances and Disease Registry (ATSDR), 1999; Clarkson, 1972, 1992; Clarkson and Magos, 2006; Clarkson and Strain, 2003). Unfortunately, the inorganic mercury released into the environment can be converted, by naturally-occurring biological processes, into methylmercury species. Methylmercury is a highly toxic organomercury species, present in much lower concentrations and is readily accumulated by aquatic organisms (Cai et al., 1996; Liu et al., 2008a; Liu et al., 2008b; Mason, 1994; Mason and Benoit, 2003; Mason et al., 1993; Sanchez-Uria, 1998; Ullrich et al., 2007; Ullrich et al., 2001; USEPA, 2002)

Methylmercury is neurotoxic, causes blockage of binding sites of enzymes, interferes with protein synthesis, impedes thymidine incorporation into DNA, among other factors (Clarkson, 1992; Halbach, 1995; National Institute of Environmental Health Science (NIEHS), 1998; National Research Council (NRC), 2000; Thayer, 1984). The short chain alkylmercury compounds are toxic and tend to bioaccumulate more readily than other species of mercury. The mercury–carbon bond is very stable, and the presence of the alkyl groups confers lipid solubility. Nearly all mercury found in fish flesh (>95%) occurs as methylmercury (Cai et al., 2000; Mason et al., 1999; Porcella, 1994), and most of the mercury present in humans originates from fish in the food supply (U.S.E.P.A., 2000) via the following processes: (1) emission of mercury to the air; (2) mercury air transport and deposition on land and water; (3) transformation of mercury to

methylmercury in water bodies; (4) methylmercury uptake and bioaccumulation in fish; and (5) consumption of contaminated fish by mammals, including humans. Mercury and methylmercury exposures can result in permanent damage to the brain and kidneys, in both humans and wildlife. Many organizations and agencies have addressed the level of methylmercury exposure to humans (NRC, 2000; U.S.E.P.A., 2000).

Several pollution events have been associated with the anthropogenic use of organomercurials. The most documented case of methylmercury poisoning occurred in Minamata Bay, Japan (from 1932 until diagnosed in 1968), from which the name Minamata Disease derived (Clarkson, 1972, 1992; Hosokawa, 1993; Smith, 1975). More than 2,000 people were poisoned by the consumption of fish and shellfish contaminated with methylmercury. This event was the first known case of mercury pollution in the aquatic environment. It was caused by the discharge of methylmercury into the drainage channel that leads into the Minamata Bay. Methylmercury was formed during the production of PVC formed by reacting acetaldehyde and inorganic mercury used as a catalyst. Also organomercurials were used as fungicides for cereal infections in the 1960's. This use of organomercurials caused a particularly disastrous outbreak in 1972 in Iraq, where the seed grain coated with antifungal methylmercuric preparations were consumed as homemade bread. As a result 6,530 victims were ill (Watanabe, 1996). The impact on ecological systems was noted earlier in 1964 by Swedish ornithologists who observed a significant decrease in wild bird populations (Helander, 1982). Nowadays the pathway of exposure to methylmercury involves the emission of low concentrations of mercury, mainly from combustion sources (Environmental Reporter, 2000; Fitzgerald et al., 2007; Fitzgerald and Lyons, 1973; Fitzgerald and Watras, 1989; Lindberg et al.,

2005a; Lindberg et al., 2005b; Mason et al., 2006; Nriagu et al., 1992). These emissions lead to build up of methylmercury in water bodies and fish tissue over time (U.S.E.P.A., 1997e1997f; U.S.G.S., 1998). It is important to stress that the most likely individuals who are being exposed to a high level of methylmercury are consumers of large quantities of fish. Pregnant women and young children are particularly sensitive to exposure of high levels of mercury (NRC, 2000).

During the past decade, a new trend has emerged with regards to mercury pollution (Kambey, 1989). Investigations initiated in the late 1980s in the northern-tier states of the United States, Canada and the Nordic countries found that fish, mainly from oligotrophic lakes and often in very remote areas, commonly have high levels of mercury (Cai, 1997; Cai, 2000; Cai et al., 1997; Cai et al., 1999; Krabbenhoft et al., 1998; Krabbenhoft et al., 2000; Kranzer, 2003; Lindberg et al., 2001; Lindberg and Zhang, 2000; Liu et al., 2008a; Liu et al., 2008b; Mason, 1994; Mason et al., 2005; Mason and Benoit, 2003; Mason et al., 2000; Mason and Sullivan, 1997; O'Driscoll and Evans, 2000; O'Driscoll et al., 2005). Fish sampling surveys in other regions of the United States have shown widespread mercury contamination in streams, wetlands, reservoirs and lakes (U.S.G.S., 1998). Most of the mercury released to the atmosphere by anthropogenic activities is in the form of the elemental mercury vapor (Schroeder and Munthe, 1998; Schroeder et al., 2003). It may also be bound to airborne particles that can be widely transported from the source of emission (U.S.E.P.A., 1997b). Mercury may be deposited into surface waters and lands. Most of the mercury in waters, soils, sediments, or plants and animals is in the form of inorganic mercury salts and organic forms of mercury. However, methylmercury has been found to be the predominant form of mercury in the

tissues of fish caught in water containing predominantly inorganic mercury (Cai, 2000; Mason et al., 2005; Mason and Benoit, 2003; Mason et al., 1999; Monsalud, 1999). Therefore a chemical transformation of inorganic mercury (Hg^{2+}) to methylmercury (CH_3Hg^+) occurs in the natural environment (Gilmour et al., 2006; Gilmour and Henry, 1991; Gilmour et al., 1992; Gilmour et al., 1998; Mason et al., 2005; Mason and Benoit, 2003). Methylation of mercury has been shown to involve both biotic and abiotic pathways (Jensen and Jernel Ö.V, 1969; Nagase H.; Ose, 1982; Weber, 1993; Wood J.M. et al., 1969). By highly efficient bioaccumulation and biomagnification, neurotoxic methylmercury would eventually reach our food chain especially from seafood (NRC, 2000; Nriagu, 1993; Nuzzi, 1972; Topping and Davies, 1981). The USEPA conducted a quantitative human health risk assessment of methylmercury (U.S.E.P.A., 1997e1997f1997h). The assessment estimated that between 1-3% of women of childbearing age in the US eat sufficient amounts of fish for their fetuses to be at risk from methylmercury exposure. The EPA's reference dose for methylmercury of 0.1 μg per g of body weight per day is viewed as a scientifically justifiable level (NRC, 2000) for protecting human health from the adverse effects of methylmercury.

1.2 Sources of mercury in the environment

Natural mercury emissions include volcanoes, natural mercury deposits and volatilization from the ocean (Liu et al., 2008a; Liu et al., 2008b; Munthe et al., 2003; Murphy et al., 2006; U.S.E.P.A., 1997c; U.S.G.S., 1998), which was estimated by Mason (Mason, 1994) as 2000 tons per year. Naturally mercury-enriched material found associated with plate tectonic boundaries, areas of high crustal heat flow, precious and

base metal mineralization, recent volcanism, and organic rich sedimentary rocks (Rasmussen, 1994). Large areas of land in the western United States are enriched in mercury, and mercury deposits are abundant (Jonasson and Boyle, 1972). However, since the 19th century the total amount of mercury in the environment has grown by a factor of 2 to 5 above pre-industrial levels (Mason, 1994). Mercury was widely used in industry because of its diverse properties (U.S.E.P.A., 1997c1997i; U.S.G.S., 1998). As a consequence, it is clear that industry was an important source of mercury in the environment. Human activities are primarily responsible for mercury pollution, mainly from combustion and waste incineration (Porcella et al., 1997) from scrubber water or coal cleaning water produced by coal fired power plants and solid waste incinerators (Carroll and Truman, 1995; U.S.E.P.A., 1997c). The intentional use of mercury in products (i.e., batteries, paints, pesticides) in the US has decreased significantly in the past 20 years (U.S.D.O.I., 1994).

Elevated levels of mercury in waters remote from anthropogenic emission sources have also been documented (Rasmussen, 1994; Sorensen et al., 1994; Swain, 1992; U.S.E.P.A., 1997g, 1998; Uchino et al., 1987). This mercury levels indicate that atmospheric deposition is an important source of contamination. This situation raises concerns about increasing amounts of mercury in the global pool and the implications of mercury emissions and their impacts on both people and ecosystems worldwide. In December 2000, the EPA announced its intention to regulate mercury emissions from fossil fuel electric power plants under the Clean Air Act (Environmental Reporter, 2000). In addition to air emissions, mercury is also released in other ways, including waterborne discharges and direct disposal to the land (U.S.E.P.A., 1997c1997e).

Over the years, some mercury compounds have been specifically developed as pesticides, fungicides, and germicides to be used on grains, in paints, and with vaccines (U.S.E.P.A., 2000). The examples of the usage of organomercury compounds include methylmercury and ethylmercury and phenylmercury as a fungicide and cereal seed treatment; thiomersal and mercurochrome as antiseptics; mersalyl, chlormerodrin, mercuraphen and mercurophylline as diuretics. Although some of these compounds are not used any longer, their removal is not uniform throughout the world: ranging from outright bans, to recommendations and voluntary codes (Craig, 1986; U.S.D.O.I., 1994; U.S.E.P.A., 1997a).

1.3 Biogeochemical cycling of mercury

Once released into the environment, mercury is subject to a variety of processes and interactions. Environmental mercury is thought to move through various environmental compartments, possibly changing forms and species during this process. Like other elements, these processes are conceptualized as a cycle (Liu et al., 2008a; Liu et al., 2008b; Stober et al., 2001; Stordal et al., 1996; Tseng et al., 2004; Turner et al., 2001). Figure 1.1 illustrates mercury release by both natural and anthropogenic sources into environmental media: air, soil and water. When airborne mercury is deposited on land or in water, biological transformations can occur that converts some of the mercury to methylmercury. The amount of mercury transformed to methylmercury varies from one water body to another.

Figure 1.1 The mercury cycle. Sources and fate. Hg_p refers to mercury in the particulate. (U.S.E.P.A., 1998)

Beyond mercury loading, the environmental setting (i.e., climate, geology, land use, land cover), water chemistry and wetland density (Cleckner et al., 1999) are the most important factors controlling methylmercury production. However, these factors seem very complex and variable, and not altogether predictable. The exact mechanism by which mercury enters the food chain is largely unknown. However, EPA reported that bacteria that process sulfate in the environment plays an important role by taking up the mercury in its inorganic form and through metabolic processes, converting it to methylmercury (U.S.E.P.A., 1997b). Dimethyl- and methylmercury, Hg^{2+} and elemental mercury may interchange in a general biochemical cycle. This accounts for the formation of methylmercury in remote areas where it has not been directly introduced to the environment, but where Hg^{2+} may have been used. A scheme with a summary of the biogeochemical cycling of mercury is presented in Figure 1.2.

In lakes, rivers and reservoirs methylmercury is taken up by fish, resulting in significant methylmercury bioaccumulation in fish tissue. Nearly all the mercury that accumulates in fish tissue is methylmercury. Inorganic mercury is less efficiently absorbed and eliminated to a higher extent. In some instances the concentration of methylmercury in fish may be several orders of magnitude greater than the concentrations in the surrounding water or sediment. Research in mercury transport, transformations and fate will improve our understanding of the complexity of mercury processes once it enters the environment, and allow improved future regulatory efforts.

Figure 1. 2 Diagram summarizing the biogeochemical cycling of mercury in aquatic environments. M^a = methylation (oxidative); D^b = demethylation (bacterial reduction).

1.4 Mercury in soil

Mercury deposited in soils undergoes different chemical and biological transformations, such as $\text{Hg}^{(0)}$ oxidation, and Hg^{2+} reduction or methylation depending on soil pH, temperature and humic content. Inorganic forms of mercury in soils are quite soluble and therefore are highly mobile. However, Hg mobilization in soils through

inorganic compounds such as HgCl_2 and $\text{Hg}(\text{OH})_2$ is minor compared to mercury bound to soil humic substances. The formation of organic Hg^{2+} complexes is the dominating process due to the affinity of Hg^{2+} and its inorganic compound to sulfur containing functional groups. This tendency to complex limits the mobility of mercury in soil as most of the mercury is fixed in the bulk organic matter and can only be mobilized through elution in run off by being attached to suspended soil or humus. However, Hg^{2+} will be absorbed on soluble organic soil components such as fulvic acids and may be transferred to run off in the dissolved phase (U.S.E.P.A., 1997d, 2000). In a study done on the binding and mobility of mercury in soils contaminated by emissions from chlor-alkali plants (H. Bisester et al 2002), the highest mercury concentrations were found in the uppermost soil layer (5cm). Mercury concentrations are proportional to a decrease in depth which in turn correlates with a decrease in organic matter content. Mercury is transported to deeper soil layers as soluble organic complexes. In sandy soils deficient in organic matter, coupling to humic substance is minor. Leachable Hg is in the form of soluble organic Hg complexes and is highest in soils with a high organic matter and low clay content. Reactive Hg or weak Hg complexes are retained in the uppermost soil layer through sorption on mineral surfaces. The size of the soil particle is also important when it binds to mercury. The content of mercury and organic matter decreases with particle size. Mercury was demonstrated in a study that mercury concentration in soil was high in fine particles, and that at pH of less than 2, Hg^{2+} was the predominant species. (Wasay et al 1995).

1.5 Mercury problems in Oak Ridge Reservation

Between 1950 and 1963, the DOE Y-12 Weapons Plant used mercury as part of the lithium isotope separation and purification process. Estimates of 330 metric tons of mercury were released into the environment; of that total, 110 metric tons were lost to the East Fork Poplar Creek (EFPC) (D.O.E, 1997). The study concluded that DOE could not account for an additional 750 metric tons of mercury used during that period . Releases of mercury to the creek contaminated instream sediments, and periodic flooding contaminated floodplain soils along the creek. The floodplain width ranges from 5 to 500 meters (D.O.E, 1983). Much of the mercury is now sequestered in the Y-12 plant.

In 1983, massive mercury contamination from the Y-12 Plant was discovered in East Fork Poplar Creek, which flows through residential areas of Oak Ridge. Seeing the impacts DOE had on the region, the State of Tennessee asserted its authority over activities on the Oak Ridge Reservation (ORR). This authority included enforcement of regulations, monitoring of the environment and oversight of cleanup on the ORR. During the past 15 years the Department of Energy has been identifying and remediating the sources of mercury in and near the Upper East Fork Poplar Creek (UEFPC) at the Y-12 plant.

Physical, chemical, and biological processes in the environment have altered some of the mercury into a variety of other organic and inorganic forms. The total mercury concentrations in the area are relatively known to be high. However, little is known about the fate, transport, and potential environmental impact of the high level mercury present in the soil and sediments in some area at the Oak Ridge Reservation.

1.6 Research Objectives

The purpose of the research is to investigate the mercury speciation and to evaluate the mobility and bioavailability of mercury in the soil and sediment in the contaminated areas of Oak Ridge Reservation and to determine the factors that controls the fate, transport, and bioavailability of mercury in the ecosystem. The characterization of mercury in soil collected from this area will be conducted using sequential extractions and thermal desorption procedures. In order to obtain an overall assessment of mercury contamination in the Oak Ridge Reservation, efforts were also made to identify the different mercury species present in the soil, sediment and water surrounding the Y-12 area at Oak Ridge.

The significance of this study is that it will describe the behavior of mercury in the soil and how this behavior affects its potential impact to human health in the surrounding area. It will also lead to a better understanding of the mercury mobility in the environment, and this will directly affect the selection of the techniques used for mercury remediation in the future.

Chapter 2 Mercury speciation in Oak Ridge Reservation Soil.

2.1 Introduction

Speciation analysis of mercury (Hg) is important in assessing the risk posed by contaminated soils. This is because the fate, transport, and bioavailability of Hg in soil are dependent upon the species in which it is present (Barnett and Harris, 1997; Wall Schlager and Desai, 1998; Wall Schlager et al., 1998a). The speciation of Hg in soil and sediment may be defined functionally (e.g., bioavailable fraction) or operationally (e.g., water soluble, exchangeable, and organo-chelated Hg fractions). Mercury speciation can also be described to distinguish between specific chemical species (e.g. inorganic Hg and methylmercury) (Bloom et al., 2003). The procedures determining functionally or operationally defined Hg species are sometimes called fractionation rather than speciation (Martin-Doimeadios et al., 2000).

Sequential extraction procedures (SEP), thermal desorption analysis, and spectroscopic techniques are three major approaches to determine Hg speciation in soil. Sequential extraction, a widely used method for Hg speciation, can provide useful information related to environmental behavior of Hg in soil, such as solubility, mobility, and bioavailability (Biester and Scholz, 1997a; Han et al., 2003). Thermal desorption analysis has also been used for Hg species in solid samples. It offers the advantages of being simple, fast, and cost-effective (Bombach et al., 1994). Spectroscopic techniques, such as X-ray absorption fine structure spectroscopy or X-ray microprobe spectroscopy, can provide a direct observation of Hg speciation. The application of this approach, however, is limited by its relatively poor detection limit (Kim et al., 2003; Kim et al.,

2000). Combinations of these techniques rather than a single method are often needed to estimate Hg speciation and assess the environmental impact of Hg contaminated sites.

The Oak Ridge Reservation (ORR), especially in the area surrounding the Y-12 Weapons Complex, was heavily contaminated with Hg. In the 1950s and 1960s, an estimation of 108,000-212,000 kg of Hg was released to the headwaters of the East Fork Poplar Creek (EFPC) during the production of Lithium enriched in ^6Li in the Y-12 Plant, which resulted in a heavy Hg contamination in the floodplains of the EFPC. Efforts have been made to investigate the magnitude, speciation, mobility, and bioavailability of Hg in this area, especially the Lower EFPC (LEFPC) floodplains. The EFPC floodplain soils were found to contain Hg in concentration up to 3,000 $\mu\text{g/g}$ and in a combination of various physicochemical forms such as Hg^0 , dissolved ionic Hg, fine Hg particles attached to suspended matter, mercuric oxide, Hg covalently bound to organic matter, and mercuric sulfide (Barnett and Harris, 1995, 1997; Campbell et al., 1998; Han et al., 2009; Hollerman et al., 1999). Among these Hg forms, mercuric sulfide (~85% of total Hg) had been suggested as the predominant form (Revis and Osborne, 1989), but it was also detected in variable and sometimes relatively lower quantities (Barnett and Harris, 1995). Because of the severe contamination of Hg, this site was placed on the National Priority List to undergo remediation (Barnett and Harris, 1997; Morris, 1995).

Despite extensive studies focusing Hg contamination in the LEFPC floodplains, it is currently not very clear about the magnitude and speciation of Hg present in soils coming from the DOE Y-12 site. The present study was carried out on a soil sample collected just outside the Y-12 boundary of the ORR site. The choice of this site for sample collection was based upon several technical bases. First of all it was the first

easily accessible location beyond the Y-12 property and would still have primarily the fingerprint of any Y-12 manipulations, e.g., fresh addition of Clinch River water for flow management. Secondly, samples taken from this site would have the least exposure to any of the downstream environmental influences, e.g., residual floodplain deposition or Hg reintroduction that might alter the original Hg transport from the Y-12 site. And finally, various engineering activities on the Y-12 site over the years and near this sampling site, e.g., placement of rip-rap in the creek to reduce the transport of fine particulate, has lead to a different legacy of Hg contamination at this site than from say the LEFPC floodplains.

A prominent redoximorphic characteristic of soil was observed throughout area surrounding the Y-12 site, i.e., the soil was clearly composed of two components: a gray part (termed as redoximorphic depletions) and a brownish part (termed as redoximorphic concentrations) (Fig. 2.1). The concentration, phase association, mobility, and volatility of Hg present in these two components were inferred to be different based on the previous observation that fairly different Hg concentrations were present in these two components. The effect of soil redoximorphic features on Hg concentration and phase association has not been investigated in previous studies dealing with Hg speciation. Most of them applied operationally defined speciation techniques (SEP and/or thermal desorption) to bulk soil samples (wet or dried) (Biester et al., 2000; Biester and Scholz, 1997b; Bloom et al., 2003). In the present study, I make a new attempt to characterize Hg speciation and to evaluate Hg mobility in soils. I first fractionated the soil sample based on redox induced alteration of soil characteristics. Then, I applied SEP and thermal desorption analysis to the fractionated soil components rather than bulk soil sample. The

objective of this study is to provide a typical example for expanding and detailing the methodology characterizing Hg speciation in soil by applying multiple speciation techniques coupled with fractionation methods. I selected only a typical sample based on the results of previous survey of Hg contamination in the studied area. However, the data generated from various analytical protocols applied in the present study should be potentially useful for investigating the phase association and environmental risk of Hg probably influenced by soil features in the concerned area.

2.2 Experimental

2.2.1 Soil sample collection

The soil sample was taken from the EFPC banks at levels 4 – 8 inches above the water surface using a garden trowel just outside the Y-12 Complex site boundary in Oak Ridge. The sampling site was located approximately a quarter mile offsite, beyond the cement culvert that conveys the stream from the Y-12 site, and directly behind a commercial car wash (Mullins Car Wash). The sample was shipped to FIU on dry ice and stored at -20°C before being analyzed for Hg and Hg speciation.

2.2.2 Fractionation of soil sample

To determine whether Hg concentration and speciation in the soil sample were affected by soil composition, the redoximorphic depletions and concentrations were manually separated. In the low-chroma gray redoximorphic depletions part (Fig. 2.1), Fe and Mn oxide or a combination of Fe and Mn oxide and clay appeared to have been

partially removed via redox processes related to seasonal saturation. The brownish redoximorphic concentrations part seemed to contain more Fe and Mn oxide. The analysis for major elements in these two components confirmed that redoximorphic concentrations contained higher concentrations of Fe, Mn, Ca, and Mg than redoximorphic depletions. The mass amount of redoximorphic concentrations was much larger than redoximorphic depletions as observed during separation process of these two components. Although these two components were not separated completely in the laboratory, differences in Hg concentration and association with soil caused by these two components, if any, should be observed.

Figure 2. 1 Redoximorphic depletions (gray color) and redoximorphic concentrations (brown color) in Y-12 soil sample

Part of the two separated components was stored in a freezer and another part was freeze-dried for 72 h. The dried samples were then grinded with a mortar and separated into fine and coarse particle fractions in order to investigate the effect of particle size on Hg distribution. Number 35 and Number 60 sieves were used to separate coarse particles ($< 500\ \mu\text{m}$) and fine particles ($< 250\ \mu\text{m}$), respectively.

Contents of major elements (Al, Mg, Ca, Mn, Fe) in the fractionated samples were determined by inductively coupled plasma mass spectrometry (ICPMS) (Mg, Ca, Mn) or atomic absorption spectrometry (AAS) (Al and Fe) following $\text{HNO}_3/\text{H}_2\text{O}_2$ digestion (Cai et al., 2002). Organic carbon contents in these samples were determined by subtracting inorganic carbon content from total carbon content. Clay speciation and mineral identification were also conducted on the four fractionated subsamples using X-ray diffraction analysis (Phillips PW 1050 diffractometer) at Activation Laboratories Ltd. (Ontario, Canada).

2.2.3 Reagents and instrumentation

A cold vapor atomic fluorescence spectrometer (CVAFS) system (Merlin10.035, PS Analytical, UK) was used for Hg analysis. A Gyrotory shaker (model G2) from New Brunswick Scientific Co., Inc. (Edison, NJ) and a Blue M oven (Blue Island, IL) were used for sequential extraction and thermal desorption. A certified Hg standard (1000 ppm in 1.8% HNO_3) was purchased from Fischer Scientific (Fair Lawn, NJ). Another certified Hg standard (1000 ppm in 10% HNO_3) from second source (SPEX CertiPrep, Metuchen, NJ) was used for calibration check. A river sediment standard reference material (SRM) NIST 8406, with nominal values of 60 ng/g for Hg and 5.50% for Al, 2.96% for Fe, and

0.043% for Mn, was purchased from the National Institute of Standard and Technology (Gaithersburg, MD). Trace metal grade of HCl and HNO₃, analytical grade of potassium bromide, potassium bromate, stannous chloride, and other reagents were purchase from Fisher Scientific.

2.2.4 Determination of Hg in fractionated samples

Samples (0.1 to 0.3 g wet or dry) were placed inside a 10 ml Wheaton glass ampoule to which 1ml of H₂O and 2 ml of concentrated HNO₃ were added (Jones et al., 1995). The samples were allowed to settle for 20 minutes, then sealed using an Ampulmatic Ampule Sealer, and digested in an autoclave at 120 °C for 1 hour. The samples were analyzed after cooling down. All results were calculated based on dry weight unless stated otherwise.

2.2.5 Thermal desorption experiments

Thermal desorption experiments were performed on NIST 8406 and on the wet and dry redoximorphic depletions and redoximorphic concentrations of the ORR soil sample without further differentiation into particle size. Soil samples (0.1 to 0.2 g) were weighed into a 10 ml Wheaton glass ampule. The thermal desorption experiments were performed at temperatures ranging from 60 to 180 °C for a period of 15 hours inside an oven. The glass ampules were then removed from the oven and allowed to cool. The concentration of Hg remained in the samples were determined using HNO₃ digestion-CVAFS procedure as described above. Triplicates of the sample and three blanks were carried out for each temperature. Each ampule was analyzed three times.

2.2.6 Sequential extraction procedure

A sequential extraction procedure reported previously by Bloom et al. (2003) was conducted on the fine and coarse freeze-dried redoximorphic depletions and redoximorphic concentrations (Fig. 2.2). Listed in Table 2.1 are definitions of the five different fractions and the correspondent extractant used in each step. An aliquot of approximately 0.4 g of sample was used in the sequential extraction. For each step, 40 ml of extractant was added except for step 5 in which 13 ml of aqua regia was used. The extraction was conducted by shaking on an orbital shaker at 200 rpm at room temperature for 24 hours. After centrifuging at 3000 rpm for 5 minutes, the supernatant was carefully decanted into a 250 ml plastic bottle and the precipitate was rinsed with 40 ml of the same corresponding extractant by shaking vigorously and followed by centrifugation. The two supernatant solutions were then combined. The concentration of Hg in the supernatants was determined by CVAFS according to the laboratory procedure (Jones et al., 1995).

Table 2.1 Extractants and Hg fractions used in the sequential extraction procedure.

Extractions were conducted at room temperature (20 °C) for 24 hours.

Fraction ID	Extractant	Extractant:soil ratio	Hg fraction
F1	deionized water	100:1	Water soluble Hg
F2	0.1 M CH ₃ COOH + 0.01 M HCl	100:1	human stomach acid soluble Hg
F3	1 M KOH	100:1	organic matter bound Hg
F4	12 M HNO ₃	100:1	Hg ⁰
F5	aqua regia	32.5:1	mercuric sulfide

Figure. 2.2 A scheme showing the sequential extraction procedure used in this study.

Fig. 2.2 (cont'd) A scheme showing the sequential extraction procedure used in this study

2.3 Results and Discussion

2.3.1 Soil characterization

The results of X-ray minerals identification revealed a similar pattern for the manually separated redoximorphic depletions and redoximorphic concentrations, with quartz alpha, sericite, muscovite or mica, and orthoclase the major mineral forms. The X-ray diffraction patterns of the clay speciation for these two components were also similar. However, differences in clay mineral compositions between redoximorphic depletions and redoximorphic concentrations were observed. Vermiculite and kaolinite/dickite or nacrite were present in both components, but interstratified vermiculite/illite was identified only in the redoximorphic concentrations. Additionally, two peaks at 10.09 and 4.96 Å observed in the redoximorphic concentrations clearly indicate the presence of illite. Only one peak at 4.96 Å was found in the redoximorphic depletions, which could not confirm the presence of illite because of the possible interferences of sericite or muscovite. It seemed that the redoximorphic concentrations contained more types of minerals containing Fe/Mg than the redoximorphic depletions.

The concentrations of some major elements (Al, Mg, Ca, Mn, Fe) in the redoximorphic depletions and redoximorphic concentrations were different as seen in Table 2.2. As expected, significantly higher concentrations of non-silica mineral elements such as Mg, Ca, especially Mn and Fe, were observed for the redoximorphic concentrations compared with redoximorphic depletions. This seemed to be related to the presence of more types of Fe/Mg minerals such as illite and interstratified vermiculite/illite in the redoximorphic concentrations. The organic carbon content in the redoximorphic concentrations was also higher than redoximorphic depletions.

Table 2.2 Content of major elements and organic carbon in fractionated subsamples

Subsample type			Major elements (%)					Organic
			Al	Mg	Ca	Mn	Fe	carbon (%)
Redoximorphic depletions	coarse	mean	0.25	0.08	0.08	0.01	0.98	0.08
		SD	0.01	0.00	0.00	0.00	0.06	0.01
	fine	mean	0.30	0.09	0.10	0.01	1.05	0.06
		SD	0.01	0.00	0.00	0.00	0.01	0.01
Redoximorphic concentrations	coarse	mean	0.37	0.10	0.11	0.08	2.11	0.17
		SD	0.01	0.00	0.00	0.01	0.04	0.01
	fine	mean	0.34	0.09	0.11	0.04	1.70	0.10
		SD	0.001	0.00	0.01	0.00	0.01	0.01

2.3.2 Hg in the redoximorphic depletions and redoximorphic concentrations with different particle sizes

It was observed that loss of Hg occurred for the redoximorphic depletions during the freeze-drying process (Table 2.3). The concentration of Hg in wet redoximorphic depletions sample (91.8 ± 11.6 ng/g) was significantly different ($P < 0.01$) from that in the freeze-dried sample (57.3 ± 1.2 ng/g). For the redoximorphic concentrations, there was no significant difference between Hg concentrations before and after freeze-drying (206.6 ± 57.8 versus 235.9 ± 7.8 ng/g). The high standard deviations for the wet samples could be attributed to the lack of homogeneity of the sample used. As discussed in the following paragraph, the redoximorphic concentrations has stronger binding affinity to Hg resulted from higher Fe/Mn and organic carbon contents than redoximorphic depletions. This appeared to be partially responsible for the difference of Hg loss during

the freeze-drying process between redoximorphic depletions and redoximorphic concentrations.

Table 2.3 Hg concentrations in the redoximorphic depletions and redoximorphic concentrations from the ORR soil sample with different particle size

	Redoximorphic depletions				Redoximorphic concentrations			
	Wet	Dry	Fine	Coarse	Wet	Dry	Fine	Coarse
Hg concentration (ng/g)	91.8	57.3	76.7	50.5	206.6	235.9	203.2	121.9
SD	11.6	1.2	3.8	5.7	57.8	7.8	13.7	22.9

Hg concentrations in the redoximorphic concentrations were significantly higher than in the redoximorphic depletions ($P < 0.01$) (Table 2.3). The Hg concentration in the fine redoximorphic concentrations (203.2 ng/g) was almost three-fold of the fine redoximorphic depletions (76.7 ng/g), whereas the Hg concentration in the coarse redoximorphic concentrations (121.9 ng/g) was twice as much as that in the coarse redoximorphic depletions (50.5 ng/g). This is not unexpected because the redoximorphic concentrations contained higher Fe and Mn than the redoximorphic depletions (Table 2.1). The minerals of Fe and Mn such as iron hydroxide and hydrated manganese oxides have been known to have high affinity to Hg (Andersson, 1979; Dudas, 1976). Organic matter present in soils could also strongly bind Hg (Andersson, 1979). It was observed that organic carbon was higher in the redoximorphic concentrations than the redoximorphic depletions for both fine and coarse particle sizes (Table 2.2). Although organic carbon content in the studied sample seems to be low (0.06-0.17%), such an

organic carbon content was likely high enough for combining an accountable portion of Hg. This presumption was based on a previous observation that binding of Hg to organic carbon, the predominant process of Hg sorption in the studied soils, showed no correlation with soil organic carbon content (Biester et al., 2002b). It was reported that about 82.5% of total Hg was found as humic/fulvic acid-bound form in a soil sample with 0.28% of organic carbon content whereas only 21.8% was found in another soil sample with 0.69% of organic carbon content (Biester et al., 2002a).

Particle size had an apparent effect on Hg distribution in the soil sample. For both redoximorphic depletions and redoximorphic concentrations, fine particles contained higher concentration of Hg compared with coarse particles (Table 2.3). The difference in Hg concentration between coarse and fine fraction was statistically significant as confirmed by a t-test ($P < 0.01$). Apparently the specific surface area of fine particles was higher than that of coarse particles, which was likely the reason for higher Hg concentration in the fine fraction. It has often been observed that adsorption of Hg is increased with decreasing particle size and increasing specific surface area (Andersson, 1979).

2.3.3 Thermal desorption experiments

Illustrated in Fig 2.3 is the Hg concentration for wet and dry redoximorphic depletions and redoximorphic concentrations of the ORR soil sample and NIST 8406 after thermal treatment at different temperatures. The differences in Hg concentration between untreated and thermally treated samples indicated the amount of Hg released. As

expected, thermal treatment released certain amounts of Hg and the amounts of Hg vaporized varied with sample types and temperatures.

Significant Hg release was observed only when treatment temperature was 140 °C or higher except for the wet redoximorphic depletions subsample. For this sample, significant ($P = 0.05$) reduction in Hg concentration was not observed after thermal treatment from 80 to 180 °C, whereas an unexpected significant ($P < 0.05$) increase in Hg concentration was observed for 80 and 120 °C treatments. The reason for the increase in Hg is not very clear. However, it is plausible that the difficulty of obtaining a homogenized sample from the wet soil could cause the sample unrepresentative. As for the amount of Hg released, about 20-30% of total Hg was released from the freeze-dried samples after they were heated at 180 °C for 15 hours. The percentage of the released Hg was somewhat lower (10-25%) from the wet redoximorphic concentrations through the same treatment. It was observed that placing wet soil in ampoules generated relatively large and dense soil particles after drying at high temperatures. The presence of these large particles was thought to affect the release of Hg under varying temperatures. Therefore, it is likely that Hg was released more from the freeze-dried compared to the wet soil samples when heated. Compared with the freeze-drying process, less loss of Hg was observed for the wet redoximorphic depletions during thermal desorption treatments. This could be attributed to the inhomogeneity of wet sample or formation of these large and dense particles. It was also noted that much more Hg (>50%) was released in NIST 8406 after 180 °C treatment compared with the ORR soil sample possibly due to the differences of soil properties and Hg binding forms between them (Fig. 2.3).

Fig. 2.3 Hg concentration in the ORR soil sample and SRM NIST 8406 after thermal desorption treatments. (a) Wet redoximorphic depletions; (b) Freeze-dried redoximorphic depletions; (c) Wet redoximorphic concentrations; (d) Freeze-dried redoximorphic concentrations; (e) NIST 8406

Since different Hg species present in solid samples are expected to be released at different temperatures (Bombach et al., 1994; Windmüller et al., 1996), thermal desorption may provide some information on Hg species present in soils. It has been reported that Hg^0 , Hg_2Cl_2 , HgCl_2 , HgS , and Hg associated with organic matter could be released at <150, 170, 220-250, 300-400, and 200-300 °C, respectively (Biester et al., 2000; Bombach et al., 1994; Windmüller et al., 1996). Therefore, it can be assumed that thermal desorption with temperature lower than 180 °C adopted in the present study would primarily release Hg^0 and Hg_2Cl_2 , and probably a small portion of other forms of Hg such as HgCl_2 , $\text{Hg}(\text{NO}_3)_2$, HgO (Windmüller et al., 1996). It is estimated that Hg^0 and/or other “easily” vaporized Hg species appeared to account for 10-30% of Hg species in the soil studied. Although large amount of Hg^0 was initially discharged to the environments in the studied area (Barnett and Harris, 1997), it may have been converted to other Hg species during discharge or aging processes in the complex environments. In addition, lack of significant Hg release at less than 120 °C indicated that the Hg in this soil was relatively thermal stable and would not be thermally released under real-world environmental conditions. Temperature higher than 180 °C was not tested in the present study because this study was designed to investigate Hg species with high mobility or volatility simulating the real environment.

Mercury retained in different soil mineral fractions was believed to have different mobility potential because of difference in texture of soil fractions (Andersson, 1979). It was observed that Hg retained in the redoximorphic concentrations had stronger interactions with the matrix and thus was more resistant to be mobile than Hg in the redoximorphic depletions for the ORR soil sample. An apparent Hg release occurred

from 140 °C for the freeze-dried redoximorphic depletions whereas it did from 160 °C for the freeze-dried redoximorphic concentrations. Moreover, 30.7% of total Hg was released for the redoximorphic depletions at 180 °C while 18.1% was observed for the redoximorphic concentrations after the same treatment. This could be indicative of the fact that Hg retained in the redoximorphic concentrations was less volatile than Hg in redoximorphic depletions.

2.3.4 Sequential extraction

Mercury extracted in each step (F1-F5), representing different forms of Hg associated with different soil phases, is presented in Table 2.4. The sum of the amount removed by each extractant was in good agreement with the amount released by digestion with concentrated nitric acid with recoveries ranging from 94.3 to 125.1%. In addition, a recovery of 68.8% for SRM NIST 8406 was achieved, suggesting higher residual Hg left after these five extraction steps.

The distribution of Hg in each fraction showed considerable similarities for all four subsamples of the ORR soil and SRM NIST 8406. Figure 2.4 shows the percentage of Hg extracted in each step calculated against the sum of Hg recovered in all five steps. In all cases the most abundant Hg fraction was organic matter bound Hg fraction (F3) with percentage higher than 50% of total Hg. The second highest fraction was F4 (20-30%), representing Hg^0 based on the fact that all free Hg^0 present in a sample could be dissolved in the cold 12 M HNO_3 (Bloom et al., 2003; Gerlach CL, 1995). It should be noted that some other classes of Hg compounds such as Hg(I) , Hg associated with amorphous organo-sulfur, Hg-Ag amalgams, and Hg associated with crystalline Fe/Mn

oxide phases may be extracted into F4 fraction. Besides F3 and F4, the aqua regia soluble Hg fraction, F5, operationally termed as mercuric sulfide (HgS) including both cinnabar and metacinnabar and mercuric selenide (HgSe), also contributed an accountable portion to total Hg in the samples (about 10%). The first two sequentially extracted fractions F1 and F2, representing water soluble and human stomach acid soluble Hg, respectively, were relatively small portions.

These five Hg fractions have different mobility and potential bioavailability. The first two fractions (F1 and F2) were probably most important Hg classes in view of environmental concerns. Water soluble (F1) Hg fraction is likely the most labile and able to migrate in interstitial soil solutions (Kot et al., 2001), and even moves downward into deeper soil layer or groundwater. F2 fraction, simulating human stomach acid soluble Hg species, was determined as the fraction of Hg in soil potentially available for absorption in the human digestive system.

Table 2.4 Concentrations of different Hg species in different fractions of the ORR soil and SRM NIST 8406 by using sequential extraction procedure

Subsample type		Hg concentrations (ng/g) in different fractions							Recovery (%)
		F1	F2	F3	F4	F5	Sum	Total Hg	
redoximorphic	fine	3.4±0.1	2.5±0.4	44.0±2.8	16.6±1.0	5.9±0.8	72.4	76.7	94.3
depletions	coarse	3.7±0.8	2.0±0.1	35.6±3.6	15.0±1.8	6.8±0.4	63.1	50.5	125.1
redoximorphic	fine	3.8±0.7	3.2±0.5	117.4±1.3	47.3±9.1	20.4±4.8	192.1	203.2	94.5
concentrations	coarse	5.4±1.1	3.1±0.1	77.4±6.9	33.3±6.7	10.4±1.6	129.6	121.9	106.3
NIST 8406		1.7±0.2	1.3±0.2	23.6±1.5	10.2±0.8	4.5±0.4	41.3	60.0	68.8

Fig. 2.4 Distribution of Hg in the freeze-dried subsamples from the ORR soil sample and the SRM NIST 8406 using sequential extraction. (a) Coarse redoximorphic depletions; (b) Fine redoximorphic depletions; (c) Coarse redoximorphic concentrations; (d) Fine redoximorphic concentrations; (e) NIST 8406

This kind of absorption through the gastrointestinal tract appears to be the most critical endpoint and exposure pathway for human community around Hg contaminated soil sites. Compared with the first two Hg fractions that were weakly associated with soil phase, F3 (Hg bound to organic matter) was regarded as stronger complex (Wallschlager et al., 1998b) and thus has limited mobility and bioavailability. As a result of its very low solubility, F4 (Hg^0 likely plus other slightly soluble Hg species associated with soil particles) and F5 (insoluble mercuric sulfide) were not subject to transport or availability for chemical or biological transformation. It also should be borne in mind that: (1) Hg

bound to organic matter (F3) could include methylmercury species (mainly monomethylmercury) in spite of being a very small proportion in general (Bloom et al., 2003); (2) organo-chelated Hg (F3) was observed to be strongly correlated with methylation potential and thus seems to play an important role in the biogeochemical cycle of Hg in some cases (Bloom et al., 2003; Ogrinc et al., 2007) and (3) Hg fractionation (and speciation) in soil/sediment is dynamic (Wallschlager et al., 1998b; Wallschlager et al., 1998c) and subject to shift with alteration of environmental conditions including physical, chemical factors, and especially microbial population and activities. For example, it has been reported that the presumably non-soluble cinnabar appeared to become soluble and form aqueous complexes with sulfide if it accumulated to a high enough concentration (Jay et al., 2000; Ravichandran M, 1998) because of sulfate reduction mediated by sulfate reducing bacteria (SRB) (Mason and Benoit, 2003).

It was observed that Hg in the redoximorphic concentrations was less labile than Hg in the redoximorphic depletions. In the redoximorphic depletions, the sum of F1 and F2 fraction (labile and bioavailable Hg fractions) accounted for 11.4% for coarse particles and 7.7% for fine particle. Lower proportions of F1 together with F2 were observed for the redoximorphic concentrations (7.7 and 3.4% for coarse and fine particle, respectively).

2.3.5 Environmental implications

Thermal desorption analysis showed that approximately 10-30% of total Hg in the ORR soil sample was Hg^0 and other “easily” vaporized Hg species. Such a proportion was comparable with the F4 fraction (about 20-30%) obtained in the sequential extraction

procedure. The identical results obtained in these two different methods of speciation analysis provided a good estimation for Hg^0 and other “easily” vaporized Hg species present in the ORR soil sample. Despite such an accountable “volatile” proportion, Hg in the studied soil seemed to be unfavorable to volatilization or to potentially produce inhaling toxicity because of bonding with the solid matrix. Lack of significant Hg release at less than 120 °C indicated that Hg in this soil was relatively thermally stable and would not be thermally released under real-world environmental conditions.

The result of the present study suggested that both labile and bioavailable Hg fractions with high environmental risks were relatively small proportions in the studied ORR soil sample. Mercuric sulfide, previously reported as the dominant form of Hg, was found not to be the most abundant form (~10% of total Hg) in the studied soil sample. Such differences in Hg speciation could be attributed to the differences in sampling locations selected and probably, to a less extent, to the different sequential extraction procedures employed.

2.4 Conclusions

The redoximorphic concentrations contained higher Hg than the redoximorphic depletions. The higher content of Fe/Mn and organic matter was probably responsible for the higher Hg concentration in the redoximorphic concentrations. As expected, fine soil particles contained higher Hg compared with the coarse ones.

The results obtained using thermal desorption and sequential extraction procedure suggested that Hg retained in the redoximorphic concentrations was less volatile and labile than Hg in the redoximorphic depletions. With regards to the speciation of Hg in

the soil, 10-30% of Hg species appeared to be Hg^0 and other “easily” vaporized Hg species whereas organic matter bound Hg fraction was the major form of Hg species (accounting for 50% of total Hg).

Chapter 3 Analysis of mercury species in samples from ORR

3.1 Introduction

During the 1950's large amounts of mercury were released from Oak Ridge National Laboratories around the area of the East Fork Poplar Creek (EFPC) in Tennessee (Campbell et al., 1998; Han et al., 2009; Hollerman et al., 1999; Liu et al., 2006). Previous studies have indicated that the amount of total mercury in the soil ranges from 0.5 to 3000 ppm (Revis and Osborne, 1989). Because of the severe contamination of Hg, EFPC was placed on the National Priority List to undergo remediation through thermal desorption treatment and other techniques (Barnett and Harris, 1995, 1997; Barnett and Turner, 1995). A remedial investigation and feasibility study of Lower EFPC resulted in the signing of a Record of Decision (ROD) in August 1995. In response to the ROD, soil contaminated with Hg above 400 mg/kg was removed from two sites (NOAA facility and Bruner's) in LEFPC and the floodplain. Additional remediation practices were also and are being conducted in this area. It is not very clear about the magnitude of Hg contamination in this area after all these remedial activities. An extensive sampling in this area was conducted (see section 3.23) and samples were analyzed for THg and MeHg for water, soil, and sediment samples collected at a series of sites located along the water flow direction of the EFPC. The objective of this study is to characterize the magnitude of Hg contamination post remediation in the ORR area and determine the distribution patterns of THg and MeHg along the creek.

3.2 Experimental

3.2.1 Instrumentation

A cold vapor atomic fluorescence spectrometer (CVAFS) system (Merlin 10.035, PS Analytical, UK) was used for mercury analysis. A Gyrotory shaker G2 from New Brunswick Scientific Co. Inc. and a Blue M oven were used for the sequential extraction procedure as well as for the thermal desorption analysis. For additional samples, a DMA-80 Direct Mercury Analyzer from Milestone Inc. was used to determine the total mercury concentration in soil. A BioScience Ampulmatic Bench-Scale Ampule Sealer is also used to prepare the soil samples prior to digestion.

3.2.2 Chemicals and Reagents

Trace metal grade HCl and HNO₃, analytical grade potassium bromide, potassium bromate, stannous chloride and other reagents all from Fisher Scientific were used for the mercury analysis. Mercury free DDI H₂O was obtained in house produced by filtering tap water through a Culligan system consisting of activated charcoal and two mixed bed ion exchange cartridges. The filtered water is piped to a mercury-free clean room, where is passed through a Barnstead Mega-ohm B Pure system. A certified Hg standard 1000 ppm in 1.8% HNO₃ from Fischer Scientific was used as the primary standard. As a secondary mercury standard 1000 ppm in 10 % HNO₃ from SPEX was used as a calibration check. In addition, a river sediment standard reference material (SRM) NIST 8406, with nominal value of 60 ng/g of Hg and 5.50% for Al, 2.96% for Fe, and 0.043% for Mn, obtained from the National Institute of Standard and Technology.

For total mercury analysis the following reagents will be prepared before the actual analysis begins. A solution of 0.2 M Potassium bromide (KBr) is prepared by weighing 11.900 g of KBr and heating overnight in a glass scintillation vial (Kimble 74511) at $250\text{ }^{\circ}\text{C} \pm 20\text{ }^{\circ}\text{C}$ in a furnace to remove mercury. After cooling, the KBr is dissolved in 500 ml of DIW and stored in a borosilicate bottle. This solution is prepared on a weekly basis.

A 0.1 M Potassium bromate (KBrO_3) is prepared by weighing approximately 8.385 g of KBrO_3 and heating it also overnight in a glass scintillation vial (Kimble 74511) at $250\text{ }^{\circ}\text{C} \pm 20^{\circ}\text{C}$ in a furnace to remove mercury. After cooling, the KBrO_3 is dissolved in 500 ml of DIW and stored in a borosilicate bottle. It is prepared on a weekly basis.

A Mixed brominating reagent (0.1 M Potassium bromide (KBr) : 0.05 M Potassium bromate (KBrO_3)) is then prepared by mixing equal volumes (100 ml) of potassium bromate and potassium bromide solutions in a 250 borosilicate bottle with a Teflon cap. It is also prepared on a weekly basis.

A 12 % (w/v) Hydroxylamine hydrochloride ($\text{NH}_2\text{OH}.\text{HCl}$) is prepared by weighing 6.0 g of $\text{NH}_2\text{OH}.\text{HCl}$ and dissolving it in 50 ml of DIW in a 60 ml Teflon bottle. It is prepared on a weekly basis. It is added to destroy the excess bromine before analysis. Also, to reduce Hg^{2+} compounds present in solution to Hg^0 , a 2% (w/v) stannous chloride (SnCl_2) is prepared by adding 50 ml of 12 N HCl and 40 g of $\text{SnCl}_2.2\text{H}_2\text{O}$ and the volume is then completed up to 2000 ml using DIW. Purged with argon for 20 minutes before running samples. It is also prepared on a weekly basis. In

addition, a 1% HCl solution is prepared to be used as wash water for the AFS system during the actual analysis.

3.2.3 Sampling site selection

A total of 54 environmental samples were taken from the LEFPC area. Creek water, creek bank soil cores at 4–8” above water level, sediment cores, and creek-creek bank vegetation samples were taken at points along the length of the creek. The sampling site was located ¼ mile from the Y-12 complex site, and directly behind a commercial car wash (Mullins Car Wash). After collection the samples were sent overnight under dry ice from Oak Ridge to Miami and then placed either in a -20°C freezer for storage until analyzed. Figure 3.1 shows the locations of the sampling sites.

Figure 3.1 Sampling points along the LEFPC: (A) behind Mullins' Car Wash; (B) behind the NOAA facility; (C) at the Bruner Site; (D) Pre-Wastewater Treatment Plant; (E) Post-Wastewater Treatment Plant; (F) at Robertsville Junior High School; (G) at the Horizon Center on the ORR.

3.3 Procedure

3.3.1 Total mercury in soil and sediment

Soil and sediment samples (0.1 to 0.3 g) were placed inside a 10 ml of Wheaton glass ampule. Effort was made to select homogenized samples by taking them from different areas of the bulk sample. Triplicates were made for each sample, and each of these was analyzed at least three times. To each ampule 1ml of H₂O and 2 ml of concentrated HNO₃ were added. Then the samples were allowed to settle for at least 20 minutes before sealing so that any gas produced was released from the ampule prior to closing. Afterward, each ampule was sealed using an Ampulmatic Ampule Sealer and digested in an autoclave at 120°C for 1 hour. After removing the ampules from the autoclave, they were allowed to cool and were then analyzed. An extra sample for each type of sediment and soil was weighed and dried overnight at 80°C in a regular oven in order to determine the wet-to-dry ratio. This ratio was used to report the mercury concentration on a dry-weight basis.

3.3.2 Total mercury in water

The procedure used is based on the SERC standard operating procedure for total mercury determination in water. Prior to analysis, 5 ml of concentrated trace metal grade HCl is added per liter of sample (0.5 %) for preservation purpose. These additions are done in an Hg clean room. For each individual sample, three 125 ml Teflon bottles are filled to the 125 ml line with the sample water. The samples are placed in an ultraviolet cabinet for 12 hours and allowed to cool. Placing the samples in the UV cabinet

destroys any organic matter present in the solution. Then, 0.6 ml of 12 N HCl (to complete 1 % HCl) and 2.5 ml of KBrO₃/KBr mixed brominating reagent are added to each bottle. After one hour, 500 µl of 12 % (w/v) hydroxylamine hydrochloride are added to inhibit any further reaction. Samples are allowed to settle for at least 10 min before analysis.

An extra 125 ml aliquot of one of the samples included in the run (one per sample set) is obtained to be used as a Matrix Spike sample. Then 1.25 ml of the sample is removed from the bottle and replaced by 1.25 ml of the 100 ppt working calibration standard to yield a final spiked mercury concentration of 1 ppt.

A six point calibration curve is prepared (0, 0.5, 2.5, 5, 10, and 25 ppt) in 1% HCl from the 1000ppm primary standard from Fisher. Also, an additional standard 5 ppt using the SPEX total mercury standard is prepared as a check standard.

Three reagent blanks containing different amounts of reagents are digested to determine the amount of mercury added to each sample by them. The reagent blanks are prepared by filling three 125 ml bottles with DIW from the mercury-free room and carrying out the following procedure: Reagent blank I : 1.8 ml of DIW are removed from the Reagent I bottle and 1.25 ml KBrO₃/KBr mix, 0.3 ml HCl, and 0.25 ml hydroxylamine are consecutively added. Reagent blank II: 3.6 ml of DIW are removed from the Reagent II bottle and 2.50 ml KBrO₃/KBr mix, 0.6 ml HCl, and 0.50 ml hydroxylamine are consecutively added. Reagent blank III: 7.2 ml of DIW are removed from the Reagent III bottle and 5.00 ml KBrO₃/KBr mix, 1.2 ml HCl, and 1.00 ml hydroxylamine are consecutively added. The reagent blanks are analyzed in 125 ml Teflon bottles along with the samples and each bottle is analyzed at least three times.

3.3.3 Methylmercury in soil and sediment

A total of 41 sediment samples were sent to Frontier Geosciences Inc. (414 Pontius Ave. North. Seattle, WA 98109), because of the lack of available working equipment. Methylmercury samples were analyzed via cold vapor gas chromatography fluorescence spectrometry (CV-GC-AFS).

Samples were processed using ultra- clean sample handling techniques in laminar flow clean areas known to be low in atmospheric trace metals. Reagents, gases, and deionized water are all reagent or ultra pure grade, and were previously analyzed for trace metals to ensure low blank results. Daily analytical runs were begun with a 5 point standard curve, spanning the entire analytical range of interest, with an additional run every 10 samples. The daily standard curves were calculated using the blank-corrected initial standards, with a linear regression forced through zero. For each analytical set, one matrix duplicate, two matrix spikes, and at least three method blanks were co-processed and analyzed in exactly the same manner as ordinary samples.

Because of significant positive monomethylmercury MMHg artifact formation during the distillation of samples containing high levels of inorganic Hg (Bloom et al., 1997), the sediment and soil samples were cold extracted rather than distilled. Aliquots of these samples, approximately 0.5g, were accurately weighed into 40 ml Teflon centrifuge tubes, and 5 ml of H₂SO₄/KBr solution plus 1ml of 1 M CuSO₄ were added. After mixing, 10ml of methylene chloride (CH₂CL₂) was added to each tube, and the samples were shaken for 1 hour. The samples were then centrifuged at 3000 RPM for 30 minutes to separate the solvent from the aqueous layer. Exactly 2.0 ml of CH₂CL₂ were removed

from each sample and pipetted into a Teflon vial containing 57.6 ml of deionized water. The samples were heated to 45 °C and purged with N₂ to volatilize the CH₂Cl₂, thus releasing the MMHg to the pure aqueous phase.

Aliquots of extracted samples were analyzed using aqueous phase ethylation, purging onto Carbotrap, isothermal GC separation, and cold vapor atomic fluorescence spectrometry (CVAFS) detection. Prior to ethylation, the pH of the sample was brought to 4.9 with the addition of acetate buffer. Samples were ethylated by the addition of sodium tetraethyl borate, and then the volatile ethyl analogs purged with N₂ onto Carbotrap. After a trap drying step, the mercury ethyl analogs were thermally desorbed into a 1 m isothermal GC column (15% OV-3 on Chromasorb WAW-DMSC) held at 100°C for separation. The column resolves the following peaks: elemental Hg, dimethyl Hg, methyl ethyl Hg, and diethyl Hg. Because of the wet chemistry used, only methyl ethyl Hg, the MMHg analog is quantified for this assay. The organo-Hg compounds are pyrolytically broken down to Hg⁰ prior to entering the CVAFS detector for quantification.

3.4 Results and Discussion

3.4.1 Initial evaluation of total mercury concentrations in ORR area.

Prior to the large scale sampling and sample analysis for soil, sediment, and water samples in the ORR area, a pilot study was conducted to evaluate the concentration levels of Hg in this area. Another purpose of conducting such a pilot study was to identify potential problems associated with sampling, sample transfer, sample storage, and sample analysis that may be encountered during the large scale study. In this pilot study, four

samples were originally received: a soil sample HCET-D094-004-S, a sediment sample HCET-D094-003-SD, and 2 water samples HCET-D094-001-W and HCET-D094-002-W. Additional water samples labeled as HCET-D094-005-W, HCET-D094-006-W, and sediment samples HCET-D094-0-11-50 BOTTOM, HCET-D094-0-11-50 TOP, HCET-D094-0-10-S BOTTOM, HCET-D094-0-10-S TOP were also received. These samples were analyzed to assess the level of mercury contamination just outside the Y-12 boundary of the ORR site.

Total mercury concentrations in the Oak Ridge samples for the initial sampling episode are found in Table 3.1. The results for soil and sediment samples were calculated on a dry weight basis. It should be noted that for this analytical round, high standard deviations (STDEV) were observed for soil samples. The high STDEV could be attributed to the lack of homogeneity in the samples received. The original sample was analyzed as received, without freeze-drying, in an effort to minimize possible losses of elemental and volatile species of mercury. The soil, however, was clearly composed of two parts, a brownish part or “clay”, redoximorphic concentrations and a gray part or the “sandy” fraction, redoximorphic depletions. Higher concentrations have been obtained for all samples analyzed, compared to the background levels of Hg in water (generally less than 10 ng/L) and soil (about 100 ng/g), indicating that this area has been heavily contaminated with Hg. In consideration of high concentrations of Hg present in ORR soil, a DMA-80 Direct Mercury Analyzer (DMA) from Milestone Inc. was used to determine the total mercury concentration in soil. The selection of DMA-80, over acid digestion-CVAFS method, for soil THg determination can significantly reduce the cost and time associated sample analysis.

Table 3.1 Total mercury concentrations in ORR samples during initial sampling event

Sample ID	Concentration	STDEV
<i>Soil/sediment</i>	<i>(ng/g)</i>	<i>(ng/g)</i>
HCET- D094-004-S	137.9	72.2
HCET-D094-003-SD	10,489	2,043
HCET-D094-0-11-50 TOP	394.7	217.2
HCET-D094-0-11-50 BOTTOM	587.3	167.2
HCET-D094-0-10-S TOP	833.9	113.6
HCET-D094-0-10-S BOTTOM	72.7	32.1
<i>Water</i>	<i>(ng/L)</i>	<i>(ng/L)</i>
HCET- D094-001-W	670.3	31.0
HCET- D094-002-W	280.5	5.3
HCET-D094-005-W	596.6	18.7
HCET-D094-006-W	637.6	12.7

3.4.2 Survey of the mercury problem in the ORR area

Over 40 samples (including soil, sediment and water samples) were analyzed at mercury contaminated site surrounding the Y-12 area in order to assess the dimensions of the Hg contamination in the area. The results (Table 3.2) showed that environmental compartments surrounding the Oak Ridge contained high concentration of Hg, though varying remarkably depending upon different environmental media types and sampling locations. The Hg concentrations in surrounding the Oak Ridge area ranged from 50 to 45,000 ng/g. The soil samples had similar magnitude of Hg concentration with sediment samples. Four water samples in this area were analyzed and very high Hg concentrations

with the range from 280.5 to 670.3 ng/L were observed. All these analysis data indicated that this sampling area was heavily contaminated with Hg in comparison to a background concentration of 112 ng/g for soil in continental USA (Andersson, 1979). The Hg concentration observed in the present study appeared to be comparable with previous results (15-2630 µg/g) determined by other authors in related area though present results seemed to be a bit lower than previous data probably due to different sampling locations (Barnett and Harris, 1997).

It should be noted that, however, high standard deviations (STDEV) were observed for certain samples such as HCET-D094-004-S, HCET-D094-038-S, HCET-D094-0-11-50 TOP, HCET-D094-0-10-S BOTTOM soil samples and HCET-D094-043-SD sediment sample (about 40-50% RSD). The high STDEV could be attributed to the lack of homogeneity of the sample used. Original sample was used without freeze-drying in an effort to minimize possible loss of elemental and volatile species of Hg.

Table 3.2 Mercury concentrations in the selected soil, sediment, and water samples collected from Oak Ridge LEFPC mercury-contaminated samples

Sample Name	Location	Average Conc. (ng/g)	STDEV	RSD
SOIL				
HCET-D094-004-S	Behind Mullins' Car Wash	137.91	72.19	52.35
HCET-D094-031-S	LEFPC @ NOAA Site	37155.41	4764.63	12.82
HCET-D094-032-S	LEFPC @ NOAA Site	30485.83	3044.91	9.99
HCET-D094-038-S	LEFPC @ Bruner's Site	4389.80	1680.85	38.29
HCET-D094-039-S	LEFPC @ Bruner's Site	1042.26	36.88	3.54
HCET-D094-018-S	Pre WWTP (S. Monterey Rd.)	26368.89	1297.56	4.92
HCET-D094-024-S	Post WWTP (Gum Hollow Rd.)	1626.92	120.30	7.39
HCET-D094-052-S	Robertsville	23219.50	4580.60	19.73
HCET-D094-053-S	Robertsville	28554.32	5163.77	18.08
HCET-D094-045-S	Horizon Center	10173.76	3405.76	33.48
HCET-D094-046-S	Horizon Center	2299.01	163.57	7.11
HCET-D094-058-S	Mouth of Fork	226.61	26.27	11.59
HCET-D094-065-S	South Perimeter Road	1208.20	78.17	6.47

HCET-D094-072-ORNL-4	Hinds Creek	58.97	8.70	14.75
HCET- D094-0-11-50 BOTTOM		587.3	167.2	28.47
HCET- D094-0-11-50 TOP		394.7	217.2	55.03
HCET- D094-0-10-S BOTTOM		72.7	32.10	44.15
HCET- D094-0-10-S TOP		833.9	113.6	13.62
SEDIMENT				
HCET - D094 -003-SD	Behind Mullins' Car Wash	10488.67	2043.06	19.48
HCET-D094-029-SD	LEFPC @ NOAA Site	5436.58	749.65	13.79
HCET-D094-030-SD	LEFPC @ NOAA Site	8955.74	1509.66	16.86
HCET-D094-036-SD	LEFPC @ Bruner's Site	57.68	6.60	11.44
HCET-D094-037-SD	LEFPC @ Bruner's Site	65.80	5.94	9.03
HCET-D094-015-SD	Pre WWTP (S. Monterey Rd.)	12534.24	166.63	1.33
HCET-D094-016-SD	Pre WWTP (S. Monterey Rd.)	13849.02	1824.54	13.17
HCET-D094-022-SD	Post WWTP (Gum Hollow Rd.)	60.32	6.18	10.25
HCET-D094-023-SD	Post WWTP (Gum Hollow Rd.)	975.07	148.94	15.27
HCET-D094-050-SD	Robertsville	2592.19	335.17	12.93
HCET-D094-051-SD	Robertsville	13231.95	1939.75	14.66
HCET-D094-043-SD	Horizon Center	13117.65	5979.92	45.59
HCET-D094-044-SD	Horizon Center	23764.76	3516.43	14.80
HCET-D094-057-SD	Mouth of Fork	550.48	50.27	9.13
HCET-D094-059-SD	Mouth of Fork	9354.38	1895.61	20.26
HCET-D094-060-SD	Mouth of Fork	89.50	3.76	4.20
HCET-D094-064-SD	South Perimeter Road	5069.25	1621.11	31.98
HCET-D094-066-SD	South Perimeter Road	1837.62	153.70	8.36
HCET-D094-067-SD	South Perimeter Road	1798.03	335.91	18.68
HCET-D094-069-ORNL-1	Hinds Creek	132.99	39.45	29.66
HCET-D094-070-ORNL-2	EFK 23.4	45102.34	2826.45	6.27
HCET-D094-071-ORNL-3	EFK 6.3	6913.36	683.09	9.88
WATER				
HCET- D094-001-W	Behind Mullins' Car Wash	670.27	30.96	4.62
HCET- D094-002-W	Behind Mullins' Car Wash	280.45	5.30	1.89
HCET- D094-005-W	Behind Mullins' Car Wash	596.6	18.70	3.13
HCET- D094-006-W	Behind Mullins' Car Wash	637.6	12.70	1.99

3.4.3 Methylmercury in ORR soil and sediment

The methylmercury concentrations in ORR soil and sediment samples were illustrated in Table 3.3. Samples were collected from three locations, i.e., Mullins Carwash, Bruner's site, and Horizon center (see Fig. 3.1). For each site, both soil and sediment samples were collected. The results of MeHg analysis suggested that, similar to THg, MeHg exhibited a fairly wide concentration range in the ORR soil and sediment (Table 3.3). The soil MeHg can vary from 0.4 (similar to background levels in uncontaminated areas) to up to 60 ng/g (a level rarely observed in environmental

matrices). The sediment MeHg in the ORR can range from 0.2 to over 20 ng/g, depending upon the sampling location. The observation of fairly high MeHg concentrations in a variety of samples (including soil and sediment) collected from the ORR is indicative of heavy Hg contamination in this area.

It was observed that soil MeHg exhibited a different pattern of distribution among these 3 sampling sites than sediment MeHg did. For soil MeHg, Mullins carwash was the highest while no significant difference was observed between Bruner's site and Horizon center (Fig. 3.2A). The mean concentrations of soil MeHg for mullins carwash, Bruner's site, and Horizon center were 30.1, 4.79, 4.05 ng/g, respectively. For sediment MeHg, Horizon center was highest, compared to the other two locations (Fig 3.2B). The mean concentrations of sediment MeHg for mullins carwash, Bruner's site, and Horizon center were 3.46, 0.632, 10.4 ng/g, respectively.

In consideration that these 3 sampling sites located along the downward direction of the EFPC, with the water flow direction from Mullins carwash site to Bruner's site to Horizon center. The Hg source to the EFPC is located around the headwater of this creek. One might speculate that the distribution of MeHg in soil and sediment should be related to THg distribution patterns along the creek. A quick check of THg distribution along the EFPC suggested that clear spatial patterns were not present for THg in soil (Fig. 3.3A) or in sediment (Fig. 3.3B), which might be a result of the long-time discharge of Hg from the DOE facility around the headwater of EFPC during the past several decades. The discrepancy between THg and MeHg distribution along the creek suggested that the differences in Hg methylation/demethylation among different sampling site, in addition to THg distribution, play an important role in determining MeHg distribution patterns.

Further studies in respect of biogeochemical characteristics of different sampling sites and their effects on Hg methylation/demethylation are needed to better understand the Hg problems in this area.

Table 3.3 Methylmercury concentrations in ORR soil and sediment samples

Sample ID	Site location	Sample type	% total Solids	Methyl Hg (ng/g)	
				wet weight	dry weight
HCET-D094-MT1	Mullins Carwash	Soil	73.9	17.9	24.2
HCET-D094-MT2	Mullins Carwash	Soil	72.7	43.8	60.2
HCET-D094-MT3	Mullins Carwash	Soil	71	26.2	36.9
HCET-D094-MT4	Mullins Carwash	Soil	74.7	19.4	26
HCET-D094-MT5	Mullins Carwash	Soil	77.5	11.3	14.6
HCET-D094-MT6	Mullins Carwash	Soil	76.3	14.2	18.7
HCET-D094-MT1SD	Mullins Carwash	Sediment	43.3	3.28	7.58
HCET-D094-MT2SD	Mullins Carwash	Sediment	83.5	4.06	4.87
HCET-D094-MT3SD	Mullins Carwash	Sediment	76.7	1.11	1.44
HCET-D094-MT4SD	Mullins Carwash	Sediment	73.6	1.66	2.26
HCET-D094-MT5SD	Mullins Carwash	Sediment	80	1.79	2.24
HCET-D094-MT6SD	Mullins Carwash	Sediment	71.9	1.7	2.36
HCET-D094-BG1B	Bruner's Site	Soil	82.4	1.34	1.63
HCET-D094-BG2B	Bruner's Site	Soil	85.7	0.32	0.373
HCET-D094-BG3B	Bruner's Site	Soil	82.8	0.326	0.394
HCET-D094-BG4B	Bruner's Site	Soil	83	0.787	0.948
HCET-D094-BG5B	Bruner's Site	Soil	80.1	9.28	11.6
HCET-D094-BG6B	Bruner's Site	Soil	78.7	5.52	7.02
HCET-D094-BG7B	Bruner's Site	Soil	80	7.79	9.73
HCET-D094-BG8B	Bruner's Site	Soil	81.8	7.63	9.33
HCET-D094-BG9B	Bruner's Site	Soil	85.7	1.21	1.41
HCET-D094-BG10B	Bruner's Site	Soil	85	0.703	0.827
HCET-D094-BG11B	Bruner's Site	Soil	82.7	7.78	9.41
HCET-D094-BG2D-SD	Bruner's Site	Sediment	80.8	0.148	0.183
HCET-D094-BG4C-SD	Bruner's Site	Sediment	74.6	0.154	0.206
HCET-D094-BG6C-SD	Bruner's Site	Sediment	78.2	0.149	0.191
HCET-D094-BG6E-SD	Bruner's Site	Sediment	79.1	1.02	1.29
HCET-D094-BG7-A	Bruner's Site	Sediment	77.5	1.41	1.82
HCET-D094-BG11-A	Bruner's Site	Sediment	74.5	0.075	0.101
HCET-D094-HT1	Horizon Center	Soil	79.7	4.38	5.49
HCET-D094-HT2	Horizon Center	Soil	81.8	2.99	3.65
HCET-D094-HT3	Horizon Center	Soil	83.6	2.35	2.82
HCET-D094-HT4	Horizon Center	Soil	89.2	4.08	4.57
HCET-D094-HT5	Horizon Center	Soil	82.8	2.91	3.52
HCET-D094-HT6	Horizon Center	Soil	81.9	3.48	4.25
HCET-D094-HT1SD	Horizon Center	Sediment	63.6	14.8	23.3
HCET-D094-HT2SD	Horizon Center	Sediment	70	5.29	7.56
HCET-D094-HT3SD	Horizon Center	Sediment	61.9	5.51	8.9
HCET-D094-HT4SD	Horizon Center	Sediment	66.6	12.6	18.9
HCET-D094-HT5SD	Horizon Center	Sediment	76.2	1.45	1.9
HCET-D094-HT6SD	Horizon Center	Sediment	71.3	1.1	1.55

Fig. 3.2 Distribution of MeHg in soil and sediment along the EFPC

Fig. 3.3 Distribution of THg in soil and sediment along the EFPC

3.5 Conclusions

Total mercury concentrations ranged from 50 to 45,000 ng/g while MeHg varied from 0.2 to 60 ng/g in the ORR soil and sediment samples. The observation of fairly high THg as well as MeHg concentrations indicated that this area still has severe Hg

contamination problem, despite that some remedial measures were adopted in the past two decades. Both THg and MeHg concentrations varied remarkably depending upon different sampling locations and environmental matrices sampled. Clear spatial patterns were not present for THg distribution along the EFPC, suggesting that long-time discharge of Hg from the DOE facility has extensively spread Hg contamination in this area. Spatial patterns were observed for MeHg in soil and in sediment, although the patterns were not identical for these two matrices. The discrepancy between THg and MeHg distribution along the creek suggested that, in addition to THg distribution, the differences in biogeochemical characteristics among different sites (which affects Hg methylation and demethylation) are important role in determining MeHg distribution patterns.

Chapter 4 Conclusions

Higher mercury concentrations were found in the redoximorphic concentrations than in the redoximorphic depletions. The higher content of Fe/Mn and organic matter was probably responsible for the higher Hg concentration in the redoximorphic concentrations. As expected, fine soil particles contained higher Hg compared with the coarse ones. The results obtained using thermal desorption and sequential extraction procedure suggested that Hg retained in the redoximorphic concentrations was less volatile and labile than Hg in the redoximorphic depletions. With regards to the speciation of Hg in the soil, 10-30% of Hg species appeared to be Hg^0 and other “easily”

vaporized Hg species whereas organic matter bound Hg fraction was the major form of Hg species (accounting for 50% of total Hg).

Total mercury concentrations ranged from 50 to 45,000 ng/g while MeHg varied from 0.2 to 60 ng/g in the ORR soil and sediment samples. The observation of fairly high THg as well as MeHg concentrations indicated that this area still has severe Hg contamination problem, despite that some remedial measures were adopted in the past two decades. Both THg and MeHg concentrations varied remarkably depending upon different sampling locations and environmental matrices sampled. Clear spatial patterns were not present for THg distribution along the EFPC, suggesting that long-time discharge of Hg from the DOE facility has extensively spread Hg contamination in this area. Spatial patterns were observed for MeHg in soil and in sediment, although the patterns were not identical for these two matrices. The discrepancy between THg and MeHg distribution along the creek suggested that, in addition to THg distribution, the differences in biogeochemical characteristics among different sites (which affects Hg methylation and demethylation) are important role in determining MeHg distribution patterns.

Chapter 5 Future Work

Additional work will be necessary to have a complete understanding of the mercury problems in the East Fork Poplar Creek. Additional samples might be helpful especially if the samples are closer to the actual Oak Ridge reservation. This could give a better understanding of the situation and condition of the total mercury released originally.

A greater number of samples and sampling areas might be needed and this might require the use of a more direct and easy to use technique such as the Direct Mercury Analyzer thus reducing sample preparation procedures and time.

The results obtained for methyl mercury concentrations indicate that a correlation exists between methyl mercury and total mercury concentration and location. In the future, to understand how the nature of that trend relates to the overall mercury contamination problem an in depth study should be conducted.

The interesting problem of mercury bioavailability should be considered. For example using soil from that area, and small fishs and a fish tank, a study could be performed on the amount of mercury absorbed by fish and how this could be related to a real natural environment.

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