TECHNICAL PROGRESS REPORT

Remediation and Treatment Technology Development and Support for DOE Oak Ridge Office: Preliminary Results Summary of Laboratory Experiments of Mercury Transport Processes

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1. Introduction

The overall objective of this task is to provide laboratory measurements for critical mercury (Hg) transport, transformation, and exchange processes (i.e., methylation/demethylation, and dissolution) to be used in the numerical model. The laboratory experimental work will provide insight on parameters relevant to the Oak Ridge Reservation (ORR) and which are required in the numerical model, such as dissolution rate of mercury. In addition, experimental work will be conducted to analyze the effect of significant environmental factors (pH, Eh, thiols) on the major transport and transformation processes of Hg.

Under this task we will systematically investigate the stability, bioavailability, and mobility of the aged mercury species in soils and sediments. New techniques will be developed and applied in the analysis of Hg species and the study of Hg transport and transformation processes. Effects of environmental factors, such as oxidation-reduction, pH, and complexation with ligands (e.g., cysteine, glutathione, and large molecular NOM), on mobilizing cinnabar will be particularly investigated. From June 2012 to January 2013, we 1) developed an isotope dilution method for analyzing inorganic Hg concentration in water; 2) evaluated the relative importance of thiol group versus other groups in L-cysteine in cinnabar dissolution; 3) tested the difference of reduced glutathione (GSH) and oxidized glutathione(GSSG) in promoting cinnabar dissolution; 4) are developing an isotope dilution (ID)-phenylation-purge and trap-ICP-MS technique for analyzing organomercury species; 5) are developing a new technique using isotope tracers to simultaneously determine the dissolution of cinnabar and re-adsorption of released Hg^{2+} on the cinnabar surface.

2. Background

Mercury occurs in a variety of species, such as elemental mercury (Hg^0), mercury sulfide (HgS), mercury (hydr)oxides (e.g., HgO and $Hg(OH)_2$), ionic mercury salts (e.g., $HgCl_2$), and methylmercury (MeHg), in the environment. At historically mercury contaminated sites (e.g., the DOE Oak Ridge site), the originally discharged mercury would undergo complicated aging processes in the environment and eventually be sequestered in the soil and sediment in relatively stable forms (e.g. mercury bead and HgS). The mercury species sequestered in soils and sediments is generally considered low in solubility and reactivity, which prevents this mercury from being released into the solution and from being transported into the aquatic environment. Despite the limited solubility, mobility, and reactivity, the aged mercury species in soils and sediments may undergo a series of physical and chemical processes under certain environmental conditions, releasing dissolved mercury species into the solution. Cinnabar has often been suggested to act as an important sink for mercury in soils and sediments because of its extremely low solubility product(Mikac et al., 2002b; Mikac et al., 2003b). However, recent studies suggested that cinnabar can also release mercury to environment, which could be promoted by the oxidization of S(II) by Fe(III)-(hydr)oxides or dissolved oxygen (DO)(Burkstaller et al., 1975; Pyzik and Sommer, 1981; Barnett et al., 2001a; Mikac et al., 2002a; Mikac et al., 2003a; Poulton et al., 2004; Holley et al., 2007a) and the presence of ligands such as sulfide,

polysulfides, NOM (e. g. natural organic matter), and chloride in the environment(Burkstaller et al., 1975; Paquette and Helz, 1995; Paquette and Helz, 1997; Ravichandran et al., 1998b; Waples et al., 2005). The dissolution of cinnabar is an important process of Hg cycling in aquatic environments as it can provide a sufficient and continuous source of inorganic mercury and subsequently enhance the production of a more toxic species of Hg, methylmercury (MeHg).

Several possible mechanisms have been previously proposed for the dissolution of cinnabar in the environment. The most common one is that cinnabar dissolution is enhanced via the formation of HgL_x complexes, especially the formation of Hg-thiol complexes (MAHALINGAM RAVICHANDRAN et al., 1998; Ravichandran et al., 1998a; Aiken et al., 2001; Ravichandran, 2004; Waples et al., 2005). The coordination between dissolved Hg^{2+} and ligands will reduce the concentration of free Hg^{2+} and thus promote the dissolution of cinnabar. Another proposed mechanism is that the oxidation of S^{2-} will decrease the concentration of S^{2-} and thus promote the dissolution of cinnabar (Burkstaller et al., 1975; Barnett et al., 2001b). However, little is known about the relative importance of the oxidation of S^{2-} and the formation of Hg complexes in HgS dissolution. In addition to the dissolution of HgS, adsorption of Hg^{2+} could also play an important role in the release of Hg^{2+} from cinnabar. Several studies have found that Hg^{2+} could be quickly absorbed on cinnabar in DI water (Burkstaller et al., 1975; MAHALINGAM RAVICHANDRAN et al., 1998; Barnett et al., 2001b; Holley et al., 2007b), indicating the released Hg^{2+} from cinnabar could be re-adsorbed on the cinnabar surface. However, this process has been omitted in most recent studies on cinnabar dissolution and there is lack of a technique that can simultaneously measure the dissolution and re-adsorption of released Hg^{2+}. Such a technique is necessary for measuring the 'real' dissolution rate of cinnabar and elucidating the pathways through which cinnabar dissolute in natural environment.

3. Technical Approach

3.1. Development of the isotope dilution method for analyzing inorganic Hg concentration in water

Isotope dilution method is based on the addition of a known amount of enriched isotopes to samples. The alteration of the isotope ratio can be used to calculate the concentration of Hg in samples. Prior to analysis of the water sample, a certain amount of [199]Hg will be added to samples, serving as an internal standard. Then, signals of [199]Hg, and [202]Hg isotopes will be analyzed using flow injection (FIAS 400 from Perkin-Elmer company) coupled with ICP/MS (ELAN DRC-e ICP/MS from Perkin-Elmer company). Concentration of Hg in samples can be calculated according to the ratio of [199]Hg and [202]Hg.

3.2. Relative importance of thiol group versus other groups in L-cysteine in cinnabar dissolution

Effects of L-serine and L-cysteine on cinnabar dissolution were tested and compared. The initial concentrations of L-cysteine and L-serine were 10 μM. pH was adjusted to 8.0 with 10 mM

NaOH. Samples (~1.0 mL) were collected after 24 h of dissolution experiments, filtered by 0.22 μm polyethylene membrane and analyzed for total Hg.

3.3. Comparision of reduced glutathione (GSH) and oxidized glutathione(GSSG) in promoting cinnabar dissolution

Effects of GSH and GSSG on cinnabar dissolution were tested and compared. The initial concentrations of GSH and GSSG were 10 μM. pH was adjusted to 8.0 with 10 mM NaOH. Samples (~1.0 mL) were collected after 24 h of dissolution experiments, filtered by 0.22 μm polyethylene membrane and analyzed for total Hg.

3.4. Development of the isotope dilution (ID)-phenylation-purge and trap-ICP-MS technique for analyzing organomercury species

Prior to analysis of the water samples, a certain amount of $Me^{200}Hg$ and $Et^{199}Hg$ will be added to samples, serving as internal standards. $Me^{200}Hg$ was synthesized from ^{200}HgO by methylcobalamin. $Et^{199}Hg$ was synthesized from ^{199}HgO by $(C_2H_5)_4Sn$. $Me^{200}Hg$, $Me^{202}Hg$, $Et^{199}Hg$, and $Et^{202}Hg$ were then detected using phenylation-purge trap-ICP-MS. Concentrations of MeHg and EtHg in samples were then calculated according to the ratios of $Me^{200}Hg/Me^{202}Hg$ and $Et^{199}Hg/Et^{202}Hg$.

4. Results

4.1. Development of the isotope dilution method for analyzing inorganic Hg concentration in water

- *Coupling of a Flow Injection System (FIAS 400) to ICP-MS for analyzing mercury isotopes*

As shown in Figure 1, a Flow Injection System (FIAS 400) was successfully coupled to ICP-MS and it could be used to analyze mercury isotopes in samples. Influence of nebulizer gas flow rate (0.5 L/min, 0.6 L/min, 0.8 L/min, 0.96 L/min) on the sensitivity was tested. 0.8L/min was chosen as the flow rate of nebulizer gas.

Figure 1. Coupling of a Flow Injection System (FIAS 400) to ICP-MS for analyzing mercury isotopes

- ***Development of the isotope dilution method for analyzing inorganic Hg concentrations in water***

Prior to analysis of the water sample, a certain amount of ^{199}Hg was added to samples to form a final concentration of 10 ppt. Concentrations of Hg^{2+} in samples were then calculated according to Eq. 1. The method detection limit was estimated to be 6.7 ppt.

$$C_s = \frac{C_{199}A_{199}^{202} - RC_{199}A_{199}^{199}}{RA^{199} - A^{202}}$$

(1)

R: ratio of ^{202}Hg^{2+} to ^{199}Hg^{2+} in samples
C_s: the concentration of Hg in samples.
C_{199} : concentrations of spiked ^{199}Hg.
    : the abundance of ^{199}Hg in ^{199}Hg.
    : the abundance of ^{202}Hg in ^{199}Hg.
    : the abundance of ^{199}Hg in natural Hg.
    : the abundance of ^{202}Hg in natural Hg.

4.2. Relative importance of thiol group versus other groups in L-cysteine in cinnabar dissolution

As shown in Figure 2, Hg^{2+} released from cinnabar in $10\mu M$ L-cysteine was observed to be 40~60 times higher than that in $10\mu M$ of L-serine or sodium nitrate control medium (Figure 2), indicating that thiol is the major functional group in L-cysteine that promote the dissolution of cinnabar.
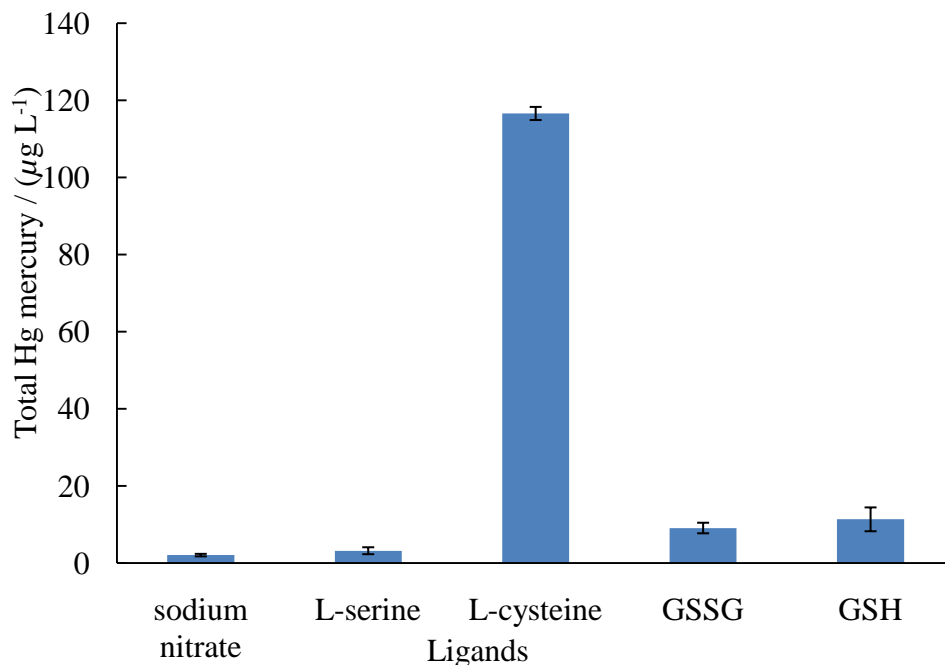
Figure 2 Effect of thiol group on the release of dissolved Hg from cinnabar

4.3. Comparision of reduced glutathione (GSH) and oxidized glutathione(GSSG) in promoting cinnabar dissolution

Concentrations of released Hg (II) from cinnabar were analyzed to be 9.1±1.4, 11.4±3.1 and 116.6±1.7 μg L^{-1} in the presence of in 10 μM of GSSG, GSH and L-cysteine, respectively. Total concentration of Hg released from cinnabar in the presence of GSH was only about 10% of that in the presence of L-cysteine. Hg^{2+} released in the presence of GSSG was slightly less than that in the presence of GSH (Figure 2).

4.4. Development of the isotope dilution (ID)-phenylation-purge and trap-ICP-MS technique for analyzing organomercury species

35 µl 2.16 µg/L Me^{200}Hg was added to water samples. Me^{202}Hg and Me^{200}Hg were detected using phenylation-purge and trap-ICP-MS technique (Figure 3). Concentrations of MeHg in water sample could be calculated by the ratio of Me^{202}Hg/ Me^{200}Hg according to Eq. 2.

$$C_s = \frac{C_{200}A_{200}^{202} - R C_{200} A_{200}^{200}}{R A^{200} - A^{202}} \tag{1}$$

R: ratio of Me^{202}Hg to Me^{200}Hg in samples

C_s : the concentration of MeHg in samples.

C_{200} : concentrations of spiked Me^{200}Hg.

    : the abundance of ^{200}Hg in Me^{200}Hg.

: the abundance of ^{202}Hg in Me^{200}Hg.

: the abundance of ^{200}Hg in natural Hg.

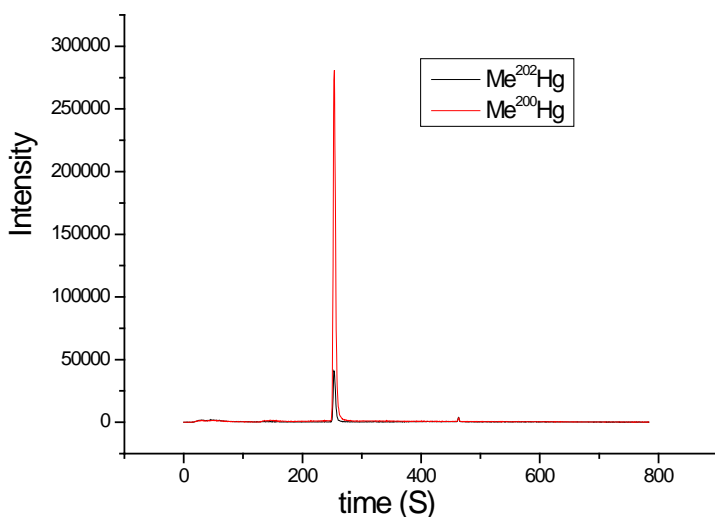: the abundance of ^{202}Hg in natural Hg.

Figure 3 Typical chromatogram of water sample spiked with Me^{200}Hg and analyzed by aqueous phenylation followed by purge and trap-ICP-MS

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