Performance of Treatment Media for the Stabilization of Mercury under Variable Geochemical Conditions

by

Shannon Daugherty

A thesis
presented to the University of Waterloo
in fulfillment of the
thesis requirement for the degree of
Master of Science
in
Earth Sciences

Waterloo, Ontario, Canada, 2010

I hereby declare that I am the sole author of this thesis.

This is a true copy of this thesis, including any final required revisions, as accepted by my examiners.

I understand that this thesis may be made electronically available to the public.

Shannon Daugherty

ABSTRACT

Mercury-contaminated sediments are found in many locations throughout North America and the world. Release of Hg from such sediments and subsequent biological uptake can result in biomagnification in associated ecosystems. This study focused specifically on a stabilization technique involving the addition of reactive media to the sediment matrix to immobilize Hg and reduce its bioavailability. A series of batch and column experiments was conducted over a range of physical and geochemical conditions to evaluate the propensity of a diverse set of reactive media to stabilize Hg in sediment with high organic carbon and clay content. The additives, selected to promote adsorption and precipitation of Hg, included natural attapulgite (palygorskite) clay, organically-modified clay, elemental sulfur, a strong reducing agent, and mixtures thereof. The results of the batch experiments indicated that addition of reactive media to the sediment led to substantially lower aqueous concentrations of Hg relative to untreated sediment. The stabilization of Hg was observed to be dependent on mass of added reagent, with generally greater treatment observed for the higher masses of reagent evaluated. Aqueous concentrations of Hg were reduced from > 800 ng L^{-1} in control samples to < 50 ng L^{-1} in treated samples for all of the reactive media at the highest mass proportions evaluated. The effectiveness of Hg stabilization using the sulfur-based blends was strongly affected by contact with atmospheric oxygen, with better treatment observed in oxygen-limited conditions. The results of the column tests showed that relatively low concentrations of Hg (< 50 ng L^{-1}) were leached from untreated sediment, maintained under anoxic conditions, with steadily percolating water. However, increased concentrations of Hg (> 200 ng L^{-1}) were observed in column effluent collected from the untreated sediment following flow interruption. This release of high concentrations of Hg was not observed for the columns containing treated sediment after stagnation. Particularly low Hg concentrations were maintained in effluent collected from the sulfur-based treatment mixtures (< 40 ng Hg L^{-1}) for the entirety of the experimental duration, regardless of flow perturbations.

Acknowledgements

I extend many thanks to my supervisor, Carol Ptacek, for offering me this great opportunity and for all her guidance and support through the course of my degree. I also thank Dave Blowes for inspiring me to pursue my degree at the University of Waterloo and to both he and Doug Gould for their thoughtful insight into this thesis. Your interest and dedication to the sciences serve as a model for each of us.

My sincere thanks go to Rich Landis, for all of his kind encouragement and guidance over the past two years. His endless appreciation and support for our work, and his cheerful attitude have helped me to stay focused and enthusiastic about the project. I would also like to thank Blair Gibson and Matt Lindsay for all of their thoughtful discussion and advice. Endless thanks to Laura Groza for her endless hours spent in the lab, to Corina MacDonald for welcoming me and orienting me to the research group, and to James Tordiff and all the many other students who have helped me with my research.

I would also like to thank DuPont and NSERC for their generous funding for our research project, and additionally for their support of the scientific advancement and the protection of our environment.

Special thanks to all my dear friends for the laughs, love, and encouragement. Jen Parks, Brenda Bailey, Nathan Cleven, and Luiz Celso Gomes Jr., you’ve been an endless source of light in my life and I can’t imagine being here without each of you. Finally, my deepest gratitude is with my family, for your love, loyalty, and support. Thank you.

Table of Contents

List of Tables

List of Figures

List of Abbreviations

AF	Atomic flourescence
ATP	Attapulgite clay
CEC	Cation exchange capacity
CONTROL	Sediment control
DI	Deionized water
DMeHg	Dimethylmercury
HH	Hydroxylamine hydrochloride
IC	Ion chromatography
ICP-MS	Inductively coupled plasma-mass spectrometry
IRB	Iron-reducing bacteria
LCW	Laurel Creek Water
MeHg	Methylmercury
MRM	Organically-modified bentonite clay
PV	Pore volume
S	Elemental sulfur
SI	Saturation index
SRB	Sulfer-reducing bacteria
ZVI	Zero-valent (elemental) iron

Chapter 1:

Introduction

1.1 Background

Mercury (Hg) is a highly toxic contaminant that can have severe impacts on ecosystems and human health, but its ecological and toxicological effects are species-dependent (Fitzgerald and Lamborg, 2005). Mercury occurs naturally in the environment, cycling between air, land, and water. There are three known naturally-occurring oxidation states of Hg, including Hg^{2+}, Hg^{+}, and Hg^{0}, and two organic forms, monomethylmercury (MeHg) and dimethylmercury (DMeHg). The methyl forms of Hg are highly toxic and readily bioaccumulate in the food web. Due to this bioaccumulative effect, Hg poisoning is most threatening to predatory animals, including humans.

Anthropogenic activities have increased the global cycling of Hg and have caused the unnatural accumulation of Hg in many locations throughout the world (Fitzgerald and Lamborg, 2003). The unique physio-chemical properties of Hg make its use in various industrial and agricultural operations widespread. For example, the extremely high surface tension and volatility of Hg make it useful for the processing of Ag and Au-ores. Mercury amalgamates with precious metals due to the high surface tension and affinity for other metals and can later be easily separated by exploiting the low volatilization temperature of Hg. Historically, Hg was released into the environment through a number of processes including precious metal mining, chloralkali manufacturing of pulp and paper, and mining and smelting activities (Boening, 2000). Release of Hg to the environment is now largely controlled in the western world, but continues to be a concern in developing countries. Currently, the most significant anthropogenic inputs of Hg to the environment are atmospheric and result from high temperature combustion processes, including burning of fossil fuels and municipal waste (Fitzgerald and Lamborg, 2005).

Mercury is persistent in the environment, and as a result of past industrial activities, sediments containing elevated concentrations of Hg are found throughout the world. Sediments can act as a sink for atmospheric and aqueous Hg and other contaminants, but also behave as a source as weathering of contaminated sediments releases low levels of Hg to the environment over long periods of time (Renholds, 1998). The tendency for Hg to methylate and bioaccumulate to concentrations in organisms that are millions of times higher than in the water column, means even trace concentrations of Hg are problematic in the environment (Zillioux et al., 1993). Therefore, remedial strategies focused on the stabilization of Hg-contaminated sediments are required for locations where release of Hg into aquatic environments and subsequent methylation and bioaccumulation are concerns.

Methods to remediate contaminated sediment focus either on limiting the bioavailability of Hg to prevent its uptake by organisms (e.g., sediment washing to remove Hg, thermal extraction, solidification/stabilization) or inhibiting Hg-methylation (e.g., through addition of reactive media to suppress the activity of microorganisms responsible for the methylation of Hg) (Mulligan et al., 2001). Due to the species-dependent nature of Hg mobility and toxicity (Compeau and Bartha, 1985; Benoit et al, 1999), remedial approaches that promote formation of non-bioavailable forms of Hg can be highly successful.

Treatment methods can be classified into three general categories, including: a) *ex-situ* recovery, b) *in-situ* recovery, and c) immobilization and stabilization methods (e.g., Hinton and Viega, 2001; Mulligan et al., 2001). Due to the complex biogeochemical cycling of Hg in the environment, large variations in remediation costs, and other socioeconomic factors, the choice of remediation option for a particular location is usually site-specific and rarely clear. Extensive research into site characterization as well as the mechanisms influencing Hg-release into the aqueous phase is necessary.

1.2 Research Objectives

The primary objective of this study was to evaluate a novel approach for stabilizing Hg in a sediment matrix. Addition of reactive media to contaminated sediments has the potential to provide a cost-effective management strategy for many sites. The goal of investigating sediment additives is to provide a long-term solution for minimizing bioavailable Hg. The specific objectives of this study include:

- Evaluate a series of reactive media to determine the most effective media / media combinations at stabilizing Hg in a contaminated lacustrine sediment.
- Determine the optimum reagent ratio for stabilization of Hg under variable redox conditions.
- Investigate the impact of reactive media addition on pore water composition.

- Monitor long-term performance of the media combinations in anoxic conditions.

1.3 Thesis Organization

This thesis is presented as two research papers related to the objective outlined out in the previous section. Chapter 2 describes a series of batch experiments designed to determine the reactive media / media combinations most effective at immobilizing Hg in an organic-rich lacustrine sediment. The sensitivity experiments described in Chapter 2 were designed to assess the influence of reagent ratio and redox environment on media performance. Chapter 3 describes a series of column experiments designed to evaluate the long-term effectiveness of the reagent combinations under anoxic conditions. The conclusions from this work are summarized in Chapter 4.

Chapter 2:

Assessment of Treatment Media Performance for the Stabilization of Mercury under Variable Geochemical Conditions

2.1 INTRODUCTION

Sediments containing elevated concentrations of mercury (Hg) are found in many locations throughout the world, often the result of past industrial releases. Mercury can be problematic to ecosystems, primarily due to its tendency to methylate and bioaccumulate. Because the mobility and toxicity of Hg are speciation-dependent (Compeau and Bartha, 1985; Benoit et al, 1999), remedial approaches promoting the formation of non-bioavailable or stable species have the potential to be highly successful at treating Hg-contaminated sediments. Due to the large variability in remediation costs and the complex biogeochemical cycling of Hg in the environment, the selection of an optimum approach for Hg remediation is rarely clear.

Sediments are commonly thought of as the ultimate sink for Hg and other contaminants in the environment (Renholds, 1998). Therefore, strategies targeting the immobilization or stabilization of Hg within the sediment matrix present appealing remedial options. The tendency for Hg to methylate and bioaccumulate often make *ex-situ* management of Hg-contaminated sediments an appealing alternative to *in-situ* treatment. Sediments can be dredged from the location where bioaccumulation is a primary concern (such as lake or river systems), and either remediated directly or treated and buried in an alternate location where conditions can be managed to enhance Hg stability and suppress methylation. Many treatment approaches focus on the removal of Hg from the sediment, such as washing, thermal extraction, and electrokinetics (Mulligan et al., 2001), but these approaches require further containment or treatment of the concentrated Hg and are therefore only cost-effective for heavily contaminated sites. E*x-situ* solidification/stabilization is any process involving the addition of a chemical agent to the sediment with the intent of forming a stable solid to immobilize the contaminant, and includes cementation and polymerization (Mulligan et al., 2001). This approach offers an alternative means of managing Hg-contaminated sediments, through intentional immobilization of Hg.

Immobilization can likewise be accomplished by addition of reactive media which target adsorption as the primary mechanism of contaminant removal. Manufactured media with increased adsorption capacity include various forms of activated carbon and organically-modified clays (e.g. Viana et al., 2008; Say et al., 2007). The processing of these treatment materials can make their use in field application costly, as well. Trace concentrations of Hg (ng L^{-1}) can bioaccumulate to potentially toxic levels if conditions conducive to methylation exist (Zillioux et al., 1993), making it necessary to explore treatment options for sites considered to have relatively low level Hg contamination (µg g^{-1}). For sites containing lower amounts of Hg, a more natural, less expensive treatment media may be preferred.

The complex biogeochemical cycling of Hg requires development of site-specific remedial approaches, and implementation of an effective remediation strategy necessitates a detailed understanding of mechanisms contributing to the cycling and release of Hg. Findings by Benoit et al. (1999) have shown methylation to be directly related to the concentration of dissolved HgS^0, which is passively taken up by sulfate-reducing bacteria (SRB), the primary methylators of Hg. Therefore, it follows that if this species can be limited from solution, methylation can be suppressed. Accumulation of excess sulfide is found to result in decreased methylation, presumably due to the increased precipitation of mercury sulfide solids (Benoit et al, 1999), an effect commonly referred to in the literature as sulfide inhibition.

Sediments may be exposed to a wide range of geochemical conditions upon dredging and reburial (i.e. oxic, anoxic, changing aqueous composition, pH, etc.), thus, it is necessary to evaluate the robustness of the media under expected exposure conditions. The focus of this study is to evaluate the effectiveness of a range of reactive media additives to promote either adsorption of Hg or precipitation of sparingly-soluble Hg-sulfide solids under varied geochemical conditions. Experimental investigations were performed to assess the effectiveness of two clay additives including a natural and widely available attapulgite (palygorskite) clay and a commercially available organically-modified clay to stabilize Hg in sediment. Elemental iron and elemental sulfur were also investigated to assess the ability of these treatment media to limit Hg concentrations. Elemental forms of S and Fe were selected as stabilizing additives rather than solid iron-sulfides due to the slow dissolution kinetics of iron-sulfides (Wersin et al., 1991; Svensson et al., 2006), and the strong reducing potential of Fe^0. The effects of redox condition (oxic vs. anoxic), mass of reagent, and the chemical composition of the aqueous phase (pH, alkalinity, competing ions) on the effectiveness of treatment of Hg-contaminated sediments by the four treatment additives were examined.

2.2 METHODOLOGY

2.2.1 Experimental Approach

Batch experiments that included mixtures of lake sediment, treatment media, and water were conducted to evaluate the short-term stabilization potential of selected media and to determine the optimal sediment to media ratio. The additives were mixed and allowed to react in contact with an O_2-rich atmosphere (oxic experiments) or within an enclosed chamber filled with 95 % N_2/ 5% H_2 gas (anoxic experiments). The stabilization and/or adsorption capacity of four reactive materials (Section 2.2.2.3) were thoroughly evaluated, individually and in combination under oxic and anoxic conditions.

2.2.2 Materials

2.2.2.1 Sediment

Five sediment samples were collected from the delta of a eutrophic lake in the northeastern United States known to contain elevated concentrations of inorganic Hg, as well as relatively high concentrations of carbon and sulfur (Table 2.1). The sediments were collected from the lake using a sediment coring device and refrigerated until shipped to the University of Waterloo by overnight courier, where they were stored at 4° C. To minimize sediment oxidation, sample containers were opened for handling in an anoxic chamber (COY glovebox containing a 95% N_2, 5% H_2 atmosphere). For the initial batch experiments, Sediment A was selected for experimentation based on results of previous characterization studies, which indicated that the total Hg concentration (115 mg kg^{-1}) was elevated and the sediment had the potential to readily leach Hg into interstitial waters (Table 2.1) (Gibson et al., in progress). For the long-term and mass sensitive experiments, the five sediment samples were blended in equal mass proportions to yield a larger bulk sample.

2.2.2.2 Water

The water added to the reactive mixtures was obtained from the headwaters of Laurel Creek, Waterloo, Ontario (LCW). This water contained low concentrations of total Hg and measurable dissolved organic carbon (Table 2.2) and was similar in composition to the water in contact with the lake sediments.

2.2.2.3 Treatment media

The treatment media evaluated included oxidized elemental sulfur (S) (Adventus, Mississauga, Ontario), attapulgite clay (ATP) (Zemex, Attapulgus, GA), organically-modified bentonite clay (MRM) (Cetco, Hoffman Estates, IL), and $H_2Omet^{TM}58$ granular zero-valent iron (ZVI) (QMP, Sorel-Tracy, Quebec) (Table 2.3). Coarse-grained material was selected in preference to fine-grained material such as nanoparticles to facilitate longevity of treatment. Treatment media was obtained from suppliers and used without further processing.

2.2.3 Batch experiments

Experimental samples containing 4 g reactive media, 40 g wet sediment, and 160 mL LCW were prepared and reacted for 1, 14, and 21 days, after which time concentrations of aqueous Hg in contact with the sediment were measured. Control samples contained 40 g wet sediment, 160 mL LCW, and no reactive media. Samples were hand-shaken to homogenize the additives, loosely capped to allow excess oxygen to remain in the head space, and left to stagnate for the designated reaction time. Stagnation was implemented to mimic anticipated post-depositional field conditions.

2.2.4 Sensitivity tests

Experimental mixtures showing optimal reactivity were further evaluated by modifying the ratio of reactive materials to assess the minimum amount of treatment media required to promote Hg immobilization/stabilization. Experiments were performed on each individual media (single-media tests), and in combination (bi-media tests). Concentrations of major ions and trace elements also were determined to evaluate effects of reactive media addition. Each sample contained 40 g of the homogenized sediment, 160 mL LCW, and varying amounts of media (Table 2.4). Single-media samples were prepared with 5% (1.0 g), 10% (2.0 g) and 20% (4.0 g) reactive media on a dry-weight basis. The effectiveness of Hg stabilization for the bi-media treatment mixtures was evaluated using the same total percentages of treatment media, but with variations of the media selected in a step-wise progression so that as mass of one reagent was increased the mass of the other reagent was decreased. All treatment mixtures were allowed to equilibrate under stagnant conditions for 14 days.

2.2.5 Collection of Water Samples

At the end of the reaction time each sample was destructively sampled by the following procedure. Samples were vigorously hand-shaken for ~20 s and then poured from the 250 mL amber bottle into new polypropylene centrifuge tubes. The samples were centrifuged at 6000 rpm for 15 min to separate the solids and facilitate the filtering process. The supernatant water was filtered using 0.45 µm Supor® membrane fiber filters. For the Hg analyses, four 20 mL aliquots were collected in trace-clean amber glass vials (VWR); two samples were preserved with concentrated Omni trace ultra high purity HCl (Baker Instra-Analyzed) and two samples were preserved with ultra purity HNO_3 (EMD Chemicals) to a $pH < 2.0$. Samples were individually bagged to minimize cross-contamination among the samples. Samples for cation analyses were collected in 10 mL polypropylene bottles and acidified with Omni trace HNO_3 to a $pH < 2.0$. Samples for anion analyses were collected in 10 mL polypropylene bottles without the addition of a preservative. All samples were stored at 4°C until analysis.

Measurements of pH were made using an Orion Ross combination pH electrode (model number 8156BNWP) and Eh measurements were made with an Orion Pt - Ag/AgCl combination redox electrode (model number 9678BNWP), both on unfiltered water. The pH electrode was calibrated with standard buffer solutions of pH 4, 7, and 10, and the response of the Eh electrode was checked regularly against Zobell's (Nordstrom, 1977) and Light's (Light, 1972) solutions. Measurements of alkalinity were made on filtered samples using a Hach digital titrator with bromylcresol green/methyl red indicator and 0.16 N H_2SO_4.

2.2.6 Mitigation of Contamination

Throughout the course of experimentation, progressive modifications were made to the procedures to minimize contamination of samples, surfaces, and the glovebox atmosphere. For the oxic samples, after initially allowing excess oxygen to enter the headspace of the reaction vessels, further exposure of the samples to atmospheric Hg was minimized by lightly capping bottles with teflon-lined lids. For the anoxic experiments, glovebox surfaces were frequently wiped to remove residual Hg and trays of activated carbon were placed in the glovebox to adsorb volatile Hg and H_2S. Experimental controls consisting of deionized water (DI) were exposed to the atmosphere for the same time as the reactive media mixtures to assess whether contamination was occurring during sample handling. Control samples containing only water were included for every 10-15 samples and were centrifuged, filtered, and preserved in the same manner as the sediment samples. Concentrations of Hg in the controls were consistently < 5 ng L^{-1} throughout the duration of the sensitivity experiments.

2.2.7 Analytical Methods

Analysis of total aqueous Hg was performed according to US EPA Method 1631, Revision E (US EPA, 2002). Acid-preserved samples were oxidized with 0.5% BrCl at least 12 hours prior to analysis. A 0.1% hydroxylamine hydrochloride (HH) solution was added to the samples before analysis to remove residual halides. Stannous chloride ($SnCl_2$) was added in excess during analysis to reduce oxidized Hg to its elemental form. Reduced Hg was concentrated on a dual gold trap and analyzed by an atomic fluorescence (AF) detector using a Tekran® Series 2600 Ultra-trace Hg Analyzer. Concentrations of major cations and trace elements were analyzed by inductively coupled plasma-mass spectrometry (ICP-MS) (Thermo X Series II quadrupole) and concentrations of anions were determined by ion chromatography (IC) (Dionex DX-600).

2.2.8 Geochemical and Speciation Modeling

Saturation indices (SIs) were calculated using the geochemical equilibrium/mass-transfer code MINTEQA2 (Allison et al., 1990). Thermodynamic constants in the database were modified to be consistent with WATEQ4F (Ball and Nordstrom, 1991). Dissolved sulfide concentrations were not determined during the experiment. To assess the potential effects of dissolved sulfide, the calculations were conducted assuming equilibrium with respect to FeS, which provided estimates of sulfide concentrations based on the measured iron concentrations. This assumption was made based on observations by Wersin et al. (1991), which showed that water is typically in equilibrium with respect to iron sulfide in organic-rich, sulfate-reducing environments. Speciation modeling was not performed for the bi-media sensitivity samples, because the water collected from both combinations contained high levels of sulfate and were assumed not to have become strongly sulfate-reducing.

2.3 RESULTS AND DISCUSSION

2.3.1 Batch Experiments

Batch-style experiments were designed to evaluate the effect of multiple variables on the stabilization of Hg, including: reaction time, reagent mass, reagent combinations, and redox conditions. The sediment control, containing only sediment and LCW, released between 700 and 1000 ng Hg L^{-1} to the water under oxic conditions. Lower aqueous concentrations of Hg (25-40% decrease) were observed in the sediment control mixture under anoxic conditions (Figure 2.1). The addition of treatment media resulted in further decreases in aqueous Hg concentrations, 25-75% below the control concentrations. The decreases in concentrations were more subdued under oxic conditions than under anoxic conditions. No obvious temporal trends were observed over the time frame evaluated. The most promising media combinations included S+ZVI and MRM+ATP, which were investigated to assess mass-dependency in the subsequent sensitivity experiments. The clay ATP was also selected for a more thorough investigation considering its low cost, availability, and the results of the short-term experiments.

2.3.2 Sensitivity Tests

For this set of experiments, four individual treatment media and two media combinations were selected based on results from previous screening tests; including: ZVI, S, ATP, MRM, S+ZVI and MRM+ATP. Treatment efficiency, as determined by low aqueous Hg concentrations, was found to be dependent on reagent combination, reagent ratio, and redox environment (Figures 2.2 and 2.3). With the exception of samples containing only

S, which exhibited distinctive behavior, the single-media treatment of Hg under anoxic conditions did not display a strong dependence on reagent mass. For all of the single-media anoxic samples, aqueous Hg concentrations were consistently maintained below 100 ng L^{-1}, with the exception of mixtures containing 1 g S, 10 g S, and 1 g ATP (Table 2.4). Given that ATP has a relatively low cation exchange capacity (CEC) (Weaver and Pollard, 1973) sorption limitations likely played a role in the modest effectiveness of the 1 g ATP addition.

Concentrations of Hg were likewise maintained at < 200 ng L^{-1} for all bi-media combinations. A more pronounced mass-dependency was observed for the bi-media mixtures. Concentrations of aqueous Hg were maintained below 100 ng L^{-1} for samples containing a minimum of 2.25 g of treatment reagent. The low mass of Hg released under anoxic conditions suggests that the Hg is likely bound in a stable reduced form in the unoxidized sediment. This observation is consistent with studies by Gibson et al. (in progress), which indicated that Hg contained in the untreated sediment is bound predominantly as a stable mercury sulfide or possibly mercury selenide. Under anoxic conditions, the mass of Hg released from sediment was more strongly dependent on the mass of reagent added than the type of reagent used.

Treatment efficiency under oxic conditions was affected by both mass and type of reagent added. Aqueous Hg concentrations were much more variable, and more dependent on the mass of treatment media under oxic conditions than under anoxic conditions, although this effect was subdued for the MRM+ATP mixture relative to the

S+ZVI mixture. For the single-media treatment addition of 1 g, aqueous Hg was lowest for the two clays evaluated. A decrease in aqueous Hg concentrations corresponded with increasing mass of treatment media, and concentrations were consistently maintained at < 65 ng L^{-1} for all reagents evaluated at 4.0 g. The lowest aqueous Hg concentration for the single-media treatment was observed for S (4.0 g) under oxic conditions, from 400 ng L^{-1} in the unamended sediment to 40 ng L^{-1} for the treated sediment. The best overall treatment for oxic conditions was observed for the reactive media combination containing S (2.0 g) + ZVI (0.5 g), with aqueous Hg concentrations maintained at < 30 ng L^{-1}.

The results from the sensitivity tests indicated generally lower aqueous Hg concentrations under anoxic conditions than under oxic conditions. These results are expected according to thermodynamic calculations which show a far greater stability of HgS under anoxic conditions, and a thermodynamic instability of HgS in the presence of oxygen (Barnett et al., 2000).

$$HgS_{(s)} + 2H_2O \leftrightarrow Hg(OH)_2^0 + H_2S \qquad K = 10^{-38} \qquad (2.1)$$

$$HgS_{(s)} + 2O_{2(aq)} + 2H_2O \leftrightarrow Hg(OH)_2^0 + SO_4^{2-} + 2H^+ \qquad K=10^{93} \qquad (2.2)$$

In support of these thermodynamic calculations, Svenssen et al. (2006) reported that the addition of elemental sulfur to vials containing HgO or Hg^0 formed HgS almost 100% of the time under anoxic, alkaline conditions after two years of reaction time. For anoxic conditions, saturation indices (SIs) calculated for the sensitivity tests predict supersaturation with respect to mercury sulfide phases (Figure 2.6). For oxic conditions, other Hg-phases, such as $HgCO_3$ and $Hg(OH)_2$, approach, but do not attain saturation. Possible Hg-controlling phases are listed in Table 2.5.

The reduction of H_2O by Fe^0 produces H_2 gas, which can be used by sulfate-reducing bacteria (SRB) as an electron donor. The reduction of sulfate by SRB can result in the production of sparingly-soluble mercury sulfide minerals (Weisener et al., 2005).

$$SO_4^{2-} + 2CH_2O \rightarrow H_2S + 2HCO_3^- \tag{2.3}$$

where CH_2O represents a generic form of organic carbon. The release of high concentrations of H_2S into solution and the accompanying shift in pH can result in the precipitation of sparingly soluble mercuric sulfide solids.

$$Hg^{2+} + HS^- \rightarrow HgS_{(s)} + H^+ \tag{2.4}$$

The lowest concentrations (< 40 ng L^{-1}) were observed for oxic mixtures containing the highest masses of treatment media [Oxic: MRM (4g), ATP (4g), S (4g), MRM (2g) + ATP (2g), and S (2g) + ZVI (0.5g); Anoxic: S (2g) + ZVI (2g)]. This deviation from expected results may be due in part to contamination of the enclosed atmosphere within the anoxic glovebox by volatile Hg^0, leading to slight contamination of water samples during sampling.

The pH, Eh, and alkalinity of the equilibrated mixtures were not substantially affected by mass of reagent added, with pH and Eh remaining nearly constant for the different masses evaluated (Figures 2.2 and 2.3). Values of pH were slightly lower under oxic conditions than under anoxic conditions, although the difference never exceeded 0.5 pH units. The lower pH under oxic conditions most likely resulted from acid-production during oxidation of organic carbon (Equation 2.5) and iron sulfide minerals (Equation 2.6).

$$CH_2O + O_2 \leftrightarrow CO_3^{2-} + 2H^+ \qquad (2.5)$$

$$FeS_{2(s)} + 14Fe^{3+} + 8H_2O \leftrightarrow 15Fe^{2+} + 2SO_4^{2-} + 16H^+ \qquad (2.6)$$

Minor shifts in pH (< 1 pH unit) corresponded with increased mass of some reagents. A slight increase in pH was observed with increasing mass of ATP, likely due to base-releasing minerals associated with the clay. An opposite shift in pH was observed with increased mass of S, decreasing in pH from 6.7 with 1 g S to a pH of 5.9 with 4 g S, likely due to acid formed from sulfur oxidation reactions prior to use. The pH was relatively constant for samples with variable masses of ZVI and MRM. For the bi-media combinations, decreases in pH corresponded to increases in mass for the S+ZVI mixtures. The pH of the water in contact with all mixtures ranged from 5.9 to 7.6. Values of Eh were generally 100 to 300 mV lower under anoxic conditions than under oxic conditions, as expected. The range of Eh is consistent with expected values for both oxic (250 to 450 mV) and anoxic conditions (< 0 mV), with the exception of the anoxic MRM (4 g) sample, which was approximately 200 mV.

The alkalinity was slightly lower (15 to 150 mg L^{-1} as $CaCO_3$) for all of the treatment mixtures reacted under oxic conditions than for those reacted under anoxic conditions (100 to 300 mg L^{-1} as $CaCO_3$). This decline in alkalinity was likely due to consumption of alkalinity through reaction with acid generated from organic carbon and sulfide mineral oxidation (Evangelou and Zhang, 1995, Benner et al., 1999). Alkalinity was observed to increase with increasing mass of ATP under anoxic conditions, but not under oxic conditions. The alkalinity was consumed almost completely (< 20 mg L^{-1} as $CaCO_3$) by the high masses of S (2 g and 4 g), suggesting the potential loss of buffering capacity with the addition of this media. Addition of a carbonate buffer may be required to maintain near neutral pH values during field applications of S additions. If alkaline pH can be maintained, elemental S may present a promising remedial option. These results are consistent with results reported by Svensson et al. (2006), who observed HgS to form in the presence of elemental S in aqueous systems under anoxic, alkaline conditions.

The composition of the aqueous phase requires consideration when selecting a remedial option for a specific site. For instance, electrolyte concentration can have a strong effect on Hg speciation, and in turn control the speciation and bioavailability of Hg (Nriagu, 1979). Following equilibration of sediment and reactive media, the chemical composition of the aqueous phase was analyzed for the sensitivity tests, including analysis of major, minor, and trace elements. Major changes in water chemistry were not observed in response to the addition of ATP or ZVI. Aqueous concentrations of Na, Mg, Mn, Sr, Cl, and SO_4 increased by 300 to 400%, Fe increased by ~ 50%, and Ca increased by ~ 250% with increasing mass of MRM from 1 g to 4 g (Figure 2.4). Increasing MRM in the bi-media combinations resulted in an increase of the same constituents, but only from 50 to 200%, in most cases. Addition of S also corresponded to an increase in aqueous SO_4 concentration, similar to that observed for the MRM mixtures. Similar trends were observed for the bi-media combinations (Figure 2.5). Addition of soluble SO_4 in the range of 30-100 μM SO_4 may be undesirable due to its potential to promote Hg methylation under reducing conditions (Gilmore et al., 1998). However, in the presence of high concentrations of dissolved SO_4, Weisener et al. (2005) found that aqueous Hg was successfully removed from contaminated pore water by passage through ZVI-packed columns under constant flow conditions. Furthermore, Weisener observed the formation of mercuric sulfide, inferred to be metacinnabar, on the ZVI surfaces. Therefore, while the presence of SO_4 can lead to methylation, SO_4 also may be a beneficial component for the stabilization of Hg if redox conditions conducive to the reduction of sulfate prevail.

Increasing mass of MRM and S was accompanied by a corresponding increase in Si by approximately 5 mg L^{-1}. Increasing mass of ATP and ZVI had the opposite effect of decreasing concentrations of Si by approximately 3 mg L^{-1}. Concentrations of Si were nearly four times higher under anoxic conditions (17 to 42 mg L^{-1}) than under oxic conditions (4-13 mg L^{-1}), indicating the possible dissolution of silicate minerals under anoxic conditions. Concentrations of the elements Al, Cu, Co, Sr, and As were not substantially affected by the mass of reagent added and are not included in the figures.

Concentrations of Al were maintained below 0.3 mg L^{-1}. The upper bound of the trace element concentrations are as follows: Cu < 50 μg L^{-1}, Co < 1.2 μg L^{-1}, Sr < 0.4 μg L^{-1}, and As < μg L^{-1}.

2.4 CONCLUSIONS

The results from the stabilization experiments indicate that over the time frame of the experiments (up to 21 days), the mass of Hg released from the sediment could be reduced with the addition of reactive media. The greatest decreases in aqueous Hg concentrations were observed for reagent mixtures, including S+ZVI and MRM+ATP. Sediment that leached in excess of 1000 ng Hg L^{-1} in the control samples leached as little as 30 ng L^{-1} for the treatment combinations. Aqueous Hg concentrations were independent of redox conditions for the sediment mixtures containing MRM+ATP. At low masses of reactive media added, the sediment mixtures containing S+ZVI did display a redox-dependency with greater treatment observed under anoxic conditions. Increasing the mass of these reagents lowered aqueous Hg and eliminated the strong redox-dependency observed at the lower mass additions. Values of pH and alkalinity also declined with the addition of this reactive mixture, suggesting that a carbonate buffer also may be warranted for field applications.

It is expected that different primary geochemical stabilization mechanisms were promoted by the two media combinations. The clay combination most likely promoted immobilization through adsorption, and possibly precipitation reactions with sulfide. If the sulfate released from the addition of MRM were reduced, formation of mercury sulfide could be possible, as well as co-precipitation or adsorption of Hg by FeS. Mercury sulfide mineral precipitation is expected to have occurred for the S+ZVI combination, and to a lesser extent, adsorption of Hg to iron sulfide surfaces. Further analysis of the solid phase and microbial populations would be needed before removal mechanisms could be determined with greater certainty. Although both combinations show promising results in the controlled laboratory environment over the short-term, precipitation of sparingly-soluble sulfide minerals would be the preferred remedial mechanism to manage Hg in the field over longer time periods due to the high stability of HgS minerals.

The most effective of the reactive media mixtures (S+ZVI and MRM+ATP) were associated with increased SO_4 concentrations. Because high concentrations of dissolved sulfate have been found to correlate with higher rates of Hg methylation, applications utilizing these media should evaluate the potential for methylation reactions.

Table 2.1
Solid-phase concentration of selected constituents expressed on a dry weight basis. Concentrations from Gibson et al. (in progress).

SEDIMENT	**Hg (mg kg^{-1})**	**Ca (mg kg^{-1})**	**Fe (mg kg^{-1})**	**C (%)**	**S (%)**
A	115	14,400	15,500	23.3	1.2
B	79	8,950	20,500	8.4	0.3
C	335	7,150	25,000	6	0.4
D	240	7,000	26,000	5.4	0.6
E	140	5,500	18,500	7.6	0.3
MEAN	182	8,600	21,100	10	1

Table 2.2
Chemical composition of Laurel Creek Water (LCW)

PARAMETER	VALUE
pH	7.5
Eh (mV)	640
Alkalinity (mg L^{-1} as $CaCO_3$)	225
Cl (mg L^{-1})	28
NO_3 (mg L^{-1})	6
SO_4 (mg L^{-1})	35
Na (mg L^{-1})	13
Mg (mg L^{-1})	15
K (mg L^{-1})	1.6
Ca (mg L^{-1})	39
Al (μg L^{-1})	5
Mn (μg L^{-1})	1.4
Fe (μg L^{-1})	50
Se (μg L^{-1})	1.1
Pb (μg L^{-1})	2.6
Hg (ng L^{-1})	9
TP (mg L^{-1})	0.1
NH_3+NH_4 (mg L^{-1})	0.1
TKN (mg L^{-1})	1.8
TOC (mg L^{-1})	3.7
DOC (mg L^{-1})	3.8

Table 2.3 Source, abbreviation, and grain-size of treatment media

REAGENT	ABBREVIATION	SOURCE	GRAIN SIZE
Elemental Sulfur	S	Adventus	>2000 µm
Attapulgite Clay	ATP	Zemex	<125 µm
Organically-modified Clay	MRM	Cetco	250-590 µm
Zero-valent Iron	ZVI	QMP	250-590 µm

Table 2.4 Reagent mass ratios used for the sensitivity tests

Sample	ATP g (%, dry)	MRM g (%, dry)	ZVI g (%, dry)	S g (%, dry)
1	0.5 (1.9)	-	-	-
2	2.0 (7.1)	-	-	-
3	4.0 (13.3)	-	-	-
4	-	0.5 (1.9)	-	-
5	-	2.0 (7.1)	-	-
6	-	4.0 (13.3)	-	-
7	-	-	0.5 (1.9)	-
8	-	-	2.0 (7.1)	-
9	-	-	4.0 (13.3)	-
10	-	-	-	0.5 (1.9)
11	-	-	-	2.0 (7.1)
12	-	-	-	4.0 (13.3)
13	0.25 (0.62)	0.25 (0.62)	-	-
14	0.25 (0.61)	0.5 (1.2)	-	-
15	0.25 (0.59)	2.0 (4.7)	-	-
16	0.5 (1.2)	0.25 (0.61)	-	-
17	0.5 (1.2)	0.5 (1.2)	-	-
18	0.5 (1.2)	2.0 (4.7)	-	-
19	2.0 (4.7)	0.25 (0.59)	-	-
20	2.0 (4.7)	0.5 (1.2)	-	-
21	2.0 (4.5)	2.0 (4.5)	-	-
22	-	-	0.25 (0.62)	0.25 (0.62)
23	-	-	0.25 (0.61)	0.5 (1.2)
24	-	-	0.25 (0.59)	2.0 (4.7)
25	-	-	0.5 (1.2)	0.25 (0.61)
26	-	-	0.5 (1.2)	0.5 (1.2)
27	-	-	0.5 (1.2)	2.0 (4.7)
28	-	-	2.0 (4.7)	0.25 (0.59)
29	-	-	2.0 (4.7)	0.5 (1.2)
30	-	-	2.0 (4.5)	2.0 (4.5)

Table 2.5
Possible Hg-controlling phases

MINERAL NAME	FORMULA
Cinnabar	**HgS**
Metacinnabar	**β-HgS**
Mercury carbonate	**$HgCO_3$**
Mercury chloride	**$HgCl_2$**
Mercury Oxide	**HgO**
Mercury Hydroxide	**$Hg(OH)_2$**
Mercury Sulfate	**$HgSO_4$**
Pyrhhotite	**FeS**
Pyrite	**FeS_2**
Marcasite	**FeS_2**

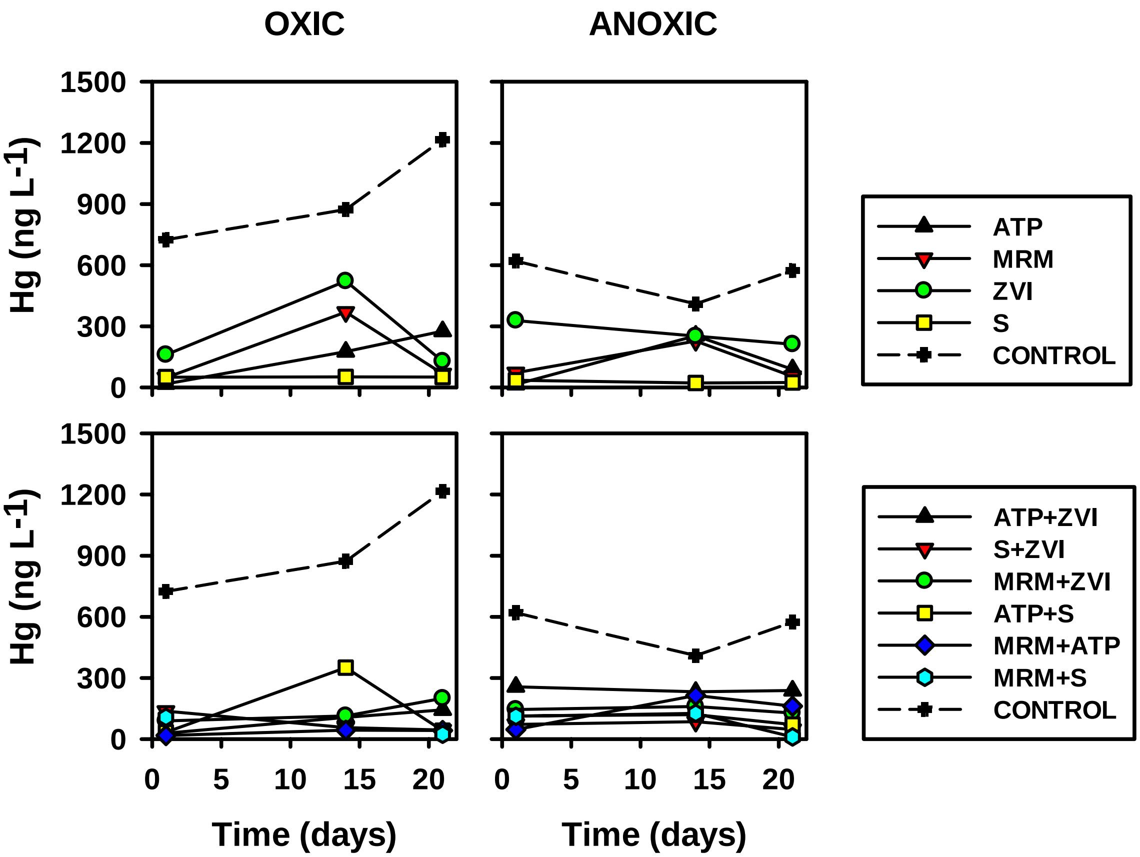

Figure 2.1 Concentrations of total dissolved Hg (ng L^{-1}) for different treatment media as a function of time and redox environment.

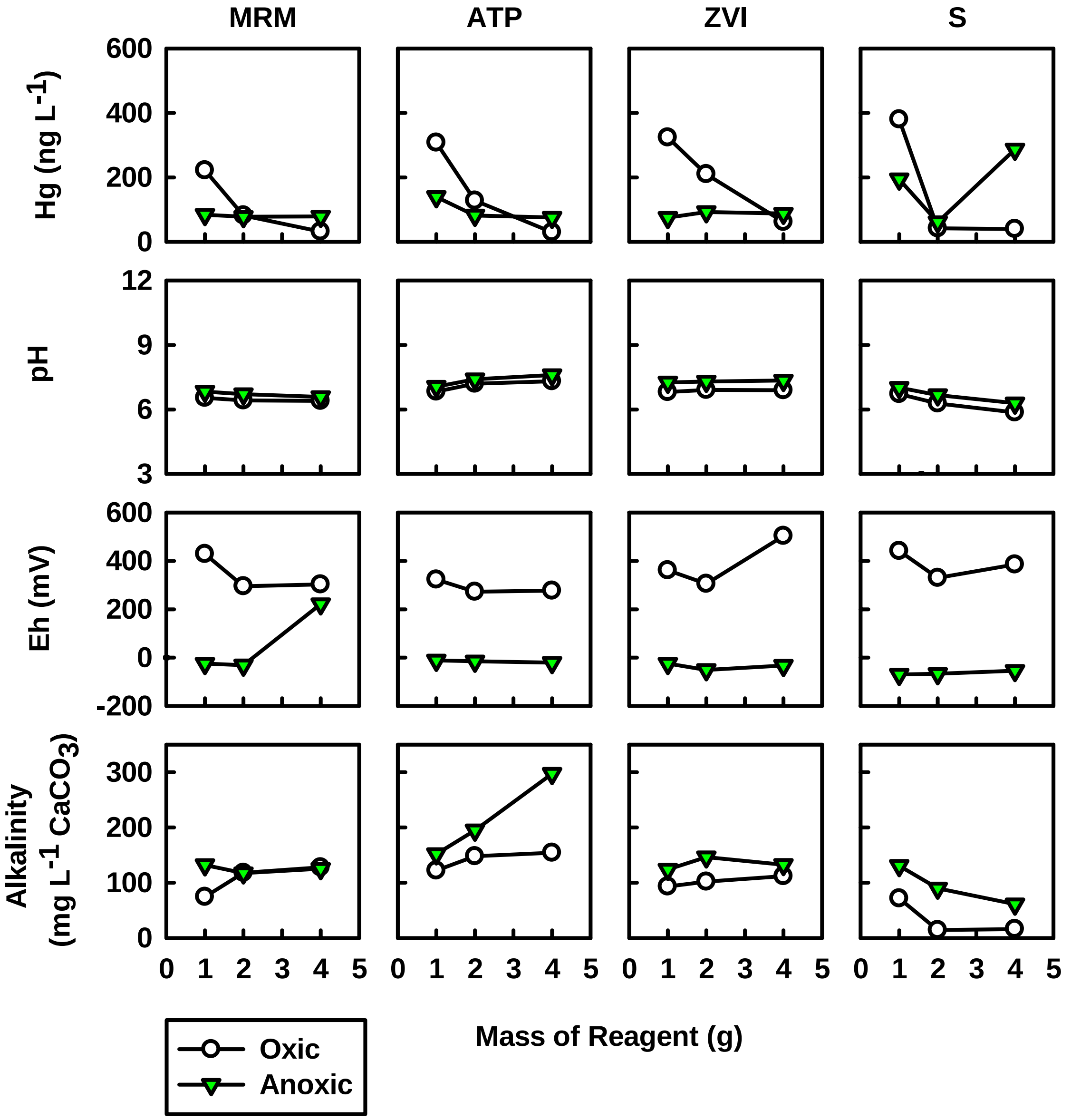

Figure 2.2 Concentrations of total dissolved Hg (ng L^{-1}), pH, Eh (mV), alkalinity (mg L^{-1} as $CaCO_3$) for individual treatment media as a function of mass of reagent added.

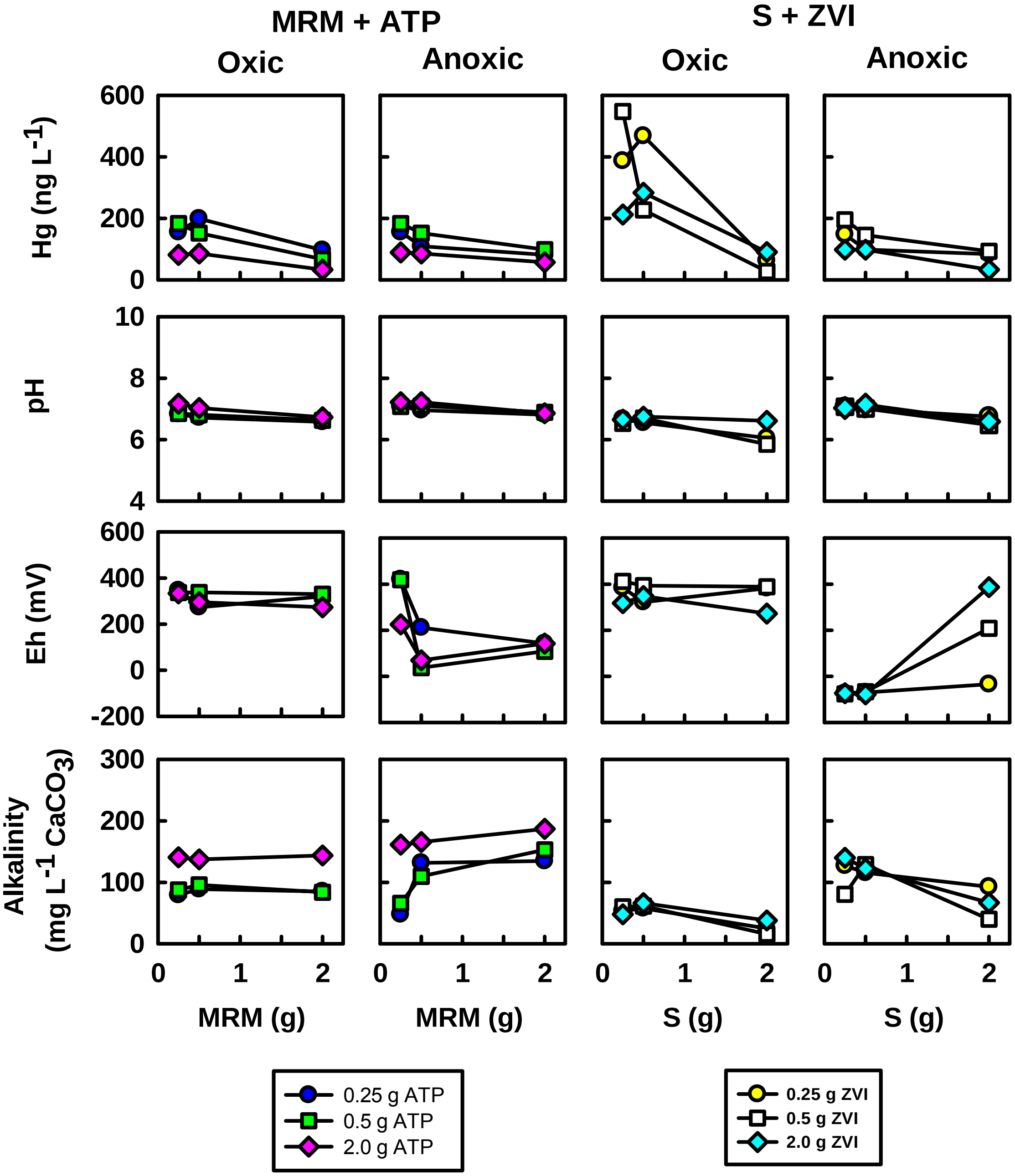

Figure 2.3 Concentrations of total dissolved (< 0.45 μm) Hg (ng L^{-1}), pH, Eh (mV), alkalinity (mg L^{-1} as $CaCO_3$) for bi-media combinations as a function of mass of reagent added.

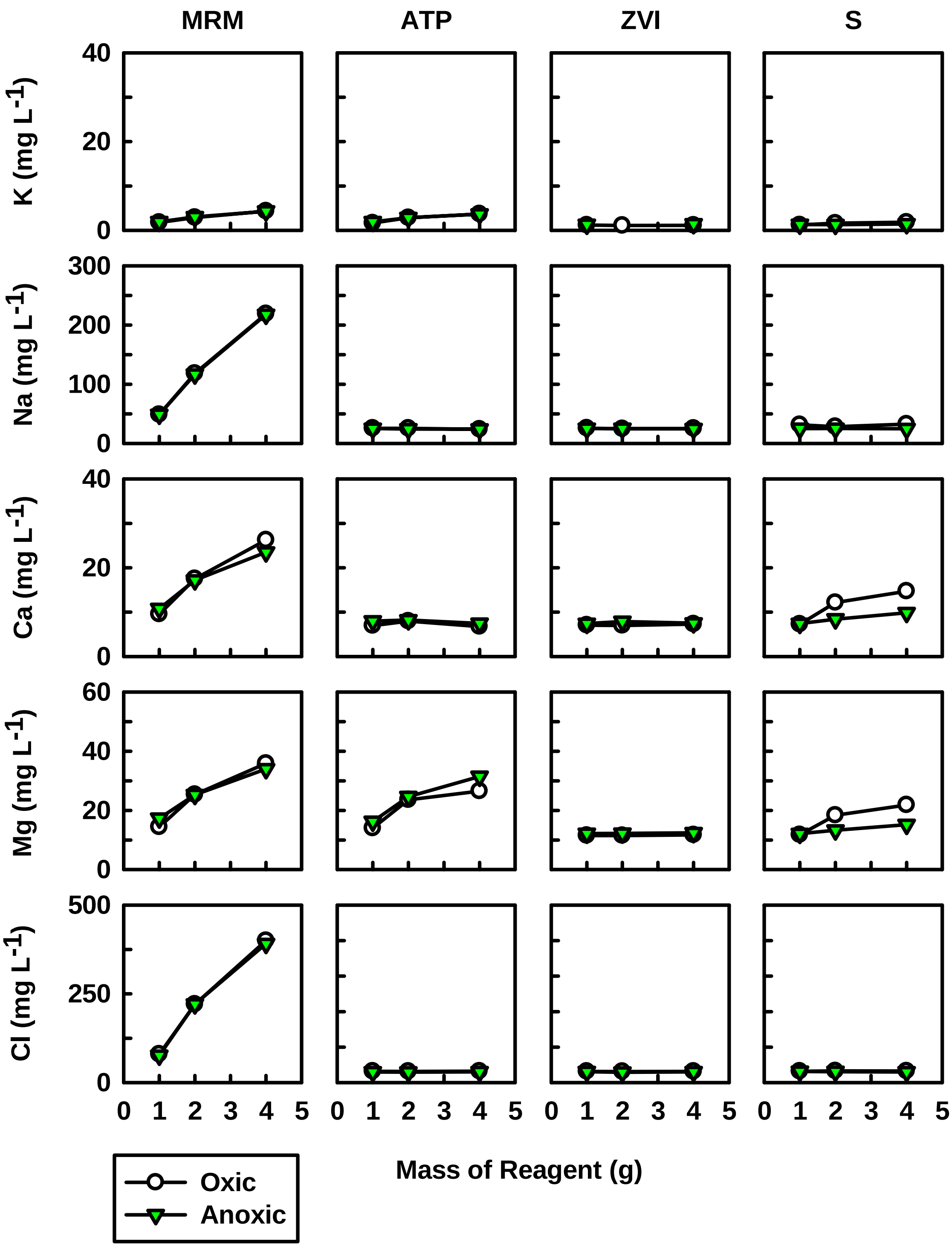

Figure 2.4.a Concentrations of K (mg L^{-1}), Na (mg L^{-1}), Ca (mg L^{-1}), Mg (mg L^{-1}), and Cl (mg L^{-1}) for single-media batch experiments as a function of mass of reagent added.

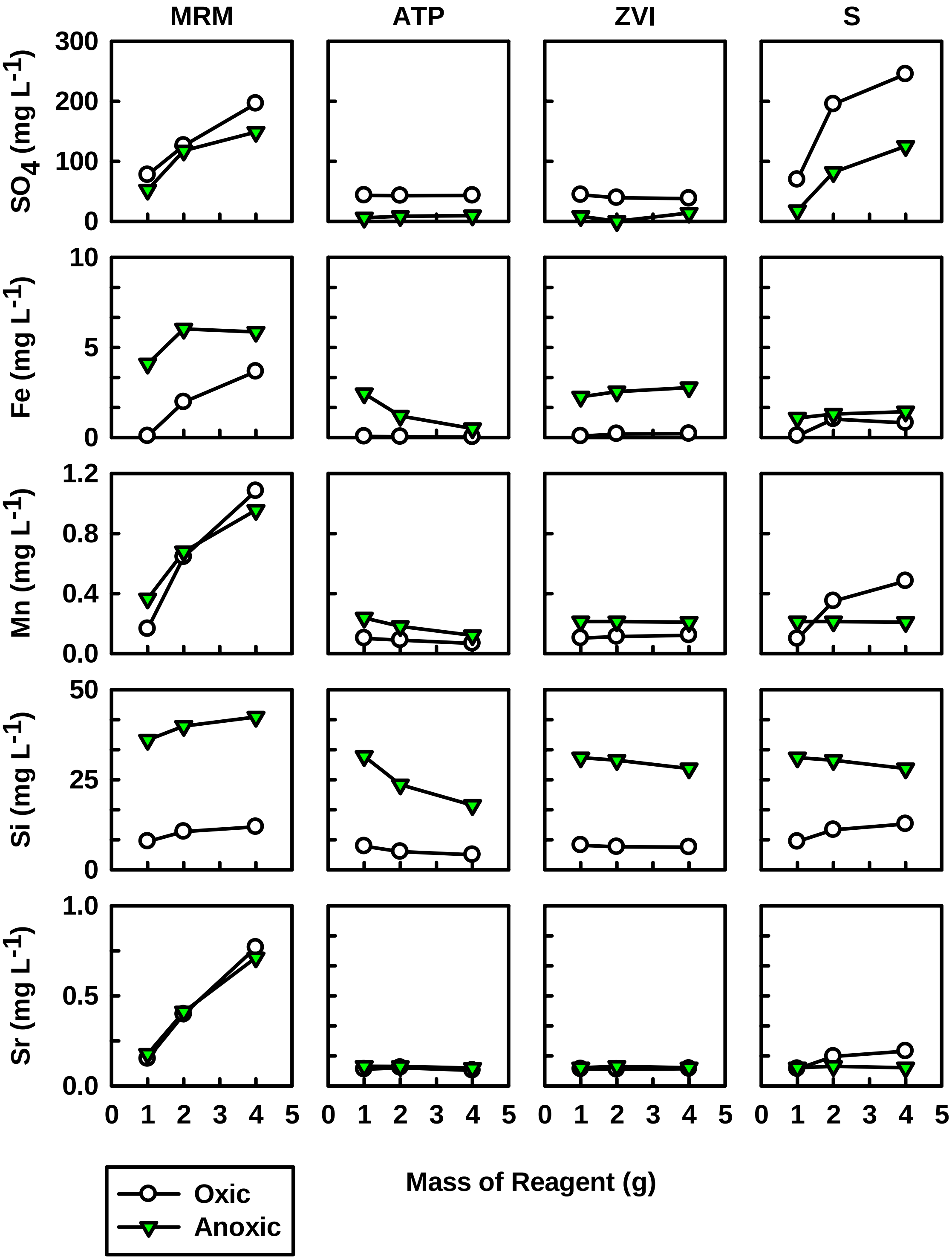

Figure 2.4.b Concentrations of SO_4 (mg L^{-1}), Fe (mg L^{-1}), Mn (mg L^{-1}), Si (mg L^{-1}), and Sr (mg L^{-1}) for single-media batch experiments as a function of mass of reagent added.

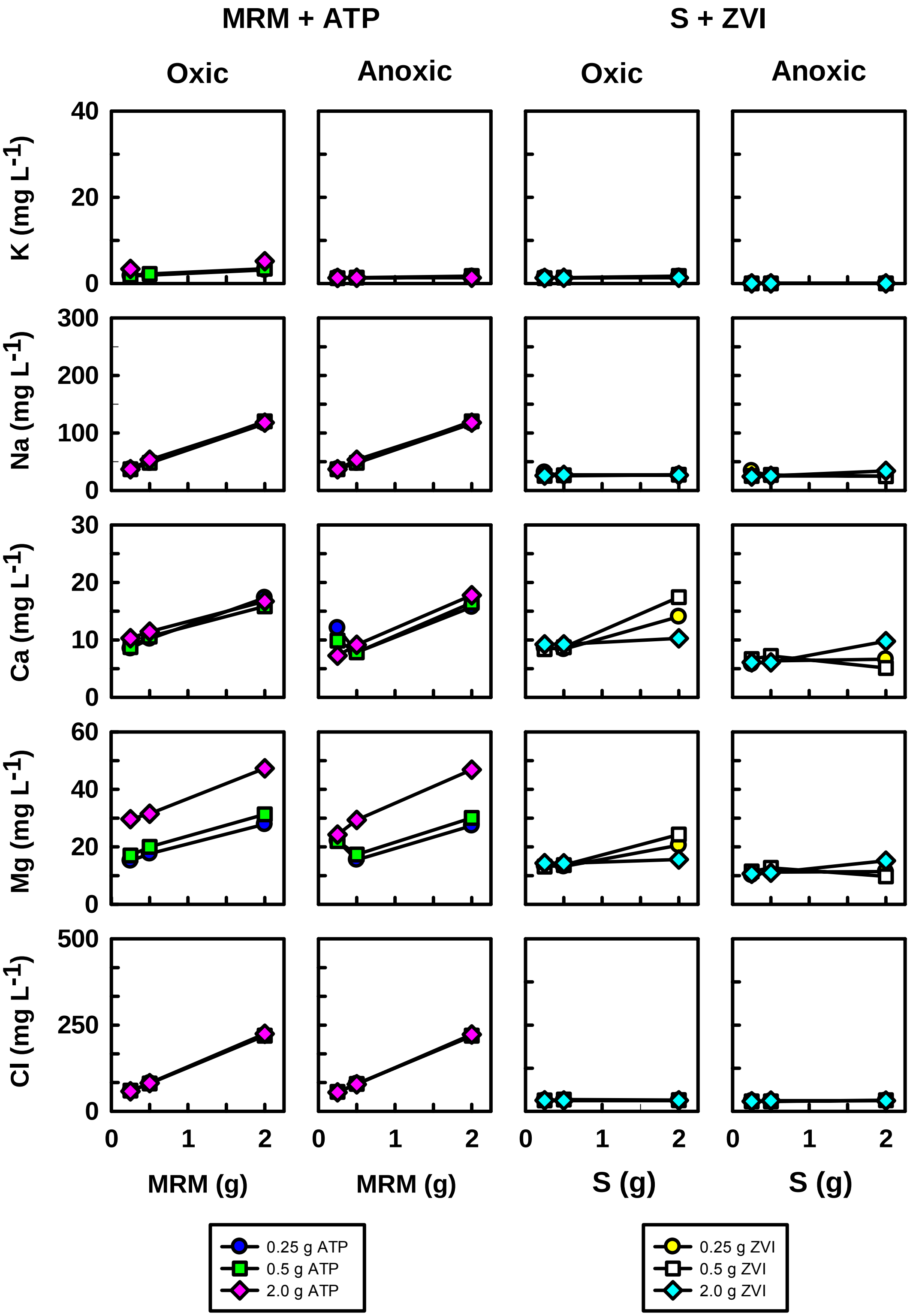

Figure 2.5.a Concentrations of K (mg L^{-1}), Na (mg L^{-1}), Ca (mg L^{-1}), Mg (mg L^{-1}), and Cl (mg L^{-1}) for bi-media combinations of reactive media as a function of mass of reagent added.

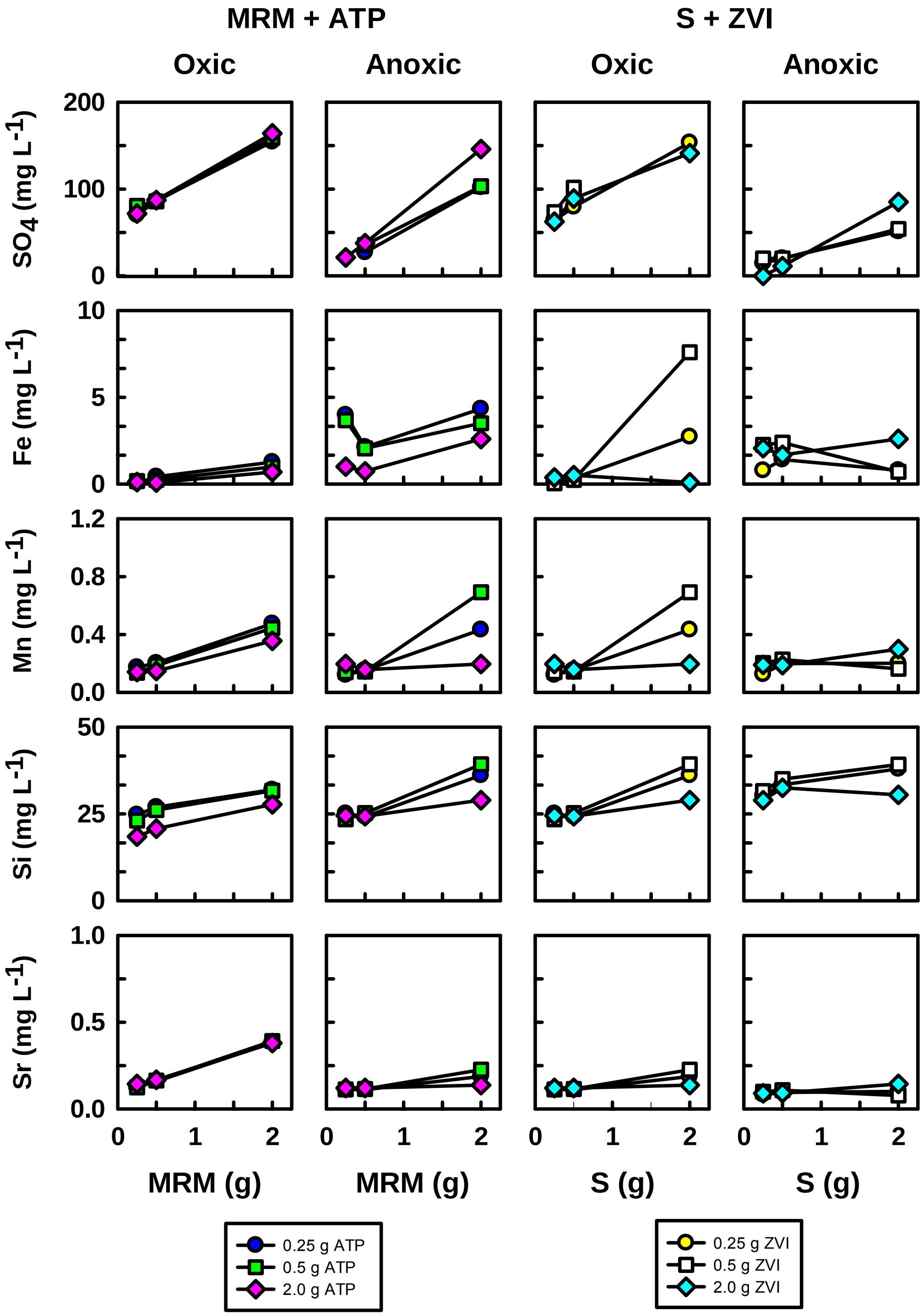

Figure 2.5.b Concentrations of SO_4 (mg L^{-1}), Fe (mg L^{-1}), Mn (mg L^{-1}), Si (mg L^{-1}), and Sr (mg L^{-1}) for bi-media combinations of reactive media as a function of mass of reagent added.

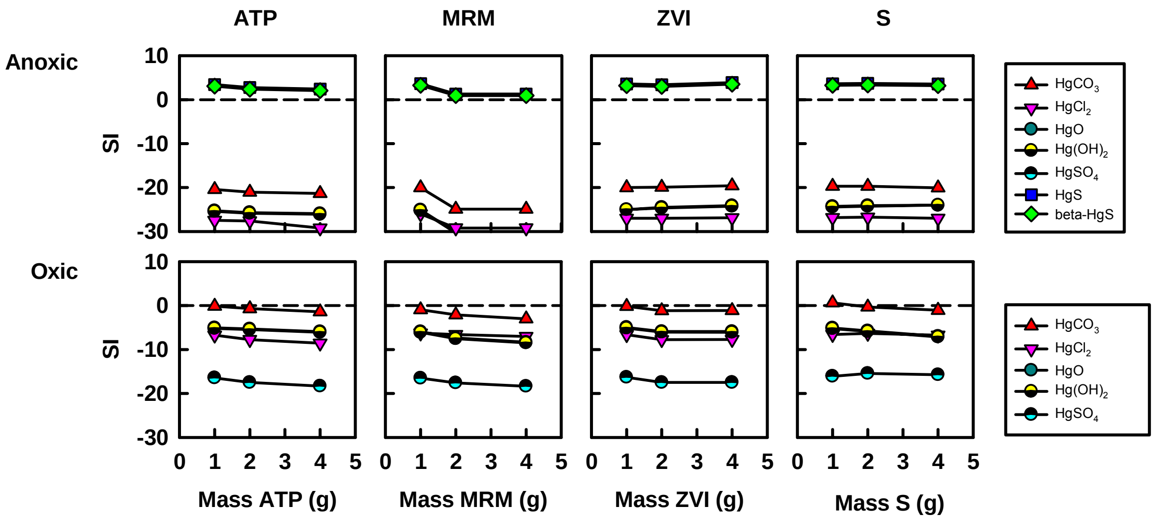

Figure 2.6 Saturation indices (SIs), calculated for Hg-bearing solid-phases using the aqueous composition obtained from single-media sensitivity tests.

Chapter 3:

Long-term Assessment of Treatment Media Performance for the Stabilization of Mercury: A Column Study

3.1 INTRODUCTION

Mercury is one of the most toxic elements known and persists at elevated concentrations in sediments in many locations around the world. The slow release of Hg from the sediment matrix and subsequent biological uptake and transformation to alkylmercury compounds represents a substantial threat for most predatory organisms, including humans, due to a tendency for these compounds to bioaccumulate. The release of legacy Hg from contaminated sediments is expected to continue for extended periods, unless mitigation steps are taken. Assessment of the effectiveness of solid-phase reactive media additives as stabilization agents of Hg in sediment is the primary focus of this study.

Cycling of Hg between organic and inorganic species is a complex problem, but sulfate-reducing bacteria (SRB) and, to a lesser extent, iron-reducing bacteria (IRB), have been identified as the primary methylators of Hg (Zillioux et al., 1993; Han et al., 2008). Increasing concentrations of aqueous sulfate in contact with sediment cores increases the potential for Hg methylation, most likely due to stimulation of SRB activity (Gilmour et al., 1998). The production of reduced sulfide by SRB in sediment pore water is increased by excess quantities of labile organic carbon and sulfate (Pallud and Van Cappellen, 2006).

$$SO_4^{2-} + 2CH_2O \rightarrow H_2S + 2HCO_3^- \qquad (3.1)$$

where CH_2O represents organic carbon. Accumulation of pore water sulfide inhibits Hg methylation in cores collected from sediments having contrasting mineral and organic content; an effect commonly referred to as sulfide inhibition (Benoit et al., 1999; Han et al. 2008). Therefore, sulfur content and speciation and redox zonation play a critical role in the methylation potential of a system.

Despite the intricate balance between sulfur speciation and methylation, sulfide minerals are still considered to be the most prevalent and stable sink for Hg in reducing environments (Barnett et al., 1997). Many remediation strategies attempt to stabilize Hg by introducing various forms of sulfur to the contaminated system. For example, Kot et al. (2007) used colloidal sulfur to immobilize Hg in spiked sediment slurries and numerous researchers have utilized iron sulfide minerals for adsorption and/or exchange of aqueous Hg (Brown et al., 1979; Svensson et al., 2006; Xiong et al., 2009). Therefore, it follows that inducing sulfide inhibition through accumulation of excess sulfide should have the dual consequence of reducing methylation and immobilizing Hg as a sulfide solid according to the following equation.

$$Hg^{2+} + HS^{-} \leftrightarrow HgS + H^{+} \tag{3.2}$$

Zero-valent iron (ZVI) is a strong reducing agent and has been successfully applied as a remedial mechanism for trace metals by forcing the reductive precipitation of metal-sulfides in laboratory studies (e.g., Lindsay et al., 2008) and a full-scale field application (Blowes et al., 1997). Weisener et al. (2005) used columns packed with ZVI to intercept groundwater with high Hg and sulfate concentrations, and observed > 90 % reduction in aqueous Hg and formation of β-HgS precipitates. We postulate that the combined addition of granular zero-valent iron (ZVI) and oxidized sulfur pellets to Hg-contaminated sediment can have the effect of forcing a rapid transition through the sulfate-reduction phase, bypassing the opportunity for methylation and stabilizing Hg as solid HgS.

Three saturated column experiments with contrasting treatment additives were conducted to test the hypothesis that addition of a strong reductant to a sulfur-based treatment system encourages sulfide inhibition of methylation and immobilization of Hg. The three treatment columns contained Hg-contaminated sediment and reactive media additions, including: a) oxidized elemental sulfur with a strong reductant (S+ZVI), b) a sulfate-rich organically-modified clay and natural attapulgite clay with no reductant (MRM+ATP), and c) natural attapulgite clay with low sulfate and no reductant (ATP). A fourth column experiment also was conducted with Hg-contaminated sediment and no amendment as a control (CONTROL).

3.2 METHODOLOGY

3.2.1 Experimental Approach

Anoxic column experiments were conducted to evaluate the stability of treatment media mixtures in an O_2 –deficient environment. Natural lacustrine sediment, reactive media and inert granite (added for sediment structure) were blended in proportions considered relevant to field-scale application (Table 3.1). Column experiments were designed to assess the performance of treatment media under transient flowing conditions over long periods of time.

3.2.2 Materials

3.2.2.1 Sediment

Lacustrine sediment collected near a historically-contaminated industrial site was used for the anoxic column experiments. Sediment characteristics are discussed thoroughly in Gibson et al. (in progress). The five sediment samples discussed in the preceding chapter were blended in equal mass proportions to yield the homogenized sediment used for the anoxic column experiments. Crushed granite was blended with the sediment at a ratio of 1:1 to enhance the structural properties of the lacustrine sediment and to increase the hydraulic conductivity to promote water flow. The average bulk density of the sediment/gravel mixture was 1.183 kg L^{-1}.

3.2.2.2 Water

Column influent water was collected from the Laurel Creek (LCW) headwaters, Waterloo, Ontario and stored at 4° C until experimental use. This water contained low concentrations of total Hg and measurable dissolved organic carbon (see Table 2.2), and was similar in composition to the water in contact with the lake sediments. LCW was purged with argon gas for a minimum of two hours prior to experimental use to remove dissolved oxygen.

3.2.2.3 Treatment Media

Treatment media selected for the anoxic columns included attapulgite clay (ATP), a mixture of zero-valent iron and elemental sulfur (S+ZVI) and a mixture of organically-modified clay and attapulgite clay (MRM+ATP). Treatment media was used as received from the suppliers with no further modification (see Table 2.3).

3.2.3 Anoxic Column Experiments

The anoxic column apparatus consisted of a reservoir of LCW, 1.5875 mm (1/16 in) Teflon tubing, a variable speed ISMATEC peristaltic pump, four plexiglass columns [inner diameter = 5.08 cm (2 in), length = 19.685 cm (7 ¾ in), fabricated at the University of Waterloo], flow-through amber glass sample bottles and polypropylene waste jugs (Figure 3.1). The experiments were conducted in an anoxic chamber (5% H_2 / 95% N_2). The headspace outlet of each waste jug was directed to an activated carbon trap to prevent the release of volatile Hg into the glovebox atmosphere. Columns were wet-packed with the homogenized lacustrine sediment, crushed granite, and respective treatment media inside the anoxic chamber to minimize sediment oxidation and avoid contamination of the sediment. Coarse-mesh nylon and 120 ASTM mesh Nytex screens were placed at each end of the columns to retain sediments. In addition, 2 cm thick silica sand margins (ASTM 20-30 mesh) were layered on the top and bottom of each column to entrap fine sediment fractions.

Effluent from each column was sampled twice weekly for the first 60 days of experimentation, after which time flow to the columns was interrupted and columns were left to stagnate for one week. After flow was resumed, samples were collected every second day for one week and once per week afterward. A second stagnation period of 30 days was initiated at day 265 for the CONTROL and S+ZVI columns, day 240 for the MRM+ATP column, and day 185 for the ATP column. Samples were collected daily for the first week after flow was resumed and then bi-weekly for the remainder of experimentation. Water was pumped through the columns at a uniform flow rate for the entire experimental period, except during the stagnation periods. Flow rate varied slightly between columns, but averaged between 0.6 pore volumes (PV) and 1.0 PV / day.

3.2.4 Collection of Water Samples

Column effluent was collected using a leur-lock syringe attached to a t-valve on the inflow line of the flow-through sample collection vial. The effluent samples were filtered using 0.45 µm Supor® membrane fiber filters. For the Hg analyses, four 20 mL aliquots were collected in trace-clean amber glass vials (VWR); two samples were preserved with concentrated Omni trace ultra high purity HCl (Baker Instra-Analyzed) and two samples were preserved with ultra purity HNO_3 (EMD Chemicals) to a $pH < 2.0$. Samples were stored at 4°C until analysis. Measurements of pH were made using an Orion Ross combination pH electrode (model number 8156BNWP) and Eh measurements were made with an Orion Pt - Ag/AgCl combination redox electrode (model number 9678BNWP), both on unfiltered water. The pH electrode was calibrated with standard buffer solutions of pH 4, 7, and 10, and the response of the Eh electrode was checked regularly against Zobell's (Nordstrom, 1977) and Light's (Light, 1972) solutions. Alkalinity was measured on filtered samples using a Hach digital titrator with bromylcresol green/methyl red indicator and 0.16 N H_2SO_4. Concentrations of sulfide in column effluent were measured during the last 2 months of flow. Measurements were made in sealed cells in the anoxic chamber using the methylene blue spectrophotometric method (Lindsay and Baedecker, 1998).

3.2.5 Analytical Methods

Analysis of total aqueous Hg was performed according to US EPA Method 1631, Revision E (US EPA, 2002). Acid-preserved samples were oxidized with 0.5% BrCl at least 12 hours prior to analysis. A 0.1% hydroxylamine hydrochloride (HH) solution was added to the samples before analysis to remove residual halides. Stannous chloride ($SnCl_2$) was added in excess during analysis to reduce oxidized Hg to its elemental form. Reduced Hg was concentrated on a dual gold trap and analyzed by an atomic fluorescence (AF) detector using a Tekran® Series 2600 Ultra-trace Hg Analyzer. Concentrations of major cations and trace elements were analyzed by inductively coupled plasma-mass spectrometry (ICP-MS) (Thermo X Series II quadrupole) and concentrations of anions were determined by ion chromatography (IC) (Dionex). Duplicate analyses of total Hg were performed on many samples, but in most cases the size of the error bars was less than the size of the symbol size on the plots.

3.2.6 Geochemical and Speciation Modelling

Saturation indices (SIs) were calculated using the geochemical equilibrium/mass-transfer code MINTEQA2 (Allison et al., 1990). Thermodynamic constants were modified in the database to be consistent with WATEQ4F (Ball and Nordstrom, 1991). To compensate when sulfide measurements are missing, the calculations were conducted assuming equilibrium with respect to FeS, which provided calculated values of sulfide concentrations from the measured iron concentrations. This assumption was made based on observations by Wersin et al. (1991), which showed that water is typically in equilibrium with respect to iron sulfide in organic-rich sulfate-reducing environments. Observation of black precipitates, presumed to be iron sulfide, on the effluent tubes was used as one line of evidence that sulfate-reduction was occurring. Speciation modeling was not performed for the MRM+ATP column as the effluent waters contained high levels of sulfate and low sulfide and were assumed not to have become strongly sulfate-reducing.

3.3 RESULTS AND DISCUSSION

Column effluent was sampled over a minimum period of 300 days to assess the long-term leaching potential of the sediment and the ability of the selected treatment media to immobilize Hg in the sediment matrix. Two intermittent phases of stagnation were implemented to evaluate the robustness of the treatment-induced Hg immobilization.

3.3.1 Column Physical Properties and Flow Characteristics

Inter-column variations in porosity and flow rate were observed (Table 3.1). The porosity was 40 vol. % for the CONTROL column, 45 vol. % for S+ZVI, 29 vol. % for MRM+ATP, and 33 vol. % for ATP. The differences in porosity likely were due to differences in the physical properties of the reactive media addition. The average flow rates for the columns ranged from 102 to 127 mL day^{-1} and the pore volume (PV) of each column was calculated as the difference between saturated and unsaturated masses and ranged from 125 to 191 mL.

3.3.2 Column Geochemistry

3.3.2.1 pH, Eh and Alkalinity

The column effluent was near neutral in pH, ranging from 6.69 to 8.39, among the four columns over the duration of the experiments (Figure 3.2). The effluent pH for the CONTROL, S+ZVI and MRM+ATP columns rose gradually until it reached a plateau between pH 7.6 and 8.0 by the completion of experimentation. The pH of the CONTROL column was 6.99 at the start of experimentation and gradually rose to 8.0 ± .12. The effluent pH from the S+ZVI column displayed a similar effect, leveling off at a pH of 7.6 ± .2 by day 22. The pH of the first PV of flow from the MRM+ATP column was approximately 6.7 and stabilized near the end of experimentation at 7.9 ± .12. The effluent pH of the ATP column was consistently 8.0 ± .16 throughout the course of experimentation. The consistent plateau across the columns at approximately 8.0 pH units is most likely attributable to the carbonate alkalinity associated with the LCW input solution, which was collected from a spring discharging from a limestone aquifer and the presence of carbonate minerals in the contaminated sediment.

The alkalinity measured in the effluent of all columns ranged between 100 and 200 mg L^{-1} (as $CaCO_3$) and is indicative of alkaline LCW water. The S+ZVI column generally had a lower alkalinity than the CONTROL and clay-amended columns. This lower alkalinity suggests that acid was generated in the S+ZVI column, possibly due to oxidation of the S prior to emplacement in the column. A steady decrease in the Eh was observed as the conditions within the column became increasingly reducing, due to depletion of the electron acceptor supply as the organic carbon was oxidized. The amended columns exhibited a more pronounced decrease in Eh than the CONTROL column.

3.3.2.2 Major Ion and Trace Element Geochemistry

The concentrations of dissolved major ions and trace elements were monitored in the column effluent as a secondary indicator of media performance. Release of high concentrations of dissolved constituents is a potential consequence of media addition, and can also be used as an indicator of mineral dissolution and instability of the solid matrix. Sulfate is of primary concern because increasing sulfate concentrations have been shown to cause a corresponding increase in methylation (Gilmour et al., 1992). However, if sulfate-reducing conditions prevail, reduced sulfate can contribute to formation of excess H_2S, which can bind with Hg to form sparingly soluble HgS solids. The concentrations of sulfate in the first few PVs from the two clay columns were high (130 to 140 mg L^{-1}) in comparison to the CONTROL column (~ 40 mg L^{-1}) and the S+ZVI column (60 mg L^{-1}). Sulfate concentrations in the CONTROL, ATP, and S+ZVI rapidly decreased to 20 mg L^{-1} or less, but elevated sulfate concentration was maintained in the range of 10 to 110 mg L^{-1} in the MRM+ATP column throughout the duration of the experiments. Concentrations of sulfate declined the greatest in the S+ZVI column to < 10 mg L^{-1} until day 118, followed by a small increase to 20 mg L^{-1}.

Dissolved sulfide concentrations were measured in the column effluent toward the end of the column experiments (Table 3.2). Excess concentrations of dissolved sulfide of up to 416 μg L^{-1} were measured in the effluent of the S+ZVI column, in contrast to the other three columns, which contained much lower concentrations (9-25 μg L^{-1}). Excess dissolved sulfide has been shown to induce sulfide inhibition of methylation in sediments containing varying organic carbon content (Benoit et al., 1999). The accumulation of sulfide in the S+ZVI column could be interpreted as an indicator of suppressed methylation. Additional analysis of the solid-phase methylation would be necessary to verify this hypothesis.

Concentrations of Cl approached 500 mg L^{-1} in the effluent for the first several PVs of flow from the MRM+ATP column, but rapidly declined to lower values of 25 mg L^{-1} (Figure 3.3). The CONTROL, S+ZVI, and ATP columns leached < 30 mg L^{-1} Cl. Chloride exerts a strong control on Hg speciation and bioavailability and tends to complex Hg as a relatively soluble mercury chloride (Nriagu, 1979). Excess dissolved Cl is therefore an undesirable component when trying to form stable Hg solids.

The first few PVs of flow were closely monitored and analyzed as an indicator of what potentially could be released from sediments immediately following treatment and deposition. Elevated concentrations of exchangeable cations (K, Na, and Mg) were observed in the first several PVs of flow from the clay-amended columns (Figure 3.3), and elevated concentrations of Na (approximately 50 mg L^{-1}) were observed in effluent collected from the CONTROL column. In contrast, much lower concentrations of the major ions were observed in effluent collected from the S+ZVI columns. Both the S+ZVI and CONTROL columns initially released elevated concentrations of Co, Sb, Ba and Pb (Figure 3.4). Concentrations of these elements were lower in the clay-amended columns, likely due to adsorption reactions. The S+ZVI treatment combination resulted in an initial release of elevated concentrations of Cu relative to the CONTROL column. Elevated concentrations of Sr were released from the MRM+ATP column relative to the CONTROL, which continued until day 75. Concentrations of U were elevated in the first few pore volumes of flow from the ATP column, but then leveled off to a level slightly higher than the CONTROL around day 50. The remaining cations showed less pronounced changes during the first PV of flow relative to the remainder of the experiments.

Between days 60 and 80, the effluent from the ATP column exhibited an increase in several elements, including Mg, Al, and Ca. Concentrations of Si steadily increased in the ATP column effluent from the start of flow. Because the primary constituents of the ATP clay are Mg, Al, and Si, the simultaneous increase of these elements in the effluent water suggests possible ATP clay dissolution.

3.3.2.3 Mercury Immobilization

The CONTROL column, which consisted of unamended sediment, was conducted to provide an indication of the concentrations of Hg and other trace contaminants that could potentially leach from the sediment after burial, if no treatment were implemented. Concentrations of Hg as high as 340 ng L^{-1} were observed in the effluent from the

CONTROL column during the first 4 days of flow, but stabilized by day 36 to 22 ± 2 ng L^{-1} (Figure 3.2). The 7-day stagnation period, which occurred at 60 days, resulted in a subtle spike in the effluent Hg concentration to 36 ng L^{-1}, but again stabilized in the range of 15-25 ng L^{-1} within 20 subsequent PVs. The second stagnation period at 265 days resulted in Hg release from the sediment of > 300 ng L^{-1} after flow was resumed. The low release of Hg under flowing conditions followed by high release of Hg after stagnation implies a mass-transfer constraint on the release of Hg from the untreated sediment. These observations suggest that under flowing conditions the concentrations of Hg in the pore water were limited due to slow sediment to pore water mass-transfer of Hg. Leaching of Hg, even in trace concentrations, may pose a substantial threat to the natural environment due to the potential for trace amounts (ng L^{-1} range) to biomagnify in the food web to concentrations on the order of a million times greater than that observed in the water column (Zillioux et al, 1993). It is therefore important to seek treatment alternatives that have the potential to immobilize Hg to the greatest degree possible.

Despite the increased concentration of Hg released following the two stagnation periods, Hg leached from the untreated sediment was low relative to concentrations observed in batch reactor experiments, which involved thorough mixing of the sediments with river water followed by a stagnation period (Chapter 2). Furthermore, the observed aqueous concentrations of Hg observed in the batch experiments were low relative to resuspension results for the same sediments reported by Gibson et al. (in progress). In the resuspension tests, in which sediment and water were continuously and vigorously mixed for up to 24 hours, concentrations of Hg as high as 1200 ng L^{-1} were observed under anoxic conditions. The release of Hg appears to be closely related to the mixing environment, with the highest concentrations observed with the most vigorous mixing.

The ATP treatment column resulted in only moderate suppression of Hg release. Concentrations of Hg were maintained at values less than observed for the CONTROL column for the first 60 days of flow. After the 7-day stagnation, effluent Hg concentrations increased steadily, eventually approaching those observed in the CONTROL column (after day 90). This increased release of Hg, coincident with release of increased Mg and Al, indicates that the potential of the clay to immobilize Hg was reached or exceeded by this time and is suggestive of possible clay breakdown.

Concentrations of Hg in the first few PVs of flow from the MRM+ATP column were around 300 ng L^{-1}, but decreased rapidly and stabilized below 10 ng L^{-1} by day 20. Organically-modified clays have exceptionally high CEC, and in general, a high affinity for Hg with varying affinity for different Hg species (Say et al., 2007). Of the three treatment columns, concentrations of Hg were consistently the lowest in the MRM+ATP column. The 7-day stagnation period resulted in little change in Hg release, and concentrations did not exceed 25 ng L^{-1} until the 30-day interruption of flow. Only one sample effluent collected at 283 days was observed to have ~ 40 ng L^{-1} Hg even after the longer interruption in flow. Speciation modeling were not performed for this column because sulfide concentrations were inferred in the model based on the assumption of equilibrium with respect to FeS, which is valid only for sulfate-reducing conditions. Neither substantial removal of sulfate nor substantial accumulation of sulfide were observed for the MRM+ATP combination, suggesting that sulfate-reducing conditions may not have fully developed. Despite the high concentrations of sulfate, effluent Hg was maintained at very low concentrations throughout experimentation. This suggests that the adsorption capacity of the MRM may have been high enough to adsorb most Hg, or small amounts of sulfide may have formed and precipitated with the Hg.

Effluent concentrations of Hg collected from the S+ZVI treatment column were approximately equal to the MRM+ATP column and consistently lower than the CONTROL and ATP columns. The initial PV of flow from the S+ZVI column contained Hg at concentrations almost 50% lower than those observed in the CONTROL and ATP columns and 40% lower than the MRM+ATP column. Within 2 days of flow, the effluent Hg concentrations decreased to < 17 ng L-1, and by day 20 concentrations were < 10 ng L^{-1} and continued to decrease until the first stagnation period. The release of Hg after the 7-day stagnation period was suppressed in the S+ZVI column relative to the CONTROL, suggesting that the addition of treatment media lead to immobilization of Hg within the sediment matrix. The 30-day stagnation period resulted in a minor increase in Hg concentrations of 19 ng L^{-1} in effluent from the S+ZVI column. However, concentrations of Hg in the S+ZVI effluent rapidly returned to very low levels of 3 ± 2.6 ng L^{-1}. Weisener et al. (2005) observed similar results using ZVI to stabilize Hg in a sulfate-rich groundwater, reducing Hg concentrations from 40 μg L^{-1} to 100-500 ng L^{-1}; with lower concentrations observed in a column with a slower flow velocity. Low concentrations of sulfate and high concentrations of sulfide (sulfide measurements made at the end of the column life) in the column effluent suggest that sulfate-reduction was actively occurring.

Thus, conditions conducive to formation of stable HgS were present, according to results reported by Svenssen et al. (2005), which showed the formation of HgS after two years in batch reactors containing Hg^0 and S^0 under alkaline, anaerobic conditions. Speciation modeling results resulted in calculated saturation indices that were close to equilibrium for an HgS phase for each of the columns analyzed. These results are also consistent with SEM imaging results obtained by Weisener et al. (2005), clearly showing the formation of β-HgS.

Concentrations of Hg in effluent collected from the S+ZVI column increased unexpectedly at day 209 and continued until day 237, when concentrations approached 30 ng L^{-1}. A similar increase in effluent Hg was observed in effluent from the CONTROL column over the same time period. The similar behavior of the CONTROL and S+ZVI columns, overlapping timing, and the fact that these two columns were attached to the same input reservoir suggest that the spike may have been associated with changes in the composition of the LCW feed solution.

3.4 CONCLUSIONS

The results from the anoxic column experiments suggest that Hg contained in the unoxidized sediment is relatively stable if maintained under steady flow in anoxic conditions. However, the sediment does have the potential to release environmentally significant concentrations of Hg if flow is perturbed. Release of Hg was observed to increase following periods of stagnation, suggesting that the concentrations of leached Hg were limited by kinetic mass-transfer processes. Similar trends of increasing concentration following flow interruption have been previously observed and are attributed to discrepancies between advection and kinetic mass transfer timescales (Wehrer and Totsche, 2008; Gong et al., 2010). The addition of reactive media resulted in lower concentrations of Hg in the effluent from the columns than observed in the untreated sediment. Concentrations following flow disruptions also were lower in the treated columns than in the untreated columns. The most immediate and lasting stabilization effects were observed for the treatment combinations containing sulfur, including S+ZVI and MRM+ATP. The lowest concentrations of Hg were achieved with the MRM+ATP additives. Very low concentrations of effluent Hg were maintained for the combination of ZVI and S, which also corresponded to rapid sulfate reduction and sulfide accumulation. Calculation of saturation indices indicated the potential for all conditions to form a mercury sulfide phase, but the greatest degree of supersaturation was predicted for the S+ZVI treatment condition. Further work will be required to determine solid-phase alterations and affect of media addition on methylation.

Table 3.1
Composition and physical parameters for anoxic column experiments

Parameter	CONTROL	MRM+ATP	ATP	S+ZVI
Sediment (%)	**50**	**50**	**50**	**50**
Gravel (%)	**50**	**40**	**40**	**40**
ZVI (%)	**-**	**-**	**-**	**5**
S (%)	**-**	**-**	**-**	**5**
MRM (%)	**-**	**5**	**-**	**-**
ATP (%)	**-**	**5**	**10**	**-**
Porosity	**0.4**	**0.29**	**0.33**	**0.45**
PV (mL)	**171**	**125**	**140**	**192**
Average Flow Rate (PV/day)	**0.74**	**0.96**	**0.73**	**0.59**

Table 3.2
Concentrations of dissolved sulfide and sulfate in column effluent at the end of experimentation

Column	Day	S^{2-} (μg L^{-1})	SO_4 (mg L^{-1})
CONTROL	**355**	**10**	**19.6**
	376	**13**	**19.1**
	369	**11**	**20.5**
S+ZVI	**355**	**329**	**43.3**
	376	**416**	**42.8**
	369	**315**	**49.9**
MRM+ATP	**320**	**5**	**22.9**
	340	**12**	**21.5**
	360	**8**	**21.3**

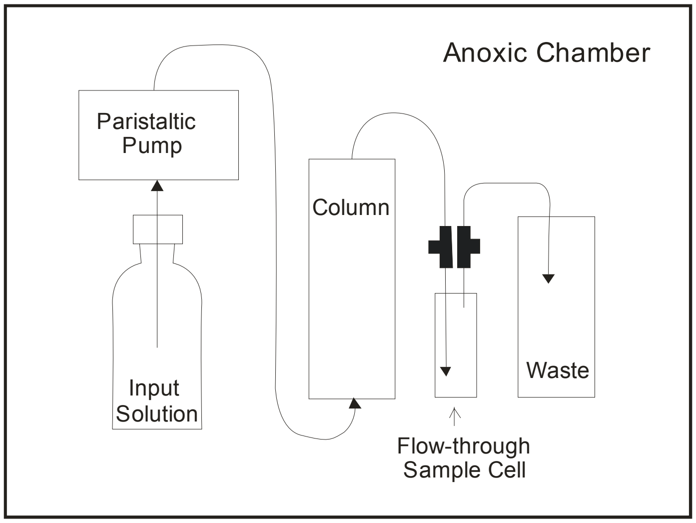

Figure 3.1 Schematic diagram of anoxic column experimental setup.

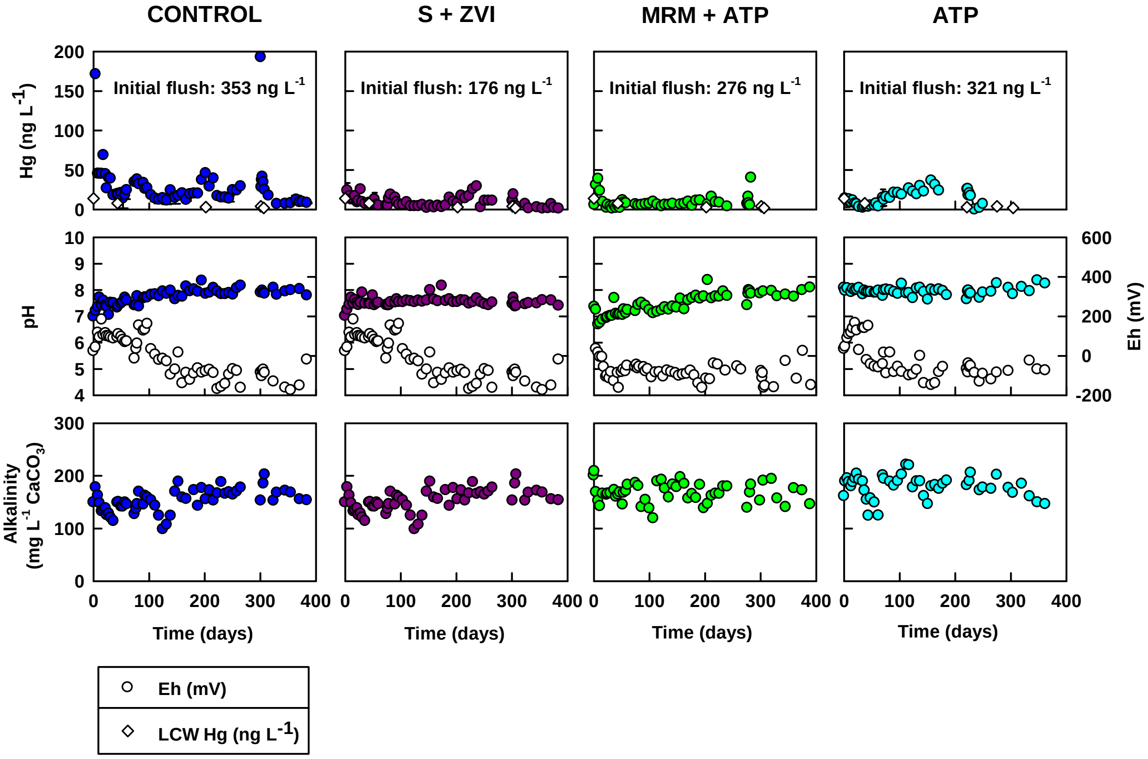

Figure 3.2 Concentrations of dissolved (< 0.45 μm) Hg (ng L^{-1}), pH, Eh (mV), and alkalinity (mg L^{-1} as $CaCO_3$) for anaerobic columns as a function of time. Hollow circles represent Eh measurements and the hollow diamonds represent Hg (ng L^{-1}) concentration in the LCW input solution.

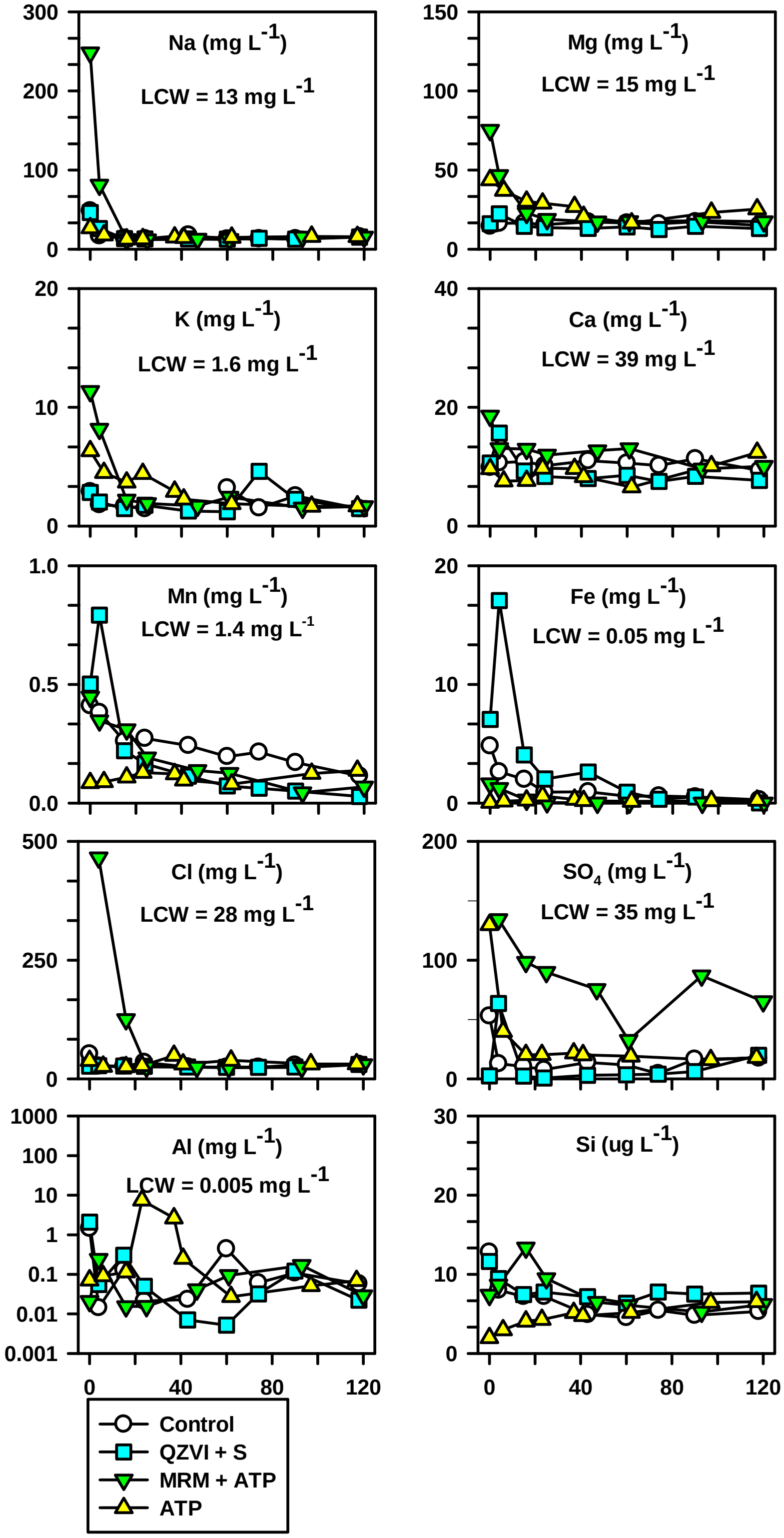

Figure 3.3 Concentrations of Na (mg L^{-1}), Mg (mg L^{-1}), K (mg L^{-1}), Ca (mg L^{-1}), Mn (mg L^{-1}), Fe (mg L^{-1}), Cl (mg L^{-1}), SO$_4$ (mg L^{-1}), Al (mg L^{-1}), and Si (µg L^{-1}) for control and treatment columns.

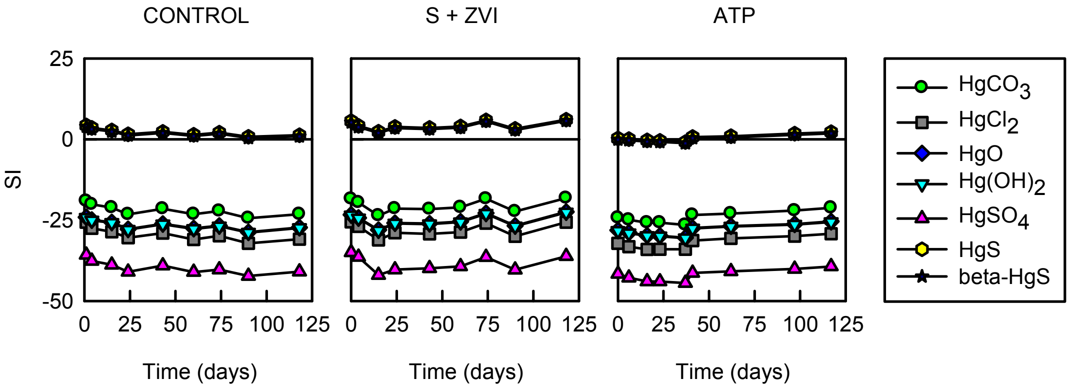

Figure 3.3 Calculated saturation indices for Hg-bearing solid phases. MRM+ATP results not included due to the high concentrations of dissolved sulfate, a violation of the assumptions made for modeling sulfide-phases.

Chapter 4:

Conclusions

6.1 Summary of Findings

The series of batch and column experiments performed suggest that addition of reactive media to Hg-contaminated sediment has the potential to effectively immobilize Hg and minimize its release to the environment. Varying levels of treatment efficiency were observed for the different media / media combinations under the manipulated conditions.

The batch reactor experiments evaluated the potential of multiple reactive media to stabilize a fixed concentration of Hg under specific redox conditions, including both oxic and anoxic conditions, and examined the mass-dependency of treatment. Treatment efficiency was generally better with increased mass of reagent. The reagent combinations that resulted in the lowest release of aqueous Hg included S+ZVI and MRM+ATP. For both of these media combinations, added in the highest mass proportions evaluated, release of Hg was suppressed below the level of the untreated sediment by > 97%, reducing aqueous Hg from > 1000 ng L^{-1} to < 30 ng L^{-1}. Evaluation of single-media performance indicated treatment efficiency under oxic conditions was highly dependent on the mass of reagent added, and greater media masses had substantially better treatment. Treatment under anoxic conditions was generally good for all reagents, independent of mass of reagent. Evaluations of bi-media combinations revealed a redox-independent treatment for the MRM+ATP mixture, although increasing mass of both reagents resulted in lower release of Hg. The ZVI+S mixture displayed a strong redox-dependency, with generally better immobilization under anoxic conditions.

Results from the anoxic column experiments were consistent with the results observed in the batch reactor experiments. In general, the release of Hg was lower in the column experiments than for the batch experiments, for both the treated and untreated sediment conditions. Release of Hg from the CONTROL column was nearly an order of magnitude lower than the concentrations released from untreated sediment in the batch experiments, which likely resulted from mass-transfer limitations. These results suggest that if the sediment is maintained under an entirely anoxic atmosphere, the potential for release of Hg from the sediment is limited, provided flow velocities are similar to those used for these experiments. The interruption of flow to the columns resulted in increased concentrations of Hg released from untreated sediment, but the S+ZVI and MRM+ATP treatment additives greatly reduced this flux. Changes in pH were not a concern for this set of experiments, given the steady supply of alkaline water, relative to the batch experiments, which had only a fixed amount of carbonate alkalinity. High concentrations of major constituents and trace elements were released from the sediments during the first several PVs of flow. With the exception of sulfate, this release leveled off to near background concentrations. High concentrations of sulfate were released from the MRM+ATP column throughout the duration of experimentation, suggesting strongly sulfate-reducing conditions were not developed for this treatment combination.

It is likely that different geochemical stabilization mechanisms were promoted by the two media combinations. The high concentrations of sulfate in the MRM+ATP effluent and very low concentrations of sulfide suggest that sulfide precipitation was not the dominant Hg-stabilization reaction. Clays are known for their high adsorption potential, but the sulfur associated with the MRM reagent could also play a role in immobilization by co-precipitating with Hg. The presence of excess sulfide in the effluent from the S+ZVI column suggests formation of HgS is probable. Speciation calculations performed for the S+ZVI effluent water support this interpretation.

6.2 Future Research

Further research into the mechanisms of Hg removal of each of these reactive media and media combinations would be beneficial. Analysis of the solid-phase composition of the anoxic column sediments would substantiate modeling results, which predicted the precipitation of HgS. The suppression of methylation is a critical concern for the treatment of any Hg-contaminated sediment. Treatment performance could be further substantiated with analysis of solid and aqueous phases for MeHg concentrations. Furthermore, because Hg remediation strategies are inherently site-specific, additional experimentation performed on multiple sediments with contrasting compositions would test the robustness of the treatment media combinations. Other possible work could investigate other types of media, such as biochar, which is becoming a popular additive for its high adsorption capacity, low-cost, and potential to reduce the carbon footprint by sequestering labile-carbon sources.

It is important to note that the anoxic column experiments were performed with sediment that had never been exposed to oxygen. It is not known how stable the reactive mixtures would remain under oxic conditions, or how effective the reagents would be over the long-term on oxidized sediment. Experiments investigating Hg stability under oxidizing conditions would be a good further test of the robustness of the media combinations.

References

Allison, J.D., Brown, D.S., Novo-Gradac, K.L., 1990. MINTEQA2/PRODEFA2, A Geochemical Assessment Model for Environmental Systems, Version 3.0 User's Manual. Environmental Research Laboratory, Office of Research and Development, US EPA, Athens, GA.

Ball, J.W., Nordstrom, D.K., 1991. User's manual for WATEQ4F with revised thermodynamic database and test cases for calculating speciation of major, trace and redox elements in natural waters. US Geol. Surv. Open-File Rep. 91–83.

Barnett, M.O., Harris, L.A., Turner, R.R., Stevenson, R.J., Henson, T.J., Melton, R.C., Hoffman, D.P., 1997. Formation of mercuric sulfide in soil. *Environ. Sci. Technol*. 31(11), 3037-3043.

Barnett, M.O., Turner, R.R., Singer, P.C., 2000. Oxidative dissolution of metacinnabar (β-HgS) by dissolved oxygen. *Appl. Geochem.* 16, 1499-1512.

Benner, S.G., Blowes, D.W., Gould, W.D., Herbert, R.B., Ptacek, C.J., 1999. Geochemistry of a permeable reactive barrier for metals and acid mine drainage. *Environ. Sci. Technol*. 22, 2793-2799.

Benoit, J.M., Gilmour, C.C., Mason, R.P., and Heyes, A., 1999. Sulfide controls on mercury speciation and bioavailability to methylating bacteria in sediment pore waters. *Environ. Sci. Technol*. 33, 951-957.

Blowes, D.W., Ptacek, C.J., and Jambor, J.L., 1997. In-situ remediation of Cr(VI)-contaminated groundwater using permeable reactive walls: Laboratory studies. *Environ. Sci. Technol.* 31 (12), 3348-3357.

Boening, D.W., 2000. Ecological effects, transport, and fate of mercury: a general review. *Chemosphere*. 40, 1335-1351.

Brown, J.A., Bancroft, G.M., Fyfe, W.S., McLean, R.A.N., 1979. Mercury removal from water by iron sulfide minerals. An electron spectroscopy for chemical analysis (ESCA) study. *Environ. Sci. Technol*. 13(9), 1142-1144.

Compeau, G.C. and Bartha, R., 1985. Sulfate-reducing bacteria: Principal methylators of mercury in anoxic estuarine sediment. *Appl. Environ. Microbiol*. 50(2), 498-502.

Evangelou, V.P., Zhang, Y.L., 1995. A Review: Pyrite oxidation mechanisms and acid mine drainage prevention. *Crit. Rev. Environ. Sci. Technol*. 25(2), 141-199.

Gibson, B.D., Ptacek, C.J., Blowes, D.W., Daugherty, S.D., in progress. *Characterization of a mercury contaminated lake sediment and Implications for remediation.*

Gilmour, C. G., Henry, E. A., and Mitchell, R., 1998. Sulfate stimulation of mercury methylation in freshwater sediments. *Environ. Sci. Technol*. 26(11), 2281-2287.

Gong, R., Lu, C., Wiu, W.-M., Cheng, H., Gu, B., Watson, D.B., Criddle, C.S., Luo, J. 2010. Estimating kinetic mass transfer by resting-period measurements in flow-interruption tracer tests. *J. Contam. Hydrol.* 117 (1-4), 37-45.

Han, S., Obraztsova, A., Pretto, P., Deheyn, D.D., Gieskes, J., and Tebo, B.M., 2008. Sulfide and iron control on mercury speciation in anoxic estuarine sediment slurries. *Marine Chem.* 111, 214-220.

Hinton, J. and Veiga, M., 2001. Mercury contaminated sites: A review of remedial solutions. In: Proc. National Institute for Minamata Disease, Forum 2001, March 19-20, 2001, Minamata, Japan, pp. 19-40.

Kot, F.S., Rapoport, V.L., Kharitonova, G.V., 2007. Immobilization of soil mercury by colloidal sulphur in the laboratory experiment. *Cen. Europ. J. Chem.* 5(3), 846-857.

Light, T.S., 1972. Standard solution for redox potential measurements. *Anal. Chem*. 44, 1038-1039.

Lindsay, S.S., Baedecker, M.J., 1988. Determination of aqueous sulfide in contaminated and natural water using the methylene blue method. In: Collins, A.G., Johnson, A.I. (Eds.), Ground-Water Contamination: Field Methods, ASTM, Philadelphia, pp. 349-357.

Lindsay, M.B.J., Ptacek, C.J., Blowes, D.W. and Gould, W.D., 2008. Zero-valent iron and organic carbon mixtures for remediation of acid mine drainage: Batch experiments. *Appl. Geochem.* 23, 2214-2225.

Mulligan, C.N., Yong, R.N., Gibbs, B.F., 2001. An evaluation of technologies for the heavy metal remediation of dredged sediments. *J. Hazard. Mater*. 85, 145-163.

Nordstron, D.K., 1977. Thermochemical redox equilibria of ZoBell's solution. *Geochim. Cosmochim. Acta.* 41, 1835-1841.

Nriagu, J.O., 1979. The biogeochemistry of mercury in the environment. North-Holland Biomedical Press, Amsterdam.

Pallud, C., Van Cappellen, P., 2006. Kinetics of microbial sulfate reduction in estuarine sediments. *Geochim. Cosmochim. Acta.* 70 (5), 1148-1162.

Renholds, J., 1998. *In Situ Treatment of Contaminated Sediments*. Washington DC: U.S. EPA Office of Solid Waste and Emergency Response, Technology Innovation Office. Retrieved from http://www.cluin.org/download/studentpapers/renhold.pdf

Say, R., Birlik, E., Erdemgil, Z., Denizli, A., Ersöz, A., 2007. Removal of mercury species with dithiocarbamate-anchored polymer/organosmectite composites. *J. Hazard. Mater*. 150, 560-564.

Svensson, M., Allard, B., and Düker, A., 2006. Formation of HgS—mixing HgO or elemental Hg with S, FeS, or FeS_2. *Sci. Total Environ.* 368, 418-423.

U.S. EPA, 2002. *Method 1631, Revision E: Mercury in Water by Oxidation, Purge and Trap, and Cold Vapor Atomic Flourescence Spectrometry.* Report No. EPA-821-R-02-019.

Viana, P.Z., Yin, K., and Rockne, K.J., 2008. Modeling active capping efficacy. 1. Metal and organometal contaminated sediment remediation. *Environ. Sci. Technol*. 42, 8922-8929.

Wang, Q., Kim, D., Dionysiou, D.D., Sorial, G.A., Timberlake, D., 2004. Sources and remediation for mercury contamination in aquatic systems – a literature review. *Environ. Pollut.* 131, 323-336.

Waybrant, K.R., Ptacek, C.J., Blowes, D.W., 2002. Treatment of mine drainage using permeable reactive barriers: column experiments. *Envrion. Sci. Technol.* 36, 1349-1356.

Weaver, C.E., Pollard, L.D., 1973. *The Chemistry of Clay Minerals*. Amsterdam, London, New York: Elsevier Scientific Publishing Company. p.125.

Weisener, C.G., Sale, K.S., Smyth, D.J., and Blowes, D.W., 2005. Field column study using zerovalent iron for mercury removal from contaminated groundwater. *Environ. Sci. Technol*. 39, 6306-6312.

Wersin, P., Höhener, P., Giovanoli, R., and Stumm, W., 1991. Early diagenetic influences on iron transformation in a fresh-water lake sediment. *Chem. Geol.* 90, 233-252.

Westerhoff, P. and James, J., 2003. Nitrate removal in zero-valent iron packed columns. *Water Res*. 37, 1818-1830.

Wehrer, M. and Totsche, K.U., 2008. Effective rates of heavy metal release from alkaline wastes – Quantified by column outflow experiments and inverse simulations. *J. Contam. Hydrol.* 101 (1-4), 53-66.

Xiong, Z., He, F., Zhao, D., Barnett, M.O., 2009. Immobilization of mercury in sediment using stabilized iron sulfide nanoparticles. *Water Res.* 43, 5171-5179.

Zillioux, E.J., Porcella, D.B., Benoit, J.M., 1993. Mercury cycling and effects in freshwater wetland ecosystems. *Environ. Toxicol. Chem.* 12, 2245-2264.