

IMMOBILIZATION OF MERCURY IN CONTAMINATED SOILS USING ALUMINUM  
DRINKING WATER TREATMENT RESIDUALS

By

ANNA HOVSEPYAN

A DISSERTATION PRESENTED TO THE GRADUATE SCHOOL  
OF THE UNIVERSITY OF FLORIDA IN PARTIAL FULFILLMENT  
OF THE REQUIREMENTS FOR THE DEGREE OF  
DOCTOR OF PHILOSOPHY

UNIVERSITY OF FLORIDA

2008

© 2008 Anna Hovsepyan

To my mother, Tatyana Chukhrukidze.

## ACKNOWLEDGMENTS

I especially thank Dr. Jean-Claude J. Bonzongo for his guidance, support, kindness, humor, and many other great qualities that made him an exceptional advisor. I thank my committee members, Dr. Gabriel Bitton, Dr. Joseph J. Delfino, and Dr. Willie G. Harris, for their valuable expertise, advice, and support that helped me bring this project to completion. My special thanks go to Mr. and Mrs. Glick, founders of the Sally and William Glick Graduate Research Award, for their generosity and interest in environmental research. It was my honor and privilege to be the recipient of this award in 2006. I thank Dr. Paul J. Lechler of the Nevada Bureau of Mines and Geology for providing mercury contaminated soil samples. I also thank Dr. Xinde Cao and Lisa Stanley for their help with soil characterization. I thank Gill Brubaker and Gary Scheiffle of the Particle Engineering Research Center of the University of Florida for their help and advice in AI-WTRs characterization. I am grateful to the students in the Department of Environmental Engineering Sciences for their friendship and support. My special thanks go to my family and friends. I greatly appreciate their love, support, and encouragement.

## TABLE OF CONTENTS

	<u>page</u>
ACKNOWLEDGMENTS .....	4
LIST OF TABLES .....	7
LIST OF FIGURES .....	8
ABSTRACT .....	10
CHAPTER	
1 INTRODUCTION: MERCURY IN SOILS AND REMEDIATION .....	12
Problem Statement .....	12
Overview of Soil Remediation Techniques and Rationale for this Study .....	15
Drinking Water Treatment Residuals (WTRs) .....	19
Research Objectives and Dissertation Outline .....	21
2 ALUMINUM- BASED DRINKING WATER TREATMENT RESIDUALS (Al-WTRs) AS A SORBENT FOR MERCURY: MATRIX CHARACTERIZATION AND DETERMINATION OF SORPTION CAPACITIES .....	27
Introduction.....	27
Materials and Methods .....	28
Collection and Characterization of Al-WTRs .....	28
Determination of the Maximum Sorption Capacity of Al-WTRs and Sorption Isotherms .....	31
Mercury Desorption from Al-WTRs .....	32
Kinetics of Hg Sorption on Al-WTRs and Effect of pH .....	33
Results and Discussion .....	34
Characterization of Al-WTRs.....	34
Determination of the Maximum Sorption Capacity of Al-WTRs and Sorption Isotherms.....	35
Mercury Desorption from Al-WTRs .....	37
Kinetics of Hg Sorption on Al-WTRs .....	37
Conclusions.....	41
3 IMMOBILIZATION OF MERCURY IN CONTAMINATED SOILS BY ALUMINUM- BASED DRINKING WATER TREATMENT RESIDUALS (Al-WTRs) ...	56
Introduction.....	56
Materials and Methods .....	59
The Al-WTRs and Soil Sample Collection, Characterization, and Site Description .....	59
Column Leaching Studies.....	62

Assessing the Bioavailability of Mercury in Al-WTRs Treated Soils .....	65
Chemical Fractionation of Mercury in Used Soils .....	66
Results and Discussion .....	68
Column Leaching Studies: General Characteristics .....	68
Florida Sandy Soil .....	69
Nevada Soil .....	73
Conclusions.....	76
4 DISTRIBUTION OF MERCURY SORBED ONTO ALUMINUM-BASED DRINKING WATER TREATMENT RESIDUALS (Al-WTRs) AND IMPLICATIONS FOR LONG-TERM STABILITY OF FORMED “MERCURY-Al-WTRs” COMPLEXES.....	89
General Introduction.....	89
Part-1: Chemical Fractionation of Mercury in Al-WTRs by Sequential Extraction .....	89
Introduction .....	89
Material and Methods.....	91
Preparation of aged mercury-spiked Al-WTRs.....	91
Sequential extraction procedure .....	92
Results and Discussion.....	94
Part-2: Mercury Incorporation in Micropores of Al-WTRs and Modeling of Intraparticle Diffusion .....	98
Introduction .....	98
Materials and Methods .....	99
Aged mercury-spiked Al-WTRs .....	99
Determination of SSA-N <sub>2</sub> and SSA-CO <sub>2</sub> of Al-WTRs before and after mercury sorption .....	99
Determination of the activation energy (E <sub>a</sub> ) of mercury sorption onto Al-WTRs particles.....	101
Results and Discussion.....	102
Determination of SSA-N <sub>2</sub> and SSA-CO <sub>2</sub> of Al-WTRs before and after mercury sorption .....	102
Modeling of intraparticle diffusion and prediction of mercury diffusivity .....	104
General Conclusions.....	106
5 CONCLUSIONS AND RECOMMENDATIONS .....	117
Conclusions.....	117
Recommendations.....	118
LIST OF REFERENCES .....	120
BIOGRAPHICAL SKETCH .....	135

## LIST OF TABLES

<u>Table</u>	<u>page</u>
1-1 Selected Hg standards for different environmental compartments.....	23
1-2 Comparison of chemical and physical properties of WTRs with typical soil levels (from Dayton and Basta, 2001).....	24
1-3 Comparison of WTR nutrient levels with soil nutrient levels adequate for growth of most crops (from Dayton and Basta, 2001) .....	25
1-4 Average concentrations of 15 metals in Al-WTRs determined using the EPA method 3050.....	26
2-1 Physicochemical properties of Al-WTRs collected from the Bradenton Drinking Water Treatment Facility (Florida, USA).....	43
2-2 Determination of Hg maximum sorption capacity (mg/g) at pH 6.5 .....	44
2-3 Sorption isotherm parameters for Hg sorption on Al-WTRs at pH 6.5 .....	44
2-4 Kinetic Parameters for Hg Sorption on Al-WTRs at pH 6.5 and initial Hg concentration of 40 mg/L.....	44
3-1 Experimental design for column studies with soil weight in each column of 300 g .....	77
3-2 Physicochemical characteristics of soils used in column leaching studies.....	78
3-3 Toxicity of Florida’s sandy soil leachate collected from the 1 <sup>st</sup> pore volume as determined by the MetPLATE™ toxicity test.....	79
3-4 Mass balance of Hg in column studies using Florida’s sandy soil. ....	80
3-5 Mass balance of Hg in column studies using Nevada’s soil.....	81
4-1 Mercury, Al, Fe, and Si concentrations and distribution (%) in different fractions of Hg-spiked Al-WTRs.....	108

## LIST OF FIGURES

<u>Figure</u>	<u>page</u>
2-1 SEM micrographs of the original Al-WTRs collected from the Bradenton Drinking Water Treatment Facility (Florida, USA) showing irregular size and non-homogeneity of particles.....	45
2-2 Elemental spectra (EDS) of the original Al-WTRs before use in Hg sorption experiments and of the recovered Al-WTRs after the sorption experiments confirming Hg sorption on Al-WTRs.....	46
2-3 Mercury sorption isotherm with initial Hg concentrations of 10, 20, 40, and 80 mg/L and pH 6.5.....	47
2-4 Langmuir plot for Hg sorption on Al-WTRs at initial Hg concentrations of 10, 20, 40, and 80 mg/L and pH 6.5.....	48
2-5 Effect of contact time on Hg sorption on Al-WTRs at 40 mg/L initial Hg concentration and pH 6.5.....	49
2-6 Lagergren, pseudo-first order kinetic plot for Hg sorption on Al-WTRs at initial Hg concentration of 40 mg/L and pH 6.5.....	50
2-7 Pseudo-second order kinetic plot for Hg sorption on Al-WTRs at initial Hg concentration of 40 mg/L and pH 6.5.....	51
2-8 Weber and Morris intraparticle diffusion plot for Hg sorption on Al-WTRs at initial Hg concentration of 40 mg/L and pH 6.5.....	52
2-9 Bangham intraparticle diffusion plot for Hg sorption on Al-WTRs at initial Hg concentration of 40 mg/L and pH 6.5.....	53
2-10 Effect of pH on Hg sorption on Al-WTRs at initial Hg concentration of 40 mg/L. The values are averages (n=3) and error bars represent standard errors of the mean.....	54
2-11 Effect of pH on Zeta Potential of Al-WTRs.....	55
3-1 Mercury concentrations in Florida sandy soil leachates of control (no Al-WTRs) and samples treated with Al-WTRs at application rates of 2.5%, 5%, and 10%.....	82
3-2 Mercury concentrations in Florida sandy soil leachates collected from the 5 <sup>th</sup> to the 13 <sup>th</sup> pore volume in control (no Al-WTRs) and samples treated with Al-WTRs at application rates of 2.5%, 5%, and 10%.....	83
3-3 Cumulative mass of Hg leached per kg of soil from the control (no Al-WTRs) and Al-WTRs treated columns of Florida sandy soil after 13 pore volumes.....	84

3-4	Concentrations of methyl-Hg produced in Florida sandy soil after 10 days of incubation under water saturation and anoxic conditions.....	85
3-5	Mercury concentrations in Nevada soil leachates of control (no Al-WTRs) and samples treated with Al-WTRs at application rates of 2.5%, 5%, and 10%.....	86
3-6	Cumulative mass of Hg leached per kg of soil from the control (no Al-WTRs) and Al-WTRs treated columns of Nevada soil after 11 pore volumes.....	87
3-7	Concentrations of methyl-Hg produced in Nevada soil after 10 days of incubation under water saturation and anoxic conditions.....	88
4-1	Mercury, Al, Fe, and Si distribution (%) in the various fractions of Al-WTR.....	109
4-2	The N <sub>2</sub> gas sorption on Al-WTRs with no Hg and Hg-spiked.....	110
4-3	The CO <sub>2</sub> gas sorption on Al-WTRs with no Hg and Hg-spiked.....	111
4-4	Mean BET (N <sub>2</sub> ) and micropore (CO <sub>2</sub> ) surface area of Al-WTRs with no Hg (black bars) and Hg-spiked (white bars) Al-WTRs.....	112
4-5	Micropore volume based on pore size distribution of Al-WTRs with no Hg (black bars) and Hg-spiked Al-WTRs (grey bars).....	113
4-6	Mean micropore volume of Al-WTRs with no Hg (control) and Hg-spiked Al-WTRs.....	114
4-7	Arrhenius plot of Hg sorption on Al-WTRs at 11 <sup>0</sup> C, 25 <sup>0</sup> C, and 35 <sup>0</sup> C.....	115
4-8	Diffusivities ( <i>D</i> ) of Hg in Al-WTRs as a function of varying $\lambda$ values (mean distance between sorption sites).....	116

Abstract of Dissertation Presented to the Graduate School  
of the University of Florida in Partial Fulfillment of the  
Requirements for the Degree of Doctor of Philosophy

IMMOBILIZATION OF MERCURY IN CONTAMINATED SOILS USING ALUMINUM  
DRINKING WATER TREATMENT RESIDUALS

By

Anna Hovsepyan

August 2008

Chair: Jean-Claude J. Bonzongo  
Major: Environmental Engineering Sciences

The goal of this project is to evaluate the potential of aluminum drinking water treatment residuals (Al-WTRs) as sorbent for the immobilization of mercury (Hg) in contaminated soils. The Al-WTRs are readily available and non-hazardous waste by-products of the municipal drinking water treatment process composed primarily of amorphous aluminum (hydr)oxides and are produced daily in very large quantities at both national and global scales. While numerous studies have evaluated the use of Al-WTRs in controlling water pollution from agricultural phosphorus runoffs, the potential of Al-WTRs for the immobilization of metals in contaminated soils remains poorly studied. To our knowledge, no data on the interaction between Hg and Al-WTRs exists in the peer-reviewed literature. To evaluate the use of this waste material in remediation of Hg-contaminated soils, the following tasks were completed: (1) characterization of Al-WTRs and assessment of Al-WTRs potential to sorb Hg from aqueous solutions under varying conditions such as pH and contact time (2) assessment of the ability of Al-WTRs to sorb and immobilize Hg in contaminated soils using column studies mimicking the effect of acid rain (3) assessment of the ability of Al-WTRs to reduce/eliminate the bioavailability and toxicity of Hg from treated soils using microbial Hg methylation as a surrogate for its bioavailability and MetPLATE<sup>®</sup> toxicity test, and (4) evaluation of mechanisms of Hg immobilization on Al-WTRs

with implications for long-term stability. The overarching hypothesis of this work is that both chemical and physical characteristics of Al-WTRs would favor the sorption, and therefore, the immobilization of Hg by formation of Hg-[Al-WTRs] complexes that are highly stable under environmental conditions. Results suggest that Al-WTRs have an average specific surface area of 48 m<sup>2</sup>/g and an internal micropore surface area of 120 m<sup>2</sup>/g. Obtained sorption isotherms in aqueous solutions indicated a strong affinity of Hg for Al-WTRs. Using the Langmuir adsorption model, a relatively high maximum sorption capacity of 79 mg Hg/g Al-WTRs was determined. Sorption kinetic data was best fit to a pseudo-first order model, while the use of the Weber-Morris and Bangham models suggested that the intraparticle diffusion could be the rate-limiting step. Also, Al-WTRs effectively immobilized Hg in the pH range of 3 to 8. The results showed that the leachability, toxicity, and methylation potential of Hg was reduced by the addition of Al-WTRs to soils, pointing out the ability of Al-WTRs to immobilize Hg in soils. However, the effect was more pronounced in newly-contaminated soil compared to well-aged soil. The findings of this study suggest that it is likely that Hg was incorporated into micropores of Al-WTRs as shown by the porosity and chemical fractionation data. Finally, future studies are needed to determine the exact binding sites of Hg on Al-WTRs. Overall the results suggest that the addition of Al-WTRs to Hg-contaminated soils could be an efficient remediation method.

CHAPTER 1  
INTRODUCTION: MERCURY IN SOILS AND REMEDIATION

**Problem Statement**

Heavy metals found in the environment originate from both anthropogenic and natural sources. Unlike organic pollutants, metals are not biodegradable and their persistence, transformation, and transfer to the food chain can lead to negative effects on ecological functions and human health (Steinnes 1997). Currently, the United States Environmental Protection Agency (US-EPA) Priority Pollutant List includes Ag, As, Be, Cd, Cr, Cu, Hg, Ni, Pb, Sb, Se, Tl, and Zn as metals of serious environmental concern (Adriano, 2001). Additionally, more than 50% of the reported contaminated soil sites listed on the US National Priority List are impacted by heavy metals (Mulligan et al. 2001). Unfortunately, the remediation of metal contaminated soils remains one of the most intractable problems of environmental restoration (Mulligan et al. 2001), and this is both a national and international concern. It requires the development of cost-effective and efficient remedial approaches for metals and other contaminants, while avoiding adverse effects on the treated systems.

Mercury (Hg) is a naturally occurring element in the earth's crust, with natural background concentrations in soils ranging from a few parts per billion (ppb) to levels in hundreds of ppb (Adriano 2001; Steinnes 1997). Natural sources of Hg in the environment include volcanoes, hot springs, and the weathering of rocks (D'Itri 1972; Drasch et al. 2004). However, concerns related to the effects of Hg on the environment and human health arise primarily from the anthropogenic inputs of this pollutant to different environmental compartments. Anthropogenic activities that release Hg into the environment include, but are not limited to, the combustion of fossil fuels, mining, waste incineration, rubber processing, the improper disposal of commercial and industrial products containing Hg, and industrial activities such as the paper and pulp industry,

and chlor-alkali plants (Chen et al. 1999; D'Itri 1972; Drasch et al. 2004). With regard to soils, the major sources of Hg pollution are chlor-alkali plants, mine tailings, and diffuse sources such as the burning of fossil fuels in coal-fired power plants (D'Itri 1972; Drasch et al. 2004; Steinnes 1997).

Concerns over the biogeochemical cycling of Hg in the environment have been driven primarily by the toxicity of its alkyl-compounds, namely methyl-Hg. However, both inorganic and organic Hg species represent a hazard to living organisms, even when present at trace levels in the environment (Drasch et al. 2004). The toxicity of Hg species has been the subject of abundant research (D'Itri 1972; Kazantzis 1980; Magos and Clarkson 2006; Patra and Sharma 2000), and although not the focus of this dissertation, it is noteworthy that studies on Hg methylation dominate the current literature on Hg biogeochemistry. Despite some ongoing controversies on the role of different microbial groups and abiotic factors, processes leading to Hg methylation and methyl-Hg accumulation in soils and sediments are quite well-understood. Methyl-Hg is a lipid-soluble organometallic compound which passes easily through cell membranes to then bioaccumulate and biomagnify in food chains (Baldi 1997; Boudou and Ribeyre 1997). As a neurotoxin, methyl-Hg attacks the central nervous system (Grieb et al. 1990; Lindqvist et al. 1991), and the principal pathway for human exposure to this toxic pollutant is the consumption of contaminated fish in which the majority, if not all, of Hg bioaccumulates in the methylated form. Accordingly, regulatory agencies focus primarily on fish as the target organism to protect human health and other sensitive organisms. In fact, Hg found in aquatic systems and which ultimately accumulates in fish originates predominantly from watershed soils (Babiarz et al. 1998; Hurley et al. 1995; St. Louis et al. 1996). This is due to soil's high capacity to sequester Hg and to behave as both sink and source of Hg over long periods of time (Johansson et al. 1991;

Piao and Bishop 2006). This is also linked to the high ratio of dry land surfaces to water covered surfaces within watersheds where atmospheric deposition is the main source of Hg contamination. Therefore, in addition to erosion processes that introduce Hg from top soils to surface waters via runoffs, hydrologic and biogeochemical perturbations are the principal agents for Hg mobilization accumulated in surface and vadose zone soils and contamination of waterways.

As a result of strict regulations by the US-EPA, emissions of Hg in the US have been decreasing since the 1990's (Hylander and Meili 2003; Jackson et al. 2000; Pirrone et al. 1996), and research on the development of new solutions for pollution prevention as well as for remediation of sites already contaminated with Hg has been stimulated. Table 1-1 summarizes selected Hg standards enforced by either the US-EPA or the Florida's Department of Environmental Protection (FDEP 2005; US-EPA 2003a; US-EPA 2003b). On a worldwide scale, several sites remain heavily contaminated with Hg from both historic and present anthropogenic activities (Adriano 2001; Hylander and Goodsite 2006; Nriagu and Wong 1997). For instance, soil samples collected from gold mining impacted soils in North-West USA exhibit total-Hg (THg) concentrations that range from 132 mg/kg to 635 mg/kg (Kim et al. 2003), while soils from areas surrounding a chlor-alkali plant in the Netherlands had THg concentrations ranging from 4.3 mg/kg to 1150 mg/kg (Bernaus et al. 2006).

Unfortunately, the negative effects of certain pollutants such as Hg become known only several years after their initial intentional (e.g. landfills) and/or non-intentional disposal (e.g. diffuse sources) (Pacyna and Keeler 1995). Consequently, reactive approaches such as the development of efficient and cost-effective remediation methods remain crucial.

## **Overview of Soil Remediation Techniques and Rationale for this Study**

Although much is now known on the biogeochemistry of metals in soils and sediments, research on the development of cost-effective and environmental-friendly remediation techniques remains challenging. Various *ex situ* and *in situ* technologies have already been proposed for the remediation of Hg contaminated soils. These technologies include conventional engineering-based methods employing techniques such as physical separation, thermal processes, washing, stabilization and solidification, (D'Itri 1972; Suer and Allard 2003; Wasay et al. 1995), and other emerging technologies such as phytoextraction (Moreno et al. 2005). While these methods can be efficient in removing Hg from soil, only a few of these techniques have been tested commercially, and their widespread use remains limited due to the prohibitive costs and other disadvantages discussed below.

Excavation is the most traditional method for soil remediation and it involves the removal and transport of contaminated soils for disposal in hazardous landfills or for off-site treatment (McGowen et al. 2001). However, through this process there is a risk of spreading the contaminated soil and dust. Excavation could be very efficient in removing metal contaminants from very small contaminated areas. However, it becomes very expensive and impracticable when dealing with very large contaminated areas (Basta and McGowen 2004). Also, excavation of large areas should be followed by restoration of the soil, which includes backfilling of the area with clean soil and landscaping. The major disadvantage of excavation is high cost, therefore for areas with no immediate risks of metal exposure to living organisms, other methods should be considered.

Soil washing involves physical separation or chemical extraction to remove metals from contaminated soil (Dermont et al. 2008; Tsang et al. 2007). Physical separation processes that could be used specifically for Hg involve techniques such as screening and gravity concentration

and separation (US-EPA 1995). However, the efficiency of physical separation depends on various factors that include metal speciation, soil texture, moisture content, heterogeneity of soil matrix, etc. (Dermont et al. 2008). The treatment is not effective if there is a high variability of metal chemical forms or if there is a high silt/clay or high humic content in treated soils (Dermont et al. 2008; Tsang et al. 2007). Chemical extraction uses fluids to solubilize metals from soils and to allow the transfer of released metals from the solid soil phase to the aqueous phase (Dermont et al. 2008). Various extracting fluids such as acids/bases, surfactants, chelating agents, salts, or redox agents have been proposed (Dermont et al. 2008; Ehsan et al. 2006). Acid solutions are extracting agents that could be used for chemical extraction of Hg (Vanbenschoten et al. 1994). Soil leaching with strong oxidizing agents such as  $\text{Cl}_2$  and  $\text{OCl}^-$  could be used to destroy organic complexes of Hg and to transfer Hg to the liquid phase (Szpyrkowicz et al. 2007). However, these strong oxidizing agents may also oxidize minerals that are in the reduced form and are part of the soil structure (Tessier et al. 1979). Similar to the physical separation, the effectiveness of this technique depends on metal speciation and soil quality including texture, buffering capacity, and organic matter content (Hamby 1996; Tsang et al. 2007). Another disadvantage of this process is the production of large volumes of hazardous liquid wastes that require further treatment and safe disposal (US-EPA 1997a).

Electro-remediation involves movement and subsequent removal of ionic metal forms from the soil in an imposed electric field (Altin and Degirmenci 2005; Cox et al. 1996; Hakansson et al. 2008; Page and Page 2002). For Hg remediation, as a pretreatment iodide/iodine complexing agent could be used to mobilize Hg (Hakansson et al. 2008). Similar to soil washing, this process creates liquid wastes which require subsequent treatment (Hakansson et al. 2008). One of the limitations of this technique is that it is effective only when the moisture

content of the soil is between 14 and 18% (Hamby 1996). Another disadvantage is that reduced immobile forms of Hg present in soils can become mobile, and if not removed properly, they can lead to toxicity in contact with living organisms. Also, electro-remediation gives poor results in soils with low permeability (e.g., high clay content), which limits the transfer of Hg from solid to aqueous phases (Suer and Lifvergren 2003).

Methods for removal of elemental Hg from soil include amalgamation by adding aluminum, copper or other metals to soils. This ability of Hg to form amalgams with certain metals allows its removal from the bioavailable Hg pool, and therefore, from the methylation/demethylation cycle (D'Itri 1972).

Volatilization or thermal desorption is another method for removal of Hg from soils (Chang et al. 1998; Kunkel et al. 2006). This process requires special equipment at the contaminated site to collect Hg vapor so that it does not contaminate the ambient air (Takeuchi et al. 2001; US-EPA 1997a; US-EPA 2007).

The encapsulation process involves either mixing of the soil with cementing agents or glassification of the soil in order to encapsulate the contaminated area (D'Itri 1972; Hamby 1996). One of the key disadvantages of encapsulation is that it permanently restricts future soil use.

Phytoextraction, which makes use of plants to remove Hg and other metals from contaminated soils, has economic advantages over traditional engineering-based remediation methods (Barocsi et al. 2003; Garbisu and Alkorta 2001; LeDuc and Terry 2005; Meagher and Heaton 2005). However, to be efficient, hyper-accumulator plant species are needed and they should possess certain traits such as ability to tolerate metals, high biomass production, rapid growth, high bioaccumulation of the targeted metal (Bismarck et al. 2000; Weatherford et al.

1997). Another disadvantage of this method is that although many heavy metal cations can be taken up and accumulated in plant roots, translocation of these cations to the shoots is often limited (Huang et al. 1997; Wang and Greger 2006). To enhance the bioavailability of metals and hence the uptake by plants, chelating agents such as EDTA may be added to the soil (Barocsi et al. 2003; Huang et al. 1997; Stanhope et al. 2000). Only a few studies have proposed the use of phyto-extraction for Hg (Meagher and Heaton 2005; Moreno et al. 2005). In a study by Moreno et al. (2005), Hg uptake by *Brassica juncea* (Indian mustard) was facilitated by the application of sodium thiosulphate to the soil. However, it was found that Hg volatilized from above ground portion of plants, raising questions on the implications of Hg emission (Moreno et al. 2005).

An alternative to the conventional engineering-based methods is immobilization of Hg in soil via adsorption to render it harmless. Adsorption processes are of great importance in determining the fate and transport of Hg and other metals in soils (Sarkar et al. 2000). The main approach of Hg immobilization is to stabilize Hg thus reducing its bioavailability and consequently the environmental risks. The process is inexpensive depending on what adsorbents are used to stabilize Hg. A number of adsorbents such as activated carbon, zeolites, silica gels, clays, and ion-exchange resins (Chen et al. 2004; Chiarle et al. 2000; Huang and Blankenship 1984; Mercier and Detellier 1995; Prado et al. 2002; Zamzow et al. 1990) have been proposed to remove Hg from solutions, while only a few adsorbents, such as used tire rubber, have been proposed for Hg adsorption in soils (Meng et al. 1998). Even though used tire rubber was reported to have a relatively high adsorption capacity for Hg (14.6 mg/g), it is not known how its application would affect the overall soil quality. In the search for an “ideal” adsorbent for Hg

immobilization, drinking water treatment residuals (WTRs) are considered in this doctoral research.

### **Drinking Water Treatment Residuals (WTRs)**

Aluminum and iron based WTRs are the most common by-products of drinking water treatment facilities. WTRs are formed as a result of addition of aluminum or iron salts and other coagulants (such as polymers) to raw water to remove colloids, silt and clay-size particles, and color (Dayton and Basta 2001; Makris and Harris 2006). WTRs are produced daily during drinking water treatment processes and are either disposed in landfills, stored in onsite lagoons, or simply discharged into the river systems (Novak and Watts 2004). The disposal of this waste product is expensive and may increase the overall cost of water purification (Novak and Watts 2004).

Extensive research has shown that as a result of their chemical composition and high reactivity, WTRs can potentially be used as amendments to increase soil phosphorus (P) sorption capacity and reduce the impacts of runoff and infiltration on water quality (Codling et al. 2000; Dayton et al. 2003; Silveira et al. 2006). Based on laboratory studies, it has been suggested that the mechanism of P sorption onto WTRs matrices tends to be biphasic, with an initial fast sorption reaction on the surface due to electrostatic interactions between P and WTRs, followed by a slower sorption step associated with the intraparticle diffusion of P into micropores (Makris et al. 2004b). With regard to P sorption kinetics, reports on reaction order are not consistent. In a study by Novak and Watts (2005), P sorption data on WTRs were best fit to a first-order reaction model, while P kinetic data by Makris et al. (2005) fitted best to a second-order reaction model. This discrepancy can be attributed to factors such as the lack of homogeneity and the difference in the composition of WTRs used in these two studies. However, these authors concur on the strong ability of WTRs to sorb P.

Overall, previous research has now established the strong ability of WTRs to immobilize anions such as phosphate (Dayton et al. 2003), fluoride (Sujana et al. 1998), and perchlorate (Makris et al. 2006). Unlike the above anionic species, Hg and most metals occur in soil solutions primarily as cations. Reports on the efficiency of WTRs in binding heavy metals are still lacking. Some preliminary efforts, such as the work by Brown et al. (2001) found that WTR amendments in soil reduced the  $\text{NH}_4\text{NO}_3$  extractable Cd, Pb, and Zn, suggesting that WTRs might have a strong ability for immobilization of these metals of environmental concern. Although WTRs are found abundantly as Fe- or Al-based materials, it is believed that the use of Fe-WTRs in the remediation of Hg contaminated soils is less attractive due to the highly redox sensitive nature of iron, which could result in iron dissolution under anoxic conditions and release of previously sorbed metal cations. Therefore, in this study we will focus only on aluminum-based WTRs (Al-WTRs).

Dayton and Basta (2001) investigated the prospect of seventeen WTRs (fourteen of which were Al-WTRs) to be used as soil substitutes by comparing physicochemical properties and nutrient composition of the WTRs with typical soils. They found that most of the studied Al-WTRs had soil-like qualities with the potential to be used as soil substitutes for land reclamation purposes (Table 1-2). The physicochemical properties of WTRs were found adequate for plant growth (Table 1-3). If used solely for crop growth, the drawback of WTR application would be the reduction of P bioavailability, which could lead to P deficiency in plants if applied at excessively high rates (>10% WTRs) (Dayton and Basta 2001). However, this shortcoming can be easily corrected by applying a P-fertilizer to the treated soil whenever necessary (Hyde and Morris 2000).

Dayton and Basta (2001) also evaluated the potential toxicity of Al-WTRs using the toxicity characteristic leaching procedure (TCLP), a US-EPA standard procedure used to profile waste materials as hazardous or non-hazardous for the purpose of landfilling. The heavy metal content of all studied Al-WTRs was significantly below the regulatory levels for TCLP and therefore categorized as non-hazardous waste. Indeed, metal concentrations of WTRs are not regulated by the US-EPA 40 CFR Part 503 for sewage sludge disposal (US-EPA 1997b). Studies have shown that metal concentrations of studied WTRs were lower than the U.S. EPA regulatory limits for metals of environmental concern (Table 1-4) (Hyde and Morris 2000), and the dissolved Al concentrations in Al-WTRs extracts did not produce toxicity symptoms in soybeans and corn (Dayton and Basta 2001). Studies also demonstrated that Al-WTRs did not cause acute toxicity to the aquatic invertebrate *Daphnia similis* in a 48 hour toxicity assay (Sotero-Santos et al. 2005). In addition, no evidence of aluminum toxicity was found when alum-based sludge was used as a growth medium (Babatunde and Zhao 2007).

Adsorption capacity, non-toxic nature, ease of use, low cost, and availability are the factors that should be taken into account when choosing an adsorbent for soil Hg remediation (Stoodley et al. 2002). The results of our research demonstrate that Al-WTRs, as Hg adsorbents, seem to fit the above mentioned criteria. An added advantage to this adsorbent is that it exhibits soil-like qualities.

### **Research Objectives and Dissertation Outline**

The purpose of this doctoral research is to evaluate the potential of using Al-WTRs in the remediation of Hg-contaminated sites. While numerous studies have evaluated the use of Al-WTRs in controlling water pollution from agricultural-P runoffs, the potential of this material for the immobilization of metals in contaminated soils has not been adequately studied. Based on a

thorough review of the peer-reviewed literature, no data on the interaction between Hg and WTRs exist.

Experiments consisted primarily of laboratory assays to determine Hg sorption capacities of Al-WTRs, the ideal Al-WTRs rate for Hg immobilization in soils, reduction of Hg toxicity and bioavailability, and the potential for the stability of formed Hg-complexes.

The overarching hypothesis of this study is that both chemical and physical compositions of Al-WTRs favor the sorption and therefore the immobilization of Hg by formation of Hg-[Al-WTRs] complexes that are highly stable under environmental conditions. Therefore, Al-WTRs can be used to immobilize Hg in soils where Hg levels have been increased above natural background by anthropogenic activities.

The study was designed to meet the following main objectives.

**Objective 1:** Evaluate the potential of Al-WTRs to sorb Hg from aqueous solutions through determination of the Hg sorption capacities of Al-WTRs and identify the effect of contact time and pH on Hg adsorption.

**Objective 2:** Assess the potential of Al-WTRs to sorb and immobilize Hg in contaminated soils using column studies mimicking the effect of acid rain.

**Objective 3:** Assess the ability of Al-WTRs to reduce/eliminate the bioavailability and toxicity of Hg from treated soils using microbial Hg methylation as a surrogate for its bioavailability and MetPLATE™, a microbial test that is specific for heavy metal toxicity.

**Objective 4:** Initiate an investigation of the mechanisms of Hg immobilization on Al-WTRs and the implications of such mechanisms on the long-term stability of formed Hg-[Al-WTRs] complexes.

Table 1-1. Selected Hg standards for different environmental compartments

Maximum Contaminant Level (mg/L) <sup>a</sup>	Hazardous Waste Disposal (mg/L) <sup>b</sup>	Florida Soil Clean Up Target Level Direct Exposure (mg/kg) <sup>c</sup>		Florida SCTL Leachability based on groundwater criteria <sup>c</sup> (mg/kg)
		Commercial/Industrial	Residential	
0.002	0.2	17	3	2.1 <sup>a</sup>

<sup>a</sup> Established under the Safe Drinking Water Act (US-EPA 2003a); <sup>b</sup> Based on TCLP leachate concentration, if greater than the limit, land disposal is prohibited (US-EPA 2003b); <sup>c</sup> Soil Clean Up target levels (SCTL) vary by states (FDEP 2005)

Table 1-2. Comparison of chemical and physical properties of WTRs with typical soil levels (from Dayton and Basta, 2001)

WTR	pH	Electrical conductivity (dS/m)	Cation-exchange capacity (cmol/kg)	Total N (g/kg)	Organic carbon (g/kg)	Bulk density (g/cm <sup>3</sup> )	Plant available water (g/kg)
1	7.1	0.63	56.5	10.1	80	0.58	134
2	7.7	0.54	46.7	7.1	75	0.74	301
3	7.0	1.09	18.8	18.4	128	N/A	416
4	7.8	0.60	51.0	8.2	69	0.81	142
5	7.8	1.08	44.2	12.	65	N/A	144
6	7.6	0.37	13.6	1.3	17	N/A	172
7	7.7	0.44	34.8	3.9	28	0.95	71.8
8	6.6	0.28	29.6	7.6	32	0.91	130
9	7.0	0.27	20.3	5.6	46	0.79	27.3
10	6.9	0.40	29.5	4.8	62	0.82	26
11	7.7	0.59	29.9	2.3	48	1.17	206
12	5.3	0.43	31.7	5.9	78	0.63	16.3
13	7.5	1.03	29.7	14.6	149	0.56	194
14	7.2	0.67	30.5	7.9	86	0.93	139
15	7.0	0.22	17.8	7.3	60	0.96	100
16	7.0	0.80	31.9	7.9	63	0.97	77
17	6.6	0.22	16.4	2.8	23	1.3	66.8
WTR RANGE	5.3-7.8	0.22-1.1	13.6-56.5	1.3-18.4	17-149	0.56-1.3	26-416
WTR MEDIAN	7.1	0.5	30.0	7.0	63	0.9	139
SOIL TYPICAL	5.0-8.0	<4.0	3.5-35.6	0.2-5.0	<30	1.0-1.55	63-300

Table 1-3. Comparison of WTR nutrient levels with soil nutrient levels adequate for growth of most crops (from Dayton and Basta, 2001)

WTR	Soluble P, μG/L	Olsen P, mg/k g	M III P, mg/kg	NH <sub>4</sub> - N, mg/kg	NO <sub>3</sub> -N, mg/kg	K, mg/kg	Mg, mg/kg	Fe, mg/kg	Zn, mg/kg	Ca, g/kg
1	180.5	17.04	6.81	71.1	18.7	197	56.2	8	0.55	2.63
2	96.1	6.35	3.57	68.2	66	79	341.2	50.1	5.2	21
3	240.4	8.56	5.89	55.8	5.3	42.7	102.9	85.9	70	0.6
4	227.7	24.74	12.2	69.8	7.3	76	252.7	61.5	1.5	2.81
5	274.2	23.24	9.93	101.5	56.1	186	438	110.3	3	7.23
6	48.55	4.37	6.53	22	5.7	216.6	750	56.2	1.1	4.93
10	34	4.9	6.53	47.4	3.5	94.4	40.2	60.4	2.3	2.2
11	66	7.7	2.3	25.2	35.3	161.4	788	23.4	17:9	15.3
12	79	4.0	1.6	117.8	11.9	58	8.0	34.8	0.12	0.18
13	116.6	47.1	29.7	140	123	68.3	56	58.8	1.3	9.1
14	576	49	54.4	40.6	50	206.2	278.6	101	19.8	3.5
15	49.6	8.9	24.3	41.5	41.3	109	474	34.3	2.9	1.8
16	53.2	17.7	23.3	63.1	16	102.4	89	22	23.4	1.1
17	69.2	15	16.8	26.9	13.9	19	117	89.8	4	1.1
WTR RANGE	34-576	4-49	1.6- 54.4	22-140	3.5-123	19-278	8- 1231	8-231	0.12-70	0.18- 21
WTR MEDIAN	98	13.1	6.8	51	17	109	117	60.4	3	2.6
ADEQUATE SOIL LEVEL	50-200	>12	32.5	TOTAL INORGANIC N 50-200		125	50	4.5	0.8	>0.38

Table 1-4. Average concentrations of 15 metals in AI-WTRs determined using the EPA method 3050. Samples were collected every 3 weeks over a period of 1 year (from Hyde and Morris 2000)

Analyzed Metal	Concentration Range (mg/kg)	Mean (mg/kg)	Median (mg/kg)	SD	Regulation Limits <sup>a</sup> (mg/kg)
Ag	0.25-2.7	1.08	0.65	0.79	--
As	1.9-10.3	5.8	4.3	3.0	41
Ba	66.2-353	175.5	185.8	77.5	--
Be	0.03-2.18	0.81	0.78	0.60	--
Cd	0.03-9.31	1.56	0.26	3.04	39
Cr	8.1-253	105.8	63.1	103	1200
Cu	120-475	247.5	232.2	113	1500
Hg	0.01-0.12	0.04	0.03	0.03	17
Ni	8.1-62	29.2	18.8	21.3	420
Pb	1.5-13.5	6.6	6.6	3.3	300
Sb	0.03-0.80	0.13	0.03	0.24	--
Se	0.05-5.9	2.0	1.7	1.7	36
TI	0.03-0.25	0.08	0.05	0.07	--
V	14.0-130	57.3	34.0	45.1	2800
Zn	44.4-206	90.4	70.9	50.3	

<sup>a</sup> Regulation limits are the US-EPA 40 CFR Part 503 concentration limits for land application of sewage sludge

CHAPTER 2  
ALUMINUM- BASED DRINKING WATER TREATMENT RESIDUALS (AL-WTRs) AS A  
SORBENT FOR MERCURY: MATRIX CHARACTERIZATION AND DETERMINATION  
OF SORPTION CAPACITIES

**Introduction**

Mercury (Hg) is one of the 13 metals in the US-EPA priority pollutant list with known negative impacts on both human health and ecological functions (Adriano, 2001). Its strong ability to bioaccumulate and biomagnify in food chains leads to toxicity in living organisms. The major sources of anthropogenic Hg in soils include chlor-alkali plants, mine wastes, and Hg from several diffuse sources such as coal-fired power plants (D'Itri 1972; Drasch et al. 2004). Although much is now known on the biogeochemistry of Hg in sedimentary environments, research on the development of cost-effective and environment-friendly remediation techniques remains challenging. So far, only a few remediation techniques (e.g. stabilization/solidification and soil washing/acid extraction) have been tested commercially. However, their widespread use remains limited due to several factors including their prohibitive costs (US-EPA 2007). In fact, the remediation of metal-contaminated soils remains one of the most intractable problems of environmental restoration (Mulligan et al. 2001), and this is both a national and international issue. It requires the development of cost-effective and efficient remedial approaches that render Hg and other metal contaminants harmless, while avoiding adverse effects on the treated systems.

Drinking-water treatment residuals (WTRs) are waste by-products of the drinking water treatment processes and are produced daily in large quantities in most municipalities worldwide. They are formed as a result of the addition of aluminum or iron salts to raw water in order to remove colloids, silt and clay-size particles, color, and pathogenic microorganisms (Dayton and Basta 2001; Makris and Harris 2006; Ward et al. 2005). Accordingly, WTRs consist of particles

that settle as a result of coagulation and flocculation processes. In the United States and in Europe, several million tons of WTRs are produced yearly (Babatunde and Zhao 2007; Prakash and Sengupta 2003). Previous studies have focused primarily on the ability of WTRs to immobilize negatively charged ions such as phosphate (Dayton et al. 2003), fluoride (Sujana et al. 1998), and perchlorate (Makris et al. 2006). Studies on the efficiency of WTRs in binding cations are still lacking. Some preliminary efforts, such as the work by Brown et al. (2005) found that WTR amendments in soil would reduce the  $\text{NH}_4\text{NO}_3$ -extractable Cd, Pb, and Zn, suggesting that WTRs might have the capacity to immobilize these metals in soils.

In this study, the potential of the inexpensive and readily available waste Al-WTRs material to sorb and immobilize Hg from aqueous solutions was assessed in batch experiments. Although WTRs are found abundantly as either Al- or Fe-based materials, the limited choice to Al-WTRs in this study stems from the fact that Fe-based WTRs could be prone to redox driven changes. This could potentially lead to the dissolution of previously immobilized metals, and therefore negate the potential for WTRs use in soil remediation. In this study, the maximum sorption capacities, sorption isotherms, as well as the effect of pH on Hg sorption on Al-WTRs were determined. Kinetic and intraparticle diffusion models were used to gain insight in the potential sorption mechanisms of Hg on tested Al-WTRs particles.

## **Materials and Methods**

### **Collection and Characterization of Al-WTRs**

Al-WTRs samples were collected from the Manatee County Drinking Water Treatment Plant in Bradenton, Florida, USA. In this water treatment plant, Al-WTRs is produced following the addition of alum and a small amount of copolymers of sodium acrylate and acrylamide (Makris et al. 2005). The Al-WTRs samples used in this study were collected from the Treatment Plant disposal site (open dry land in the vicinity of the water treatment plant) using a shovel.

Samples were transferred into high density polyethylene (HDPE) containers and transported back to the University of Florida in Gainesville. In the laboratory, Al-WTRs samples were first air-dried at room temperature for a period of 4 weeks. Relatively homogeneous material was then obtained by passing dried Al-WTRs through a 2 mm screen.

The pH and the electrical conductivity (EC) of Al-WTRs were measured in 1:1 (mass/volume (m/v)) and 1:2 (m/v) Nanopure<sup>®</sup> water suspensions respectively, after a 4 hr equilibration period using a pH-meter (model 240, Corning) and EC meter (model 1054, Markson), respectively. The organic carbon content was measured according to the Walkley-Black method in which organic carbon is oxidized by potassium dichromate (Walkley and Black 1934). This method is one of the most widely used procedures for obtaining a good estimate of oxidizable organic matter in soil samples (Hesse 1972). The effective cation exchange capacity (CEC<sub>e</sub>) which is a measure of the quantity of sites on soil surfaces that can retain cations by electrostatic forces, was determined as described by Sumner and Miller (1996). Briefly, CEC<sub>e</sub> was determined by extracting base cations (Ca<sup>2+</sup>, Mg<sup>2+</sup>, K<sup>+</sup>, and Na<sup>+</sup>) and aluminium (Al<sup>3+</sup>) with ammonium chloride, the concentrations of which were then determined by the Inductively Coupled Plasma Atomic Emission Spectrometry (ICP-AES). The toxicity of Al-WTRs extracts was assayed with the MetPLATE<sup>™</sup> toxicity test, after equilibration by shaking of the mixture with Nanopure<sup>®</sup> water in a 1:2.5 solid to liquid ratio for 2 hours (Boularbah et al. 1996). MetPLATE<sup>™</sup> is a metal specific toxicity test that is based on the inhibition of the enzyme β-galactosidase by metals at toxic levels in a mutant strain of *E. coli*, and does not respond to organic toxicants (Bitton et al. 1994). For total metal analysis, about 1 g of dry Al-WTRs sample was digested overnight at 110<sup>0</sup>C with 30 ml of HNO<sub>3</sub>/H<sub>2</sub>SO<sub>4</sub> mixture (7:3, v/v) in a closed Teflon<sup>®</sup> vessel. The mixture upon cooling was diluted to 50 ml with Nanopure<sup>®</sup> water. The

solution was then analyzed for total concentrations of Al, Fe, Ca, Cu, Cr, Zn, and Pb by ICP-AES and Hg by Cold Vapor Atomic Fluorescence Spectrometry (CV-AFS).

An emphasis in the characterization of used Al-WTRs was on the measurement of the specific surface area (SSA), a key parameter that strongly influences the sorption capacity of solid surfaces (Goldberg et al. 2001). As a pretreatment to SSA characterization, a known amount of Al-WTRs was introduced in a capillary glass tube and outgassed for 4 hours under helium flow at 70°C (Makris et al. 2004a). The SSA was then measured by a nitrogen adsorption (SSA-N<sub>2</sub> at 77 K) and carbon dioxide (SSA-CO<sub>2</sub> at 273 K) methods using Quantachrome Autosorb-1 (Quantachrome Corp.) apparatus. The SSA-N<sub>2</sub> was calculated using the Brunauer-Emmett-Teller or BET equation (Equation 2-1), where  $W$  is the weight of the gas adsorbed at a relative pressure  $P/P_0$ ,  $W_m$  is the monolayer capacity, and  $C$  is a BET constant.

$$\frac{1}{W \times \left(\frac{P_0}{P} - 1\right)} = \frac{1}{W_m \times C} + \frac{C - 1}{(W_m \times C) \times \frac{P}{P_0}} \quad (\text{Eq. 2-1})$$

The SSA-CO<sub>2</sub>, which describes microporosity, was calculated using the Dubinin-Radushkevich (DR) equation modified by Kaganer, also known as DRK equation (Equation 2-2) (Gregg and Sing 1982), and where  $W$  is the amount of the gas adsorbed at relative pressure  $P/P_0$ ,  $W_m$  is the monolayer capacity,  $D$  is a constant that characterizes Gaussian distribution,  $P_0$  is the vapor saturation pressure of CO<sub>2</sub> (26,140 mm Hg), and  $P$  is the equilibrium pressure (mm Hg).

$$\log W = \log W_m - D \left[ \log \frac{P_0}{P} \right]^2 \quad (\text{Eq. 2-2})$$

The BET-N<sub>2</sub> method is applied in the region of relative pressures from  $P/P_0=0.05$  to  $P/P_0=0.3$ , while the SSA-CO<sub>2</sub> is carried out in the interval of relative pressures of  $P/P_0=10^{-5}$  to  $P/P_0=0.0029$  (Gregg and Sing 1982).

Finally, the zeta potential (ZP) of Al-WTRs as a function of pH was measured using the EKA electrokinetic analyzer (Anton–Paar). The EKA is used to determine the ZP of larger (non-colloidal) particles and is based on the streaming potential method. The EKA automatically calculates the ZP by using the Helmholtz-Smoluchowski equation (AntonPaar 2003). The pH of the electrolyte solution (1mM KCl) was adjusted with 0.1 M HCl or 0.1M NaOH to the desired value in the pH range of 3 to 11. The electrolyte solution was pumped through a cylindrical cell that has two silver electrodes coated with AgCl. The ZP is then calculated based on the streaming potential, the flow of the solvent (pressure drop), the current, and the conductivity of the solution as the solvent flows across the samples. More detailed information about this methodology can be found elsewhere (Bismarck et al. 2004).

#### **Determination of the Maximum Sorption Capacity of Al-WTRs and Sorption Isotherms**

The maximum sorption capacity of Al-WTRs for Hg was determined in batch adsorption experiments. A commercial  $\text{Hg}(\text{NO}_3)_2$  standard solution obtained from Fisher Scientific was used to prepare Hg solutions in Nanopure<sup>®</sup> water with final Hg concentrations of 10, 20, 40, and 80 ppm. Obtained solutions were put in contact with dry Al-WTRs materials in a 3 to 5 ratio (m/v). All experiments were conducted at pH 6.5 and carried out in 50 ml capped and acid-cleaned polyethylene tubes which were continuously rotated at about 30 rpm on a Roto-Shake Genie<sup>®</sup> (Scientific Industries, Inc). After 96 hours of equilibration, Al-WTRs slurries were centrifuged and the supernatant filtered (0.45 $\mu\text{m}$ ) and analyzed for total Hg. Total Hg concentration in solution was measured by CV-AFS, following sample digestion according to EPA method 1631 (US-EPA 2001). Briefly, filtered samples were subjected to cold digestion using bromine monochloride ( $\text{BrCl}$ ) and analyzed using the stannous chloride ( $\text{SnCl}_2$ ) reduction method (US-EPA 2001) and a Tekran Series 2600 system (Tekran, Ontario, Canada). QA/QC criteria were met by running reagent blanks and standard solutions. The concentration of 10 analytical blanks

averaged 0.72 ng/L (n=10), and the detection limit determined as 1 standard deviation was 0.5 ng/L. All containers used in this study were acid washed and only Teflon<sup>®</sup> containers were used for storage of Hg containing solutions.

The Hg loading capacities of Al-WTRs (mg/g) were calculated using equation 2-3, and where  $C_i$  and  $C_e$  are initial and equilibrium Hg concentrations in mg/L,  $M$  is the weight of used Al-WTRs in grams, and  $V$  is the volume of solution in liters.

$$\text{Hg Loading Capacity (mg/g)} = \frac{(C_i - C_e) \times V}{M} \quad (\text{Eq.2-3})$$

The percentage of Hg sorbed was calculated from the difference between the initial Hg concentration and Hg concentration remaining in the solution at equilibrium. The sorption data was then fit to Langmuir and Freundlich models and the best fit was used to calculate the maximum sorption capacity.

The solid Al-WTRs material used in these sorption experiments was recovered and examined for sorbed Hg via scanning electron microscopy (SEM), carried out in the JSM-6330F field emission scanning electron microscope unit equipped with an X-ray energy dispersive spectrometer (SEM-EDS). To account for Hg mass balance, the solid Al-WTRs material was also analyzed for total Hg by CV-AFS.

### **Mercury Desorption from Al-WTRs**

For desorption study, Hg-spiked Al-WTRs were prepared by bringing Al-WTRs into contact with Hg solution to achieve a Hg concentration of 30,000 mg/kg and equilibrated for 7 days (no shaking was applied). The amount of Hg sorbed was determined by analyzing the dried Hg-spiked Al-WTRs for total Hg concentration. Desorption of Hg was studied by first adding dried Hg-spiked Al-WTRs in a 1:20 (m/v) to an extracting solution with a pH of 4.22, prepared according to the US-EPA Synthetic Precipitation Leaching Procedure (SPLP) (US-EPA 2003b)

and to simulate the leaching effect of acid rain. Next, the samples were rotated in capped centrifuge tubes at about 30 rpm for 18 hours on a Roto-Shake Genie<sup>®</sup>, centrifuged, and the supernatant analyzed for total Hg as described in earlier in this chapter. The percentage of Hg desorbed was calculated using equation 2-4, where  $C_{des}$  is the desorbed Hg concentration in SPLP extracting solution (mg/L),  $C_{ads}$  is the Hg sorbed concentration on Al-WTRs (mg/kg),  $V$  is the volume of extracting solution (mL), and  $M$  is the weight of Al-WTRs (g).

$$\% \text{ Hg Desorbed} = \frac{C_{des} \times V}{M \times C_{ads}} \times 100\% \quad (\text{Eq. 2-4})$$

### **Kinetics of Hg Sorption on Al-WTRs and Effect of pH**

Batch kinetic studies were performed to obtain data on Hg sorption behavior versus time. Hg solution with an initial concentration of 40 ppm was used for this experiment. The Hg solution and Al-WTRs were mixed in a 2 to 5 ratio (m/v), pH adjusted to 6.5, and the mixture agitated by continuous stirring for the duration of the experiment. The contact time and sampling intervals were selected based on preliminary experiments. Thus, at pre-decided time intervals, the supernatant was withdrawn, filtered (0.45 $\mu$ m), and analyzed for total Hg. To investigate the possible mechanisms of sorption, obtained data were fit in to different kinetic (first and second order) and intraparticle diffusion models.

Finally, in addition to the above kinetic experiment at a fixed pH, batch studies were also conducted to investigate the effect of changing pH on Hg sorption onto Al-WTRs. In these sorption experiments, 40 ppm Hg solutions were used and the pH of Al-WTRs slurries (3:5 ratio; m/v) adjusted with either 0.1N HCl or 0.1N NaOH. The Hg solutions were then equilibrated with Al-WTRs for 96 hours. After the equilibration period, the supernatant was analyzed for total Hg.

## Results and Discussion

### Characterization of Al-WTRs

Images obtained from scanning electron microscopy showed that collected Al-WTRs are heterogeneous mixtures of particles with irregular shape and variable sizes (Figure 2-1). The EDS elemental spectra analysis showed that Al-WTRs are predominantly composed of Al, Si, P, S, Ca, and Fe (Figure 2-2(A)). Other measured physicochemical characteristics of Al-WTRs are presented in Table 2-1. Overall, these parameters are similar to Al-WTRs composition reported by others in previous studies (Dayton and Basta 2001; Dayton et al. 2003; Hyde and Morris 2000; Makris et al. 2004b; Makris et al. 2005). Although not regulated by the US-EPA 40 CFR Part 503 for sewage sludge (US-EPA 1997a), it was confirmed that the concentration of Hg (0.02 mg Hg/kg Al-WTR) and that of other metals present in these Al-WTR samples were lower than the US-EPA regulatory limits for land application of sewage sludge (Table 2-1) (US-EPA 40 CFR Part 503). With regard to high Al levels and its potential leachability and toxicity, the MetPLATE™ bioassay showed no measurable toxic effect of Al-WTRs extracts. This observation is in line with previous studies where no aluminum toxicity was found in tomatoes (Dayton and Basta 2001) and broad beans (Skene et al. 1995) when grown in Al-WTRs used as a soil substitute.

The SSA-N<sub>2</sub> characterization based on the BET method (BET-N<sub>2</sub>) revealed a rather high surface area averaging 48 m<sup>2</sup>/g. The BET-N<sub>2</sub> is applicable mostly to non-porous or mesoporous materials and tends to underestimate the SSA of internal micropores when present (Lowell et al. 2004). The CO<sub>2</sub> is a preferred adsorbent in micropore analysis even though CO<sub>2</sub> (2.8 Å) and N<sub>2</sub> (3.0 Å) have similar molecular dimensions (Lowell et al. 2004; Makris et al. 2004b). The reason being that CO<sub>2</sub> analysis is performed at a higher temperature compared to N<sub>2</sub> (T=273 K for CO<sub>2</sub> and T=77 K for N<sub>2</sub>), as a result CO<sub>2</sub> passage through micropores is less constricted (Gil and

Gandia 2003; Lowell et al. 2004). Our measured SSA-CO<sub>2</sub> of 120 m<sup>2</sup>/g Al-WTR suggests that the Al-WTRs materials tested in this study have a large internal surface area that is not accounted by the BET-N<sub>2</sub> (Table 2-1). The values for SSA-N<sub>2</sub> and SSA-CO<sub>2</sub> compare quite well with those reported for Al-WTRs collected from the same water treatment plant by Makris et al. (2004b; 2005).

### **Determination of the Maximum Sorption Capacity of Al-WTRs and Sorption Isotherms**

Table 2-2 summarizes the results obtained from these experiments. The Hg loading capacities and the percentage of Hg adsorbed onto Al-WTRs calculated for each treatment show that Al-WTRs can efficiently remove dissolved Hg. Samples with 10 mg/L of initial Hg concentration had Hg levels reduced by almost 100%, while solutions with initial Hg levels of 20 mg/L were reduced by about 90%. The maximum sorption capacity of 75.4 mg/g was obtained based on experiments with initial Hg dissolved concentration of 80 mg/L. The EDS elemental spectra analysis of Al-WTR particles recovered at the end of the Hg sorption experiments verified the presence of sorbed Hg on Al-WTR-particles (Figure 2-2(B)), and mass balance calculation on the distribution of Hg between the aqueous and solid phases accounted for 99 ± 10% of the initial Hg concentrations. Additionally, the shape of the obtained sorption isotherm (Figure 2-3) suggests that sorption sites with high affinity for Hg are present on Al-WTRs, leading to very low aqueous Hg equilibrium concentrations for samples with 10 and 20 mg/L initial Hg concentrations (Polo and Utrilla 2002).

The sorption data was best fit to a Langmuir model (Figure 2-4, R<sup>2</sup>=0.98). Based on equation 2-5, a plot of  $C_e/q$  versus  $C_e$  allowed the determination of the maximum sorption capacity ( $q_m$ ) and the binding constant ( $K_{ads}$ ) from the slope and the intercept of the linear regression. In this equation,  $q$  is the adsorption density (mg/g),  $C_e$  is the equilibrium Hg

concentrations (mg/L),  $q_m$  is the maximum sorption capacity (mg/g),  $K_{ads}$  is the binding constant that measures the affinity of adsorbate for adsorbent (L/mg) (Sawyer et al. 2003).

$$\frac{C_e}{q} = \frac{1}{K_{ads} q_m} + \frac{C_e}{q_m} \quad (\text{Eq. 2-5})$$

The maximum sorption capacity determined from the Langmuir model was 79.3 mg/g, which compares well with the maximum sorption capacity of 75.4 mg/g determined experimentally (Table 2-3). This sorption capacity is considerably larger than that of some of the previously tested waste adsorbents such as used tire rubber with a maximum sorption capacity of 14.6 mg Hg/g (Meng et al. 1998).

Additionally, the favorable nature of sorption processes can be expressed in terms of a dimensionless constant separation factor ( $r$ ) defined as:  $r=1/(1+K_{ads}C_0)$ , where  $C_0$  is the initial Hg concentration (mg/L) and  $K_{ads}$  is the binding constant from equation 2-5. For this study, the calculated ( $r$ ) values were less than 1 and greater than 0, indicating a favorable sorption (McKay et al. 1982).

It is worth noting that the Langmuir model assumes that the adsorption is limited to a single monolayer coverage and that all surface sites on the adsorbent have the same affinity for the adsorbate (Sawyer et al. 2003). Accordingly, this model applies well to these short-term sorption experiments, dominated primarily by sorption of Hg to Al-WTRs external surface sites (Axe and Trivedi 2002). However, for microporous adsorbents such as Al-WTRs, there is also a possibility for the intraparticle diffusion of Hg into the micropores. Therefore, it is likely that the true sorption capacity of Al-WTRs is even greater than the value obtained in these short-term sorption experiments. Intraparticle diffusion is a much slower sorption process and is observed by maintaining a constant boundary condition of a metal in the bulk aqueous phase (Xu et al.

2006). Further long-term experiments are therefore needed to study the potential diffusion mechanisms of Hg into Al-WTRs micropores.

### **Mercury Desorption from Al-WTRs**

Finally, Hg desorption studied by leaching of formed Hg-[Al-WTRs] complexes with synthetic acid rainwater solution (SPLP) led to the release of just 1.5% of Hg previously sorbed onto Al-WTRs particles. Although preliminary, these results suggest that the leaching potential of Hg from Al-WTRs could be very low.

### **Kinetics of Hg Sorption on Al-WTRs**

Figure 2-5 shows the effect of contact time on Hg adsorption on Al-WTRs in a series of sorption experiments with initial Hg concentration of 40 mg/L and pH 6.5. Equilibrium was attained in about 32 hours, with nearly all initial dissolved Hg (~99%) sorbed onto Al-WTRs particles. Based on these studies, kinetic and intraparticle diffusion models were used to gain insight in the potential mechanisms of Hg sorption and fixation on Al-WTRs.

**Pseudo-first order Lagergren model:** The Lagergren's pseudo-first order equation (Lagergren 1898) is widely used for modeling sorption of metals from solutions (Goel et al. 2005; Gupta and Sharma 2002; Manchon-Vizuete et al. 2005). In linear form it is expressed as follows

$$\log_{10}(q_e - q_t) = \log_{10} q_e - \frac{k_1 t}{2.303} \quad (\text{Eq. 2-6})$$

where  $q_e$  is Hg concentration at equilibrium per unit mass of Al-WTRs (mg/g),  $q_t$  is the amount of Hg adsorbed at time ( $t$ ) per unit mass of Al-WTRs (mg/g), and  $k_1$  is the sorption rate constant of the pseudo-first order ( $\text{h}^{-1}$ ). By plotting  $\log(q_e - q_t)$  versus time ( $t$ ), a straight line with a correlation coefficient of  $R^2=0.9944$  was obtained (Figure 2-6). The parameters  $k_1$  and  $q_e$  determined from the slope and the intercept of the plot are presented in Table 2-4. Based on the

heterogeneous composition of Al-WTRs, it is likely that several reaction types/mechanisms are involved in the fixation of Hg on Al-WTRs. However, the use of equation 2-6 tends to suggest that the rates of these reactions could be approximated by a pseudo-first order kinetic model.

**Pseudo-second order model:** Figure 2-7 was obtained by plotting  $t/q_t$  versus time ( $t$ ), based on equation 2-7 (Ho and McKay 2000), where  $q_{e2}$  is the Hg concentration at equilibrium per unit mass of Al-WTRs (mg/g),  $q_t$  is the amount of Hg adsorbed at time ( $t$ ) per unit mass of Al-WTRs (mg/g), and  $k_2$  is the sorption rate constant (g/mg h).

$$\frac{t}{q_t} = \frac{1}{k_2 q_{e2}^2} + \frac{t}{q_{e2}} \quad (\text{Eq. 2-7})$$

The parameters  $q_{e2}$  and  $k_2$  obtained from the intercept and the slope of the plot are listed in Table 2-4. The correlation coefficient for this pseudo-second order model ( $R^2=0.9901$ ) is slightly lower when compared to the pseudo-first order model, suggesting that the adsorption of Hg by Al-WTRs under these experimental conditions can be described by a pseudo-first order kinetic model.

**Intraparticle diffusion:** The potential role of intraparticle diffusion on Hg sorption process was first explored by using the Weber-Morris intraparticle diffusion model shown in equation 2-8 (Ho and McKay 1998; Weber and Morris 1963), and where,  $q_t$  is the amount of Hg adsorbed at time ( $t$ ) per unit mass of Al-WTRs (mg/g),  $k_i$  is the intraparticle diffusion rate constant (mg/g  $\sqrt{h}$ ), and  $C$  is the sorption constant, which describes the thickness of the boundary layer.

$$q_t = k_i \sqrt{t} + C \quad (\text{Eq. 2-8})$$

Figure 2-8 was obtained by plotting  $q_t$  versus  $\sqrt{t}$  and the obtained relationship ( $R^2=0.9915$ ), seems to indicate that intraparticle diffusion may play a role in the sorption

process. Indeed, Figure 2-8 can be divided in two distinct linear portions. The first portion could be attributed to either boundary layer diffusion effects or the mass transfer effects on external surfaces, while the second portion tends to suggest an additional slower and gradual sorption stage during which intraparticle diffusion would likely dominate (Mane et al. 2007). The role of intraparticle diffusion as a rate-limiting step on sorption process was further investigated by use of the Bangham's model shown in equation 2-9 (Aharoni et al. 1979; Tutem et al. 1998), and where  $C_0$  is the initial concentration of adsorbate in solution (mg/L),  $V$  is the volume of solution (mL),  $m$  is the weight of adsorbent used per liter of solution (g/L),  $q_t$  is the amount of Hg adsorbed at time ( $t$ ) per unit mass of Al-WTRs (mg/g),  $\alpha$  ( $<1$ ) and  $k_b$  are constants.

$$\log \log \left( \frac{C_0}{C_0 - q_t m} \right) = \log \left( \frac{k_b m}{2.303 V} \right) + \alpha \log(t) \quad (\text{Eq.2-9})$$

A plot of the Bangham's model is presented in Figure 2-9. The linearity of the plot ( $R^2=0.9948$ ) confirms the applicability of Bangham's equation and indicates that intraparticle diffusion is a likely rate-limiting step of Hg sorption on Al-WTRs (Jain et al. 2004). The mechanism of intraparticle diffusion is also supported by the fact that Al-WTR particles have a large internal network of micropores as mentioned in earlier sections.

In general, the amorphous structure of Al-WTRs is believed to be caused by the formation of amorphous Al oxides and hydroxides (Makris et al. 2005; Novak and Watts 2005). The concentrations of amorphous aluminum (hydr)oxides in Al-WTRs have been found to range from 50 to 150 g/kg (Dayton and Basta 2001). Theoretically, the prevalence of such geochemical phases in Al-WTRs would make them behave like aluminum oxyhydroxides. Results from previous studies tend to suggest that sorption of heavy metals to amorphous metal oxides is usually a two-step process with a rapid sorption of the metal first to the external surface, followed by a slow intraparticle diffusion along the oxide micropore walls (Trivedi and Axe

2000). For remediation purposes, it is the long-term slow process which might play the most significant role in the sorption of the Hg fraction that becomes non-exchangeable, and therefore fully immobilized. Further studies are necessary to validate these observations and to help determine surface diffusivities.

**Effect of pH on Hg sorption by Al-WTRs:** In interfacial phenomena involving liquids, pH is a key parameter governing the surface charge of solid materials (Stumm and Morgan 1996). Although Al-WTR is a heterogeneous material, its reactivity has been found to be similar to that of amorphous aluminum (hydr)oxides. The reported point of zero charge (PZC) of aluminum (hydr)oxides is usually greater than 7.7 (Gayer et al. 1958; Goldberg et al. 2001). Theoretically, the affinity of Hg and other metal cations for (hydr)oxides and therefore Al-WTRs should increase for pH greater than  $pH_{zpc}$  and decrease at  $pH < pH_{zpc}$ , based on electrostatic interactions. The effect of the pH of the solution on the sorption of Hg on Al-WTRs is presented in Figure 2-10. These results show the highest Hg removal from aqueous phase at the highly acidic pH of 3, while the lowest Hg removal level was observed at pH 5. Overall, Hg sorption decreased first from pH 3 to 5, and then increased gradually with increasing pH from 5 to 8. This trend is not supported by the empirical PZC concept described above. Zeta potential (ZP) of the Al-WTRs was measured across a wide range of pH (3 to 11) to tentatively help explain the unusual sorption trend shown in Figure 2-11. Usually, the ZP should become more positive with the decrease in pH because of the build up of positively charged protons. The experimental data show that as the pH decreases from about 5.5 to 3, the ZP of Al-WTRs becomes more negative. This unusual trend could explain the high Hg sorption at pH 3. Similar ZP trends have been reported for several organic polymers such as cellulose and lignin, the most abundant organic polymers in nature (Bismarck et al. 2001; Bismarck et al. 2000). The organic carbon (OC)

content of used Al-WTRs averaged 13%, and besides the anthropogenic inputs due to the addition of organo-compounds during the treatment process, OC originates from natural raw waters that undergo the treatment process. This high OC content as well as the chemical composition of these organic compounds may be influencing the ZP vs. pH trend of Al-WTRs. The fact that Hg removal was very efficient at low pH values is significant from remediation standpoint, because often times contaminated soils may have a very low pH and, if left untreated, may leach out the Hg.

As the pH increases from about 5.5 to 11, the ZP becomes more negative, because of the build up of negatively charged hydroxyl ions. Figure 2-10 and Figure 2-11 show correlation of Hg sorption behavior vs. pH on one hand, and between the measured ZP vs. pH, indicating that electrostatic attractions play a role in Hg sorption onto Al-WTRs. However, as the pH increases above about pH 4, Hg should occur predominantly as  $Hg(OH)_{2(aq)}^0$  based on geochemical equilibrium predictions calculated using MINEQL<sup>+</sup> (Schecher and McAvoy 2001). Therefore, it is likely that electrostatic attraction does not constitute the only force that governs the sorption of Hg onto Al-WTRs. These data suggest that additional forces are involved in Hg sorption. One could speculate on the role of steric and hydrophobic interactions in the Hg sorption process on Al-WTRs. However, further investigations are needed to study the mechanism of Hg sorption on Al-WTRs.

### **Conclusions**

Al-WTRs are readily available and non-hazardous waste by-products of drinking water treatment processes, produced daily and in large quantities in most municipalities worldwide. They have been used successfully in experimental settings to sorb and immobilize phosphorus from agricultural impacted soils. However studies on retention of metal cations such as Hg by

Al-WTRs are lacking. In this study, the potential of Al-WTRs to sorb and immobilize Hg from aqueous solutions was evaluated. Sorption isotherms indicated a strong affinity of Hg for Al-WTRs and a relatively high maximum sorption capacity of 79 mg Hg/g Al-WTRs. Also, Al-WTRs effectively immobilized Hg in the pH range of 3 to 8. Sorption kinetic data was best fit to a pseudo-first order model, while the use of the Weber-Morris and Bangham models suggested that the intraparticle diffusion could be the rate-limiting step for Hg immobilization onto Al-WTRs particles. Overall, the results from these short-term experiments demonstrate that Al-WTRs can be effectively used to remove Hg from aqueous solutions. This ability points to the potential of Al-WTRs as sorbent in soil remediation techniques based on Hg-immobilization.

Table 2-1. Physicochemical properties of AI-WTRs collected from the Bradenton Drinking Water Treatment Facility (Florida, USA)

Parameter	Mean Value <sup>a</sup>	Units	Regulatory Limit <sup>f</sup> (mg/kg)
pH <sup>c</sup>	5.6±0.01 <sup>b</sup>		n/a <sup>g</sup>
EC <sup>d</sup>	0.36±0.01	dS/m	n/a
CEC <sup>e</sup>	45.80±0.09	cmol/kg	n/a
SSA-N <sub>2</sub> (BET)	48±0.3	m <sup>2</sup> /g	n/a
SSA-CO <sub>2</sub> (micropore)	120±0.3	m <sup>2</sup> /g	n/a
Organic Carbon	12.7±0.08	%	n/a
Al	73.8±3.2	g/kg	Nd <sup>h</sup>
Fe	3.7±0.1	g/kg	Nd
Ca	2.263±0.5	g/kg	Nd
As	8.01±1.1	mg/kg	41
Cu	141±3.4	mg/kg	1500
Cr	81.1±1.3	mg/kg	1200
Hg	0.02±0.003	mg/kg	17
Pb	1.99±0.4	mg/kg	300
Zn	14.37±1.3	mg/kg	2800

<sup>a</sup> All the values are means of triplicates; <sup>b</sup> ±values represent standard errors of the mean; <sup>c</sup> At a soil/water ratio of 1:1 (m/v); <sup>d</sup> At a soil/water ratio of 1:2 (m/v); <sup>e</sup> Effective cation exchange capacity; <sup>f</sup> US-EPA 40 CFR Part 503, pollutant limits for meeting land exceptional quality criteria; <sup>g</sup> Not applicable. <sup>h</sup> Not defined

Table 2-2. Determination of Hg maximum sorption capacity (mg/g) at pH 6.5

Initial Hg (mg/L)	Mean Equilibrium conc. (mg/L) <sup>a</sup>	Loading capacity (mg/g)	% Hg adsorbed
10	0.03±0.01 <sup>b</sup>	16.6	99.7
20	2.01±0.33	29.9	90.0
40	8.72±0.37	52.1	78.2
80	45±8.13	75.4	56.6

<sup>a</sup>All the values are means of four replicates. <sup>b</sup>±values represent standard errors of the mean

Table 2-3. Sorption isotherm parameters for Hg sorption on Al-WTRs at pH 6.5

Parameter	Value
$K_{ads}$ (L/mg)	0.4
$q_m$ (Langmuir)	79.3
$q_m$ experimental (mg/g)	75.4
$R^2$ (Langmuir)	0.9858

Table 2-4. Kinetic Parameters for Hg Sorption on Al-WTRs at pH 6.5 and initial Hg concentration of 40 mg/L

Parameter	Value	Parameter	Value
Pseudo-first order		Pseudo-second order	
$k_1$ (h <sup>-1</sup> )	0.057	$K_2$ (g/mg h)	9.12*10 <sup>-4</sup>
$q_e$ (mg/g)	80.2	$q_{e2}$ (mg/g)	103
$R^2$	0.9944	$R^2$	0.9901
Intraparticle diffusion			
Weber and Morris Model		Bangham Model	
$k_i$ (mg/g √h)	0.0677	$k_b$ (mL/g/L)	297
$C$	0.1328	$A$	0.7375
$R^2$	0.9915	$R^2$	0.9948

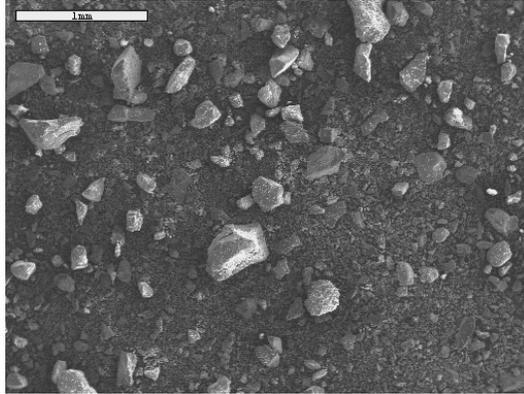


Figure 2-1. SEM micrographs of the original Al-WTRs collected from the Bradenton Drinking Water Treatment Facility (Florida, USA) showing irregular size and non-homogeneity of particles.

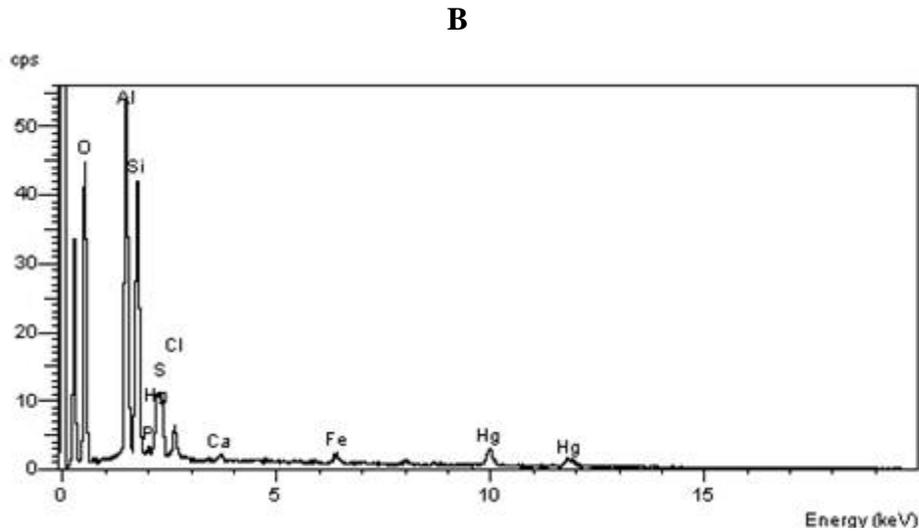
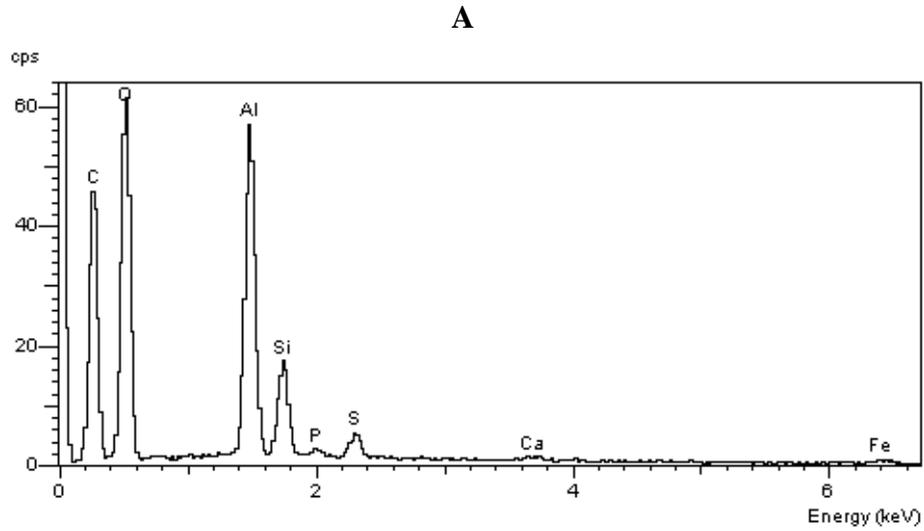


Figure 2-2. Elemental spectra (EDS) of the (A) original Al-WTRs before use in Hg sorption experiments and of the (B) recovered Al-WTRs after the sorption experiments confirming Hg sorption on Al-WTRs.

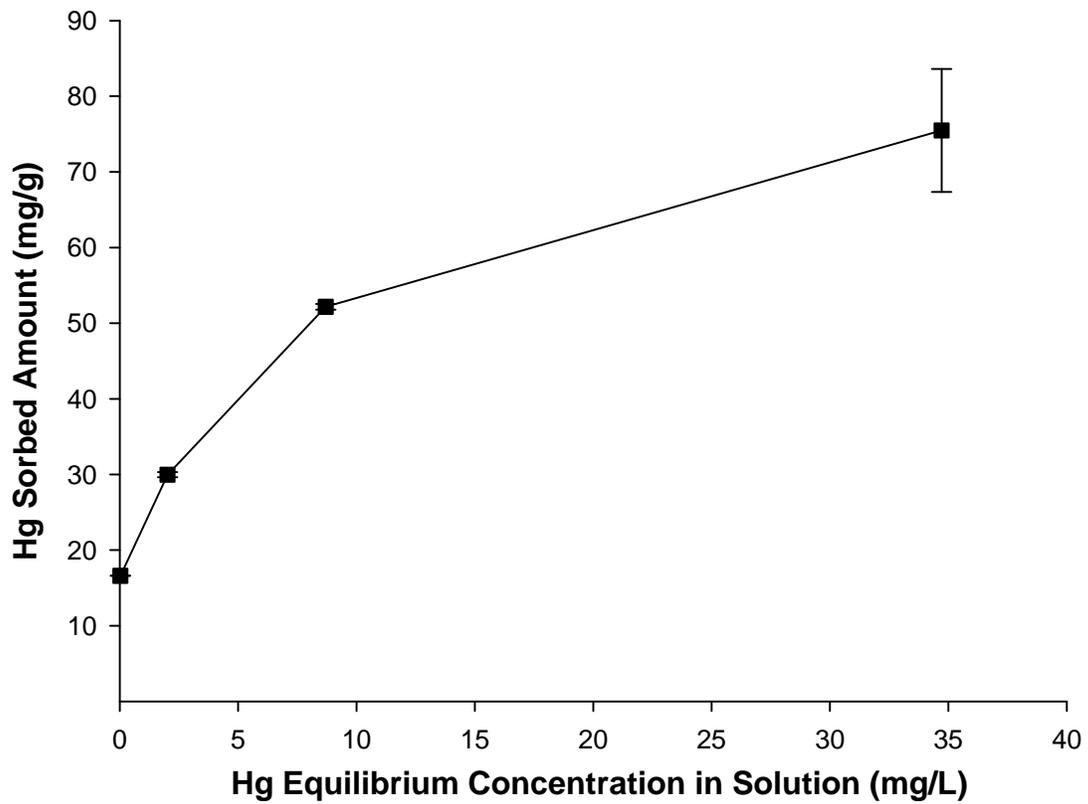


Figure 2-3. Mercury sorption isotherm with initial Hg concentrations of 10, 20, 40, and 80 mg/L and pH 6.5. Plotted values are averages (n=4) and error bars represent standard errors of the mean. Error bars for 10, 20, and 40 mg/L are very small and overlap with the point.

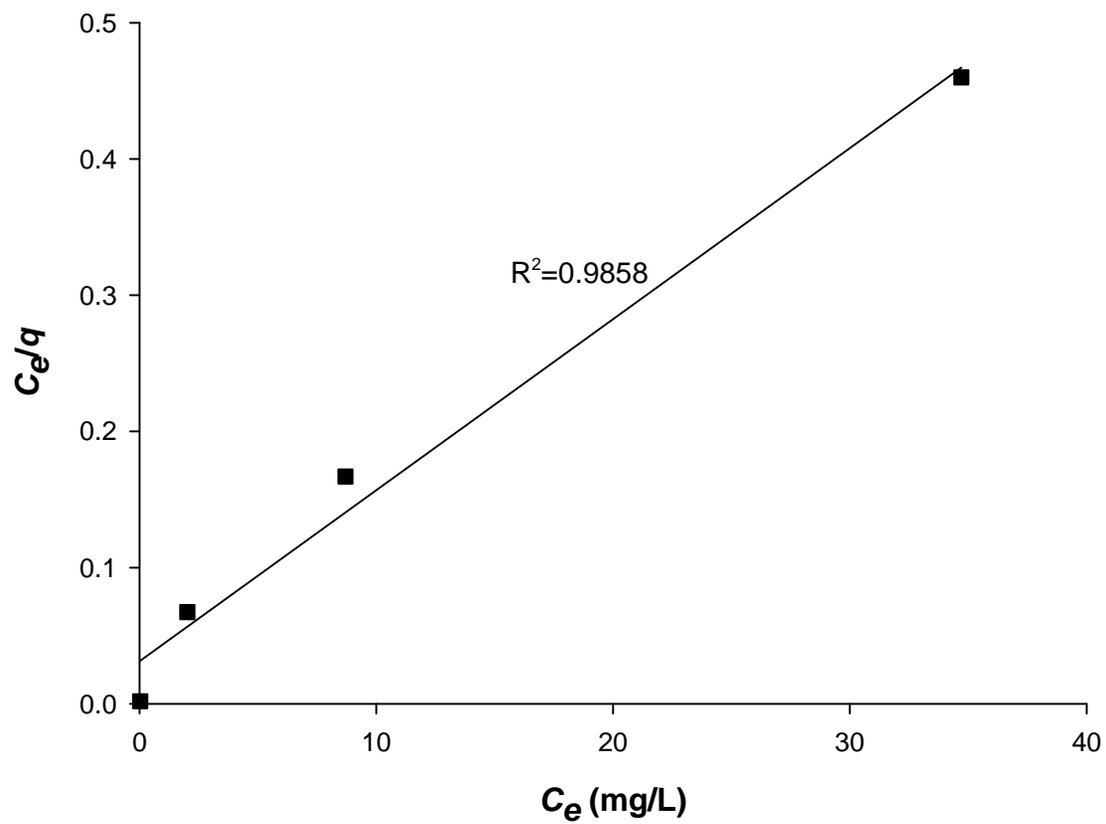


Figure 2-4. Langmuir plot for Hg sorption on Al-WTRs at initial Hg concentrations of 10, 20, 40, and 80 mg/L and pH 6.5. Where  $q$  is the adsorption density (mg/g) and  $C_e$  is the equilibrium Hg concentration (mg/L).

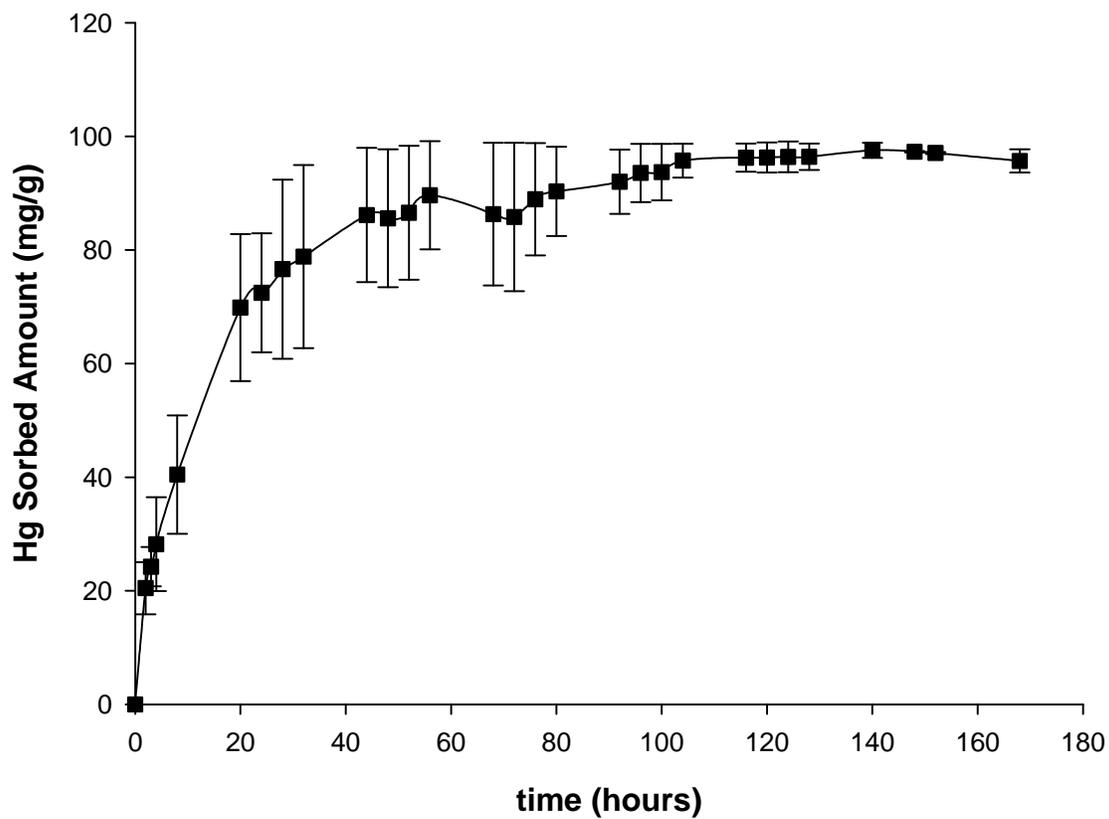


Figure 2-5. Effect of contact time on Hg sorption on Al-WTRs at 40 mg/L initial Hg concentration and pH 6.5. The values are averages (n=2) and error bars represent standard errors of the mean.

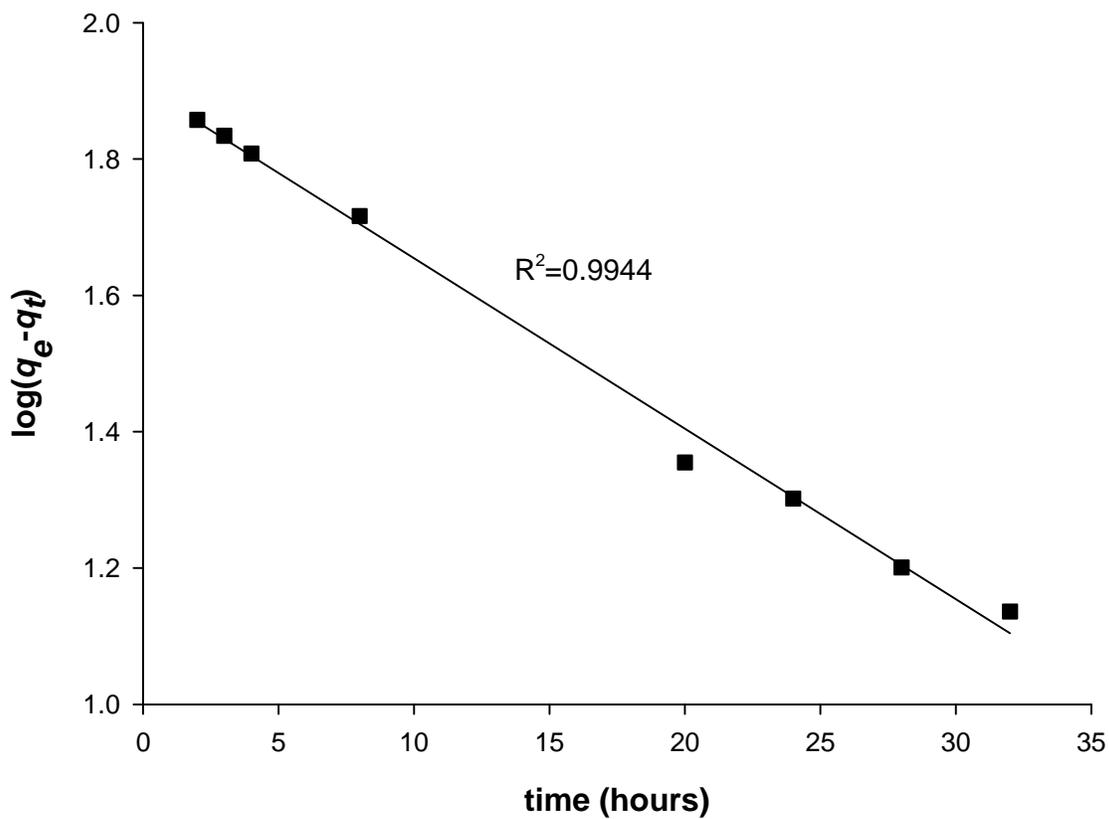


Figure 2-6. Lagergren, pseudo-first order kinetic plot for Hg sorption on Al-WTRs at initial Hg concentration of 40 mg/L and pH 6.5. Where  $q_e$  and  $q_t$  are Hg concentrations at equilibrium and at time (t) (mg/g).

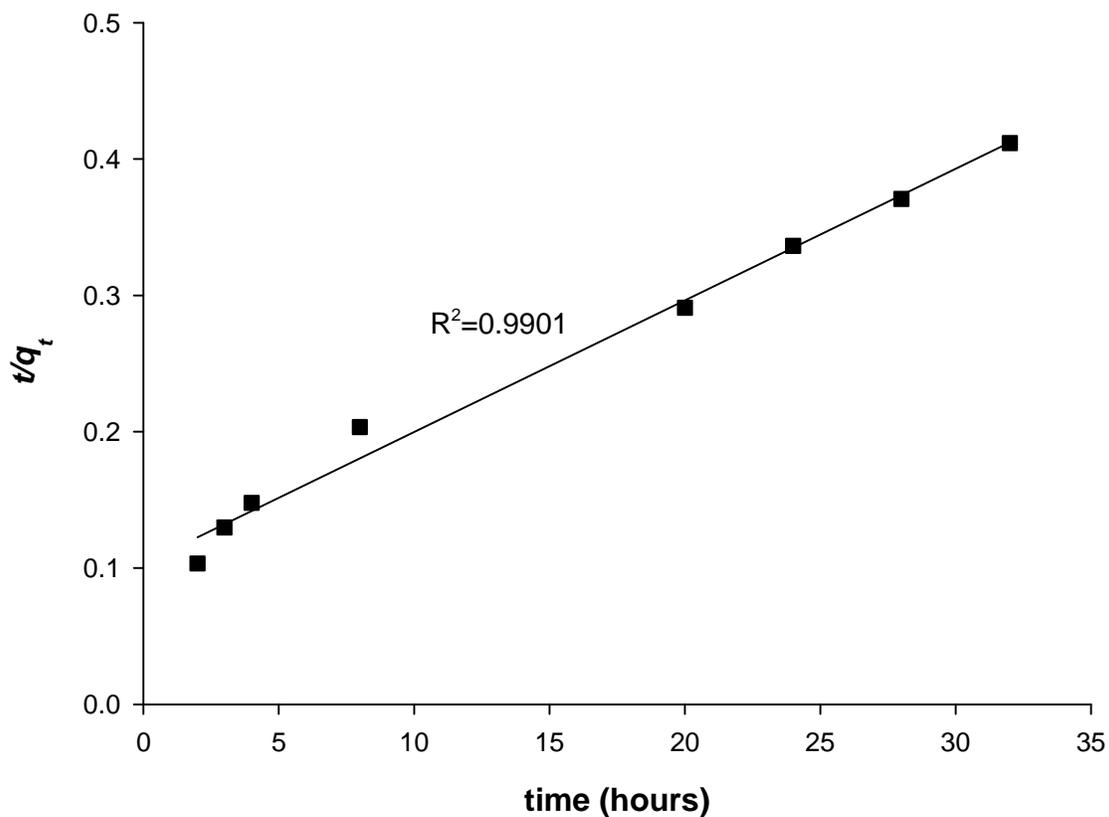


Figure 2-7. Pseudo-second order kinetic plot for Hg sorption on Al-WTRs at initial Hg concentration of 40 mg/L and pH 6.5. Where  $q_t$  is the amount of Hg adsorbed at time ( $t$ ) per unit mass of Al-WTRs (mg/g).

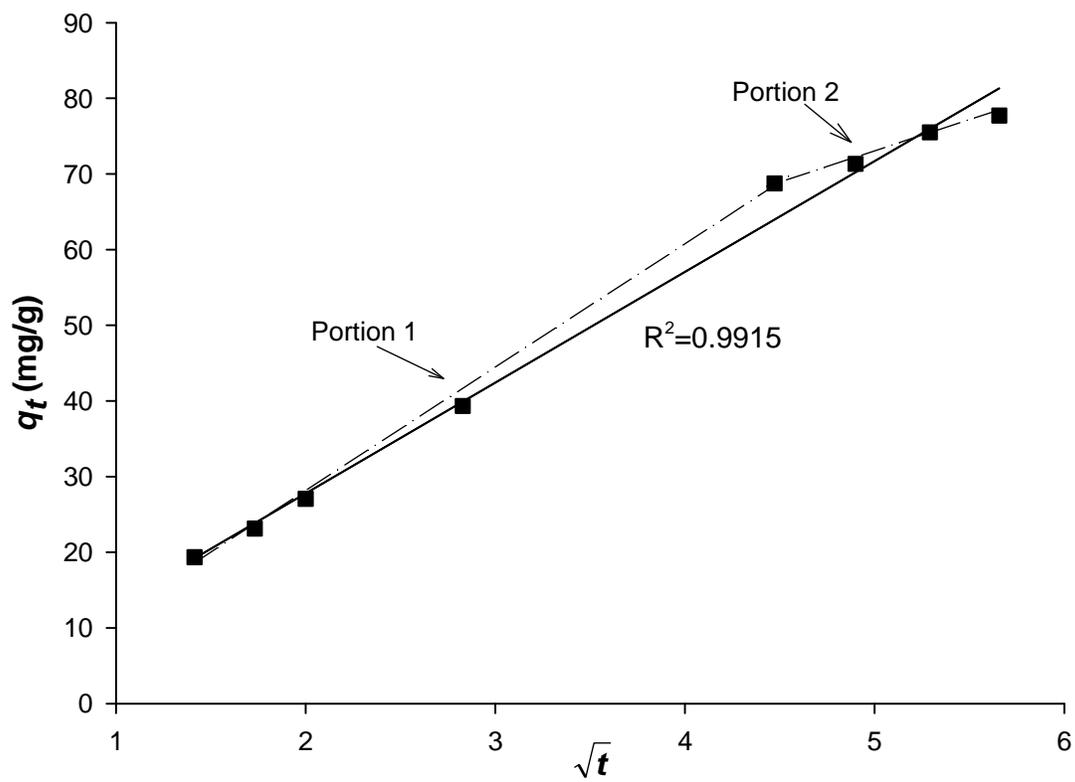


Figure 2-8. Weber and Morris intraparticle diffusion plot for Hg sorption on Al-WTRs at initial Hg concentration of 40 mg/L and pH 6.5. Where  $q_t$  is the amount of Hg adsorbed at time ( $t$ ) per unit mass of Al-WTRs (mg/g).

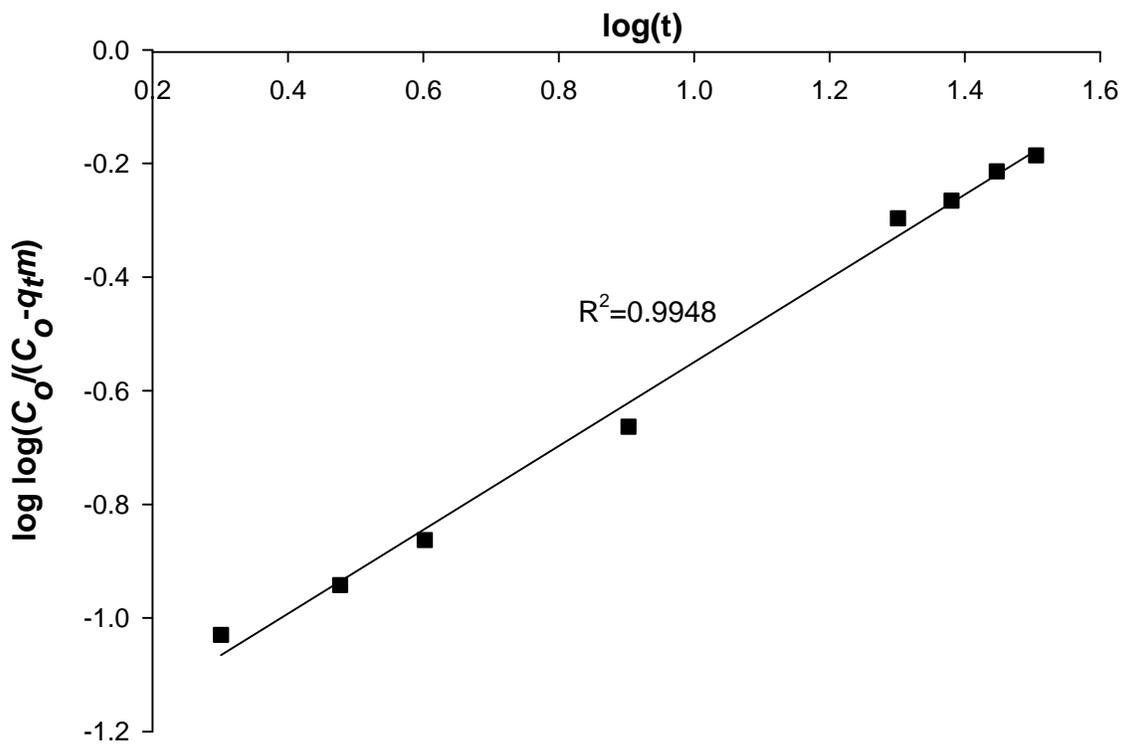


Figure 2-9. Bangham intraparticle diffusion plot for Hg sorption on Al-WTRs at initial Hg concentration of 40 mg/L and pH 6.5. Where  $C_0$  is the initial concentration of adsorbate in solution (mg/L),  $m$  is the weight of adsorbent used per liter of solution (g/L), and  $q_t$  is the amount of Hg adsorbed at time ( $t$ ) per unit mass of Al-WTRs (mg/g).

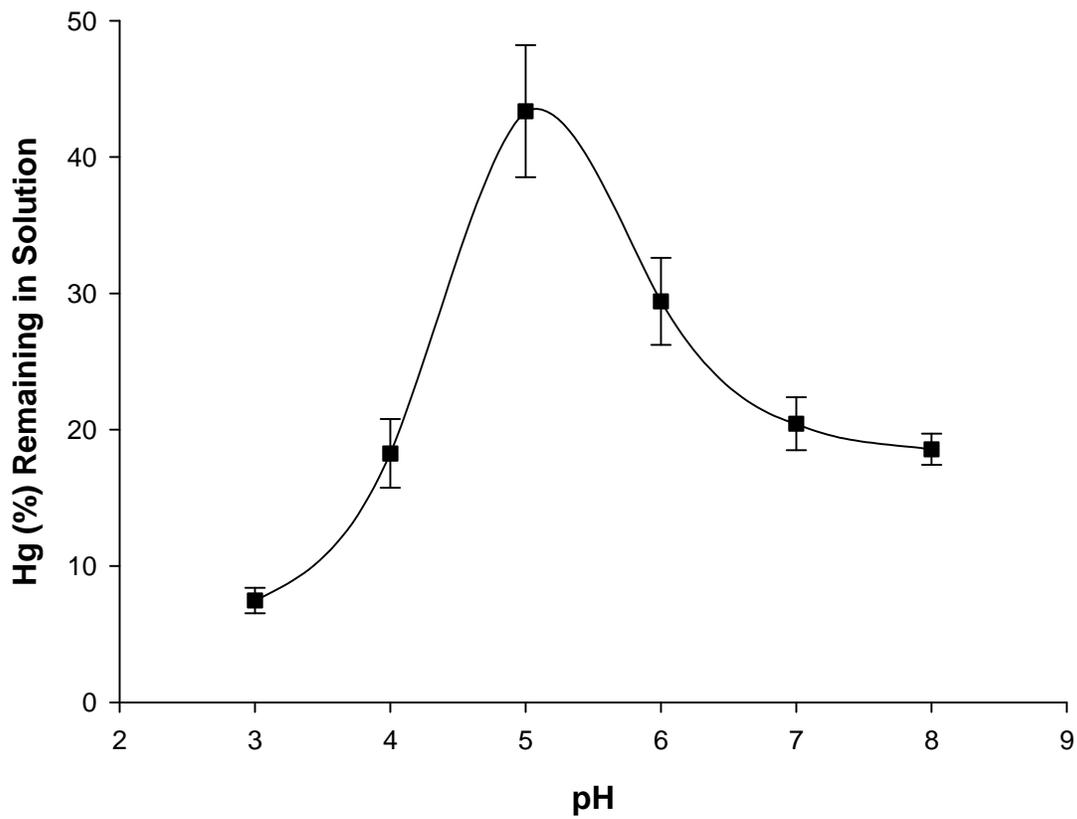


Figure 2-10. Effect of pH on Hg sorption on Al-WTRs at initial Hg concentration of 40 mg/L. The values are averages (n=3) and error bars represent standard errors of the mean.

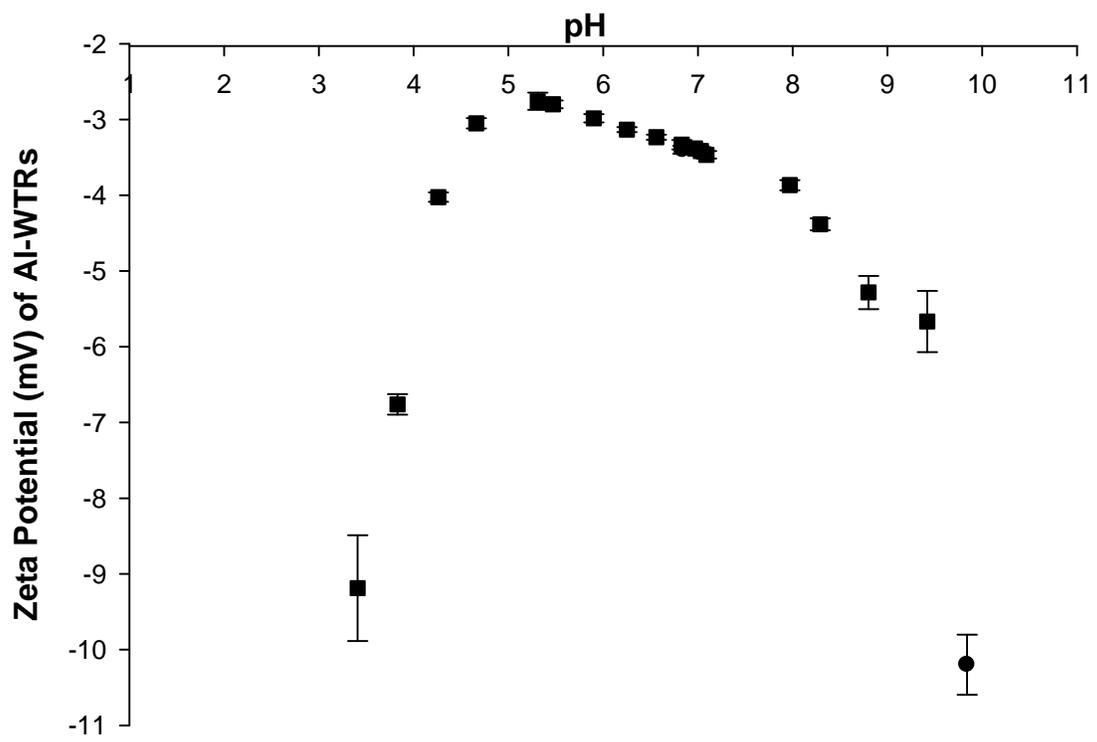


Figure 2-11. Effect of pH on Zeta Potential of Al-WTRs.

CHAPTER 3  
IMMOBILIZATION OF MERCURY IN CONTAMINATED SOILS BY ALUMINUM-  
BASED DRINKING WATER TREATMENT RESIDUALS (Al-WTRs)

**Introduction**

The average background concentration of mercury (Hg) in “pristine” soils in the United States has been estimated to be about 0.11 mg/kg (Adriano 2001; Bringmark 1997). The introduction of Hg to the environment through different anthropogenic activities increases levels of this toxic metal in the atmosphere and in both terrestrial and aquatic systems. Because of the well-established ability of Hg to bioaccumulate and biomagnify in food chains (Adriano 2001), its introduction into natural systems and the resulting environmental and health implications have been the subject of numerous investigations worldwide (Adriano 2001; Lacerda et al. 1995; Sigel and Sigel 1997). With regard to soils, anthropogenic Hg originates mainly from sources such as mine tailings, chlor-alkali plants, and diffuse sources such as emissions from coal-fired power plants and waste incinerators (D’Itri 1972; Drasch et al. 2004). For example, soils collected from gold-mining impacted sites were reported to contain total Hg (THg) concentrations ranging from 132 mg/kg to 635 mg/kg (Kim et al. 2003), while soils from areas surrounding a chlor-alkali plant had THg concentrations ranging from 4.3 mg/kg to 1150 mg/kg (Bernaus et al. 2006). Overall, Hg contamination of soils remains a worldwide problem due to either historic or present anthropogenic activities (Biester et al. 2002; Gray et al. 2002; Nriagu and Wong 1997).

The toxicity and bioavailability of Hg in soil depends greatly on Hg speciation (Bringmark 1997). Mercury present in soils occurs primarily in three different oxidation states: 0, +1, and +2 (Alloway 1995). In its elemental form ( $\text{Hg}^0$ ), Hg is poorly retained onto soil particles, and is therefore easily lost through volatilization, infiltration, and horizontal transport mechanisms (Bringmark 1997). Although not abundant, Hg is also present in soil in the +1 oxidation state in a number of Hg-minerals. While  $\text{Hg}_2\text{I}_2$ , is considered the most stable Hg(I)-mineral, several other

Hg(I)-minerals exist and most are very soluble. Examples include the following in decreasing order of solubility:  $\text{Hg}_2\text{SO}_4 > \text{Hg}_2\text{CO}_3 > \text{Hg}_2(\text{OH})_2 > \text{HgHPO}_4$ . In fact,  $\text{Hg}_2\text{SO}_4$ ,  $\text{Hg}_2\text{CO}_3$ , and  $\text{Hg}_2(\text{OH})_2$  are so soluble that they rarely precipitate in soils (Lindsay 1979). In contrast, Hg(II)-compounds are not only more stable but also the most common and the most abundant in soils (Alloway 1995; Martinez and McBride 1998). Besides the prevalent occurrence of Hg compounds in the inorganic form, soil-Hg occurs also in alkylated forms. Unlike the inorganic Hg species, alkylated Hg species, namely methyl-Hg, are produced primarily through microbial methylation of soluble and bioavailable inorganic Hg-species, while the potential for non-biological (abiotic) Hg-alkylation has been also reported under specific laboratory conditions (Adriano 2001; Alloway 1995; Bringmark 1997; Celo et al. 2006).

Mercury speciation and mobility in soils are greatly affected by certain key environmental parameters such as pH and redox conditions (Alloway 1995). The pH and pe of most soils range from 3.5 to 9 and -6 to +12; respectively (Bourg and Loch 1995). The pH is one of the most important parameters that can influence Hg adsorption to soil particles and thus its fractionation and mobility (Mulligan et al. 2001; Yin et al. 1996). In general, metals are more mobile and bioavailable under acidic conditions (Alloway 1995). In soil solution with acidic pH, positively charged (e.g.  $\text{HgCl}^+$ ) and neutral ( $\text{HgCl}_2$ ) species are formed. As the pH increases, hydroxo-Hg species such as  $\text{Hg}(\text{OH})_2$  become more predominant (Adriano 2001). Mercury chloride compounds (e.g.  $\text{HgCl}_2$ ,  $\text{Hg}_2\text{Cl}_2$ ) and hydroxo-Hg species (e.g.,  $\text{Hg}(\text{OH})_2$  and  $\text{HgO}$ ) are predominant under oxidizing conditions (Adriano 2001). Under moderately oxidizing to reducing conditions and for  $\text{pH} > 5$ , inorganic Hg can also be found in the elemental ( $\text{Hg}^0$ ) form (Schuster 1991). In addition, redox processes can induce strong acidification of soils because oxidized components are more acidic than their reduced counterparts (Bourg and Loch 1995).

Under reducing conditions in soils with high sulfur content, Hg is precipitated as Hg sulfide, which has a very low solubility (Adriano 2001; Schuster 1991). If sulfur is not available under such reducing conditions, the Hg fraction that is bound to Fe and Mn (hydr)oxides in soils may be mobilized and released to soil pore water (Bourg and Loch 1995). Studies suggest that reducing conditions are the most favorable for the formation of methyl-Hg by anaerobic bacteria (Adriano 2001; Chen et al. 1997; Compeau and Bartha 1984).

The speciation of Hg in soils is rather complex, and besides the effects of pH and redox discussed above, it is also affected by the interactions of Hg with various ligands present in soils. In fact, concentrations of free metal ions in soil solutions are mostly determined by levels of binding to the solid phase (Weng et al. 2001), and would therefore be a function of soil physicochemical composition (Bernaus et al. 2006; Lestan et al. 2003). This specific aspect controls metal adsorption-desorption reactions which occur mainly due to chemical bond formation, complex formation, and ion-exchange (Lestan et al. 2003). Accordingly, adsorption and desorption processes are of a special importance in pollutant dynamics in soils as they tend to control the fate and transport of metals including Hg in soils (Sarkar et al. 2000; Yin et al. 1996). In addition to the interactions with the solid phase, metal ions can also form complexes with dissolved organic matter and several other dissolved ligands. Therefore, the quantity and quality of dissolved organic carbon (DOC) as well as the type and abundance of inorganic soluble ligands in soil pore water tend to enhance both the solubility and mobility of Hg (Adamo et al. 2002, Weng 2002). In contaminated soils, DOC would likely act as vehicle for Hg infiltration from the surface and vadose zone soils to the groundwater.

Overall, Hg in soils may occur as: (i) dissolved (free ion or soluble complex), (ii) non-specifically adsorbed (binding mainly due to electrostatic forces), (iii) specifically adsorbed

(strong binding due to covalent or coordinative forces), (iv) chelated (bound to organic substances), and (v) precipitated (e.g. sulfides, carbonates, hydroxides, etc) species (Schuster 1991).

With regard to the remediation of metal-contaminated soils, several methods have been proposed. The advantages and disadvantages of these methods have been discussed in chapter 1, and the *in-situ* immobilization of Hg in soils through addition of sorbents is believed to be a cost-effective alternative to most conventional remediation techniques (Gray et al. 2006).

Immobilization techniques do not remove Hg from soils; but they reduce Hg mobility and bioavailability *in-situ* through adsorption processes. Preliminary investigations discussed in chapter 2 point to the ability of Al-WTRs to efficiently immobilize Hg that may leach from contaminated soils. In addition, Al-WTRs are waste by-products of water treatment facilities widely distributed nationwide. Therefore, they can be considered as low low-cost sorbents with a very high Hg adsorption capacity of ~79 mg Hg/g Al-WTRs.

In natural systems, rain is the dominant source of water, and the decrease in soil pH as a result of acid rain could increase the mobility and bioavailability of Hg (Goyer et al. 1985; Schwedt 2001). In this study, the potential of Al-WTRs to sorb and immobilize Hg from contaminated soils was assessed using column studies mimicking the effect of acid rain. The ability of Al-WTRs to reduce/eliminate the bioavailability and toxicity of Hg was evaluated through biogeochemical and toxicological approaches.

## **Materials and Methods**

### **The Al-WTRs and Soil Sample Collection, Characterization, and Site Description**

The Al-WTRs samples used in this study were collected from the Manatee County Drinking Water Treatment Plant in Bradenton, FL. The material was first air dried at room temperature for 4 weeks, and then sieved through a 2 mm screen. Selected physiochemical

properties such as pH, electrical conductivity (EC), effective cation exchange capacity (CEC), and total metal concentrations were determined. A detailed description of different characterization methods used in this study has been described earlier (chapter 2).

Two types of Hg-contaminated soils were used to investigate the ability of Al-WTRs to immobilize Hg from contaminated soil matrices. The first soil was an initially non-contaminated but Hg-spiked soil used in studies evaluating the efficiency of Al-WTRs for Hg immobilization in a freshly contaminated and low adsorption capacity soil. The non-contaminated soil was collected from the top 3 feet of the “E” horizon at the McCarty Woods of the University of Florida campus. This sandy soil was chosen because it was expected to have a high Hg leaching potential. The second type of soil used in this study came from a historically contaminated site in the Carson River watershed in Nevada. Mercury in this soil was introduced over a century ago during the 30 years of intense gold and silver mining activities of late 1800s (Gustin et al. 1994). Amalgamation with Hg was used to extract gold and silver from the ores. Unfortunately, the negative effects of Hg introduced to the Carson River watershed by mining activities became known as a serious environmental issue only several decades after the end of the intense use of Hg in gold and silver extraction by amalgamation processes. Thus, Hg accumulated in mine tailings has been redistributed throughout the Carson River watershed resulting in some of the highest environmental Hg levels reported in North America (Gustin et al. 1994). As a result, soils, surface waters, sediments, fish and wildlife in the Carson River basin are contaminated or have been affected by Hg contamination (Bonzongo et al. 1996; Lechler et al. 1997). Because of these elevated Hg levels, the Carson River watershed was placed on the National Priorities List by the US-EPA in 1990 (Gustin et al. 1994). This Hg-contaminated site offers the opportunity to obtain soil samples in which Hg has been in contact with soil particles for several decades and to

use such soil in comparison with newly contaminated materials through Hg-spiking. Soil samples from the Carson River Basin were collected with a shovel from the top 1 foot layer and placed into plastic bags. The soil samples were then shipped overnight in coolers to the University of Florida in Gainesville.

In the laboratory, all soil samples used in this study were first air-dried at room temperature and then sieved through a 2-mm screen to remove coarse debris. The non-contaminated sandy soil was spiked with a  $\text{HgCl}_2$  solution added in excess of the soil saturation level, and the mixture of soil and Hg solution was left to equilibrate for 7 days in capped plastic containers before being air dried again. At this point, the Hg contaminated soils were well homogenized and aliquot samples taken for acid digestion and determination of total-Hg concentration as described later.

The pH and the electrical conductivity (EC) of AI-WTRs and soils were measured in 1:1 (mass/volume (m/v)) and 1:2 (m/v) Nanopure<sup>®</sup> water suspensions respectively, after a 4 hr equilibration period using a pH-meter (model 240, Corning) and an EC meter (model 1054, Markson). The organic carbon content was measured according to the Walkley-Black method (Walkley and Black 1934). The effective cation exchange capacity was determined as described by Sumner and Miller (Sumner and Miller 1996). Particle size distribution of soils was determined according to the USDA Soil Survey Lab Method (USDA 1992).

For total metal analysis, about 1 g of dry soil sample was digested overnight at  $110^\circ\text{C}$  with 30 ml of  $\text{HNO}_3/\text{H}_2\text{SO}_4$  mixture (7:3, v/v) in a closed Teflon<sup>®</sup> vessel. Upon cooling, the mixture was diluted to 50 ml with Nanopure<sup>®</sup> water and analyzed for total metal concentrations by inductively coupled plasma atomic emission spectrometry (ICP-AES) and Hg by cold vapor atomic fluorescence spectrometry (CV-AFS).

The analysis of crystalline mineral phases of clay fraction of the Nevada soil was conducted by X-ray diffraction (XRD) in the soil mineralogy laboratory in the Department of Soil and Water Sciences, University of Florida on a computer-controlled X-ray diffractometer equipped with a stepping motor and a graphite crystal monochromator. Samples were scanned from  $2-60^{\circ} 2\theta$  at a rate of 2 degrees per minute using  $\text{CuK}\alpha$  radiation (Yong et al. 2001).

### **Column Leaching Studies**

**Experimental Design:** Soil columns used in this study were custom-made out of clear PVC (3.8 cm internal diameter, 30 cm length), equipped with a 2 cm drainage hole at the base and covered with netting and a layer of glass wool to prevent soil loss and to minimize the dead end volume. The columns were packed with 300 g of contaminated soil mixed with Al-WTRs to reach a final concentration of 2.5%, 5%, and 10% of Al-WTRs (mass Al-WTRs/mass soil). In columns with 2.5% and 5% treatments, Al-WTRs was uniformly mixed with the entire soil column. The 10% treatment included two incorporation schemes: (i) uniform mixing of Al-WTRs with the entire soil mass placed in the column, and (ii) Al-WTRs added as a bottom layer at the base of the column. The latter will be referred to from now on as the “liner” treatment. The experimental design resulted in four Al-WTRs treatments and a control (i.e. no Al-WTRs addition) and is summarized in Table 3-1. Soil columns were vertically held on a wooden rack placed on a lab bench. Studies using the Florida’s sandy soil were run in triplicates, while experiments with the Nevada soil were based on duplicate due to limited availability of soil samples.

**Leaching Protocol:** The US-EPA Synthetic Precipitation Leaching Procedure (SPLP) solution (EPA method 1312) obtained by dissolving 40 g of  $\text{HNO}_3$  and 60 g of  $\text{H}_2\text{SO}_4$  into 2 liters of Nanopure<sup>®</sup> water with a final pH of  $4.22\pm 0.05$ , was used as leaching solution to mimic the effect of acid rain (Townsend et al. 2005). The pore volume of packed columns was

determined by first saturating the soil within a bottom plugged column with the leaching solution and then draining out the column. The pore volume was then calculated as the difference between the volume of leaching solution added initially to the column and the volume of leachate drained out of the column. For the two soils used in this study, the determined pore volumes averaged 75 and 85 ml for the Nevada and Florida soil, respectively. Using the SPLP solution, each column was leached with 1 pore volume once a week to mimic the wet and dry cycles for rainy versus non rainy days. Following each leaching event, soil leachates were collected in acid pre-cleaned Teflon<sup>®</sup> containers, immediately filtered through 0.45 µm filters, and aliquots of the filtrate analyzed for (i) total-Hg concentrations by CV-AFS and (ii) toxicity using the MetPLATE<sup>™</sup> bioassay (Bitton et al. 1994). The Al concentrations and pH of the leachate were also measured to make sure that Al-WTRs was not a major source of soluble aluminum due to the acidic pH of the SPLP solution used.

Differences in Hg concentrations in leachates obtained from different treatments were evaluated by use of the Independent-Sample t-test with SPSS statistical software (vs. 11.0). Tests were performed at a confidence level of 95%.

At the end of the leaching experiments, soil columns were taken apart and the column contents air dried in plastic containers for post-leaching analyses of the solid phase. One gram of the material from each column was digested as described earlier and analyzed for total Hg by CV-AFS. For the columns where Al-WTRs was used as liner, soil materials from the column and sample Al-WTRs from the liner were removed, air-dried and analyzed separately.

**Toxicity of leachates:** The metal toxicity of soil leachates was assessed only on leachates collected from leaching with the first and last pore volumes by using MetPLATE™ toxicity assay (Bitton et al. 1994). MetPLATE™ is a toxicity test specific to heavy metals and is based on the inhibition of the  $\beta$ -galactosidase enzyme by metals at toxic levels in a mutant strain of *Escherichia coli* (Bitton et al. 1994). The assay was performed in triplicate with four dilutions which allowed the determination of the  $EC_{50}$ . First, 0.1 mL of bacterial reagent suspension was added to 0.9 mL of soil leachates and to negative control in culture tubes which were then incubated at 35°C for 90 minutes. Moderately hard water (60 mg/L Ca, 60 mg/L Mg, pH = 7.4-7.8) served as the negative control and it was also used to prepare the four dilutions of soil leachates. After the incubation, 0.2 mL from each tube was pipetted to a 96-well microplate and 0.1 mL of rehydrated MetPLATE™ chromogenic substrate was added to each well. The microplate was then incubated at 35°C until the purple color developed in the negative control. The  $\beta$ -galactosidase activity was evaluated by the conversion of chlorophenol red galactopyranoside to chlorophenol red, which was determined by measuring absorbance with a microplate spectrophotometer (Maxline Microplate Readers, Molecular Devices, Sunnyvale, CA) at 570 nm. The  $EC_{50}$  values of soil leachates were then calculated based on four dilutions using a regression analysis.

The toxicity unit (TU) (Bitton 1998) was used to express the metal toxicity. The TU relates to  $EC_{50}$  as shown in equation 3-1, and the higher the TU, the higher the toxicity.

$$TU = \frac{100}{EC_{50}} \quad (\text{Eq. 3-1})$$

This approach allows the expression of experimental data in terms of percent toxicity removal calculated as follows:

$$\% \text{ Toxicity Removal} = \frac{TU_{control} - TU_{treatment}}{TU_{control}} \times 100 \quad (\text{Eq. 3-2})$$

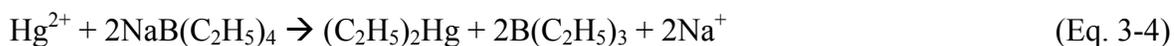
and where  $TU_{control}$  is the toxicity unit for leachate of control soils (no Al-WTRs added) and  $TU_{treatment}$  is the toxicity unit for leachate of soil with the Al-WTRs treatment.

### **Assessing the Bioavailability of Mercury in Al-WTRs Treated Soils**

At the end of the leaching experiments, aliquot soil samples were taken from the columns and used in laboratory incubations to assess the potential of the Al-WTRs treatment to limit the methylation potential of Hg. The premise behind this approach is that the formation of methyl-Hg could be used as a surrogate for bioavailability. To promote the production of methyl-Hg, thick soils slurries were prepared in pre-cleaned 50 ml glass serum bottles using Nanopure<sup>®</sup> water in a 3:1 ratio (mass/volume). The prepared slurries were first bubbled with ultra high purity nitrogen to expedite the development of anoxic conditions that favor Hg methylation (Adriano 2001), and then capped with rubber stoppers and sealed with aluminum caps. The slurries were next incubated in the dark for 10 days at room temperature. At the end of the incubation process, Hg methylation reactions were stopped by freezing (-18°C) the samples pending methyl-Hg analysis.

Methyl-Hg was first separated from the soil matrix by extraction with 15 ml of an acidic solution containing a mixture of 18% (w/v) KBr and 5% (v/v) H<sub>2</sub>SO<sub>4</sub>, and 3 ml of a 1M CuSO<sub>4</sub> solution. After shaking for 1 hour at 200 rpm and room temperature, the slurry was centrifuged at 10,000 rpm for 30 minutes and the supernatant was transferred to a different clean container. Then, 10 ml of methylene chloride (CH<sub>2</sub>Cl<sub>2</sub>) were added to the supernatant, the container tightly capped and the mixture shaken for another hour at 300 rpm at room temperature. The separation of the two liquid phases was accelerated by centrifugation. Only 2 ml out of the 10ml of CH<sub>2</sub>Cl<sub>2</sub> added initially to the sediment extract were transferred to a centrifugation tube containing 10 ml

of Nanopure<sup>®</sup> water. The mixture was next placed in a water bath at 65<sup>0</sup> C for a back extraction of methyl-Hg into the aqueous phase as the organic solvent (i.e. CH<sub>2</sub>Cl<sub>2</sub>) evaporated over time. Prior to the analysis of the aqueous sample, 8 ml of the extracted methyl-Hg solution were transferred into headspace vials. Next, 0.5 ml of 2 M acetate buffer (mixture of sodium acetate and glacial acetic acid in Nanopure<sup>®</sup> water, pH 5) was added, followed by the addition of 0.5 ml of a 1 wt % of sodium tetra-ethylborate (NaB(C<sub>2</sub>H<sub>5</sub>)<sub>4</sub>) solution for derivatization, sealed and allowed to react for 30 minutes (Leermakers et al. 2005). This overall process was adapted from Bloom et al. (1997), in which Hg species are converted to highly volatile alkyl-species except for Hg<sup>0</sup> (Equations 3-3 and 3-4).



Methyl-Hg was then determined using headspace gas chromatography separation of different volatile Hg species (Hg<sup>0</sup>, H<sub>3</sub>C-Hg-C<sub>2</sub>H<sub>5</sub>, and (C<sub>2</sub>H<sub>5</sub>)<sub>2</sub>Hg), followed by thermo-decomposition to produce elemental Hg from the separated Hg species, and then detection by atomic fluorescence spectrometry at 253.7 nm. All tests were run in triplicates to allow the determination of statistical differences between treatments. The differences in methyl-Hg concentrations in treatments were evaluated by use of the Independent-Sample t-test with SPSS statistical software (vs. 11.0) at a confidence level of 95%.

### **Chemical Fractionation of Mercury in Used Soils.**

The chemical fractionation of Hg was conducted only on soil collected from Nevada. Samples (~1g) of air-dried soil were extracted sequentially using a procedure adapted from Tessier et al. (1979). The following fractions were targeted and all extractions were carried out in triplicate.

**Fraction 1 (F1), Water Soluble:** One gram of soil was extracted at room temperature with 8 ml of Nanopure<sup>®</sup> water for 3 hours with continuous agitation at a rate of 200 rpm. Following the agitation step, the mixture was centrifuged at 10,000 rpm for 30 min (Beckman J2-HS, Tritech Field Eng. Inc.) and the supernatant removed with a pipette. Next, the residue was rinsed with 8 ml of Nanopure<sup>®</sup> water for 5 minutes and the mixture centrifuged again at 10,000 rpm for 30 min. The supernatant was carefully withdrawn and added to the first supernatant fraction. The combined supernatant was then filtered (0.45 $\mu$ m) and used for the analysis of total-Hg. The solid residue was then used in the next extraction step. Besides the extraction step, the centrifugation, rinsing, and filtration steps were identical for all fractions (F1 to F5), except for F6.

**Fraction 2 (F2), Exchangeable:** The residue from F1 was treated with 8 mL of 1M magnesium chloride (MgCl<sub>2</sub>, pH 7). The mixture was agitated on at 200 rpm at room temperature for 1 hour, prior to centrifugation, rinsing, and filtration as described in F1.

**Fraction 3 (F3), Bound to carbonates:** The residue from F2 was extracted with 8 mL of 1M sodium acetate (NaOAc) solution with a pH adjusted to 5.0 with acetic acid (HOAc). The mixture was agitated on an orbital shaker at 200 rpm at room temperature for 5 hours, prior to centrifugation, rinsing, and filtration.

**Fraction 4 (F4), Bound to Fe-Mn oxides:** The residue from F3 was extracted with 20 ml of 0.04 M hydroxylamine hydrochloride (NH<sub>2</sub>OH.HCl) in 25% (v/v) HOAc in containers placed in a water bath for 6 hours at 96  $\pm$  3 $^{\circ}$ C, with occasional agitation by hand. Upon cooling, the mixture was centrifuged, rinsed, and the supernatant filtered as described in F1.

**Fraction 5 (F5), Bound to organic matter:** The residue from F4 was extracted with 3 mL of 0.02 M nitric acid (HNO<sub>3</sub>) and 5 mL of 30% hydrogen peroxide (H<sub>2</sub>O<sub>2</sub>) that had pH adjusted to 2 with HNO<sub>3</sub>. The mixture was heated to 85  $\pm$  2 $^{\circ}$ C in a water bath for 3 hours with

intermittent agitation by hand. An additional 3 mL of 30% H<sub>2</sub>O<sub>2</sub> (pH adjusted to 2 with HNO<sub>3</sub>) was added and the mixture heated for an additional 3 hours at 85 ± 2°C. Upon cooling, and to prevent the adsorption of extracted Hg onto oxidized Al-WTRs components, 5 mL of 3.2 M ammonium acetate (NH<sub>4</sub>OAc) in 20% (v/v) HNO<sub>3</sub> was added and the sample diluted to 20 mL and agitated continuously for 30 min on an orbital shaker at 200 rpm. These steps were then followed by centrifugation and filtration as described in F1.

**Fraction 6 (F6), Residual:** The residual fraction was quantified by subtracting the sum amount of Hg obtained in fractions F1-5 from the amount of Hg obtained from the total Hg analysis.

The determination of total Hg in supernatants were conducted comparatively by inductively coupled plasma atomic emission spectrometry (ICP-AES) and cold vapor atomic fluorescence spectrometry (CV-AFS), following overnight digestion with bromine monochloride (mixture of KBr and KBrO<sub>3</sub> dissolved in concentrated HCl) at room temperature.

## **Results and Discussion**

### **Column Leaching Studies: General Characteristics**

The main physicochemical characteristics of Al-WTRs were presented earlier in chapter 2 (Table 2-1), and were found to be rather similar to Al-WTRs composition reported in the literature by other researchers (Dayton and Basta 2001; Dayton et al. 2003; Hyde and Morris 2000; Makris et al. 2004b; Makris et al. 2005).

The two soils used in this study differed in their physicochemical properties (Table 3-2). Based on the United States Department of Agriculture (USDA) soil texture triangle, the Florida's soil can be characterized as "sand" and the Nevada soil as "sandy loam" (Schwedt 2001). The average measured pH for Florida sandy soil was 6.4, while the Nevada soil had an average pH of 7.2; falling within the 5-7 and 7-9 pH ranges characteristic of humid and arid regions,

respectively (Alloway 1995; Essington 2003). Thus, in arid regions rainfall is not heavy enough to leach out basic cations such as  $\text{Ca}^{2+}$  and  $\text{Mg}^{2+}$  from soils and these soils exhibit high CEC (Bourg and Loch 1995; Schwedt 2001). The high CEC of Nevada soil could be attributed to the presence of secondary clay minerals such as montmorillonite in the composition of the soil as determined by the X-ray diffraction analysis (data not shown) (Sparks 1995). In contrast, in humid regions, basic cations are mainly leached from the soils and the cation exchange sites are occupied by acidic ions such as hydrogen and aluminum (Bourg and Loch 1995; Schwedt 2001). Hence, pH in sandy soil of this study was lower than in Nevada soil.

A total of 13 and 11 pore volumes of SPLP solution were used for the Florida and Nevada soils, respectively in leaching events that extended over a period of 13 weeks. The pH of leachate solutions obtained from Nevada soil varied from 7.46 to 8.39 and did not differ significantly among treatments. Thus, the pH of collected leachate solutions were always  $>4.2$  (pH of SPLP solution), indicating the high buffering capacity of the tested Nevada soil.

The pH values of leachates obtained from Florida soil columns ranged from 5.12 to 6.48 and did not differ significantly among treatments. Used Florida's soil did not have a high buffering capacity and was characterized by a low CEC. In such soils, acid rain may cause an increase in acidity of the soil over time. Soil acidification enhances heavy metal solubility, promoting leaching into deeper soil horizons (Adriano 1992; Adriano 2001).

### **Florida Sandy Soil**

**Mercury leached from columns packed with Hg-spiked Florida sandy soil:** Overall, Al-WTRs amended Florida's sandy soil showed consistently low levels of Hg in leachates in comparison to control columns, i.e. columns with no Al-WTRs addition. In fact, throughout the whole study, the Al-WTRs treated columns leached out significantly lower amounts of Hg compared to the control columns (no Al-WTRs). With the first pore volume, leachates collected

from soil columns amended with Al-WTRs at application rates of 5 and 10%, contained Hg levels 3 to 4 orders of magnitude lower than Hg levels measured in leachate obtained from control columns (no Al-WTRs) (e.g. 0.03 mg/L for the liner, 102 mg/L for control) (Figure 3-1). In fact, the first pore volume removed approximately 27% of Hg from control columns, corresponding to a Hg concentration about 4.5 times higher than the 2.1 mg/kg criteria for leachability of Hg to groundwater (FDEP 2005). Subsequent leaching resulted in much lower Hg outputs, which decreased progressively over time with subsequent leaching step. For the first 5 pore volumes, the effect of the “liner”, 10%, 5%, and 2.5% Al-WTRs on Hg immobilization differed significantly among each other, with the “liner” treatment having the lowest THg concentration in the leachate, followed by 10%, 5%, and 2.5% Al-WTRs application rates. From the time of the application of the 6<sup>th</sup> pore volume, there was no significant difference between the 2.5% and 5% treatments. However, the 10% and “liner” treatments performed slightly better than 2.5% and 5% treatments (Figure 3-2). After the last leaching event with the 13<sup>th</sup> pore volume, the amount of Hg removed from all columns became lower than the action limit for Florida groundwater leachability criteria (2.1 mg/kg) (Figure 3-3). However, even at this point, control columns still released significantly higher Hg levels as compared to Al-WTRs treated columns ( $p < 0.05$ ) (Figure 3-2(A) and Figure 3-3).

From all the treatments tested, the 5% application rate was found “ideal” for Florida sandy soil. The 2.5 % may not be recommended for low adsorption capacity soils as it fails to significantly remove Hg from pore water with up to 4.28 mg Hg/L leached out by the first 85 ml (or 1<sup>st</sup> pore volume) as compared to 0.9 and 0.06 mg/L for columns with 5% and 10% Al-WTRs application rates, respectively. Even though the 10% and the “liner” treatments had leached out lower Hg amounts than the 5%, the actual difference between the 10% and 5% treatments was

only ~0.3 mg/kg over the course of the entire experiment. This may not be significant from a pollution prevention viewpoint, and based on trends of Hg concentrations in collected leachates, one would anticipate that on a long-term basis, soil columns treated with Al-WTRs at 5% and 10% application rates would have a similar efficiency with regard to Hg immobilization. Although efficient, it would be costly to implement the liner approach *in-situ*, as the excavation of the contaminated soil layer would be required prior to the installation of the Al-WTRs liner.

Mercury was added in Florida sandy soil as  $\text{HgCl}_2$ . In fact, chloride ( $\text{Cl}^-$ ) occurs in natural soil systems and may be regarded as one the most mobile and effective complexing agents for Hg (Adriano 2001; Schuster 1991). Chloride forms highly soluble Hg-complexes (e.g.  $\text{HgCl}_2$ ) resulting in limited sorption and high mobility in porous and saturated media (Adriano, 1986; Schluter 1997). This limitation of Hg sorption by  $\text{Cl}^-$  in soils is especially pronounced under acidic pH, where Hg complexes with chloride (e.g.  $\text{HgCl}^+$  and  $\text{HgCl}_2$ ) dominate, in contrast to alkaline pH conditions which are favorable to hydroxo-Hg species (e.g.  $\text{Hg}(\text{OH})_2$ ) (Adriano 2001). The influence of  $\text{Cl}^-$  on Hg sorption by Al-(hydr)oxides has been investigated by several authors (Kim 1995; Meagher and Heaton 2005), and their findings support the fact that the formation of  $\text{HgCl}_2$  limits Hg sorption (Backstrom et al. 2003; Kasprzyk-Hordern 2004). Because of the prevalence of amorphous aluminum (hydr)oxides in the structure of Al-WTRs, the reactivity of Al-WTRs has been found to be rather similar to reactivity of Al-(hydr)oxides. However, our results suggest that when Hg is applied to soil as  $\text{HgCl}_2$ , Al-WTRs was able to immobilize a significant amount. These results point out the effectiveness of Al-WTRs and indicate that the behavior of Al-WTRs incorporated in soils may not be similar to that of Al-(hydr)oxides. It is therefore hypothesized that Al-WTRs would do even better with most particle reactive Hg species.

Finally, the analysis of the different leachate fractions for dissolved aluminum resulted only in values below the detection limit ( $<10\mu\text{g/L}$ ) of the ICP-AES used in this study.

**Toxicity of leachates obtained from Florida sandy soil columns:** Another approach in the assessment of the efficiency of Al-WTRs to immobilize Hg from contaminated soils is to evaluate the toxicity of soil leachates. MetPLATE™ has been used successfully to assess the potential toxicity of environmental samples such as raw water, wastewater, soils, sediments, and solid wastes (Bitton et al. 1994; Boularbah et al. 2006). The use of MetPLATE™ on selected leachates (i.e. leachates corresponding to the first and last pore volumes) obtained in this study helped accomplish this goal. Based on toxicity tests performed on the first pore volume leachates, the control (no Al-WTRs added) showed the lowest  $EC_{50}$ , which indicates the highest toxicity (Table 3-3). This result is in agreement with the results of the chemical analyses, in that the first pore volume leachate in control treatments had the highest Hg concentrations. The  $EC_{50}$  for the control treatment was used to calculate the toxicity removal by Al-WTRs in treated soils (Eq. 3-1 and 3-2). The  $EC_{50}$  values for the liner treatment and 10% Al-WTRs were  $>100\%$ , which implies no detectable toxicity effect. For all the treatments, the results indicated that the liner and 10% treatments resulted in the highest toxicity removal, followed in a decreasing order by soils with 5%, and 2.5% Al-WTRs application rates. In contrast, the toxicity of leachates resulting from the 13<sup>th</sup> (last pore volume) was too low ( $EC_{50}>100\%$ ). Overall, the MetPLATE™ results suggest that the application of Al-WTRs to Hg contaminated soils not only reduces the Hg concentration in leachates but also the toxicity, and therefore the bioavailability of Hg in the soil leachates.

**Mercury bioavailability in Florida sandy soil treated by Al-WTRs:** The effect of different Al-WTRs treatments on Hg methylation potentials in soil slurries is shown in Figure 3-

4. A significant difference in the potential for methyl-Hg production was observed between the control and the 3 Al-WTRs treatments (i.e. 2.5% ( $p=0.03$ ), 5% ( $p=0.04$ ), and 10% ( $p=0.03$ )). On average, produced methyl-Hg levels in control samples were one order of magnitude higher than the Al-WTRs treated-soils (Figure 3-4). Additionally, methylated-Hg represented  $\sim 0.11\%$  of the total-Hg concentration in control soils as compared to only 0.04 to 0.06% in the different Al-WTRs treated soils.

In general, rates of Hg methylation by microbial populations in soils and sediments depend on a variety of factors including pH, redox potential, temperature, nutrient availability, and Hg speciation (Baldi 1997; Han et al. 2007). Also, the ability of a given soil to release Hg in pore waters would tend to control rates of methyl-Hg production as the concentrations of methyl- and total-Hg have been found to correlate very well in pore waters (Biester et al. 2000). The results of these rather short-term experiments tend to suggest that the addition of Al-WTRs does significantly limit the production of methyl-Hg, by controlling Hg bioavailability to Hg-methylating bacteria.

### **Nevada Soil**

**Mercury leached from columns packed with the Nevada soil:** In contrast to the Hg-spiked Florida sandy soil where the amount of leached Hg decreased progressively with the number of pore volumes used, the concentration of Hg in leachates obtained from columns packed with the Nevada soil fluctuated within each treatments (Figure 3-5). On average, control columns leached out a higher Hg level than Al-WTRs treated soils. However the results were not statistically different, except for the liner treatment ( $p = 0.04$ ) (Figure 3-6). This could be due to the high variability of Hg leached out from control columns (Figure 3-6), which could be attributed to the non-uniform distribution of Hg in used soil. Once again, the liner treatment was the most effective. Overall, the Hg fraction removed from soil via leaching was very small as

compared to the total-Hg concentration. Therefore, Hg downward transport to groundwater in this soil would be negligible as illustrated by leachate Hg concentrations less than the 0.02 mg/L Hg maximum contaminant level for Hg under the Safe Drinking Water Act (US-EPA 2003a). Accordingly, the use of AI-WTRs in this type of soil would be recommended only for preventive purposes in case the stability of Hg-complexes present in soils become disturbed by changes in key environmental parameters.

The limited amount of leachable Hg indicates that Hg in Nevada soil is strongly associated with soil particles. The results of chemical fractionation studies carried out according to a procedure modified from Tessier et al. (1979), showed that the  $91.6 \pm 30$  mg Hg/kg of this used Nevada soil were distributed as follows: water soluble (0.08%), exchangeable (0.79%), carbonate (0.06%), iron/manganese bound fractions (0.16%), organic bound (2.74%), and with 96.2 % of total Hg is in the residual fraction. Hg in this Nevada soil was introduced primarily in the elemental form more than a century ago. Because of the limited rainfall amount in the arid climate characteristics of Nevada, Hg was not mobilized immediately. Over time, a significant fraction of the initial  $\text{Hg}^0$  underwent oxidation producing reactive Hg species and resulting in the formation of stable Hg-compounds. Following the interactions between Hg and soil constituents in combination with aging over time, the amount of leachable Hg diminished (Alexander 1995; Cruz-Guzman et al. 2003; Oorts et al. 2007). Mercury in tested Nevada soil could be present as insoluble minerals (e.g.  $\text{HgS}$ ) or trapped in the pores of soil particles as shown in speciation studies using samples collected from sites impacted by 19<sup>th</sup> century gold mining in the Californian Sierra Mountains (Meng et al. 1998; Yin et al. 1997). In this case, the authors found that 92 to 98% of total Hg was associated with fractions representing Hg in mineral lattice and as mercury sulfides (Bloom et al. 2003; Kim 1995).

Finally, and similar to the Florida's soil data, the analysis of collected leachate fractions for dissolved aluminum resulted only in non detectable levels (detection limit <10µg/L).

**Toxicity of leachates obtained from Nevada soil columns:** For the Nevada soil, the EC<sub>50</sub> values could not be calculated because of the low toxicity (EC<sub>50</sub>>100%), suggesting that Hg in this soil was strongly associated with soil constituents and not bioavailable.

**Mercury bioavailability in Nevada soil treated by Al-WTRs:** The effect of different Al-WTRs treatments on Hg methylation potential in tested Nevada soil is shown in Figure 3-7. Unlike the statistically significant difference observed between Hg-methylation potentials in control and Al-WTRs treatments in Florida's soil, studies with the Nevada soil show no significant difference between Hg-methylation potentials in control and Al-WTRs treated samples. However, on average the control treatment had a much higher methyl-Hg production potential. The methylated Hg fraction in this soil versus the different types of treatments ranged from 0.008 to 0.017% of the soil total-Hg concentration. Overall, the strong association of Hg to Nevada's soil particles seems to control its fate with regard to methylation. This is illustrated by the lack of a significant difference in methyl-Hg levels produced in control and Al-WTRs treated soils. In addition to Hg trends in leachates and the toxicity results described earlier, these Hg-methylation data confirm the fact that Hg speciation in the Nevada soil would downplay the efficiency of the proposed Al-WTR in *in-situ* remediation approach. In fact, despite the high total-Hg concentration in this Nevada soil, the easily leachable fraction is very negligible, and therefore, not ideal for the investigation of the efficiency of Al-WTRs to immobilize Hg, as stated in the objectives of this research.

## Conclusions

The mass balance of Hg in the Florida and Nevada soils is presented in Tables 3-4 and 3-5 and data are expressed in mg of Hg per 300 g of soil (amount of soil in each column). For the Nevada soil, the distribution of Hg was not uniform as illustrated by the large standard deviation of total Hg data and low % recoveries. This may be representative of the actual field conditions where Hg is not evenly distributed. In contrast, Florida soil was artificially contaminated, resulting in rather equally distributed amounts of Hg in soil.

The biogeochemical cycling of Hg in the soil is very complex and depends on a variety of factors such as soil composition, microbial processes, climate, pH and redox conditions (Kim 1995; Lindqvist et al. 1991). The bioavailability, mobility, and chemical reactivity of metals are often associated with their distribution among soil fractions (Tu et al. 2001). In general, a decrease in soil pH improves the solubility and availability of metals. Also, metals are more available in sandy soils as demonstrated in our study.

The results of this study demonstrated that leachability of Hg in Al-WTRs treated soils is significantly reduced compared to non-treated soil, despite the fact that Hg was complexed with chloride and the soil leached with an acidic solution (pH 4.2). Mercury in Nevada soil was strongly associated with soil particles and was not highly mobile. Therefore, the application of Al-WTRs to soil where Hg is present primarily in the residual/refractory fraction may not be an efficient remediation approach, unless used for a passive and long-term preventive measure. The biogeochemistry and chemical speciation of Hg in the contaminated soil should be investigated prior to choosing Al-WTRs as remediation technique.

Table 3-1. Experimental design for column studies with soil weight in each column of 300 g

Treatment	Control	2.5%	5%	10%	Liner
Al-WTRs ratio to soil <sup>a</sup>	None	1:40	1:20	1:10	1:10
Incorporation Method	N/A <sup>b</sup>	Mixed uniformly with an entire column	Mixed uniformly with an entire column	Mixed uniformly with an entire column	Applied at the bottom of a column as a liner

<sup>a</sup> Mass Al-WTRs/mass soil; <sup>b</sup> N/A=Not Applicable

Table 3-2. Physicochemical characteristics of soils used in column leaching studies

Characteristics	Florida's sandy soil	Nevada's soil
pH <sub>a</sub>	6.4±0.16	7.2± 0.09
Electrical Conductivity <sub>a</sub> (dS/m)	0.02±0.003	0.073±0.001
CEC (cmolc/kg)	7.7	85.4
% Organic carbon	0.08	0.21
% Sand	95.4	61.6
% Silt	2.9	31.6
% Clay	1.7	6.8
Hg (mg/kg) <sub>a</sub>	121.8±19 <sub>b</sub>	91.6±30 <sub>c</sub>

<sup>a</sup> Mean of triplicates ± one standard deviation; <sup>b</sup> Total-Hg concentration after spiking with HgCl<sub>2</sub> solution and air drying; <sup>c</sup> Nevada soil was not spiked

Table 3-3. Toxicity of Florida's sandy soil leachate collected from the 1<sup>st</sup> pore volume as determined by the MetPLATE™ toxicity test.

Al-WTRs Treatment	EC50 of soil leachates (%) <sup>a</sup>	Toxicity units (TU) of soil leachates <sup>c</sup>	Toxicity removal (%)
Bottom liner	>100 <sup>b</sup>	<1 <sup>c</sup>	100
10%	>100	<1	100
5%	7.92 <sup>d</sup>	12.6	98.7
2.5%	3.8±1.4	28±7.7	97.2
0% (Control)	0.1±0.02	1005±217	n/a <sup>e</sup>

<sup>a</sup> Mean of 3 replicates ± one standard deviation; <sup>b</sup> EC<sub>50</sub>>100% implies no toxicity;

<sup>c</sup> TU=100/EC<sub>50</sub>; <sup>d</sup> Standard deviation not reported. Only one replicate exhibited toxicity;

<sup>e</sup> not-applicable

Table 3-4. Mass balance of Hg in column studies using Florida's sandy soil. The initial total Hg (THg) mass was 36.5± 5.8 mg in each column, corresponding to a concentration of 121.8±19 mg/kg. Soil remaining in columns was analyzed after leaching with 13 pore volumes using SPLP solution

	Control (0% Al- WTRs)	Soil +2.5% Al-WTRs	Soil +5% Al-WTRs	Soil +10% Al- WTRs	Soil +10% Al-WTRs as liner
THg left in each soil column (mg) <sup>a</sup>	23.4±1.0	31.7±8.2	29.8±8.7	37.5±7.2	25.3 ±0.9
THg in leachate (mg) <sup>a</sup>	10.21±0.6	0.43±0.03	0.123±0.0 08	0.026±0.0 01	0.020±0.00 9
THg in Al-WTRs liner (mg) <sup>a</sup>	N/A	N/A	N/A	N/A	7.2±0.4
% Recovery	92% <sup>b</sup>	88% <sup>b</sup>	81% <sup>b</sup>	103% <sup>b</sup>	89% <sup>c</sup>

<sup>a</sup> Mean of triplicates ± one standard deviation;

$${}^b \%Hg \text{ Recovery} = \frac{(THg_{\text{column soil after leaching}} + THg_{\text{leached}}) \times 100}{THg_{\text{soil}}};$$

$${}^c \%Hg \text{ Recovery} = \frac{(THg_{\text{column soil after leaching}} + THg_{\text{in Al-WTRs-lining}} + THg_{\text{leached}}) \times 100}{THg_{\text{soil}}}$$

Table 3-5. Mass balance of Hg in column studies using Nevada’s soil. The initial total Hg (THg) mass was 36.5±5.8 mg in each column, corresponding to a concentration of 91.6±30 mg/kg. Soil remaining in columns was analyzed after leaching with 11 pore volumes using SPLP solution

	Control (0% Al-WTRs)	Soil +2.5% Al-WTRs	Soil +5% Al-WTRs	Soil +10% Al-WTRs	Soil +10% Al-WTRs as a liner
THg left in each soil column (mg) <sup>a</sup>	27.5± 9.2	26.1±2.2	33.0± 8.6	25.3± 11.3	22.7±5.9
THg in leachate (mg) <sup>a</sup>	2328±1033	799±81	357±12	324±62	56±1.3
THg in Al-WTRs liner (mg)	N/A	N/A	N/A	N/A	37411±3866
% Recovery	75% <sup>b</sup>	71% <sup>b</sup>	90% <sup>b</sup>	69% <sup>b</sup>	62% <sup>c</sup>

<sup>a</sup> Mean of duplicates ± one standard deviation;

$$^b \%Hg \text{ Recovery} = \frac{(THg_{\text{column soil after leaching}} + THg_{\text{leached}}) \times 100}{THg_{\text{soil}}};$$

$$^c \%Hg \text{ Recovery} = \frac{(THg_{\text{column soil after leaching}} + THg_{\text{in Al-WTRs-lining}} + THg_{\text{leached}}) \times 100}{THg_{\text{soil}}}$$

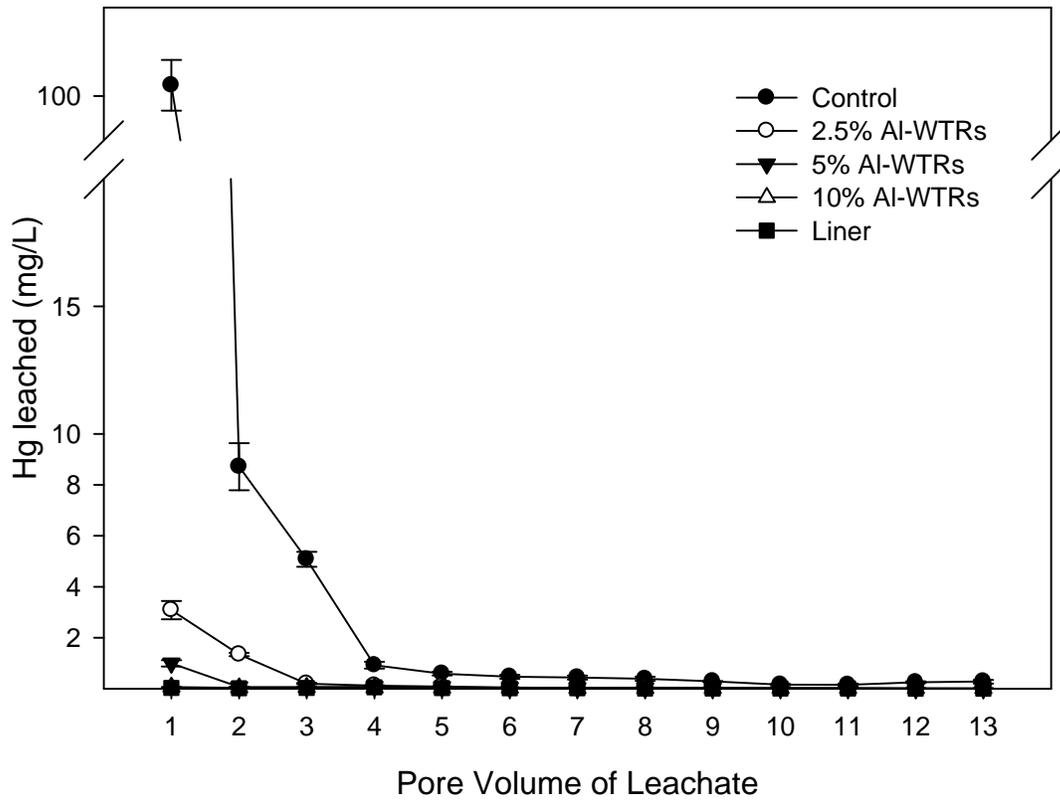


Figure 3-1. Mercury concentrations in Florida sandy soil leachates of control (no Al-WTRs) and samples treated with Al-WTRs at application rates of 2.5%, 5%, and 10%. The 10% application rate treatment had two Al-WTRs incorporation methods: (1) Al-WTRs mixed uniformly with the entire soil in the column and (2) incorporation as a liner at the bottom of the soil column (liner treatment).

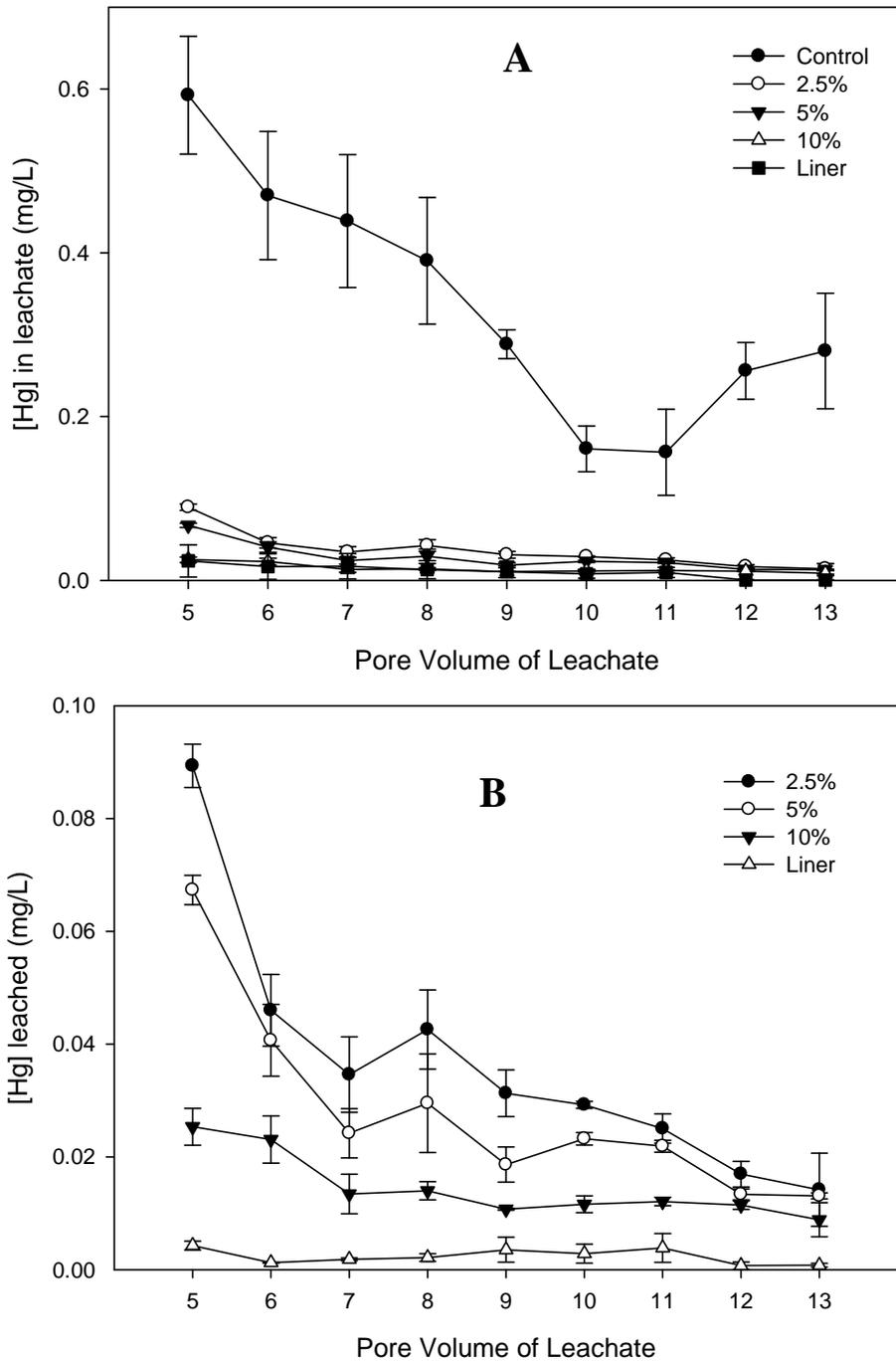


Figure 3-2. Mercury concentrations in Florida sandy soil leachates collected from the 5<sup>th</sup> to the 13<sup>th</sup> pore volume in control (no Al-WTRs) and samples treated with Al-WTRs at application rates of 2.5%, 5%, and 10%. The 10% application rate treatment had two Al-WTRs incorporation methods: (1) Al-WTRs mixed uniformly with the entire soil in the column and (2) incorporation as a liner at the bottom of the soil column (liner treatment).

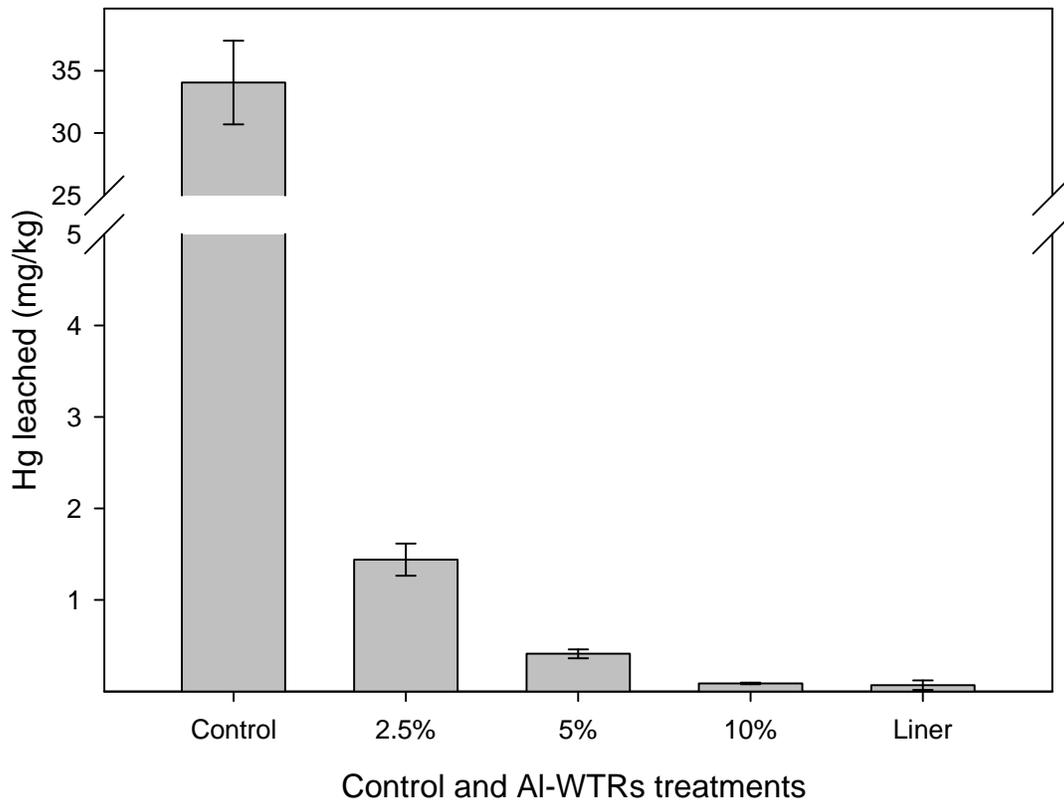


Figure 3-3. Cumulative mass of Hg leached per kg of soil from the control (no Al-WTRs) and Al-WTRs treated columns of Florida sandy soil after 13 pore volumes. Error bars represent one standard deviation of the mean.

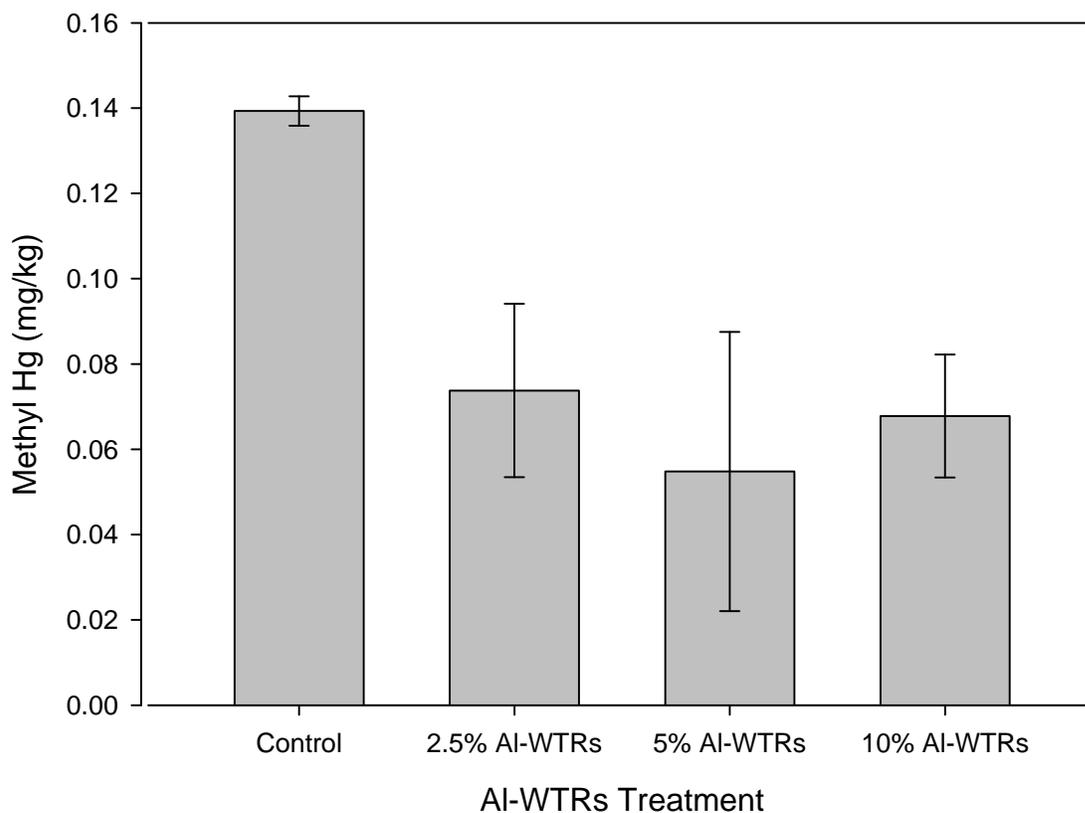


Figure 3-4. Concentrations of methyl-Hg produced in Florida sandy soil after 10 days of incubation under water saturation and anoxic conditions. On the x-axis, the control corresponds to soil without Al-WTRs addition, while shown percentages of Al-WTRs correspond to the different application rates of used Al-WTRs as treatments in column leaching experiments.

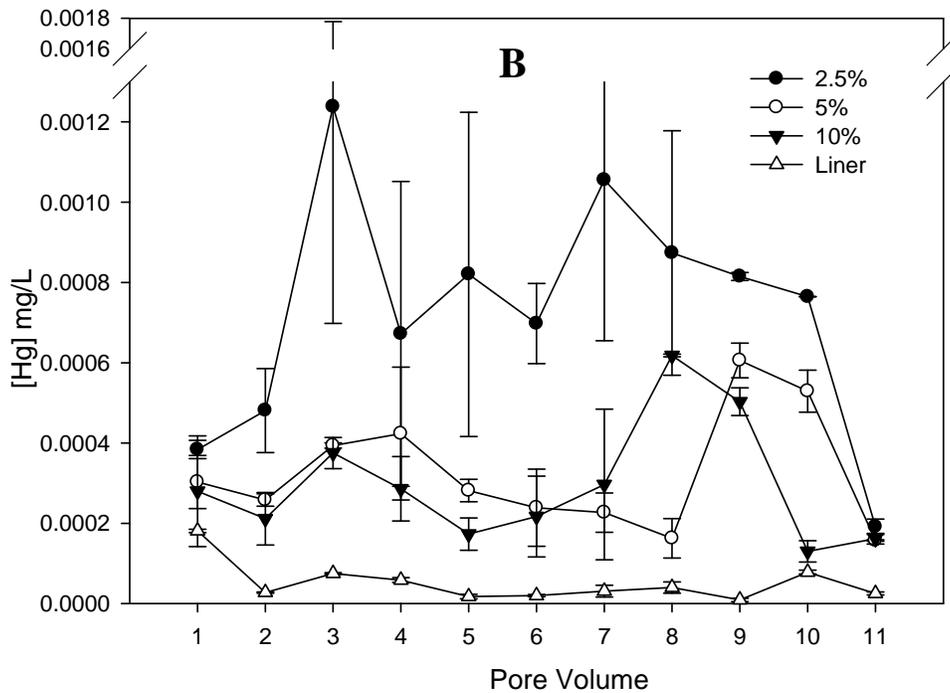
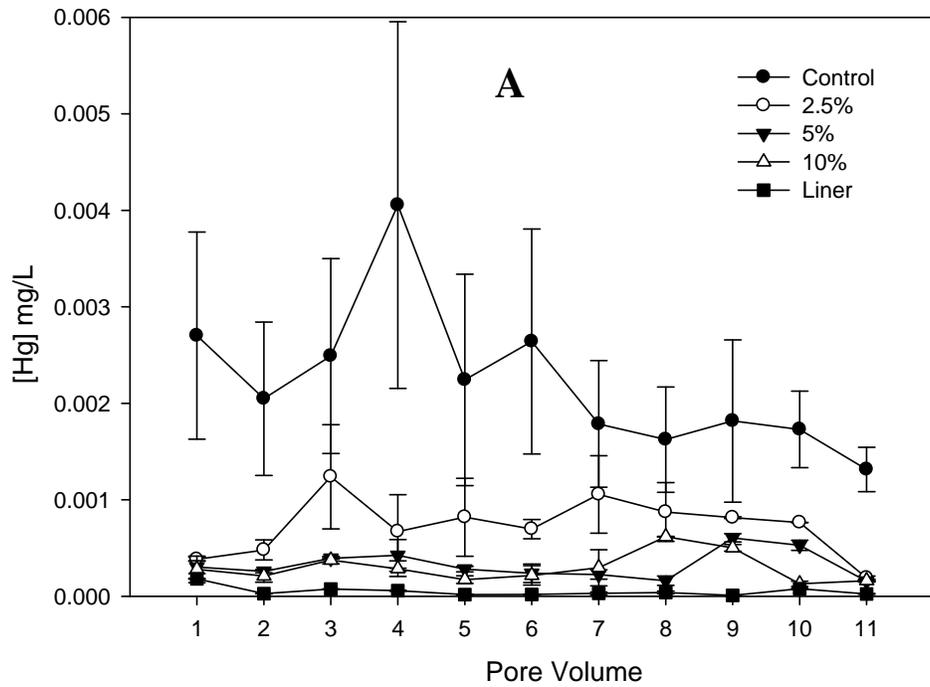


Figure 3-5. Mercury concentrations in Nevada soil leachates of control (no Al-WTRs) and samples treated with Al-WTRs at application rates of 2.5%, 5%, and 10%. The 10% application rate treatment had two Al-WTRs incorporation methods: (1) Al-WTRs mixed uniformly with the entire soil in the column and (2) incorporation as a liner at the bottom of the soil column (liner treatment).

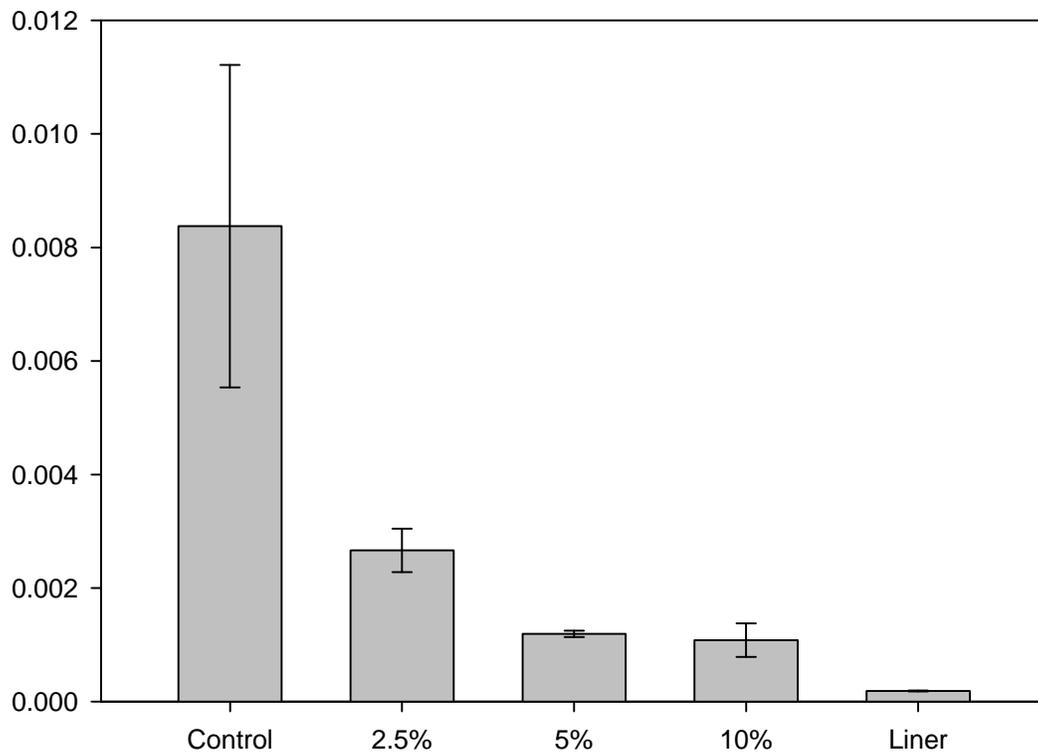


Figure 3-6. Cumulative mass of Hg leached per kg of soil from the control (no Al-WTRs) and Al-WTRs treated columns of Nevada soil after 11 pore volumes. Error bars represent one standard deviation of the mean.

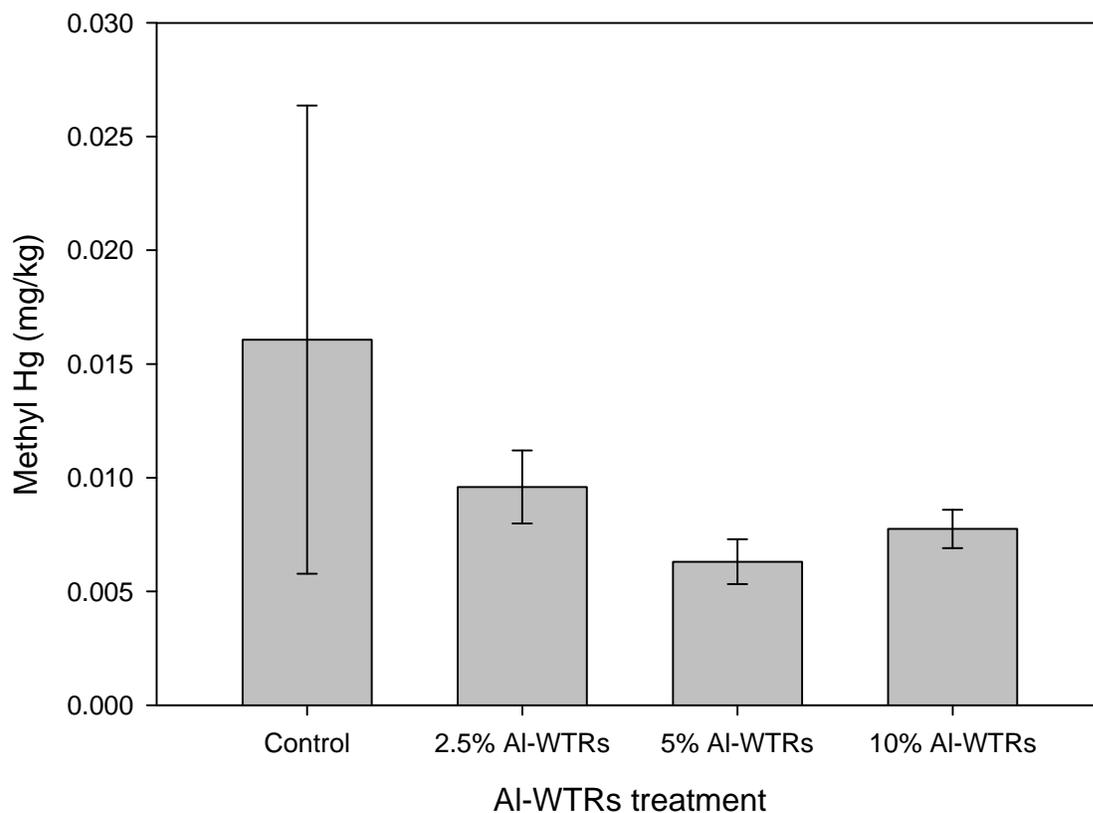


Figure 3-7. Concentrations of methyl-Hg produced in Nevada soil after 10 days of incubation under water saturation and anoxic conditions. On the x-axis, the control corresponds to soil without Al-WTRs addition, while shown percentages of Al-WTRs correspond to the different application rates of used Al-WTRs as treatments in column leaching experiments

CHAPTER 4  
DISTRIBUTION OF MERCURY SORBED ONTO ALUMINUM-BASED DRINKING  
WATER TREATMENT RESIDUALS (AL-WTRs) AND IMPLICATIONS FOR LONG-  
TERM STABILITY OF FORMED “MERCURY-AL-WTRs” COMPLEXES

**General Introduction**

The ultimate objective of this research is to establish the potential of drinking water treatment residual (Al-WTRs) to efficiently immobilize mercury (Hg) within its structure; and to determine the efficacy of Al-WTRs to form Hg-[Al-WTRs] complexes that are stable over long periods of time. If used in remediation of Hg-contaminated soils, Al-WTRs would be expected to adsorb Hg from soil pore water, and its efficiency for Hg removal from pore water and the stability of formed Hg complexes would depend on the types of Hg binding sites present in the Al-WTRs matrix. To meet the above objective, Hg distribution among different mineral and organic fractions of Al-WTRs, as well as the significance of surface versus internal sorption sites in Hg immobilization by Al-WTRs should be determined.

This study is divided into two parts. The first section uses a selective and sequential chemical fractionation approach to assess the distribution of Hg within the Al-WTRs matrix. The second part focuses on changes in sorbent's porosity due to Hg incorporation into the Al-WTRs matrix, and on the determination of Hg diffusivities into the micropores of Al-WTRs.

**Part-1: Chemical Fractionation of Mercury in Al-WTRs by Sequential Extraction**

**Introduction**

Soil contamination by Hg poses a threat to living organisms and the environment. However, the determination of total-Hg concentrations in soils is insufficient to accurately predict the environmental risks associated with Hg pollution. This is because Hg behavior and impacts in soils depend largely on its speciation (Adriano 2001; Ma and Rao 1997). The latter controls the degree of toxicity and mobility of Hg, and therefore, its bioavailability and leaching

potential from porous media (Bernaus et al. 2006; Bloom et al. 2003; Fernandez-Martinez and Rucandio 2005). In this research, it has been shown that Al-WTRs can efficiently immobilize Hg when applied to Hg-contaminated soils (chapter 3). With regard to the long-term fate of such immobilized Hg, chemical fractionation methods can be used to assess the distribution of sorbed Hg amongst the different mineral and organic fractions of Al-WTRs, and help predict the potential for leachability and bioavailability.

The distribution of Hg among the different fractions of Al-WTRs can be assessed by use of selective sequential chemical extraction procedures (Tessier et al. 1979). Although these fractionation techniques cannot identify specific compounds, they can provide much-needed information on the biogeochemical behavior of various Hg associations to both mineral and organic phases under various environmental conditions (Bloom et al. 2003). Therefore, this approach can be used to evaluate the incorporation of Hg into various fractions of Al-WTRs, and allow for the assessment of its fate (Fernandez-Martinez et al. 2006; Siegel 2002).

Selective sequential extraction techniques generally follow a procedure in which the total metal content is subdivided into several operationally defined fractions that may include (1) mobile or easily soluble fraction (e.g. water soluble compounds), (2) metal easily exchangeable through cationic substitution (e.g. exchangeable compounds), (3) metal bound to oxide minerals (e.g. associated with iron and manganese hydr(oxides)), (4) metal bound to organic matter, (5) metal present in residual fractions (e.g. mercuric sulfide) (Biester et al. 2002; Neculita et al. 2005; Tessier et al. 1979). The most bioavailable Hg is found in the easily soluble and easily exchangeable fractions. The least bioavailable Hg is generally in the residual fraction which is chemically stable over geologic time periods and represents the least toxic Hg fraction (Han et al. 2003). Chemical reagents that are used as extracting agents for each Hg-fraction are believed to

be highly “selective” in solubilizing the targeted Hg-fraction. In this study, the procedure proposed by Tessier et al. (1979), one of the most widely used metal fractionation procedures (Ayyamperumal et al. 2006; Chlopecka et al. 1996; Oygard et al. 2008) is used.

The objective of this first portion of the study is therefore to investigate the chemical partitioning of Hg in aged Hg-spiked Al-WTRs, using an operationally defined chemical fractionation procedure. This approach should allow the assessment of the potential for the long-term stability of formed Hg-[Al-WTRs] complexes, and thus the determination of the efficacy of Al-WTRs application in Hg-contaminated soils as a technique for soil remediation.

## **Material and Methods**

### **Preparation of aged mercury-spiked Al-WTRs**

A flooding approach was used in which Hg-spiked Al-WTRs were prepared by first bringing dry Al-WTRs into contact with a HgCl<sub>2</sub> solution in 1:2 ratio (m/v). The concentration of total-Hg achieved in this spiking process and determined by ICP-AES was 24,050±842 mg Hg/kg Al-WTR (n=3). Details on sample digestion and analysis are given in the “total Hg analysis” section below. Obtained slurries were then equilibrated for 7 days in closed containers in a fume hood. Next, the mixtures were allowed to dry at room temperature by opening the lid of the containers for 7 days. Following this initial step of Hg incorporation into Al-WTRs, wet and dry cycles were simulated by first saturating the Hg-[Al-WTRs] mixtures with deionized water for 5 days and then air-drying for another 5 days at room temperature. This experimental approach was designed with the intention to force Hg into the micropores of the Al-WTRs as surface sites became progressively saturated over time. After a total of 12 wet-dry cycles (~4 months), aliquots of the Hg-spiked Al-WTRs materials were used for the determination of Hg distribution among the different Al-WTRs mineral and organic fractions. The control treatment was represented by the native Al-WTRs with no Hg addition.

## **Sequential extraction procedure**

Sub-samples (~1g) of air-dried Al-WTRs samples (e.g. Hg-spiked Al-WTRs and control Al-WTRs with no Hg added) were extracted sequentially using a modified procedure originally proposed by Tessier et al. (1979). The following fractions were targeted and all extractions were carried out in triplicate.

**Fraction 1 (F1), Water Soluble:** One gram of soil was extracted at room temperature with 8 ml of Nanopure<sup>®</sup> water for 3 hours with continuous agitation at a rate of 200 rpm. Following the agitation step, the mixture was centrifuged at 10,000 rpm for 30 min (Beckman J2-HS, Tritech Field Eng. Inc.) and the supernatant removed with a pipette. Next, the residue was rinsed with 8 ml of Nanopure<sup>®</sup> water for 5 minutes and the mixture centrifuged again at 10,000 rpm for 30 min. The supernatant was carefully withdrawn and added to the first supernatant fraction. The combined supernatant was then filtered (0.45 $\mu$ m) and used for the analysis of total-Hg. The solid residue was then used in the next extraction step. Besides the extraction step, the centrifugation, rinsing, and filtration steps were identical for all fractions (F1 to F5), except for F6.

**Fraction 2 (F2), Exchangeable:** The residue from F1 was treated with 8 mL of 1M magnesium chloride (MgCl<sub>2</sub>, pH 7). The mixture was agitated on at 200 rpm at room temperature for 1 hour, prior to centrifugation, rinsing, and filtration as described in F1.

**Fraction 3 (F3), Bound to carbonates:** The residue from F2 was extracted with 8 mL of 1M sodium acetate (NaOAc) solution with a pH adjusted to 5.0 with acetic acid (HOAc). The mixture was agitated on an orbital shaker at 200 rpm at room temperature for 5 hours, prior to centrifugation, rinsing, and filtration.

**Fraction 4 (F4), Bound to Fe-Mn oxides:** The residue from F3 was extracted with 20 ml of 0.04 M hydroxylamine hydrochloride (NH<sub>2</sub>OH.HCl) in 25% (v/v) HOAc in containers placed

in a water bath for 6 hours at  $96 \pm 3^\circ\text{C}$ , with occasional agitation by hand. Upon cooling, the mixture was centrifuged, rinsed, and the supernatant filtered as described in F1.

**Fraction 5 (F5), Bound to organic matter:** The residue from F4 was extracted with 3 mL of 0.02 M nitric acid ( $\text{HNO}_3$ ) and 5 mL of 30% hydrogen peroxide ( $\text{H}_2\text{O}_2$ ) that had pH adjusted to 2 with  $\text{HNO}_3$ . The mixture was heated to  $85 \pm 2^\circ\text{C}$  in a water bath for 3 hours with intermittent agitation by hand. An additional 3 mL of 30%  $\text{H}_2\text{O}_2$  (pH adjusted to 2 with  $\text{HNO}_3$ ) was added and the mixture heated for an additional 3 hours at  $85 \pm 2^\circ\text{C}$ . Upon cooling, and to prevent the adsorption of extracted Hg onto oxidized Al-WTRs components, 5 mL of 3.2 M ammonium acetate ( $\text{NH}_4\text{OAc}$ ) in 20% (v/v)  $\text{HNO}_3$  was added and the sample diluted to 20 mL and agitated continuously for 30 min on an orbital shaker at 200 rpm. These steps were then followed by centrifugation and filtration as described in F1.

**Fraction 6 (F6), Residual:** The residual fraction was quantified by subtracting the sum amount of Hg obtained in fractions F1-5 from the amount of Hg obtained from the total Hg analysis.

**Total Hg analysis:** For solid Al-WTRs samples, 5 ml of aqua regia and 5 ml of hydrofluoric acid were added to about 1 g of dry Al-WTRs samples (i.e. Hg-spiked and control Al-WTRs) in a Teflon<sup>®</sup> vessel, capped, and digested overnight at  $110^\circ\text{C}$ . The mixture upon cooling was diluted to 50 ml with a saturated solution of boric acid to dissolve formed fluorides.

For the aqueous fractions, concentrations of Hg in supernatants were determined by inductively coupled plasma atomic emission spectrometry (ICP-AES), following overnight digestion with bromine monochloride (mixture of KBr and  $\text{KBrO}_3$  dissolved in concentrated HCl) at room temperature. This step allows the oxidation of soluble organic matter and

dissolution of colloidal Hg, therefore dissolving Hg bound to organic ligands and colloidal materials

In addition to mercury, Al, Fe, and Si were also determined to help assess the relationship between solubilized Hg and these mineral forming elements.

### **Results and Discussion**

The distribution of Hg among the different fractions of Al-WTRs is presented in Table 4-1. When expressed as percent of the initial total-Hg concentration, Hg was distributed as follows: the water soluble fraction accounted for 0.6%; the easily exchangeable fraction for 3.2%, the carbonate-bound fraction for 0.9%, the Fe and Mn oxide-bound fraction for 3.7%, the organic-bound Hg for 9.0 % and the residual fraction for 82.3 %. In contrast, control Al-WTRs samples released no Hg in any of the chemical fractions extracted, suggesting that the background Hg concentration in used Al-WTRs was mostly in the residual form and averaged 0.02 mg/kg.

In Hg-spiked Al-WTRs, the water soluble fraction (F1) had the lowest percentage (0.6%) of total-Hg present in the solid phase, and this despite the fact that Al-WTRs was flooded with HgCl<sub>2</sub> at a final concentration >24,000 mg Hg/kg Al-WTRs. In comparison with other mercury species, HgCl<sub>2</sub> is one of the most soluble forms and is generally stable in soil solution and less prone to sorption in the soil (Backstrom et al. 2003; Kasprzyk-Hordern 2004). For example, in a study by Bloom et al. (2003), almost 100% of HgCl<sub>2</sub> was extracted in the water soluble fraction after HgCl<sub>2</sub> in high concentrations was dispersed in kaolin clay. The water soluble fraction is the most mobile fraction and poses the highest environmental risk. Since Al-WTRs in this study was spiked with Hg amount rarely encountered in the environment, even in contaminated systems, the concentration of Hg leachable by water amounted to 146 mg/kg. Nonetheless, the relatively small value of Hg concentration in this fraction as compared to the initial total Hg level emphasizes the potential for Al-WTRs to limit Hg leaching if used in soil remediation.

Fraction 2 represents Hg bound to metal oxides, primarily through surface adsorption, and represents the fraction most easily substituted by ionic exchange processes (Ma and Rao 1997; Tessier et al. 1979). Although 3.2% of added Hg was recovered by extraction with sodium acetate at pH 5, similar to F1, this fraction remains relatively small as compared to the large amount of Hg added initially to the tested Al-WTRs.

The fraction F3 represents Hg associated with carbonate minerals. Mercury bound to this fraction is mobilized when the pH drops significantly, and as carbonate minerals undergo dissolution. Only 0.9% of the total-Hg added to the Al-WTR was recovered in this fraction. This rather low value could be due to either the low affinity of Hg for carbonate minerals or to the possible limited abundance of such minerals in used Al-WTRs (data not available).

Mercury co-precipitated or adsorbed onto iron and manganese (hydr)oxides (F4 fraction) is relatively stable under oxic conditions. However, such Hg can be mobilized into soil pore water if iron and manganese (hydr)oxides undergo reduction during microbial oxidation of organic matter and as these (hydr)oxides act as terminal electron acceptors under anoxic conditions (Bernaus et al. 2006; Gobeil and Cossa 1993; Tessier et al. 1979). Tested Al-WTRs contained a considerable amount of Fe, i.e. 3766 mg/kg. Fractionation results showed that most of Fe was released in the F4-fraction (Table 4-1, Figure 4-1), while Mn was not detectable (analytical detection limit of about 10µg Mn/L on used ICP-AES). However, the amount of Hg released in F4 fraction was only 3.7% of the initial total-Hg concentration, suggesting that Fe-(hydr)oxides may not play a dominant role as adsorption sites for Hg in these tested Al-WTRs.

Mercury extracted in F5-fraction (9% of total Hg) represents Hg that is bound to various forms of organic matter (Tessier et al. 1979). Organic matter plays an important role in mercury speciation (Khwaja et al. 2006; Suer and Lifvergren 2003). In chapter 2, SEM-EDS analyses

showed that Al-WTRs particles have abundant S in their chemical composition (Figure 2-2). This sulfur could be part of the different organic compounds present in Al-WTRs. In the organic fraction, Hg is probably associated with the S, N, and O containing functional groups, with the sorption affinity strongly decreasing from sulfur to oxygen (Schluter 1997). In fact, Hg is a chalcophile and therefore, the strong bonds between Hg and thiol (-SH) groups present in organic compounds could be highly specific, and when the capacity for bonding to -SH is filled, Hg would then become attached to -NH<sub>2</sub> and -COOH functional groups by somewhat weaker bonds (Bringmark 1997). Even though most of organic carbon in Al-WTRs is associated with natural organic matter of raw water, Hg may also be complexed with organic polymers which are added to treated water in very low concentrations (Makris et al. 2005). In this organic F5-fraction, Hg may become mobile only following the decomposition and/or dissolution of organic matter.

The majority of Hg was associated with the F6-residual fraction (ca. 82.3% of initial total-Hg concentration). The residual fraction is the least bioavailable and the most chemically stable. It therefore represents the least toxic Hg fraction (Han et al. 2003). This is the Hg fraction that is not expected to be released to the aqueous phase under conditions normally encountered in nature (Tessier et al. 1979). Mercury sorption onto Al-WTRs in the residual fraction is very important because of the implications for the long-term stability of formed Hg-[Al-WTR] complexes. Besides Hg, the residual fraction consisted mostly of silica and aluminum (Figure 4-1), with mean concentrations of 51.6 mg/g and 67.7 mg/g for Al and Si, respectively. Also, the acid digestion procedure used for the determination of total-Hg concentration in Al-WTRs did not achieve a complete dissolution of the solid Al-WTRs samples as evidenced by the presence of a solid residue at the bottom of the container at the end of digestion process. Therefore, it is

possible that the concentrations of extracted elements in the residual fraction could have been slightly underestimated. Finally, extracted Hg concentrations did not correlate with the concentrations of other elements (i.e. Al, Fe, and Si) measured in the supernatant solutions obtained from each of the extraction steps (Figure 4-1).

Previous studies have suggested that the oxidation of organic matter by acidified hydrogen peroxide in the organic fraction (F5) may not be complete (Tessier et al. 1979). However it represents a compromise because the use of stronger oxidizing agents may alter the material in the residual fraction (Tessier et al. 1979). To determine the percentage of the organic matter remaining in the residual fraction after the top 5 extractions, total organic matter content was measured comparatively in the native Al-WTRs and in the remaining residual fraction of Al-WTRs obtained after chemical fractionation. Loss on ignition (LOI) was used to estimate the total organic matter content. First, Al-WTRs samples were incubated for 48 hours at 130<sup>0</sup>C to dehydrate the samples. Next, the samples were combusted at 550<sup>0</sup>C for 2 hours in a muffle to ash the organic matter. Obtained results indicate that nearly 41% of total organic matter present in Al-WTRs was left in the residual fraction after the chemical fractionation that includes the oxidation of organic matter by use of 30% H<sub>2</sub>O<sub>2</sub>. The refractory organic matter likely consists of paraffin like material and highly resistant organic residues (Tessier et al. 1979). According to Makris (2004), such organic matter would likely be present in the structure of solid phase Al-WTRs. It is believed that during the formation of Al-WTRs, organic matter can become trapped in the micropores of Al-WTRs as the material coagulates and flocculates in the water.

Amorphous Al-(hydr)oxides exhibit a high affinity for Hg as illustrated in several studies (Sarkar et al. 1999, Axe and Trivedi 2002). Therefore, it is possible that Al-(hydr)oxides play a dominant role in Hg immobilized in the residual fraction. But to accurately determine the Hg

binding sites on Al-WTRs particles, studies employing analytical techniques such as X-ray absorption spectroscopy (XAS) should be used.

## **Part-2: Mercury Incorporation in Micropores of Al-WTRs and Modeling of Intraparticle Diffusion**

### **Introduction**

Results presented in earlier Chapter 2 suggest that Hg sorption onto Al-WTRs particles is a two step process, with the intraparticle diffusion being the likely rate-limiting step. The first step (rapid adsorption) could be attributed to either boundary layer diffusion effects or to the mass transfer effect on external surfaces, while the second step is a much slower and gradual sorption process during which intraparticle diffusion would dominate. Also, the chemical fractionation method used to study the speciation of Hg in aged Hg-spiked Al-WTRs revealed that most of the Hg immobilized onto Al-WTRs particles is associated with the residual fraction. These two findings are in agreement and demonstrate that Hg could be incorporated into the micropores of Al-WTRs, resulting in the formation of stable Hg complexes.

The plausibility of the intraparticle diffusion mechanism is also supported by the fact that Al-WTRs particles have a large internal surface area. The specific surface area (SSA-N<sub>2</sub>) and micropore surface area (SSA-CO<sub>2</sub>) are key parameters that strongly influence the sorption capacity of solid surfaces (Goldberg et al. 2001). According to the International Union of Pure and Applied Chemistry (IUPAC) classification, pores are divided into three categories based on their width (w): (1) micropores for  $w < 20 \text{ \AA}$ , (2) mesopores when  $20 \text{ \AA} < w < 500 \text{ \AA}$ , and (3) macropores with  $w > 500 \text{ \AA}$  (Gregg and Sing 1982). With regard to techniques used to measure the SSA of particles, the SSA-N<sub>2</sub> usually accounts for SSA of macro- and meso- pores, while SSA-CO<sub>2</sub> represents micropore surface area. In Al-WTRs under study, measured SSA-CO<sub>2</sub> is much larger than BET-N<sub>2</sub> suggesting that Al-WTRs have a large internal micropore surface area

(chapter 2). This internal network of micropores represents potential sites for Hg incorporation into the Al-WTRs matrix.

The objective of this portion of the study was to examine Hg incorporation into micropores of Al-WTRs by assessing the physicochemical properties of Al-WTRs before and after Hg sorption. Here, the specific surface area and micropore volume of Hg-free and Hg-spiked Al-WTRs were measured. In addition, to predict the diffusivity of Hg into the micropores and to assess the rates of Hg diffusion into the inner structure of Al-WTRs, site activation theory (Trivedi and Axe 1999) was used to predict Hg diffusivities into Al-WTRs particles.

## **Materials and Methods**

### **Aged mercury-spiked Al-WTRs**

Mercury-spiked Al-WTRs used in this second portion of the study were sub-samples from the Hg-spiked Al-WTRs described earlier in this chapter.

### **Determination of SSA-N<sub>2</sub> and SSA-CO<sub>2</sub> of Al-WTRs before and after mercury sorption**

The determination of specific surface area (SSA) was performed on both aged Hg-spiked and Hg-free (control) Al-WTRs. First, as a pretreatment to SSA measurement, a known amount of Al-WTRs was introduced into a capillary glass tube and outgassed for 4 hours under helium flow at 70<sup>0</sup>C (Makris et al. 2004a). The SSA was then measured by the Brunauer-Emmett-Teller nitrogen adsorption method at 77 K (BET-N<sub>2</sub>), while SSA applicable to the internal (micropore) surface area was measured using carbon dioxide at 273 K (SSA-CO<sub>2</sub>). Both BET-N<sub>2</sub> and SSA-CO<sub>2</sub> were measured using Quantachrome Autosorb-1 (Quantachrome Corp.) apparatus at the Particle Research Engineering Center (PERC) at University of Florida.

The BET-N<sub>2</sub> is applicable mostly to non-porous or mesoporous materials and tends to underestimate the SSA of internal micropores when present (Lowell et al. 2004). The CO<sub>2</sub> is a preferred adsorbent in micropore analysis even though CO<sub>2</sub> (2.8 Å) and N<sub>2</sub> (3.0 Å) have similar

molecular dimensions (Lowell et al. 2004). The reason being that CO<sub>2</sub> analysis is performed at a higher temperature (T=273 K) compared to N<sub>2</sub> (T=77 K), as a result CO<sub>2</sub> passage through micropores is less constricted (Gil and Gandia 2003; Lowell et al. 2004). The BET-N<sub>2</sub> method is applied in the region of relative pressures ranging from  $P/P_0=0.05$  to  $P/P_0=0.3$ , while the SSA-CO<sub>2</sub> is carried out in the interval of relative pressures of  $P/P_0=10^{-5}$  to  $P/P_0=0.0029$ ) (Gregg and Sing 1982).

The SSA-N<sub>2</sub> was calculated using the Brunauer-Emmett-Teller or BET equation (Equation 4-1), where  $W$  is the weight of the gas adsorbed at a relative pressure  $P/P_0$ ,  $W_m$  is the monolayer capacity and  $C$  is a BET constant.

$$\frac{1}{W \times \left(\frac{P_0}{P} - 1\right)} = \frac{1}{W_m \times C} + \frac{C - 1}{(W_m \times C) \times \frac{P}{P_0}} \quad (\text{Eq. 4-1})$$

The micropore volume was calculated from the CO<sub>2</sub> adsorption isotherm using the Dubinin-Radushkevich (DR) method (Equation 4-2), by plotting  $\left[\log \frac{P_0}{P}\right]^2$  versus  $\log W$ , from which  $V_0$  the micropore volume can then be calculated (Lowell et al. 2004).

$$\log W = \log(V_0 \rho) - D \left[\log \frac{P_0}{P}\right]^2 \quad (\text{Eq. 4-2})$$

Where  $W$  is the amount of the gas adsorbed at relative pressure  $P/P_0$ ,  $\rho$  is the liquid adsorbate density,  $V_0$  is the micropore volume,  $D$  is a constant that characterizes Gaussian distribution,  $P_0$  is the vapor saturation pressure of CO<sub>2</sub> (26,140 mm Hg), and  $P$  is the equilibrium pressure (mm Hg).

The SSA-CO<sub>2</sub>, which describes micropore specific surface area, was calculated using the Dubinin-Radushkevich- Kaganer (DRK) equation (Equation 4-3) (Gregg and Sing 1982). A plot

of  $\log W$  versus  $\left[ \log \frac{P_0}{P} \right]^2$  is used to determine the monolayer capacity  $W_m$ , from which the surface area can be calculated using equation 4-4.

$$\log W = \log W_m - D \left[ \log \frac{P_0}{P} \right]^2 \quad (\text{Eq. 4-3})$$

$$S = \frac{W_m NA}{M} \quad (\text{Eq. 4-4})$$

Where  $S$  is the specific surface area,  $A$  is the cross-sectional area,  $M$  is the molecular weight of the adsorbate, and  $N$  is the Avogadro number (Lowell et al. 2004).

The Grand Canonical Monte Carlo simulation model was used to determine the pore size distribution of Al-WTRs. All the calculations were performed using the Quantachrome Autosorb-1 Software (vs. 1.54), which incorporates an advanced built-in database of parameters and functions necessary for data analysis and the Monte Carlo simulation.

Data obtained from different experiments of Hg incorporation into the micropores of Al-WTRs was evaluated by comparing the volumes of Hg free and Hg-spiked Al-WTRs using the Independent-Sample t-test with SPSS statistical software (vs. 11.0). The tests were performed at a confidence level of 95%.

#### **Determination of the activation energy ( $E_a$ ) of mercury sorption onto Al-WTRs particles**

Short term batch kinetic studies were conducted at 11<sup>0</sup>C, 25<sup>0</sup>C, and 35<sup>0</sup>C to obtain the activation energy value needed for the determination of Hg diffusivity using the intraparticle diffusion model. A commercial standard solution of Hg(NO<sub>3</sub>)<sub>2</sub> obtained from Fisher Scientific was used to prepare solutions of 40 mg Hg /L in Nanopure<sup>®</sup> water. For each the tested three temperatures, 20 grams of Al-WTRs were mixed with 1000 ml of the Hg solution and run in duplicate. The contact time and sampling intervals were selected based on preliminary

experiments. At pre-decided time intervals, the supernatant was withdrawn, filtered (0.45 $\mu$ m), and analyzed for total Hg concentrations. Total-Hg was measured by ICP-AES, following overnight cold digestion step using bromine monochloride (i.e. KBr and KBrO<sub>3</sub> dissolved into concentrated ultra high purity HCl).

Obtained data were then fit to different kinetic models to determine the best fit and to evaluate the effect of temperature on the rate constant. The relationship between the reaction rate constant and the temperature is described by the Arrhenius equation (Equation 4-5), which can be linearized as shown in equation 4-6 (Schnoor 1996):

$$k = Ae^{-E_a/RT} \quad (\text{Eq. 4-5})$$

$$\ln k = \ln A - \left( \frac{E_a}{R} \right) \times \frac{1}{T} \quad (\text{Eq. 4-6})$$

and where  $k$  is the reaction rate constant,  $A$  is a constant that is characteristic of the reaction,  $E_a$  is the activation energy for adsorption (cal mol<sup>-1</sup>),  $T$  is the absolute temperature (Kelvin), and  $R$  is the universal gas constant (1.987 cal mol<sup>-1</sup> K<sup>-1</sup>).

Thus, the  $E_a$  can be determined from the slope of the straight line obtained by plotting  $\ln k$  versus  $1/T$  plot (Equation 4-6). The  $E_a$  value was then used to predict the diffusivities of Hg sorption on Al-WTRs.

## **Results and Discussion**

### **Determination of SSA-N<sub>2</sub> and SSA-CO<sub>2</sub> of Al-WTRs before and after mercury sorption**

The SSA-N<sub>2</sub> characterization (BET method) for control Al-WTRs revealed a rather high surface area averaging 48 m<sup>2</sup>/g. However, the measured SSA-CO<sub>2</sub> (DRK method) was even higher (120 m<sup>2</sup>/g) suggesting that Al-WTRs have a large internal surface area that is not accounted by the BET-N<sub>2</sub>. The results of N<sub>2</sub> and CO<sub>2</sub> gas sorption analysis for control (no Hg

addition) and Hg-spiked Al-WTRs are illustrated on Figures 4-2 and 4-3. The SSA characterization of Hg-spiked Al-WTRs revealed a significantly lower SSA-N<sub>2</sub> and SSA-CO<sub>2</sub> as compared to those determined in control sample ( $p=0.006$ ,  $p=0.00003$ ) (Figure 4-4).

A further interpretation of CO<sub>2</sub> sorption data was done by use of the grand canonical Monte Carlo simulation model. This technique allows for the determination of the micropore volume distribution in Al-WTRs. The model presents the pore structure as a collection of idealized slit-shaped pores with smooth graphitic walls (Ravikovitch et al. 2000). The most decrease in micropore volume was in the 3.98-5.01 Å pore width interval (Figure 4-5), and the diameter of the hydrated divalent Hg is about 4.74 Å (Trivedi and Axe 2001). Overall, Hg sorption caused significant reduction in micropore volume as calculated by the DR equation, suggesting that Hg occupied pores that would otherwise be accessible to CO<sub>2</sub> (Figure 4-6). The porosity results support the hypothesis that the predominant mechanism of Hg sorption into Al-WTRs is likely the intraparticle diffusion.

As mentioned earlier, according to the IUPAC classification, pores are divided into micro-, meso-, and macro-pores. However, this division is somewhat arbitrary and is mainly based on the difference in the types of forces that control the adsorption behavior within the different size ranges (Karger and Ruthven 1992). In mesopores, capillary forces are important, while in macropores, these capillary forces contribute very little to the adsorption capacity (Karger and Ruthven 1992). On the other hand, micropores exhibit unusually high adsorption potentials due to the wall close proximity (Lowell et al. 2004). Thus, diffusion in micropores is dominated by steric interactions between the diffusing molecule and the walls of the pores. Intraparticle diffusion of Hg into the micropores of Al-WTRs is an important aspect from the remediation viewpoint as it relates to the long-term stability of Hg. It has been suggested that the diffusing

molecules may never escape from the force field of the micropore walls (Karger and Ruthven 1992).

### **Modeling of intraparticle diffusion and prediction of mercury diffusivity**

The diffusion of molecules into micropores is an activated process proceeding by a sequence of jumps between regions of relatively low potential energy (Karger and Ruthven 1992). Understanding the mechanism of Hg incorporation in Al-WTRs is very important from remediation standpoint, as it will likely determine the long-term stability of Hg-AlWTRs complexes.

Diffusion is generally defined as a random molecular motion that occurs as a result of concentration gradient (Axe and Anderson 1997; Axe and Anderson 1998; Karger and Ruthven 1992; Reeder et al. 1999). The quantitative description of diffusion was first introduced by Adolf Fick, through an expression that is generally known as Fick's First Law of Diffusion (Karger and Ruthven 1992; Schnoor 1996) (Equation 4-7).

$$J = -D \frac{\partial c}{\partial z} \quad (\text{Eq. 4-7})$$

Where  $D$  is the transport diffusivity,  $c$  is the concentration,  $z$  is the distance, and  $J$  is the diffusive flux.

The diffusivity ( $D$ ) describes the time scale for diffusion which may vary from seconds for gases to millennia for crystalline solids at ordinary temperatures (Karger and Ruthven 1992). Therefore, the determination of the diffusivity during the intraparticle diffusion process in Al-WTRs has a practical significance as it may give an estimation of the longevity of Hg sorption process in Al-WTRs.

Several approaches have been proposed for the assessment of the intraparticle diffusion mechanism including the intraparticle diffusion model proposed for phosphorus in WTR by

Makris et al. (2004a), and the modeling approach for metal cations in amorphous oxides based on site activation theory described by Trivedi and Axe (2000). The concentrations of amorphous aluminum (hydr)oxides in Al-WTRs have been found to range from 50 to 150 g/kg (Dayton and Basta 2001). Theoretically, the prevalence of such geochemical phases in Al-WTRs would make them behave like aluminum (hydr)oxides. Therefore, we chose the site activation theory model proposed by Trivedi and Axe (2000) to determine the diffusivity of Hg intraparticle diffusion into Al-WTRs (Equation 4-8).

$$D = \lambda \times \sqrt{\frac{E_a}{2m}} \times e^{-\frac{E_a}{RT}} \quad (\text{Eq. 4-8})$$

Where  $D$  is the diffusivity,  $\lambda$  is the mean distance between sites,  $m$  is the molecular weight of the diffusing species,  $E_a$  is the activation energy required for a sorbed ion to jump to the neighboring site, and  $e^{-\frac{E_a}{RT}}$  is the Boltzmann factor. Since the molecular weight ( $m$ ),  $R$  and  $T$  have known values,  $E_a$  and  $\lambda$  should be determined in order to calculate the  $D$  (Equation 4-8). In this study,  $E_a$  was determined using rate constants of reaction from batch sorption kinetic studies conducted at 11, 25, and 35° C. First, obtained kinetic data were fit to a first order kinetic-model from which reaction rate constants were determined. The relationship between the reaction rate ( $k$ ) constant and temperature ( $T$ ) is described by the Arrhenius equation (Equation 4-5). The  $E_a$  was then determined from the slope of the straight line of the  $\ln k$  versus  $1/T$  plot (Figure 4-7). The calculated  $E_a$  value of 7.156 kcal/mol was then used to predict the intraparticle diffusion and determine theoretical diffusivities of Hg into Al-WTRs micropores (Equation 4-8). In contrast to  $E_a$ ,  $\lambda$  is usually determined through long-term lab experiments which can last from months to years. Although the literature reports several  $\lambda$  values for different amorphous metal-(hydr)oxides including  $\lambda$  values for Al-(hydr)oxides (Fan et al. 2005; Trivedi and Axe 2001), the

complex composition of Al-WTRs may result in  $\lambda$  values that are either similar to that of amorphous Al-(hydr)oxides due to its anticipated abundance in Al-WTRs matrices or far different from those reported for pure (hydr)oxide compounds. However, with the assumption that Hg binding sites on Al-WTRs are predominantly on Al- and to some extent Fe-(hydr)oxides, theoretical diffusivities of Al-WTRs can be estimated by varying the value of  $\lambda$  in equation 4-8. Accordingly, Figure 4-8 shows the range of potential diffusivity values ( $D$ ) of Hg into Al-WTRs with varying  $\lambda$  values. These predictions show that if Al-(hydr)oxides are the main sites of intraparticle diffusion ( $\lambda$  values ranging from  $2.0 \times 10^{-8}$  to  $3.5 \times 10^{-8}$  cm), then the diffusivity ( $D$ ) of Hg in Al-WTRs would range from about  $9.55 \times 10^{-11}$  to  $1.67 \times 10^{-10}$   $\text{cm}^2 \text{s}^{-1}$ . These theoretical diffusivity values for Hg diffusion into Al-WTRs would then be within the range of published diffusivities for amorphous oxides of Al and Fe ( $10^{-10}$  to  $10^{-14}$   $\text{cm}^2 \text{s}^{-1}$ ) (Axe and Trivedi 2002). Based on these predicted values of  $D$  for Hg in Al-WTRs and assuming no competition with other cations, it would take anywhere between  $4 \times 10^8$  to  $2.3 \times 10^8$  years for Hg to fully occupy the  $120 \text{ m}^2$  available in a gram of Al-WTRs. This time would likely be shortened in actual soil matrices due to competition for available binding sites between Hg and other ions. Nonetheless, these numbers suggest that if used in soil remediation, Al-WTRs could behave as a long-term sink for Hg, and more importantly, with formation of very stable Hg-Al-WTRs complexes.

### **General Conclusions**

Overall, the micro-porosity measurements with  $\text{CO}_2$  of Hg free and Hg-spiked Al-WTRs revealed the reduction of micropore volume in Hg-spiked Al-WTRs. This suggests that it is likely that Hg diffused into pores of Al-WTRs thus blocking the pores that otherwise would be accessible to  $\text{CO}_2$ ,

From the site activation theory, the theoretical diffusivities of Hg were predicted with the assumption that amorphous aluminum (hydr)oxides are the dominant geochemical phases that govern the intraparticle diffusion mechanism. To validate this interpretation, experimental diffusivities need to be determined through long term constant boundary condition (CBC) studies. In CBC studies Hg bulk adsorbate concentration is maintained constant by adding Hg into solution for prolonged periods of time (Fan et al. 2005). This approach will help saturate the sites at the surface of the particles and allow a gradual diffusion of Hg into micropores. With the obtained results, the approach proposed by Trivedi and Axe (2000) could be used to determine experimental diffusivities. If the values of theoretical diffusivities predicted in this study are comparable to the values of diffusivities obtained experimentally, then one could conclude that amorphous aluminum (hydr)oxides likely dominate the intraparticle diffusion process.

Overall, the combination of Hg accumulation in the residual fraction (based on the chemical fractionation results), and the evidence of Hg incorporation into the micropores of Al-WTRs suggest that Hg-[Al-WTRs] complexes that may form if Al-WTRs is used in remediation of Hg-contaminated soils would result in long-term immobilization of Hg in the solid phase, and therefore the elimination/reduction of Hg bioavailability and its subsequent toxicity.

Table 4-1. Mercury, Al, Fe, and Si concentrations and distribution (%) in different fractions of Hg-spiked Al-WTRs

Element	Fraction	Concentration mg/g <sup>a</sup>	% of total
Hg	Water Soluble	146±6	0.60
	Exchangeable	766±32	3.18
	Carbonate	230±23.1	0.95
	Fe/Mn Oxide	889.5±150	3.69
	Organic	2162.8±306	8.99
	Residual	19855±172	82.3
	Total	24050±842	--
Al	Water Soluble	<DL <sup>b</sup>	<DL
	Exchangeable	<DL	<DL
	Carbonate	7056±463	4.14
	Fe/Mn Oxide	85833±15269	50.37
	Organic	25875±3856	15.18
	Residual	51618±17835	30.29
	Total	170383±1820	--
Fe	Water Soluble	<DL	<DL
	Exchangeable	<DL	<DL
	Carbonate	100 ± 14	2.67
	Fe/Mn Oxide	3204± 139	85.06
	Organic	143±10	3.82
	Residual	317±239	8.4
	Total	3766±142	--
Si	Water Soluble	<DL	<DL
	Exchangeable	<DL	<DL
	Carbonate	78±8	0.11
	Fe/Mn Oxide	811±82	1.19
	Organic	44±6	0.06
	Residual	66815±1206	98.6
	Total	67750±1125	--

<sup>a</sup> Mean ± one standard deviation; <sup>b</sup>DL = detection limit

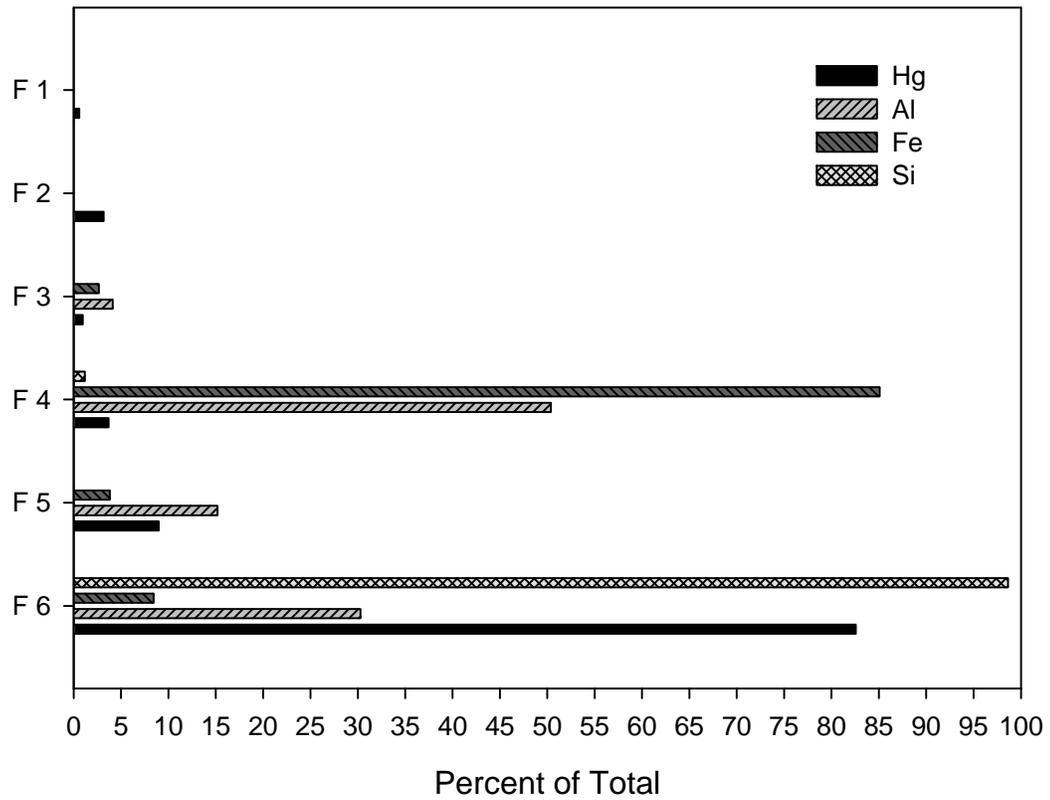


Figure 4-1. Mercury, Al, Fe, and Si distribution (%) in the various fractions of Al-WTR (F1- water soluble, F2-exchangeable, F3- carbonate, F4-Fe/Mn bound, F5- organic bound, F6-residual).

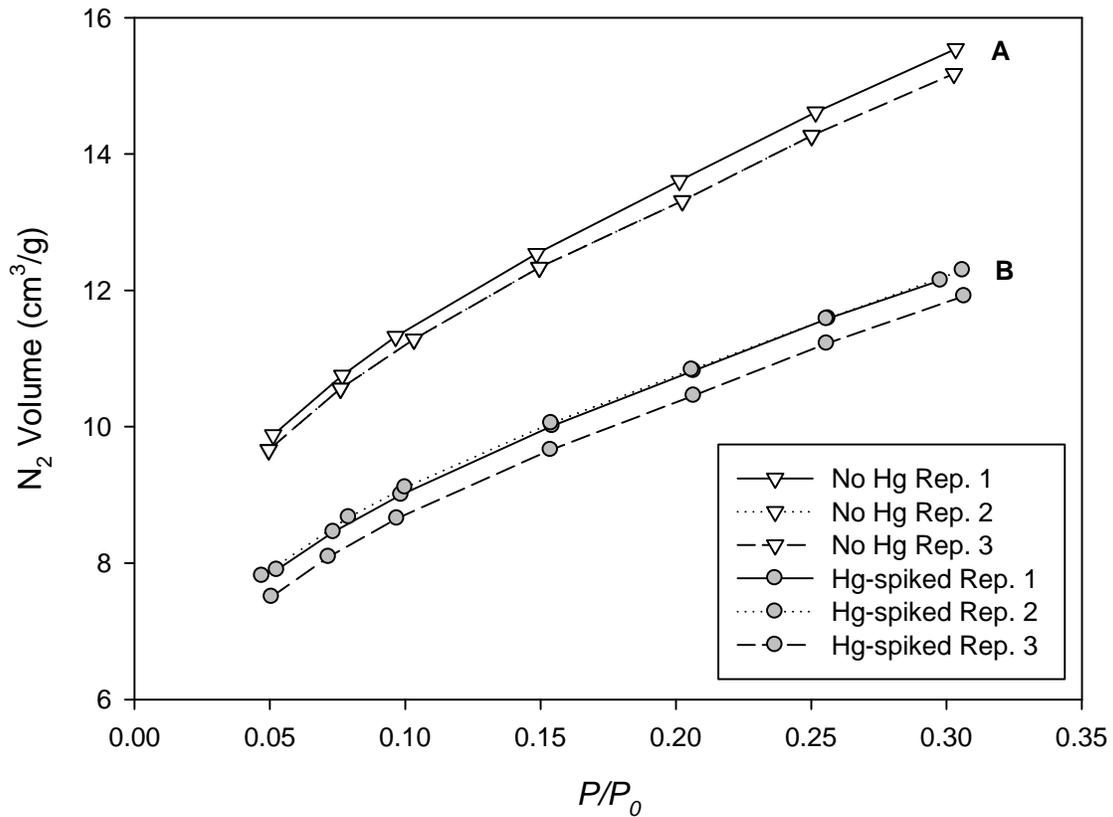


Figure 4-2. The  $N_2$  gas sorption on Al-WTRs with (A) no Hg and (B) Hg-spiked. The treatments are presented in three replicates. Replicate 1 and 2 for both (A) and (B) overlap on this graph.

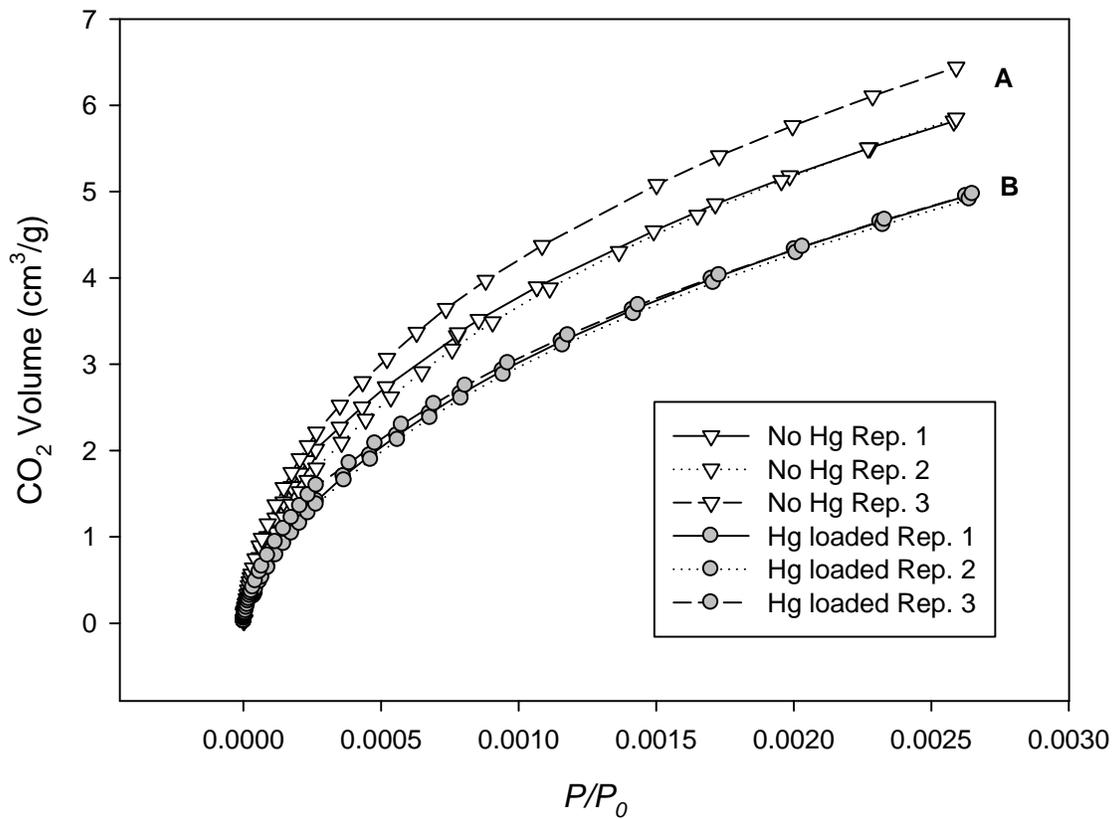


Figure 4-3. The CO<sub>2</sub> gas sorption on Al-WTRs with (A) no Hg and (B) Hg-spiked. The treatments are presented in three replicates. Replicate 2 and 3 for (A) and replicate 1 and 2 for (B) overlap on this graph.

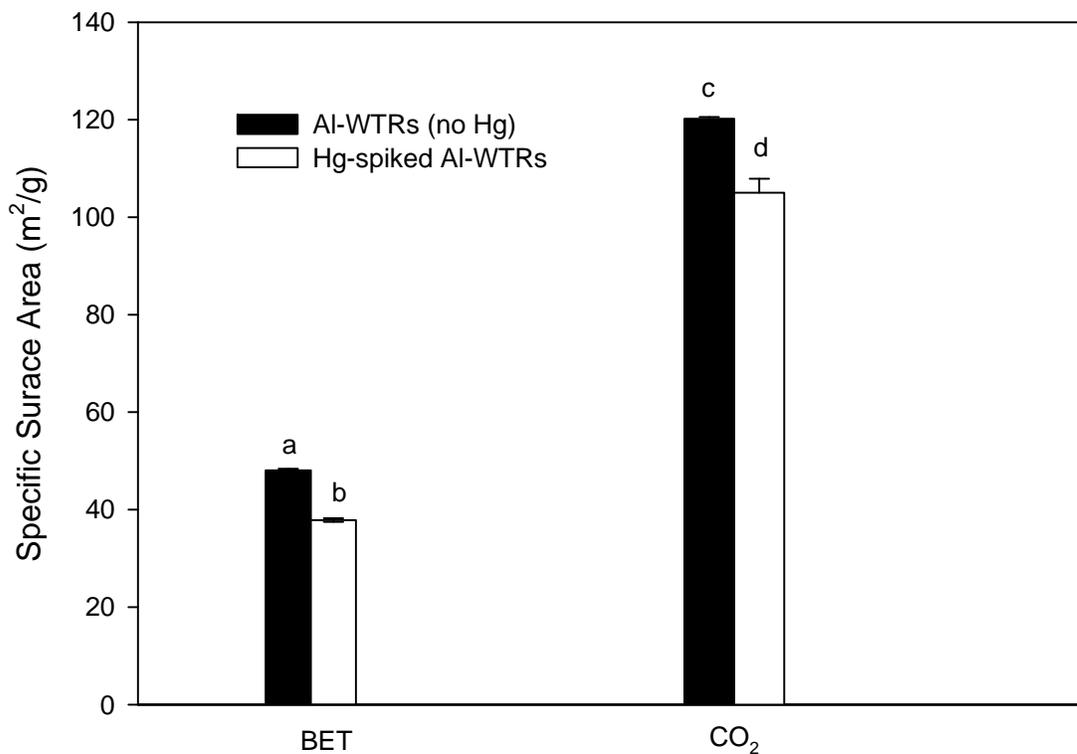


Figure 4-4. Mean BET (N<sub>2</sub>) and micropore (CO<sub>2</sub>) surface area of Al-WTRs with no Hg (black bars) and Hg-spiked (white bars) Al-WTRs. Error bars represent one standard deviation of three replicates. Different letters indicate a significant difference ( $\alpha < 0.05$ ).

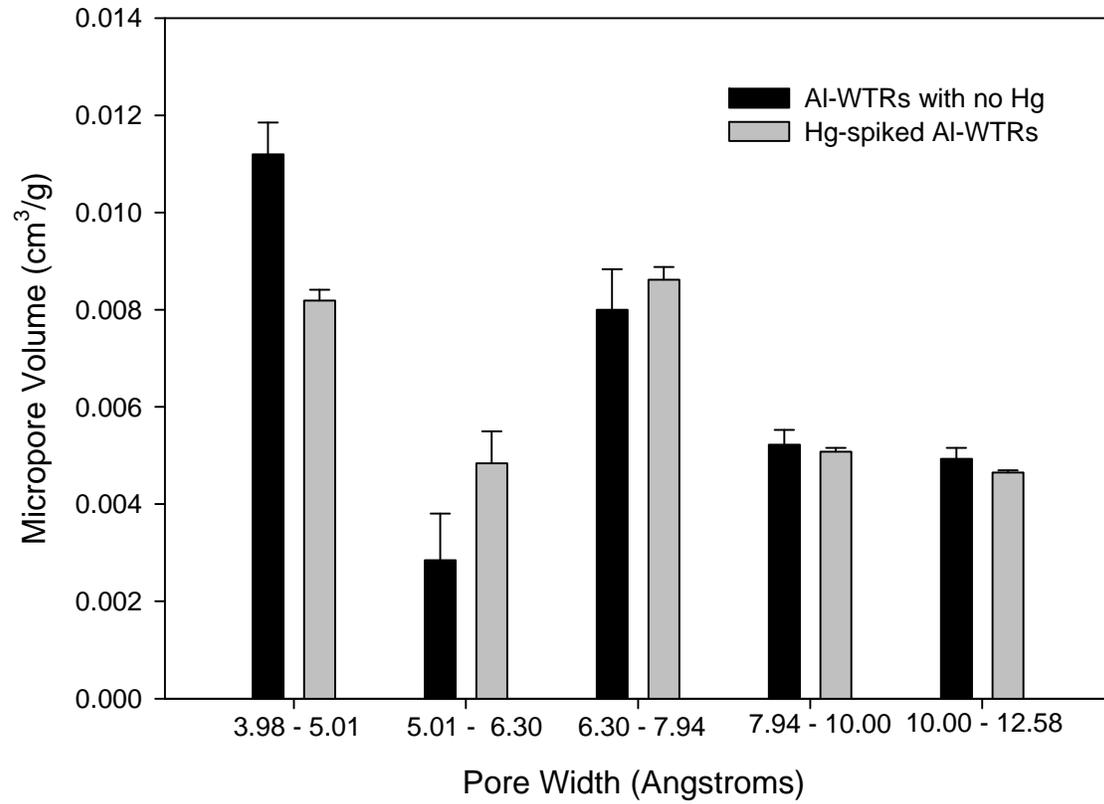


Figure 4-5. Micropore volume based on pore size distribution of Al-WTRs with no Hg (black bars) and Hg-spiked Al-WTRs (grey bars).

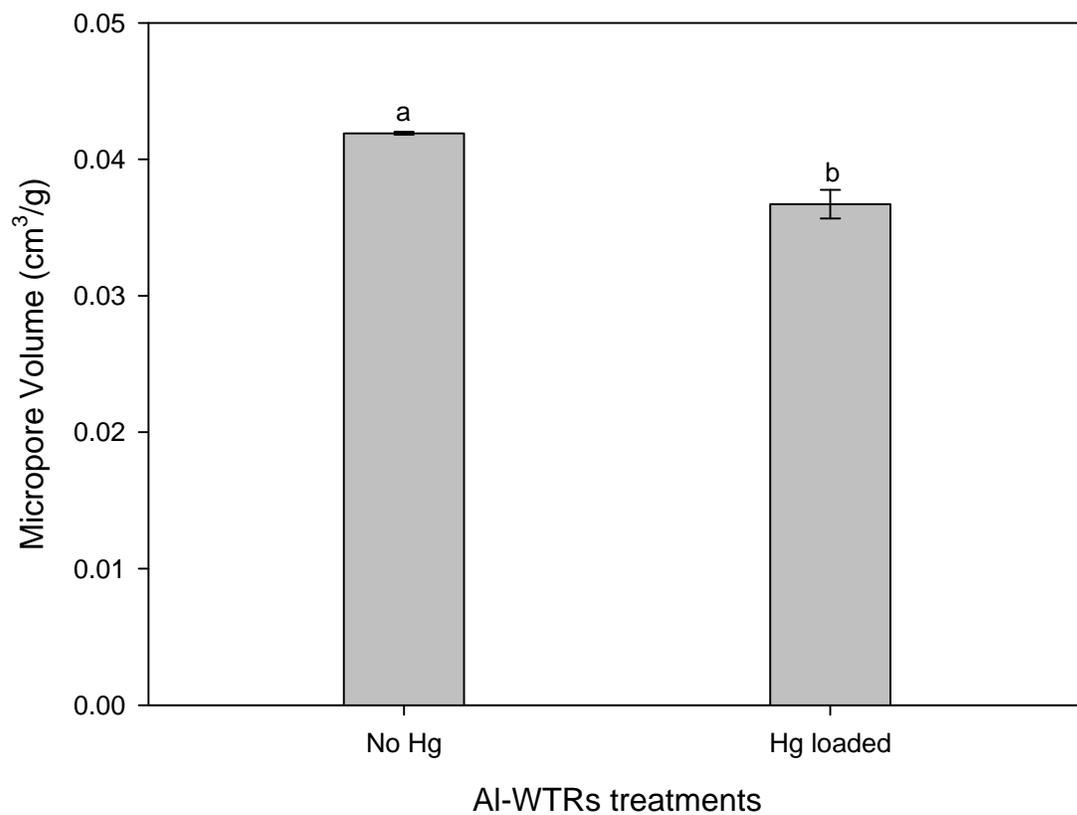


Figure 4-6. Mean micropore volume of Al-WTRs with no Hg (control) and Hg-spiked Al-WTRs. Error bars represent one standard deviation of three replicates. Different letters indicate a significant difference ( $\alpha < 0.05$ ).

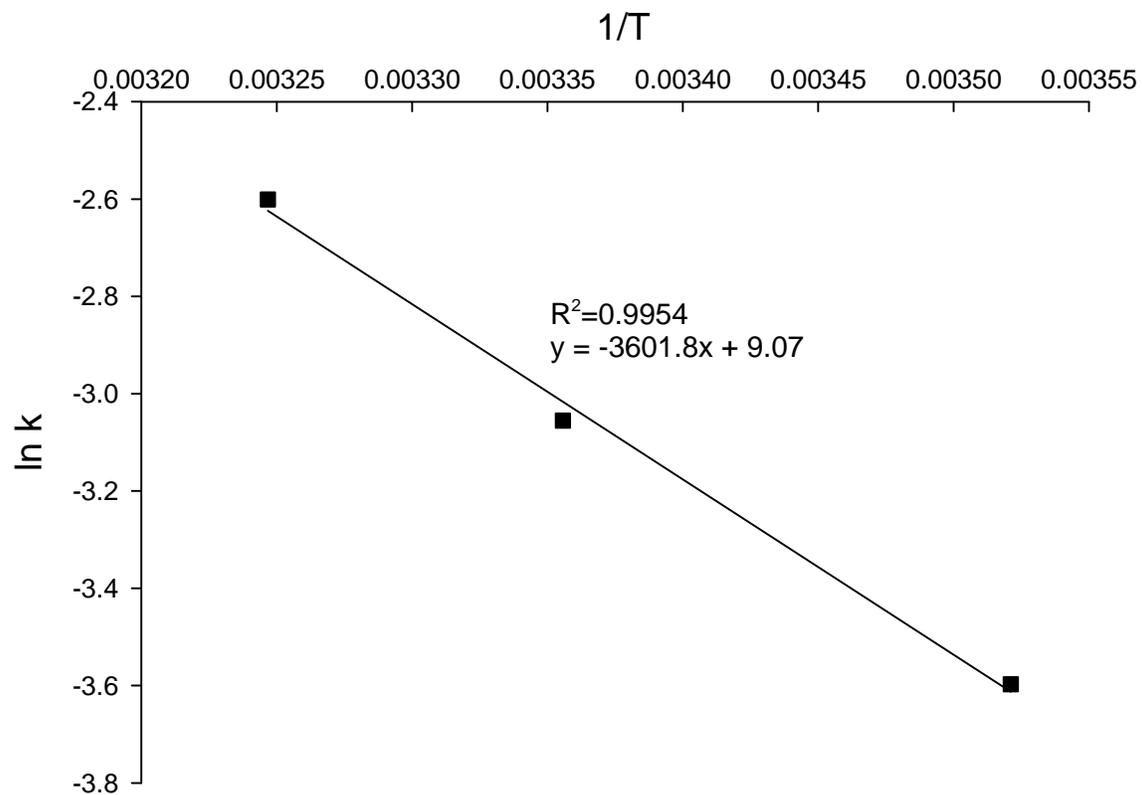


Figure 4-7. Arrhenius plot of Hg sorption on Al-WTRs at 11<sup>0</sup> C, 25<sup>0</sup> C, and 35<sup>0</sup> C, where  $T$  is the temperature expressed in Kelvin and  $k$  is the reaction rate constant.

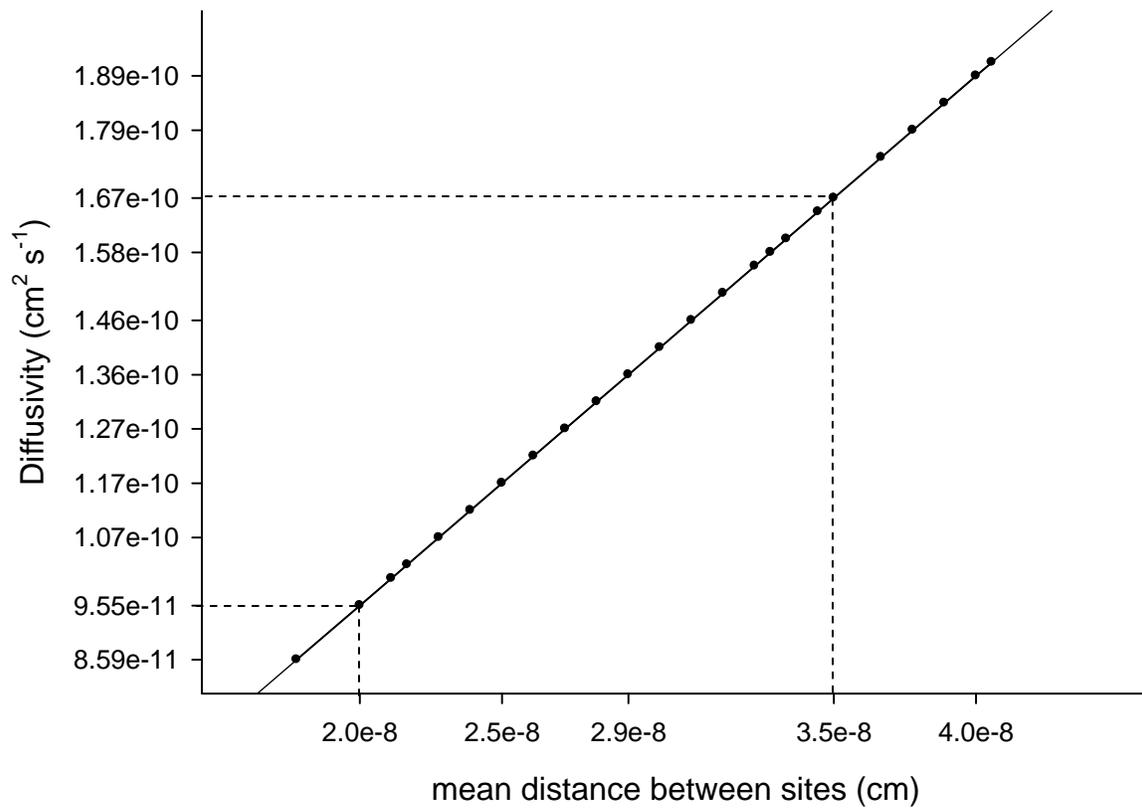


Figure 4-8. Diffusivities ( $D$ ) of Hg in Al-WTRs as a function of varying  $\lambda$  values (mean distance between sorption sites). The  $\lambda$ -values for amorphous aluminum oxides range from  $2.0 \times 10^{-8}$  to  $3.5 \times 10^{-8}$  cm (Fan et al. 2005; Trivedi and Axe 2001) and correspond to  $D$  values in the range from  $9.55 \times 10^{-11}$  to  $1.67 \times 10^{-10}$  cm<sup>2</sup> s<sup>-1</sup>.

## CHAPTER 5 CONCLUSIONS AND RECOMMENDATIONS

### **Conclusions**

Water treatment residuals (WTRs) are non-hazardous waste by-products of drinking water treatment processes. They are produced daily in large quantities worldwide and are either stored in onsite lagoons, discharged into river systems, or buried in landfills. The disposal of this waste product can be expensive as it increases the overall cost of the water purification process. Since current remediation methods of Hg-polluted soils are rather expensive and have several other disadvantages, the use of WTRs as soil amendments to immobilize Hg, and ultimately other toxic metals, would not only lower the cost of potable water by eliminating the need for landfilling of these waste materials but provide environmental benefits as a result of the reclamation of Hg-contaminated soils.

Previous research has now established the strong ability of WTRs to immobilize anions such as phosphate (e.g. Dayton et al. 2003), fluoride (Sujana et al. 1998), and perchlorate (Makris et al. 2006). Unlike the above anionic species which are the subject of several ongoing investigations related to soil remediation through in-situ immobilization of pollutants; the use of WTRs in remediation of metal-contaminated soils are nonexistent. Therefore, this study emphasized the use of aluminum-based WTRs (Al-WTRs) as a sorbent for Hg and was designed primarily to assess the ability of Al-WTRs to: (1) sorb Hg from aqueous solutions, (2) to immobilize Hg in contaminated soils, and (3) initiate an investigation of the mechanisms responsible for Hg sorption and immobilization onto Al-WTRs, as well as the potential for long-term stability of formed mercury-WTRs complexes.

The major findings of this research can be summarized as follows:

- Batch sorption experiments showed that Al-WTRs materials have a great potential as sorbent for Hg with a determined average maximum sorption capacity of 79 mg Hg/g Al-WTRs. Sorption kinetic data was best fit to a pseudo-first order model, while the use of the Weber-Morris and Bangham models suggested that Hg sorption to Al-WTRs is likely a two-step process with the intraparticle diffusion being the rate-limiting step.
- The role of intraparticle diffusion as rate-limiting step on Hg sorption process was investigated using different approaches. Overall, we compared micropore volume of Al-WTRs before and after Hg spiking, which demonstrated significant decrease in micropore volume in aged Hg-spiked Al-WTRs. The selective sequential extraction method used to study the speciation of Hg in aged Hg-spiked Al-WTRs revealed that most of the Hg is associated with the residual fraction of Al-WTRs. These findings demonstrate that it is likely that Hg was incorporated into micropores of Al-WTRs as a result of which Hg is more stable and thus is found in the residual fraction of Al-WTRs. The stability of Hg in the micropores is explained by the fact that micropores exhibit great interaction potential with the diffusing molecule due to wall proximity as a result of which the diffusing molecule may never escape from the force field of the micropore walls.
- Results from the short-term experiments, showed that Al-WTRs effectively immobilized Hg in the pH range of 3 to 8. The fact that Hg removal was very efficient at low pH values is significant from a remediation standpoint, because often times contaminated soils may have a very low pH and if left untreated, may leach out the Hg.
- The potential of Al-WTRs to sorb and immobilize Hg from contaminated soils was assessed using flow-through columns and mimicking the effect of acid rain. Two types of Hg contaminated soil were used, artificially contaminated with Hg chloride to mimic newly contaminated soils and well-aged soils from a contaminated site in Nevada. The addition of Al-WTRs to soil columns reduced Hg concentration in leachates, toxicity of leachates, as well as methylation potential of Hg compared to the control where no Al-WTRs were added, however the effect was more pronounced in the newly contaminated soil. Overall, the results point out to the ability of Al-WTRs to immobilize Hg in soils.

### **Recommendations**

- The leaching potential and therefore the mobility of Hg in soil depends on its speciation. The results of sequential extraction procedures in several studies showed that Hg concentrations  $> 100$  mg/kg can be found in mobile fractions of soils impacted by chlor-alkali plants or by Hg mining activities (Bernaus et al. 2006; Fernandez-Martinez et al. 2006). Such soils would be good candidates to be remediated through Al-WTRs additions. Hence, the chemical speciation of Hg in soil should be known before adopting this remediation approach.
- Future studies are needed to test the efficiency of Al-WTRs to immobilize Hg in a wide variety of soils that have differing physicochemical parameters. This could help develop a

predictive tool in which the ability of Al-WTRs to remediate a given soil type can be determined based on routine geological survey data for a given soil.

- Obtained results showed that applying Al-WTRs as a liner in the soils was the most effective treatment. However, it could be more difficult to implement this approach in field situations versus just mixing the top layer of soil with Al-WTRs. The liner approach could have a potential use as bottom liner in landfills. Heavy metals including Hg are often found in landfill leachates (Yong et al. 2001), therefore, use of Al-WTRs as a liner in landfills would limit the leaching of Hg and potentially other metals to the groundwater.
- Al-WTRs is a mixed adsorbent and it is possible that different constituents are responsible for sorption of Hg in different fractions. Therefore, future studies should focus on using the X-ray absorption spectroscopy (XAS), which has species-specific detection capacities, to determine the speciation of Hg in Al-WTRs. In particular, one type of XAS, the XANES (X-ray Absorption Near Edge Structure) has lower detection limits than XAS and has been suggested for determining the speciation of heterogeneous samples (Bernaus et al. 2006).
- In this study the diffusivities of Hg through intraparticle diffusion into Al-WTRs were theoretically predicted. Future studies are needed to determine the experimental diffusivities. Experimental diffusivities can be assessed through long-term experiments in which the constant boundary conditions (CBC) for Hg are maintained. During the CBC studies Hg concentrations in the aqueous phase is monitored over time and brought back to initial levels through additions of small volumes of highly concentrated Hg solutions. This approach helps saturate the sites at the surface of the particles and allows a gradual diffusion of Hg into micropores. With the obtained results, the approach proposed by Trivedi and Axe (2000) could be used to determine experimental diffusivities. If the experimental diffusivities are close to those predicted in this study, then the amorphous aluminum (hydr)oxides are likely the predominant Hg sorbents that govern the intraparticle diffusion in Al-WTRs.
- This project focused primarily on sorption of Hg without taking into account the competitive adsorption of other metal cations. Future studies are needed to validate this hypothesis by assessing the effect of competitive adsorption on Hg uptake by Al-WTRs.
- If all the above recommendations can be completed, then research on immobilization of Hg by Al-WTRs would be of greater significance because it would not only solve the problem of disposal of Al-WTRs but also will provide environmental benefits associated with the reclamation of Hg-contaminated soils. The use of the developed method will help prevent further contamination of water bodies caused by Hg leaching from contaminated soils, thus protecting human health and the environment. Drinking water treatment facilities, however, use different water sources and different additives along with the alum coagulant and therefore, the composition of Al-WTRs from different sources may vary. Accordingly, future studies are needed to validate the ability of Al-WTRs from different facilities around the nation to sorb Hg.

## LIST OF REFERENCES

- Adriano, D. C. (1992). *Biogeochemistry of Trace Metals*, Lewis Publishers, Boca Raton.
- Adriano, D. C. (2001). *Trace Elements in Terrestrial Environments: Biogeochemistry, Bioavailability, and Risks of Metals*, Springer-Verlag, New York.
- Aharoni, C., Sideman, S., and Hoffer, E. (1979). "Adsorption of Phosphate Ions by Collodion-Coated Alumina." *J. Chem. Technol. Biotechnol.*, 29(7), 404-412.
- Alexander, M. (1995). "How Toxic Are Toxic-Chemicals in Soil." *Environmental Science & Technology*, 29(11), 2713-2717.
- Alloway, B. J. (1995). *Heavy Metals in Soils*, Chapman & Hall, London.
- Altin, A., and Degirmenci, M. (2005). "Lead (II) removal from natural soils by enhanced electrokinetic remediation." *Science of the Total Environment*, 337(1-3), 1-10.
- AntonPaar. (2003). *EKA Electro Kinetic Analyzer Instruction Manual*, Anton Paar, Graz, Austria.
- Axe, L., and Anderson, P. R. (1997). "Experimental and theoretical diffusivities of Cd and Sr in hydrous ferric oxide." *Journal of Colloid and Interface Science*, 185(2), 436-448.
- Axe, L., and Anderson, P. R. (1998). "Intraparticle Diffusion of Metal Contaminants in Amorphous Oxide Minerals." Adsorption of metals by geomedia, E. A. Jenne, ed., Academic Press, New York, 193-208.
- Axe, L., and Trivedi, P. (2002). "Intraparticle surface diffusion of metal contaminants and their attenuation in microporous amorphous Al, Fe, and Mn oxides." *Journal of Colloid and Interface Science*, 247(2), 259-265.
- Ayyamperumal, T., Jonathan, M. P., Srinivasalu, S., Armstrong-Altrin, J. S., and Ram-Mohan, V. (2006). "Assessment of acid leachable trace metals in sediment cores from River Uppanar, Cuddalore, Southeast coast of India." *Environmental Pollution*, 143(1), 34-45.
- Babatunde, A. O., and Zhao, Y. Q. (2007). "Constructive approaches toward water treatment works sludge management: An international review of beneficial reuses." *Critical Reviews in Environmental Science and Technology*, 37(2), 129-164.
- Babiarz, C. L., Hurley, J. P., Benoit, J. M., Shafer, M. M., Andren, A. W., and Webb, D. A. (1998). "Seasonal influences on partitioning and transport of total and methylmercury in rivers from contrasting watersheds." *Biogeochemistry*, 41(3), 237-257.
- Backstrom, M., Dario, M., Karlsson, S., and Allard, B. (2003). "Effects of a fulvic acid on the adsorption of mercury and cadmium on goethite." *Science of the Total Environment*, 304(1-3), 257-268.

- Baldi, F. (1997). "Microbial transformation of mercury species and their importance in the biogeochemical cycle of mercury." *Metal Ions in Biological Systems: Mercury and its Effects on Environment and Biology*, A. Sigel and H. Sigel, eds., Marcel Dekker, Inc., New York, 213-257.
- Barocsi, A., Csintalan, Z., Kocsanyi, L., Dushenkov, S., Kuperberg, J. M., Kucharski, R., and Richter, P. I. (2003). "Optimizing phytoremediation of heavy metal-contaminated soil by exploiting plants stress adaptation." *International Journal of Phytoremediation*, 5(1), 13-23.
- Basta, N. T., and McGowen, S. L. (2004). "Evaluation of chemical immobilization treatments for reducing heavy metal transport in a smelter-contaminated soil." *Environmental Pollution*, 127(1), 73-82.
- Bernaus, A., Gaona, X., van Ree, D., and Valiente, M. (2006). "Determination of mercury in polluted soils surrounding a chlor-alkali plant - Direct speciation by X-ray absorption spectroscopy techniques and preliminary geochemical characterisation of the area." *Analytica Chimica Acta*, 565(1), 73-80.
- Biester, H., Gosar, M., and Covelli, S. (2000). "Mercury speciation in sediments affected by dumped mining residues in the drainage area of the Idrija mercury mine, Slovenia." *Environmental Science & Technology*, 34(16), 3330-3336.
- Biester, H., Muller, G., and Scholer, H. F. (2002). "Binding and mobility of mercury in soils contaminated by emissions from chlor-alkali plants." *The Science of The Total Environment*, 284(1-3), 191-203.
- Bismarck, A., Boccaccini, A. R., Egia-Ajuriagojeaskoa, E., Hulsenberg, D., and Leutbecher, T. (2004). "Surface characterization of glass fibers made from silicate waste: Zeta-potential and contact angle measurements." *J. Mater. Sci.*, 39(2), 401-412.
- Bismarck, A., Mohanty, A. K., Aranberri-Askargorta, I., Czapla, S., Misra, M., Hinrichsen, G., and Springer, J. (2001). "Surface characterization of natural fibers; surface properties and the water up-take behavior of modified sisal and coir fibers." *Green Chemistry*, 3(2), 100-107.
- Bismarck, A., Springer, J., Mohanty, A. K., Hinrichsen, G., and Khan, M. A. (2000). "Characterization of several modified jute fibers using zeta-potential measurements." *Colloid & polymer science* 278(3), 229-235.
- Bitton, G. (1998). *Formula Handbook for Environmental Engineers and Scientists*, John Wiley and Sons, New York.
- Bitton, G., Jung, K., and Koopman, B. (1994). "Evaluation of a microplate assay specific for heavy-metal toxicity." *Archives of Environmental Contamination and Toxicology*, 27(1), 25-28.

- Bloom, N. S., Colman, J. A., and Barber, L. (1997). "Artifact formation of methyl mercury during aqueous distillation and alternative techniques for the extraction of methyl mercury from environmental samples." *Fresenius Journal of Analytical Chemistry*, 358(3), 371-377.
- Bloom, N. S., Preus, E., Katon, J., and Hiltner, M. (2003). "Selective extractions to assess the biogeochemically relevant fractionation of inorganic mercury in sediments and soils." *Analytica Chimica Acta*, 479(2), 233-248.
- Bonzongo, J. C., Heim, K. J., Warwick, J. J., and Lyons, W. B. (1996). "Mercury levels in surface waters of the Carson River Lahontan Reservoir system, Nevada: Influence of historic mining activities." *Environmental Pollution*, 92(2), 193-201.
- Boudou, A., and Ribeyre, F. (1997). "Mercury in the Food Web: Accumulation and Transfer Mechanisms." *Metal Ions in Biological Systems: Mercury and its Effects on Environment and Biology*, A. Sigel and H. Sigel, eds., Marcel Dekker, Inc., New York, 289-319.
- Boularbah, A., Morel, J. L., Bitton, G., and Mench, M. (1996). "A direct solid-phase assay specific for heavy-metal toxicity. 2. Assessment of heavy-metal immobilization in soils and bioavailability to plants." *Journal of Soil Contamination*, 5(4), 395-404.
- Boularbah, A., Schwartz, C., Bitton, G., and Morel, J. L. (2006). "Heavy metal contamination from mining sites in South Morocco: 1. Use of a biotest to assess metal toxicity of tailings and soils." 63(5), 802-810.
- Bourg, A. C. M., and Loch, J. P. G. (1995). "Mobilization of Heavy Metals as Affected by pH and Redox Conditions." *Biogeochemistry of Pollutants in Soils and Sediments: Risk Assessment of Delayed and Non-Linear Responses*, W. Salomons and W. M. Stigliani, eds., Springer-Verlag, Berlin, Germany, 87-102.
- Bringmark, L. (1997). "Accumulation of Mercury in Soil and Effects on Soil Biota." *Metal Ions in Biological Systems: Mercury and its Effects on Environment and Biology*, A. Sigel and H. Sigel, eds., Marcel Dekker, Inc., New York, 161-184.
- Brown, S., Christensen, B., Lombi, E., McLaughlin, M., McGrath, S., Colpaert, J., and Vangronsveld, J. (2005). "An inter-laboratory study to test the ability of amendments to reduce the availability of Cd, Pb, and Zn in situ." *Environmental Pollution*, 138(1), 34-45.
- Celo, V., Lean, D. R. S., and Scott, S. L. (2006). "Abiotic methylation of mercury in the aquatic environment." *Science of The Total Environment*, 368(1), 126-137.
- Chang, J. S., Huang, J. C., Chang, C. C., and Tarn, T. J. (1998). "Removal and recovery of lead fixed-bed biosorption with immobilized bacterial biomass." *Water Science and Technology*, 38(4-5), 171-178.

- Chen, C. C., McKimmy, E. J., Pinnavaia, T. J., and Hayes, K. F. (2004). "XAS study of mercury(II) ions trapped in mercaptan - Functionalized mesostructured silicate with a wormhole framework structure." *Environmental Science & Technology*, 38(18), 4758-4762.
- Chen, X. B., Feng, X. D., Liu, J., Fryxell, G. E., and Gong, M. L. (1999). "Mercury separation and immobilization using self-assembled monolayers on mesoporous supports (SAMMS)." *Separation Science and Technology*, 34(6-7), 1121-1132.
- Chen, Y., Bonzongo, J. C. J., Lyons, W. B., and Miller, G. C. (1997). "Inhibition of mercury methylation in anoxic freshwater sediment by group VI anions." *Environmental Toxicology and Chemistry*, 16(8), 1568-1574.
- Chiarle, S., Ratto, M., and Rovatti, M. (2000). "Mercury removal from water by ion exchange resins adsorption." *Water Research*, 34(11), 2971-2978.
- Chlopecka, A., Bacon, J. R., Wilson, M. J., and Kay, J. (1996). "Forms of cadmium, lead, and zinc in contaminated soils from southwest Poland." *Journal of Environmental Quality*, 25(1), 69-79.
- Codling, E. E., Chaney, R. L., and Mulchi, C. L. (2000). "Use of aluminum- and iron-rich residues to immobilize phosphorus in poultry litter and litter-amended soils." *Journal of Environmental Quality*, 29(6), 1924-1931.
- Compeau, G., and Bartha, R. (1984). "Methylation and Demethylation of Mercury under Controlled Redox, Ph, and Salinity Conditions." *Applied and Environmental Microbiology*, 48(6), 1203-1207.
- Cox, C. D., Shoesmith, M. A., and Ghosh, M. M. (1996). "Electrokinetic remediation of mercury-contaminated soils using iodine/iodide lixiviant." *Environmental Science & Technology*, 30(6), 1933-1938.
- Cruz-Guzman, M., Celis, R., Hermosin, M. C., Leone, P., Negre, M., and Cornejo, J. (2003). "Sorption-desorption of lead (II) and mercury (II) by model associations of soil colloids." *Soil Science Society of America Journal*, 67(5), 1378-1387.
- D'Itri, F. M. (1972). *The Environmental Mercury Problem*, CRC Press, Cleveland.
- Dayton, E. A., and Basta, N. T. (2001). "Characterization of drinking water treatment residuals for use as a soil substitute." *Water Environment Research*, 73(1), 52-57.
- Dayton, E. A., Basta, N. T., Jakober, C. A., and Hattey, J. A. (2003). "Using treatment residuals to reduce phosphorus in agricultural runoff." *Journal American Water Works Association*, 95(4), 151-158.
- Dermont, G., Bergeron, M., Mercier, G., and Richer-Lafleche, M. (2008). "Soil washing for metal removal: A review of physical/chemical technologies and field applications." *Journal of Hazardous Materials*, 152(1), 1-31.

- Drasch, G., Horvat, M., and Stoeppler, M. (2004). "Mercury." Elements and their compounds in the environment: Occurrence, analysis and biological relevance, E. Merian, M. Anke, M. Ihnat, and M. Stoeppler, eds., Wiley-VCH, Weinheim, 931-1005.
- Ehsan, S., Prasher, S. O., and Marshall, W. D. (2006). "A washing procedure to mobilize mixed contaminants from soil: II. Heavy metals." *Journal of Environmental Quality*, 35(6), 2084-2091.
- Essington, M. E. (2003). *Soil and Water Chemistry: an Integrative Approach*, CRC Press, Boca Raton, FL.
- Fan, M., Boonfueng, T., Xu, Y., Axe, L., and Tyson, T. A. (2005). "Modeling Pb sorption to microporous amorphous oxides as discrete particles and coatings." *Journal of Colloid and Interface Science*, 281(1), 39-48.
- FDEP. (2005). *Soil Cleanup Target Levels*, Division of Waste Management, Florida Department of Environmental Protection, Tallahassee, Florida.
- Fernandez-Martinez, R., Loredó, J., Ordoñez, A., and Rucandio, M. I. (2006). "Physicochemical characterization and mercury speciation of particle-size soil fractions from an abandoned mining area in Mieres, Asturias (Spain)." *Environmental Pollution*, 142(2), 217-226.
- Fernandez-Martinez, R., and Rucandio, M. I. (2005). "Study of the suitability of HNO<sub>3</sub> and HCl as extracting agents of mercury species in soils from cinnabar mines." *Analytical and Bioanalytical Chemistry*, 381(8), 1499-1506.
- Garbisu, C., and Alkorta, I. (2001). "Phytoextraction: a cost-effective plant-based technology for the removal of metals from the environment." *Bioresource Technology*, 77(3), 229-236.
- Gayer, K. H., Thompson, L. C., and Zajicek, O. T. (1958). "The Solubility of Aluminum Hydroxide in Acidic and Basic Media at 25-Degrees-C." *Canadian Journal of Chemistry-Revue Canadienne De Chimie*, 36(9), 1268-1271.
- Gil, A., and Gandia, L. M. (2003). "Microstructure and quantitative estimation of the micropore-size distribution of an alumina-pillared clay from nitrogen adsorption at 77K and carbon dioxide adsorption at 273K." *Chemical Engineering Science*, 58(14), 3059-3075.
- Gobeil, C., and Cossa, D. (1993). "Mercury in Sediments and Sediment Pore-Water in the Laurentian Trough." *Canadian Journal of Fisheries and Aquatic Sciences*, 50(8), 1794-1800.
- Goel, J., Kadirvelu, K., Rajagopal, C., and Garg, V. K. (2005). "Removal of lead(II) from aqueous solution by adsorption on carbon aerogel using a response surface methodological approach." *Industrial & Engineering Chemistry Research*, 44(7), 1987-1994.
- Goldberg, S., Lebron, I., Suarez, D. L., and Hinedi, Z. R. (2001). "Surface characterization of amorphous aluminum oxides." *Soil Science Society of America Journal*, 65(1), 78-86.

- Goyer, R. A., Bachmann, J., Clarkson, T. W., Ferris, B. G., Graham, J., Mushak, P., Perl, D. P., Rall, D. P., Schlesinger, R., Sharpe, W., and Wood, J. M. (1985). "Potential human health-effects of acid-rain - report of a workshop." *Environmental Health Perspectives*, 60(MAY), 355-368.
- Gray, C. W., Dunham, S. J., Dennis, P. G., Zhao, F. J., and McGrath, S. P. (2006). "Field evaluation of in situ remediation of a heavy metal contaminated soil using lime and red-mud." *Environmental Pollution*, 142(3), 530-539.
- Gray, J. E., Crock, J. G., and Fey, D. L. (2002). "Environmental geochemistry of abandoned mercury mines in West-Central Nevada, USA." *Applied Geochemistry*, 17(8), 1069-1079.
- Gregg, S. J., and Sing, K. S. W. (1982). *Adsorption, surface area and porosity*, Academic Press, London.
- Grieb, T. M., Driscoll, C. T., Gloss, S. P., Schofield, C. L., Bowie, G. L., and Porcella, D. B. (1990). "Factors Affecting Mercury Accumulation in Fish in the Upper Michigan Peninsula." *Environmental Toxicology and Chemistry*, 9(7), 919-930.
- Gupta, V. K., and Sharma, S. (2002). "Removal of cadmium and zinc from aqueous solutions using red mud." *Environmental Science & Technology*, 36(16), 3612-3617.
- Gustin, M. S., Taylor, G. E., and Leonard, T. L. (1994). "High-Levels of Mercury Contamination in Multiple Media of the Carson River Drainage-Basin of Nevada - Implications for Risk Assessment." *Environmental Health Perspectives*, 102(9), 772-778.
- Hakansson, T., Suer, P., Mattiasson, B., and Allard, B. (2008). "Sulphate reducing bacteria to precipitate mercury after electrokinetic soil remediation." *International Journal of Environmental Science and Technology*, 5(2), 267-274.
- Hamby, D. M. (1996). "Site remediation techniques supporting environmental restoration activities - A review." *Science of the Total Environment*, 191(3), 203-224.
- Han, S., Obraztsova, A., Pretto, P., Choe, K. Y., Gieskes, J., Deheyn, D. D., and Tebo, B. M. (2007). "Biogeochemical factors affecting mercury methylation in sediments of the Venice Lagoon, Italy." *Environmental Toxicology and Chemistry*, 26(4), 655-663.
- Han, Y., Kingston, H. M., Boylan, H. M., Rahman, G. M. M., Shah, S., Richter, R. C., Link, D. D., and Bhandari, S. (2003). "Speciation of mercury in soil and sediment by selective solvent and acid extraction." *Analytical and Bioanalytical Chemistry*, 375(5), 428-436.
- Hesse, P. R. (1972). *A textbook of Soil Chemical Analysis*, Chemical Publishing Co., Inc., New York.
- Ho, Y. S., and McKay, G. (1998). "Sorption of dye from aqueous solution by peat." *Chemical Engineering Journal* 70(2), 115-124.

- Ho, Y. S., and McKay, G. (2000). "The kinetics of sorption of divalent metal ions onto sphagnum moss flat." *Water Research*, 34(3), 735-742.
- Huang, C. P., and Blankenship, D. W. (1984). "The Removal of Mercury(Ii) from Dilute Aqueous-Solution by Activated Carbon." *Water Research*, 18(1), 37-46.
- Huang, J. W. W., Chen, J. J., Berti, W. R., and Cunningham, S. D. (1997). "Phytoremediation of lead-contaminated soils: Role of synthetic chelates in lead phytoextraction." *Environmental Science & Technology*, 31(3), 800-805.
- Hurley, J. P., Benoit, J. M., Babiarz, C. L., Shafer, M. M., Andren, A. W., Sullivan, J. R., Hammond, R., and Webb, D. A. (1995). "Influences of Watershed Characteristics on Mercury Levels in Wisconsin Rivers." *Environmental Science & Technology*, 29(7), 1867-1875.
- Hyde, J. E., and Morris, T. F. (2000). "Phosphorus availability in soils amended with dewatered water treatment residual and metal concentrations with time in residual." *Journal of Environmental Quality*, 29(6), 1896-1904.
- Hylander, L. D., and Goodsite, M. E. (2006). "Environmental costs of mercury pollution." *Science of the Total Environment*, 368(1), 352-370.
- Hylander, L. D., and Meili, M. (2003). "500 years of mercury production: global annual inventory by region until 2000 and associated emissions." *Science of the Total Environment*, 304(1-3), 13-27.
- Jackson, A. M., Swain, E. B., Andrews, C. A., and Rae, D. (2000). "Minnesota's mercury contamination reduction initiative." *Fuel Processing Technology*, 65, 79-99.
- Jain, A. K., Gupta, V. K., Jain, S., and Suhas. (2004). "Removal of chlorophenols using industrial wastes." *Environ. Sci. Technol.*, 38(4), 1195-1200.
- Johansson, K., Aastrup, M., Andersson, A., Bringmark, L., and Iverfeldt, A. (1991). "Mercury in Swedish Forest Soils and Waters - Assessment of Critical Load." *Water Air and Soil Pollution*, 56, 267-281.
- Karger, J., and Ruthven, D. M. (1992). *Diffusion in Zeolites and Other Microporous Solids*, John Wiley & Sons, Inc, New York.
- Kasprzyk-Hordern, B. (2004). "Chemistry of alumina, reactions in aqueous solution and its application in water treatment." *Advances in Colloid and Interface Science*, 110(1-2), 19-48.
- Kazantzis, G. (1980). "Mercury." *Metals in the Environment*, H. A. Waldron, ed., Academic Press, 221-261.

- Khawaja, A. R., Bloom, P. R., and Brezonik, P. L. (2006). "Binding constants of divalent mercury ( $\text{Hg}^{2+}$ ) in soil humic acids and soil organic matter." *Environmental Science & Technology*, 40(3), 844-849.
- Kim, C. S., Bloom, N. S., Rytuba, J. J., and Brown, G. E. (2003). "Mercury speciation by X-ray absorption fine structure spectroscopy and sequential chemical extractions: A comparison of speciation methods." *Environmental Science & Technology*, 37(22), 5102-5108.
- Kim, J. P. (1995). "Methylmercury in Rainbow-Trout (*Oncorhynchus-Mykiss*) from Lakes Okareka, Okaro, Rotomahana, Rotorua and Tarawera, North-Island, New-Zealand." *Science of the Total Environment*, 164(3), 209-219.
- Kunkel, A. M., Seibert, J. J., Elliott, L. J., Kelley, R., Katz, L. E., and Pope, G. A. (2006). "Remediation of elemental mercury using in situ thermal desorption (ISTD)." *Environmental Science & Technology*, 40(7), 2384-2389.
- Lacerda, L. D., Malm, O., Guimaraes, J. R. D., Salomons, W., and Wilken, R. D. (1995). "Mercury and the New Gold Rush in the South." Biogeochemistry of Pollutants in Soils and Sediments: Risk Assessment of Delayed and Non-Linear Responses, W. Salomons and W. M. Stigliani, eds., Springer-Verlag, Berlin, Germany, 213-245.
- Lagergren, S. (1898). "About the theory of so-called adsorption of soluble substances." *Kungliga Svenska Vetenskapsakademiens. Handlingar*, 24(4), 1-39.
- Lechler, P. J., Miller, J. R., Hsu, L.-C., and Desilets, M. O. (1997). "Mercury mobility at the Carson River Superfund Site, west-central Nevada, USA: Interpretation of mercury speciation data in mill tailings, soils, and sediments." *Journal of Geochemical Exploration*, 58(2-3), 259-267.
- LeDuc, D. L., and Terry, N. (2005). "Phytoremediation of toxic trace elements in soil and water." *Journal of Industrial Microbiology & Biotechnology*, 32(11-12), 514-520.
- Leermakers, M., Baeyens, W., Quevauviller, P., and Horvat, M. (2005). "Mercury in environmental samples: Speciation, artifacts and validation." *Trac-Trends in Analytical Chemistry*, 24(5), 383-393.
- Lestan, D., Grcman, H., Zupan, M., and Bacac, N. (2003). "Relationship of soil properties to fractionation of Pb and Zn in soil and their uptake into *Plantago lanceolata*." *Soil & Sediment Contamination*, 12(4), 507-522.
- Lindqvist, O., Johansson, K., Aastrup, M., Andersson, A., Bringmark, L., Hovsenius, G., Hakanson, L., Iverfeldt, A., Meili, M., and Timm, B. (1991). "Mercury in the Swedish Environment - Recent Research on Causes, Consequences and Corrective Methods." *Water Air and Soil Pollution*, 55(1-2), R11-&.
- Lindsay, W. L. (1979). *Chemical Equilibria in Soils*, Wiley & Sons, New York.

- Lowell, S., Shields, J. E., Thomas, M. A., and Thommes, M. (2004). *Characterization of Porous Solids and Powders: Surface Area, Pore Size and Density*, Kluwer Academic Publishers, Dordrecht, The Netherlands.
- Ma, L. Q., and Rao, G. N. (1997). "Chemical fractionation of cadmium, copper, nickel, and zinc in contaminated soils." *Journal of Environmental Quality*, 26(1), 259-264.
- Magos, L., and Clarkson, T. W. (2006). "Overview of the clinical toxicity of mercury." *Annals of Clinical Biochemistry*, 43, 257-268.
- Makris, K. C. (2004). "Long-Term Stability of Sorbed Phosphorus by Drinking-Water Treatment Residuals: Mechanisms and Implications," Dissertation, University of Florida, Gainesville, FL.
- Makris, K. C., El-Shall, H., Harris, W. G., O'Connor, G. A., and Obreza, T. A. (2004a). "Intraparticle phosphorus diffusion in a drinking water treatment residual at room temperature." *Journal of Colloid and Interface Science*, 277(2), 417-423.
- Makris, K. C., and Harris, W. G. (2006). "Time dependency and irreversibility of water desorption by drinking-water treatment residuals: Implications for sorption mechanisms." *Journal of Colloid and Interface Science*, 294(1), 151-154.
- Makris, K. C., Harris, W. G., O'Connor, G. A., and Obreza, T. A. (2004b). "Phosphorus immobilization in micropores of drinking-water treatment residuals: Implications for long-term stability." *Environmental Science & Technology*, 38(24), 6590-6596.
- Makris, K. C., Harris, W. G., O'Connor, G. A., Obreza, T. A., and Elliott, H. A. (2005). "Physicochemical properties related to long-term phosphorus retention by drinking-water treatment residuals." *Environmental Science & Technology*, 39(11), 4280-4289.
- Makris, K. C., Sarkar, D., and Datta, R. (2006). "Aluminum-based drinking-water treatment residuals: A novel sorbent for perchlorate removal." *Environmental Pollution*, 140(1), 9-12.
- Manchon-Vizueté, E., Macías-García, A., Gisbert, A. N., Fernández-González, C., and Gómez-Serrano, V. (2005). "Adsorption of mercury by carbonaceous adsorbents prepared from rubber of tyre wastes." *Journal of Hazardous Materials*, 119(1-3), 231-238.
- Mane, V. S., Mall, I. D., and Srivastava, V. C. (2007). "Use of bagasse fly ash as an adsorbent for the removal of brilliant green dye from aqueous solution." *Dyes and Pigments*, 73(3), 269-278.
- Martínez, C. E., and McBride, M. B. (1998). "Solubility of Cd<sup>2+</sup>, Cu<sup>2+</sup>, Pb<sup>2+</sup>, and Zn<sup>2+</sup> in aged coprecipitates with amorphous iron hydroxides." *Environmental Science & Technology*, 32(6), 743-748.

- McGowen, S. L., Basta, N. T., and Brown, G. O. (2001). "Use of diammonium phosphate to reduce heavy metal solubility and transport in smelter-contaminated soil." *Journal of Environmental Quality*, 30(2), 493-500.
- McKay, G., Blair, H. S., and Gardner, J. R. (1982). "Adsorption of Dyes on Chitin .1. Equilibrium Studies." *Journal of Applied Polymer Science*, 27(8), 3043-3057.
- Meagher, R. B., and Heaton, A. C. P. (2005). "Strategies for the engineered phytoremediation of toxic element pollution: mercury and arsenic." *Journal of Industrial Microbiology & Biotechnology*, 32(11-12), 502-513.
- Meng, X. G., Hua, Z., Dermatas, D., Wang, W., and Kuo, H. Y. (1998). "Immobilization of mercury(II) in contaminated soil with used tire rubber." *Journal of Hazardous Materials*, 57(1-3), 231-241.
- Mercier, L., and Detellier, C. (1995). "Preparation, Characterization and Applications as Heavy-Metals Sorbents of Covalently Grafted Thiol Functionalities on the Interlamellar Surface of Montmorillonite." *Environmental Science & Technology*, 29(5), 1318-1323.
- Moreno, F. N., Anderson, C. W. N., Stewart, R. B., and Robinson, B. H. (2005). "Mercury volatilisation and phytoextraction from base-metal mine tailings." *Environmental Pollution*, 136(2), 341-352.
- Mulligan, C. N., Yong, R. N., and Gibbs, B. F. (2001). "Remediation technologies for metal-contaminated soils and groundwater: an evaluation." *Engineering Geology*, 60(1-4), 193-207.
- Neculita, C. M., Zagury, G. J., and Deschenes, L. (2005). "Mercury speciation in highly contaminated soils from chlor-alkali plants using chemical extractions." *Journal of Environmental Quality*, 34(1), 255-262.
- Novak, J. M., and Watts, D. W. (2004). "Increasing the phosphorus sorption capacity of southeastern Coastal Plain soils using water treatment residuals." *Soil Science*, 169(3), 206-214.
- Novak, J. M., and Watts, D. W. (2005). "Water treatment residuals aggregate size influences phosphorus sorption kinetics and p(max) values." *Soil Science*, 170(6), 425-432.
- Nriagu, J. O., and Wong, H. K. T. (1997). "Gold Rushes and Mercury Pollution." *Metal Ions in Biological Systems: Mercury and its Effects on Environment and Biology*, A. Sigel and H. Sigel, eds., Marcel Dekker, Inc., New York, 131-160.
- Oorts, K., Ghesquiere, U., and Smolders, E. (2007). "Leaching and aging decrease nickel toxicity to soil microbial processes in soils freshly spiked with nickel chloride." *Environmental Toxicology and Chemistry*, 26(6), 1130-1138.

- Oygaard, J. K., Gjengedal, E., and Mobbs, H. J. (2008). "Trace element exposure in the environment from MSW landfill leachate sediments measured by a sequential extraction technique." *Journal of Hazardous Materials*, 153(1-2), 751-758.
- Pacyna, J. M., and Keeler, G. J. (1995). "Sources of Mercury in the Arctic." *Water Air and Soil Pollution*, 80(1-4), 621-632.
- Page, M. M., and Page, C. L. (2002). "Electroremediation of contaminated soils." *Journal of Environmental Engineering-Asce*, 128(3), 208-219.
- Patra, M., and Sharma, A. (2000). "Mercury toxicity in plants." *Botanical Review*, 66(3), 379-422.
- Piao, H. S., and Bishop, P. L. (2006). "Stabilization of mercury-containing wastes using sulfide." *Environmental Pollution*, 139(3), 498-506.
- Pirrone, N., Keeler, G. J., and Nriagu, J. O. (1996). "Regional differences in worldwide emissions of mercury to the atmosphere." *Atmospheric Environment*, 30(17), 2981-2987.
- Polo, M. S., and Utrilla, J. R. (2002). "Adsorbent-adsorbate interactions in the adsorption of Cd(II) and Hg(II) on ozonized activated carbons." *Environmental Science & Technology*, 36(17), 3850-3854.
- Prado, A. G. S., Arakaki, L. N. H., and Airoidi, C. (2002). "Adsorption and separation of cations on silica gel chemically modified by homogeneous and heterogeneous routes with the ethylenimine anchored on thiol modified silica gel." *Green Chemistry*, 4(1), 42-46.
- Prakash, P., and Sengupta, A. K. (2003). "Selective coagulant recovery from water treatment plant residuals using donnan membrane process." *Environmental Science & Technology*, 37(19), 4468-4474.
- Ravikovitch, P. I., Vishnyakov, A., Russo, R., and Neimark, A. V. (2000). "Unified approach to pore size characterization of microporous carbonaceous materials from N<sub>2</sub>, Ar, and CO<sub>2</sub> adsorption isotherms." *Langmuir*, 16(5), 2311-2320.
- Reeder, D. H., McCormick, A. V., and Carr, P. W. (1999). "Structural Effects on Diffusivity Within Aggregates of Colloidal Zirconia." *Surfaces of Nanoparticles and Porous Materials*, J. A. Schwarz and C. I. Contescu, eds., Marcel Dekker, Inc., New York, 281-294.
- Sarkar, D., Essington, M. E., and Misra, K. C. (2000). "Adsorption of mercury(II) by kaolinite." *Soil Science Society of America Journal*, 64(6), 1968-1975.
- Sawyer, C. N., McCarty, P. L., and Parkin, G. F. (2003). *Chemistry for Environmental Engineering and Science*, McGraw Publishing.
- Schecher, W. D., and McAvoy, D. C. (2001). *MINEQL+: A Chemical Equilibrium Modeling System, Version 4.5 for Windows, User's Manual*, Environmental Research Software, Hallowell, ME.

- Schluter, K. (1997). "Sorption of inorganic mercury and monomethyl mercury in an iron-humus podzol soil of southern Norway studied by batch experiments." *Environmental Geology*, 30(3-4), 266-279.
- Schnoor, J. L. (1996). *Environmental Modeling: Fate and Transport of Pollutants in Water, Air, and Soil*, John Wiley & Sons, New York.
- 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 and Soil Pollution*, 56, 667-680.
- Schwedt, G. (2001). *The Essential Guide to Environmental Chemistry*, John Wiley & Sons, LTD, Chichester, UK.
- Siegel, F. R. (2002). "Analysis of Indicator Media: Samples/Protocols." *Environmental Geochemistry of Potentially Toxic Metals*, Springer, New York, 133-154
- Sigel, A., and Sigel, H. (1997). *Metal Ions in Biological Systems: Mercury and its Effects on Environment and Biology*, Marcel Dekker, Inc., New York.
- Silveira, M. L., Miyittah, M. K., and O'Connor, G. A. (2006). "Phosphorus release from a manure-impacted spodosol: Effects of a water treatment residual." *Journal of Environmental Quality*, 35(2), 529-541.
- Skene, T. M., Oades, J. M., and Kilmore, G. (1995). "Water-treatment sludge - a potential plant-growth medium." *Soil Use and Management*, 11(1), 29-33.
- Sotero-Santos, R. B., Rocha, O., and Povinelli, J. (2005). "Evaluation of water treatment sludges toxicity using the Daphnia bioassay." *Water Research*, 39(16), 3909-3917.
- Sparks, D. L. (1995). *Environmental Soil Chemistry*, Academic Press, Inc., San Diego, CA.
- St. Louis, V. L., Rudd, J. W. M., Kelly, C. A., Beaty, K. G., Flett, R. J., and Roulet, N. T. (1996). "Production and Loss of Methylmercury and Loss of Total Mercury from Boreal Forest Catchments Containing Different Types of Wetlands." *Environmental Science & Technology*, 30(9), 2719-2729.
- Stanhope, K. G., Young, S. D., Hutchinson, J. J., and Kamath, R. (2000). "Use of isotopic dilution techniques to assess the mobilization of nonlabile Cd by chelating agents in phytoremediation." *Environmental Science & Technology*, 34(19), 4123-4127.
- Steinnes, E. (1997). "Mercury." *Heavy Metals in Soils*, B. J. Alloway, ed., Chapman & Hall, London, 245-259.
- Stoodley, P., Sauer, K., Davies, D. G., and Costerton, J. W. (2002). "Biofilms as complex differentiated communities." *Annual Review of Microbiology*, 56, 187-209.

- Stumm, W., and Morgan, J. J. (1996). *Aquatic Chemistry. Chemical Equilibria and Rates in Natural Waters*, John Wiley & Sons, Inc, New York.
- Suer, P., and Allard, B. (2003). "Mercury transport and speciation during electrokinetic soil remediation." *Water Air and Soil Pollution*, 143(1-4), 99-109.
- Suer, P., and Lifvergren, T. (2003). "Mercury-contaminated soil remediation by iodide and electroreclamation." *Journal of Environmental Engineering-Asce*, 129(5), 441-446.
- Sujana, M. G., Thakur, R. S., and Rao, S. B. (1998). "Removal of Fluoride from Aqueous Solution by Using Alum Sludge." *Journal of Colloid and Interface Science*, 206(1), 94-101.
- Sumner, M. E., and Miller, W. P. (1996). "Cation exchange capacity and exchange coefficients." *Methods of Soil Analysis. Part 3: Chemical Methods.*, D. L. Sparks, ed., SSSA Book Series, Madison, WI, 1201-1229.
- Szpyrkowicz, L., Radaelli, M., Bertini, S., Daniele, S., and Casarin, F. (2007). "Simultaneous removal of metals and organic compounds from a heavily polluted soil." *Electrochimica Acta*, 52(10), 3386-3392.
- Takeuchi, F., Iwahori, K., Kamimura, K., Negishi, A., Maeda, T., and Sugio, T. (2001). "Volatilization of mercury under acidic conditions from mercury-polluted soil by a mercury-resistant *Acidithiobacillus ferrooxidans* SUG 2-2." *Bioscience Biotechnology and Biochemistry*, 65(9), 1981-1986.
- Tessier, A., Campbell, P. G. C., and Bisson, M. (1979). "Sequential Extraction Procedure for the Speciation of Particulate Trace-Metals." *Analytical Chemistry*, 51(7), 844-851.
- Townsend, T., Dubey, B., Tolaymat, T., and Solo-Gabriele, H. (2005). "Preservative leaching from weathered CCA-treated wood." *Journal of Environmental Management*, 75(2), 105-113.
- Trivedi, P., and Axe, L. (1999). "A comparison of strontium sorption to hydrous aluminum, iron, and manganese oxides." *Journal of Colloid and Interface Science*, 218(2), 554-563.
- Trivedi, P., and Axe, L. (2000). "Modeling Cd and Zn sorption to hydrous metal oxides." *Environmental Science & Technology*, 34(11), 2215-2223.
- Trivedi, P., and Axe, L. (2001). "Predicting divalent metal sorption to hydrous Al, Fe, and Mn oxides." *Environmental Science & Technology*, 35(9), 1779-1784.
- Tsang, D. C. W., Zhang, W. H., and Lo, I. M. C. (2007). "Copper extraction effectiveness and soil dissolution issues of EDTA-flushing of artificially contaminated soils." *Chemosphere*, 68(2), 234-243.

- Tu, C., Zheng, C. R., and Chen, H. M. (2001). "Distribution of copper and zinc fractions in red soil as influenced by fertilizer application." *Communications in Soil Science and Plant Analysis*, 32(5-6), 661-673.
- Tutem, E., Apak, R., and Unal, C. F. (1998). "Adsorptive removal of chlorophenols from water by bituminous shale." *Water Research*, 32(8), 2315-2324.
- US-EPA. (1995). *Contaminants and Remedial Options at Selected Metal-Contaminated Sites*, Office of Research and Development, EPA/540/R-95/512, Washington, DC.
- US-EPA. (1997a). *Best Management Practices (BMPs) for Soil Treatment Technologies*, US EPA Office of Solid Waste, EPA530-R-97-007, Washington, DC.
- US-EPA. (1997b). *Land Application of Biosolids: Process Design Manual*, CRC Press.
- US-EPA. (2001). *Method 1631, Revision C, Mercury in Water by Oxidation, Purge and Trap, and Cold Vapor Atomic Fluorescence Spectrometry*, US EPA-821-R-01-024.
- US-EPA. (2003a). *National primary drinking water standards*, Office of Water, United States Environmental Protection Agency, Washington, D.C. .
- US-EPA. (2003b). *Test Methods For Evaluating Solid Waste, SW-846*, U.S. Environmental Protection Agency, Office of Solid Waste and Emergency Response, Washington, DC.
- US-EPA. (2007). *Treatment Technologies For Mercury in Soil, Waste, and Water*, U.S. Environmental Protection Agency. Office of Superfund Remediation and Technology Innovation, Washington, DC.
- USDA. (1992). *Soil Survey Laboratory Methods Manual*, U.S. Department of Agriculture, Washington DC.
- Vanbenschoten, J. E., Reed, B. E., Matsumoto, M. R., and McGarvey, P. J. (1994). "Metal Removal by Soil Washing for an Iron-Oxide Coated Sandy Soil." *Water Environment Research*, 66(2), 168-174.
- Walkley, A., and Black, I. A. (1934). "An examination of the Degtjareff method for determining soil organic matter, and a proposed modification of the chromic acid titration method." *Soil Science*, 37(1), 29-38.
- Wang, Y. D., and Greger, M. (2006). "Use of iodide to enhance the phytoextraction of mercury-contaminated soil." *Science of the Total Environment*, 368(1), 30-39.
- Ward, M. L., Bitton, G., and Townsend, T. (2005). "Heavy metal binding capacity (HMBC) of municipal solid waste landfill leachates." *Chemosphere*, 60(2), 206-215.
- Wasay, S. A., Arnfalk, P., and Tokunaga, S. (1995). "Remediation of a Soil Polluted by Mercury with Acidic Potassium-Iodide." *Journal of Hazardous Materials*, 44(1), 93-102.

- Weatherford, J., Hammond, A., and Ratliff, J. (1997). "Investigation of the ability of plants found in western Kentucky to hyperaccumulate lead and aluminum from soils." *Microchemical Journal*, 56(1), 93-102.
- Weber, W. J., and Morris, J. C. (1963). "Kinetics of adsorption on carbon from solution." *Journal of the Sanitary Engineering Division. American Society of Civil Engineers*, 89 (SA2), 31-39.
- Weng, L. P., Temminghoff, E. J. M., and van Riemsdijk, W. H. (2001). "Contribution of individual sorbents to the control of heavy metal activity in sandy soil." *Environmental Science & Technology*, 35(22), 4436-4443.
- Xu, Y., Boonfueng, T., Axe, L., Maeng, S., and Tyson, T. (2006). "Surface complexation of Pb(II) on amorphous iron oxide and manganese oxide: Spectroscopic and time studies." *Journal of Colloid and Interface Science*, 299(1), 28-40.
- Yin, Y. J., Allen, H. E., Huang, C. P., Sparks, D. L., and Sanders, P. F. (1997). "Kinetics of mercury(II) adsorption and desorption on soil." *Environmental Science & Technology*, 31(2), 496-503.
- Yin, Y. J., Allen, H. E., Li, Y. M., Huang, C. P., and Sanders, P. F. (1996). "Adsorption of mercury(II) by soil: Effects of pH, chloride, and organic matter." *Journal of Environmental Quality*, 25(4), 837-844.
- Yong, R. N., Yaacob, W. Z. W., Bentley, S. P., Harris, C., and Tan, B. K. (2001). "Partitioning of heavy metals on soil samples from column tests." *Engineering Geology*, 60(1-4), 307-322.
- Zamzow, M. J., Eichbaum, B. R., Sandgren, K. R., and Shanks, D. E. (1990). "Removal of Heavy-Metals and Other Cations from Waste-Water Using Zeolites." *Separation Science and Technology*, 25(13-15), 1555-1569.

## BIOGRAPHICAL SKETCH

Anna Hovsepyan was born in Yerevan, Armenia in 1980. She received her bachelor's degree in environmental engineering from the State Engineering University of Armenia in 2001. In 2003, she received her master's degree in environmental analysis and management from Troy State University, Alabama, USA. Currently, she is a Ph.D. candidate under the supervision of Dr. Jean-Claude J. Bonzongo at the Department of Environmental Engineering Sciences at the University of Florida, USA.