Mechanism of Hg(II) Immobilization in Sediments by Sulfate-Cement Amendment

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ABSTRACT

Reactive amendments such as Portland and super-sulfate cements offer a promising technology for immobilizing metalloid contaminants such as mercury (Hg) in soils and sediments through sequestration in less bioavailable solid forms. Tidal marsh sediments were reacted with dissolved Hg(II) in synthetic seawater and fresh water solutions, treated with Portland cement and FeSO₄ amendment, and aged for up to 90 days. Reacted solids were analyzed with bulk sequential extraction methods and characterized by powder X-ray diffraction (XRD), electron microscopy, and synchrotron X-ray absorption spectroscopy at the Hg L_{III}- and S K-edge. In amended sediments, XRD, SEM and sulfur K-edge XANES indicated formation of gypsum in seawater experiments or ettringite-type (Ca₆Al₂(SO₄)₃(OH)₁₂·26H₂O) phases in fresh water experiments, depending on the final solution pH (seawater ~8.5; freshwater ~10.5). Analysis of Hg EXAFS spectra showed Cl and Hg ligands in the first- and second-coordination shells at distances characteristic of a polynuclear chloromercury(II) salt, perhaps as a nanoparticulate phase, in both seawater and fresh water experiments. In addition to the chloromercury species, a smaller fraction (~20-25%) of Hg was bonded to O atoms in fresh water sample spectra, suggesting the presence of a minor sorbed Hg fraction. In the absence of amendment treatment, Hg sorption and resistance to extraction can be accounted for by relatively strong binding by reduced S species present in the marsh sediment detected by S XANES. Thermodynamic calculations predict stable aqueous Hg-Cl species at seawater final pH, but higher final pH in fresh water favors aqueous Hg-hydroxide species. The difference in Hg coordination between aqueous and solid phases suggests that the initial Hg-Cl coordination was stabilized in the cement hydration products and did not re-equilibrate with the bulk solution with aging. Collectively, results suggest physical

encapsulation of Hg as a polynuclear chloromercury(II) salt as the primary immobilization mechanism.

Keywords: Mercury (Hg); Portland cement; remediation; X-ray absorption spectroscopy; sulfur XANES

1. Introduction

The use of cementitious amendments for treatment of hazardous metal and metalloid contaminants in soils and sediments is becoming increasingly accepted and applied as either an *ex situ* or *in situ* remediation option. For many inorganic contaminants, amendments are effective in reducing contaminant mobility at a lower cost relative to other options, particularly removal and disposal. One class of these materials, Portland-type cements, are attractive for soil and sediment stabilization because of their ability to immobilize a variety of contaminants and their recalcitrance under different environmental conditions (O'Day and Vlassopoulos, 2010). These cements are composed primarily of calcium silicate and calcium aluminate phases. When reacted with water, they create highly alkaline solutions and form mixtures of portlandite (Ca(OH)_2), amorphous calcium silica hydrate phases (CSH) of the tobermorite ($\text{Ca}_5\text{Si}_6\text{O}_{16}(\text{OH})_2 \cdot n\text{H}_2\text{O}$) or jennite ($\text{Ca}_9\text{Si}_6\text{O}_{18}(\text{OH})_6 \cdot 8\text{H}_2\text{O}$) types, and siliceous “hydrogarnet” solid solutions ($\text{Ca}_3\text{Al}_2(\text{SiO}_4)_{3-x}(\text{OH})_{4x}$) (Lothenbach et al., 2008; Taylor, 1997). The concentrations of iron, magnesium, carbonate, and sulfate in the cement, and potentially the composition of the treated geomedia, can affect the assemblage of solid phase products. Depending on composition, reaction time, and extent of hydration, reaction products may include calcite (CaCO_3), carboaluminate phases ($\text{Ca}_4\text{Al}_2(\text{CO}_3)(\text{OH})_{12} \cdot 8\text{H}_2\text{O}$), gypsum ($\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$), ettringite ($\text{Ca}_6\text{Al}_2(\text{SO}_4)_3(\text{OH})_{12} \cdot 26\text{H}_2\text{O}$) or related sulfoaluminate phases, and hydrotalcite-type phases ($\text{Mg}_4(\text{Al,Fe})_2(\text{OH})_{14} \cdot n\text{H}_2\text{O}$) in addition to CSH and hydrogarnet phases (Matschei et al., 2007). The presence of Fe(III) sulfate during the hydration of Portland cement commonly results in the formation of Fe-substituted ettringite, which is notable for its ability to incorporate both cations and oxyanions into its crystal structure (Moschner et al., 2008; Moschner et al., 2009).

One barrier to the use of sequestering amendments is confidence that the contaminant has been effectively immobilized for the long term (O'Day and Vlassopoulos, 2010; Randall and Chattopadhyay, 2004). Mercury (Hg), as one of the more toxic elements at low concentrations, is a particularly challenging contaminant for *in situ* remediation (Wang et al., 2012; Xu et al., 2015). Methylation of inorganic Hg under anoxic conditions by sulfate- and Fe-reducing bacteria is the primary pathway for production of methylmercury, which bioaccumulates in higher organisms mostly in the form of methylmercury (MeHg) (Benoit et al., 2003; Hsu-Kim et al., 2013). Human exposure to Hg is primarily through fish consumption (Hightower and Moore, 2003). The forms of Hg that are bioavailable to methylating bacteria are currently not well known but may include neutral Hg complexes (e.g., HgS^0 and $\text{Hg}(\text{HS})_2$) (Bessinger et al., 2012; Gilmour et al., 2008) and possibly thiol-complexed Hg and nano-HgS (i.e., colloidal HgS) (Hsu-Kim et al., 2013; Schaefer and Morel, 2009; Schaefer et al., 2011). Therefore, one strategy for reducing the extent of methylation of inorganic Hg is the addition of amendments that can sequester or stabilize inorganic forms of Hg and thus reduce its bioavailability for bacterial methylation. Another approach is to manipulate the reduction-oxidation (redox) state and/or pH of a sediment system to create conditions unfavorable for sulfate or iron reduction, thus limiting Hg methylation rate. Portland-type cement amendments, which are oxidizing and promote high pH, are amenable to use in alkaline systems such as the stabilization of fly ash wastes or sediment remediation associated with contamination from Hg chlor-alkali manufacturing facilities, or may be applied in acidic systems where pH neutralization is required in addition to contaminant immobilization.

Several studies have investigated Portland-type cement amendments for Hg remediation *ex situ*, and suggested Hg encapsulation within cement phases rather than chemical stabilization

as a sequestration mechanism (Poon et al., 1985; Roy et al., 1992), with one study suggesting formation of HgO(s) (McWhinney et al., 1990). Powdered reactivated carbon and cement were used to stabilize Hg in cube test sand used as solid waste, which resulted in sufficient retention to pass the toxicity characteristic leaching procedure (TCLP) test (Zhang and Bishop, 2002). This test was also used to assess Hg retention after treatment of liquid Hg waste streams with powdered sulfur-polymer cements and sulfide (Fuhrmann et al., 2002). A reduction in Hg concentrations in TCLP tests was observed after using ferric-lignin derivatives and Portland cement to treat high-Hg sludge from brine purification (Zhuang et al., 2004). None of these studies used spectroscopic methods to examine molecular-scale Hg speciation in cement amendment reaction products and therefore, direct evidence of the mechanism for Hg retention in cement is lacking.

In this study, we examine the ability of natural sediment treated with Portland cement and FeSO₄ to retain aqueous inorganic Hg(II) in sorption experiments with synthetic seawater and fresh water. Characterization of solid reaction products by bulk sequential extractions and microscopic and spectroscopic methods are used to directly identify the molecular-scale mechanism(s) of Hg bonding and stabilization in the cement product phases. Analysis of thermodynamic system constraints lends novel insight into controls on inorganic Hg uptake from solution and the formation of stable encapsulating phases compared with non-amended sediments.

2. Materials and methods

2.1. Materials and sediment analysis

The amendments used in sorption experiments were a mixture of 3.3:1 Portland cement type 5 (Cemex, Inc., Table 1) and iron sulfate (FeSO₄·7H₂O) (Fisher Scientific). Surface

sediment samples (0-15 cm depth) were collected from Stege Marsh (Richmond, CA, USA), a tidal marsh in central San Francisco Bay (Hwang et al., 2006) at two different locations in the tidal zone (122°19'39.53"W and 122°19'40.61"W). Samples were kept frozen (−20° C) until analysis and sorption experiments. Sediment samples were homogenized, pH was measured in deionized water (pH_w) and in 1 M KCl (pH_K) (in a 1:2.5 suspension), and total carbon (TC) was determined by combustion. Exchangeable bases were extracted with 1.0 M NH₄OAc (pH 7) (Thomas, 1982) and exchangeable aluminum (Al_K) was extracted with 1.0 M KCl (Barnhisel and Bertsch, 1982). The effective cation exchange capacity (ECEC) was calculated as the sum of Al_K and Ca, Mg, Na and K extracted by 1.0 M NH₄OAc at pH 7 (Shuman, 1990). The sediment was digested in aqua regia (HCl : HNO₃ = 3:1) by microwave-assisted digestion for analysis of trace metal and major cations following EPA Method 3051 (USEPA, 2007). Bulk mineralogical composition of the ≤ 2 mm fraction was determined by powder X-ray diffraction (XRD) on dried and ground material (see below).

2.2. Sorption experiments

Stock solutions of HgCl₂ were prepared in either synthetic seawater (De Stefano et al., 1994) or freshwater (Smith et al., 2002) using a conductivity of ~346 μS cm^{−1} based on values from Guadalupe and Almaden reservoirs (CA, USA), two sites with high Hg concentrations (Tetra Tech, 2005) (Table 2). Sorption experiments were done with amendment only (−sed), with sediment only (−amend), and with sediment and amendment (+amend). Total Hg concentrations were either ~1-2 mg L^{−1} (5-10 μmol L^{−1}) in amendment-only experiments, or ~40-50 mg L^{−1} (200-250 μmol L^{−1}) in experiments with sediments made from stock solutions of either 0.01 mM or 0.25 mM HgCl₂, respectively. Replicate experiments in Nalgene Oak Ridge high speed PPCO tubes were performed by mixing solids with HgCl₂ solutions under oxidized

conditions. In amendment (–sed) experiments, 0.53 g $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ and 0.96 g Portland cement were mixed with HgCl_2 solution (1:25 solid:solution). In sediment (+amend) experiments, 0.065 g $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$, 0.12 g Portland cement, and 1.2 g sediment were mixed with HgCl_2 solution (1:20 solid:solution). In sediment (–amend) experiments, 1.2 g of sediment was mixed with HgCl_2 solution. Suspensions were shaken in a reciprocal shaker (50 rpm) for 1, 7, 30 or 90 days at room temperature ($\sim 25^\circ\text{C}$). At the end of each reaction time, suspensions were centrifuged (10,000 rpm for 10 min) and supernatant solutions removed and filtered (0.45 μm PTFE syringe filter). Solutions were analyzed for total Hg using ICP-MS optimized for Hg measurement at low concentrations (see Serrano et al. (2012) for detailed description of Hg analysis). Calibration standards were prepared in deionized water acidified to 2% with nitric acid and contained 100 ppb Au to stabilize Hg. Standards were prepared at 10, 20, 50, 100, 200 and 500 ppt (parts per trillion) Hg. Limits of detection were calculated as three standard deviations of the instrument response from 10 repeated analyses of sample-matrix-matched blank solutions. From this analysis, a reproducible, practical instrument detection limit of 50 ng/l (ppt) was established. Mercury analyses by ICP-MS were carried out within 48 h after experiments were completed in order to minimize sample exposure time to containers. Accuracy was validated by analyzing certified reference material (NIST San Joaquin soil SRM 2709a; Mackey et al., 2010).

2.3. Sequential extractions

At the end of each reaction time, solid products from sorption experiments were homogenized and split for analyses. To extract readily exchangeable Hg, solid samples (0.5 g) were resuspended in 5 mL of 0.1 M $\text{MgCl}_2(\text{aq})$ at pH 11 and shaken for 1 h, and then centrifuged at 8000 rpm at 10°C for 20 min (Neculita et al., 2005). The supernatant solution was filtered (0.45 μm PTFE syringe filter), acidified, and measured for total Hg. Following the exchangeable

fraction, Hg associated with the poorly crystalline fractions of the amendment treatment (no sediment) was extracted with 0.2 M acidic ammonium oxalate solution (AAO) (4 h at pH 3 on a reciprocal shaker in the dark) (Jackson et al., 1986). Samples were centrifuged at 8000 rpm at 10 °C for 20 min, and the supernatant solution was removed, acidified, and measured for Hg. In sorption experiments with sediment (with and without amendment) after the exchangeable fraction was extracted, Hg associated with organic compounds was determined by two successive extractions, first using 0.2 M NaOH followed by CH₃COOH 4% (v/v) (Neculita et al., 2005). Supernatant solutions from each extraction were measured for Hg.

2.4. X-ray diffraction

Powder X-ray diffraction (XRD) was conducted on randomly oriented samples using a PanAnalytical X'Pert Pro diffractometer and X'celerator detector with Fe-filtered CoK α ($\lambda=1.74$ Å) at 40 kV and 45 mA. Additional XRD data were collected on beamline 11-3 at the Stanford Synchrotron Radiation Lightsource (SSRL) using a Si(111) monochromator with a spot size of 0.15 x 0.15 mm between 3° and 124° 2 θ in 0.006° steps. Samples were dispersed on adhesive tape and sealed with a second piece of tape. The XRD patterns were calibrated with a LaB₆ standard and converted to wavelength using non-linear curve fit and the Bragg equation. Mineral identification was performed using the ICDD reference database with the Jade software package (MDI Products).

2.5. Scanning electron microscopy and electron microprobe

Solid phases were examined using scanning electron microscopy coupled with energy-dispersive X-ray spectroscopy (SEM/EDS). Dry samples were mounted on Al-alloy stubs with double-stick carbon tape and analyzed using a FEI Quanta 200 SEM with an EDAX Genesis 2000 EDS system operated at a voltage of 25 kV and a spot size of 1 x 1 μm^2 .

Chemical mapping using electron microprobe X-ray fluorescence (XRF) was performed on solid samples embedded in epoxy and made into petrographic thin sections. Maps were collected on a CAMECA SX100 Ultra electron microprobe (Department of Planetary Sciences, University of Arizona) operating at 20 keV and 20 nA, and equipped with wavelength dispersive spectrometry (WDS) detectors. Maps were collected with a step size of 0.2 μm and a dwell time of 8 ms.

2.6. Sulfur and mercury X-ray absorption spectroscopy (XAS)

Sulfur K-edge X-ray absorption spectra were collected on beamline 4-3 at the Stanford Synchrotron Radiation Lightsource (SSRL) at ambient temperature with a Si(111) monochromator crystal in fluorescence mode with either a $\text{N}_2(\text{g})$ -filled Lytle detector or a solid-state diode detector. A reflecting mirror was used to reject higher order harmonic reflections. Dried, powdered samples were finely ground and dusted as a thin layer on S-free mylar adhesive tape. Energy was calibrated by assigning the first peak maximum in the S K-edge spectrum of $\text{Na}_2\text{S}_2\text{O}_3 \cdot 5\text{H}_2\text{O}$ to 2472.02 eV. Multiple scans (3-6) for each sample were collected and averaged over the energy range 2370-2815 eV.

Mercury L_{III} -edge absorption spectra of reacted samples were collected on beamline 11-2 at SSRL in fluorescence mode using a 30-element Ge detector and a Si(220) monochromator crystal. Samples were ground by hand and loaded undiluted into Teflon samples holders, sealed with Kapton tape, and held in a liquid-He cryostat (at 5–20 K) during data collection. Energy was calibrated using Au foil by assigning the first inflection point on the absorption edge to 11,919 eV. Up to 12 scans for each sample were collected and averaged. Analyses were performed with the programs Athena (Ravel and Newville, 2003) and EXAFSPAK (George and Pickering, 2000). Background subtraction was done using a linear fit through the pre-edge

region and a cubic spline through the spectrum above the absorption edge. Spectra were fit quantitatively using the shell-by-shell method over a k -range of 1.5 to 12.5 $\text{\AA}^{-1}$ with theoretical single- and multiple-scattering reference functions calculated by the program FEFF 8.0 (Ankudinov et al., 1998) using atomic clusters taken from the crystal structures of known Hg compounds (Serrano et al., 2012) with geometries similar to those expected in the unknown samples. In least-squares fits, distance (R) and Debye-waller factor (σ^2) were fixed on values determined from fits to reference compounds (Serrano et al., 2012) and backscatterer number (N) was varied. Photoelectron threshold energy difference (ΔE_0) was fit as a single parameter for all shells (O'Day et al., 1994).

2.7. Equilibrium speciation calculations

Thermodynamic calculations were performed using the Geochemist's Workbench modeling package with a modified version of the Lawrence Livermore National Laboratory (LLNL) thermodynamic database (Delany and Lundeen, 1990) augmented with the "cemdata 07" thermodynamic database (Lothenbach and Winnefeld, 2006) and with recently compiled thermodynamic data for inorganic Hg species (Powell et al., 2005).

3. Results

3.1. Mercury uptake and retention by amended sediments

Physical and chemical properties of the tidal marsh sediment are shown in Table 3. The sediment is characterized by low pH (3.7), a high ECEC ($137.77 \text{ cmol kg}^{-1}$), and an effective base saturation of 95%. Total organic carbon was 5.27% and background Hg concentration was 1.12 mg kg^{-1} sediment (by extraction). Uptake of Hg from seawater and fresh water solutions and sequential extractions from reacted sediment and amendment showed that Hg was retained in solid phases (90-100% uptake) after 1, 7, and 30 d in amendment only (–sed) ($\text{Hg}_T = 1\text{-}2 \text{ mg}$

L⁻¹) and sediment with amendment (+amend) ($Hg_T = 40\text{--}50 \text{ mg L}^{-1}$) experiments (Figure 1 and Table 4). Exchangeable and AAO-extracted Hg fractions in amendment (–sed) samples were less than 1 to 5.5% of total sorbed Hg. In sediment (+amend) experiments, Hg retained by solids was associated with the residual fraction, with at most a few percent of sorbed Hg extracted from the exchangeable and organic fractions (Figure 1). In sediment experiments without amendment (–amend) in seawater, ~6-10% of sorbed Hg was associated with the exchangeable fraction at 7 and 30 d, although Hg mass balance for these experiments was poor (see Table 4). In sediment (–amend) in fresh water, total Hg uptake was similar to sediment (+amend) experiments, with nearly all sorbed Hg in the residual fraction. Addition of Portland cement to sediment raised pH significantly, similar to the high pH observed in amendment (–sed) experiments in fresh water and seawater (pH 10.3-12.3). In sediment (+amend) experiments, final pH was higher in fresh water (10.4-10.8) compared to seawater (8.5-9.5), but both were strongly alkaline compared to the acidic pH of sediment solutions without amendment, which decreased from pH 6.3-6.9 at 1 d to pH 3.5-3.7 at 30 d.

3.2. X-ray diffraction

Analysis of X-ray diffractograms of amendment (–sed) experiments after 1, 30, and 90 d of reaction showed similar results for seawater and fresh water systems at 1 and 30 d, but some differences in reaction products were apparent after 90 d (Figure 2). Ettringite ($Ca_6Al_2(SO_4)_3(OH)_{12} \cdot 26H_2O$), calcite ($CaCO_3$), and calcium-silica-hydrate ($Ca_{1.5}SiO_{3.5} \cdot xH_2O = CSH$) were identified as the primary phases at all time steps. Gypsum $Ca(SO_4) \cdot 2H_2O$ was present at 1 and 30 d, but not identified at 90 d in either seawater or fresh water amendment (–sed) experiments. Tricalcium silicate ($Ca_3SiO_5 = CS$), a major cement clinker phase, was identified by XRD at 1 d, but peak intensities associated with this phase decreased with time and

disappeared by 90 d in fresh water. Peak intensities of ettringite increased with reaction time, while those attributed to calcite decreased with time, particularly in fresh water. Identification of CSH, CS, and other cement phases is complicated by overlap of primary reflections with each other and with calcite at low abundance. Hydrotalcite ($\text{Mg}_6\text{Al}_2\text{CO}_3(\text{OH})_{16} \cdot 4\text{H}_2\text{O}$) was detected in the seawater amendment only, probably because of the higher Mg concentration in seawater versus fresh water. No Hg mineral phases were identified by XRD.

In sediment with and without amendment, bulk XRD patterns are dominated by minerals in the sediment, primarily quartz, illite/montmorillonite, and kaolinite (Figure 3). Sediment (+amend) solids also contained ettringite and calcite after 7 d, but other cement-type phases were not identified. An orange precipitate was observed in the sediment samples after 1 d of reaction, but no crystalline Fe phases were identified by XRD.

3.3. Scanning electron microscopy and electron microprobe analysis

Characterization of amendment (–sed) solids reacted in seawater for 7 d by SEM/EDX showed the formation of ettringite (Figure 4a). Needle-like particle morphology typical of ettringite (Goetz-Neunhoeffler and Neubauer, 2006; Goetz-Neunhoeffler et al., 2006) was observed by SEM and corroborated by EDX analysis. Detection of Mg, Si and Fe by EDX suggests the presence of additional phases in the sample, probably C-S-H (identified by XRD), and Fe and Mg oxides, possibly as amorphous phases and therefore not detectable by XRD. Monosulfoaluminate ($\text{Ca}_4\text{Al}_2(\text{SO}_4)(\text{OH})_{12} \cdot 6\text{H}_2\text{O}$) was the other hydrated product phase observed by SEM in the solid sample after 7 d of reaction (Figure 4b) based on its characteristic morphology (Matschei et al., 2007) (sample not analyzed by EDX).

Electron microprobe analysis of sediment (+amend) in seawater using backscatter imaging and element fluorescence mapping ($45 \mu\text{m} \times 45 \mu\text{m}$ region) showed a diffuse

distribution of Hg, but counts were above the average background in the epoxy adjacent to the sample. Increased Hg fluorescence was associated with a particle dominated by Ca and S (Figure 4c), which was probably gypsum based on its S XANES spectrum (next section). Areas with increased Fe within the particle (~2-3 μm diameter) were not strongly correlated with Hg or Ca, and appear as inclusions (Figure 4c).

3.4. Sulfur XAS

Normalized bulk S XANES spectra of sediment with and without amendment reacted for up to 90 d were compared with the spectra of S reference compounds and one amendment (–sed) sample reacted in seawater for 12 months (Figure 5). The spectra of all sediment samples with and without amendment were dominated by a major absorption peak corresponding to SO_4^{2-} at 2478.2 eV, indicating predominately oxidized sulfate. In the absence of sediment, the spectrum of amendment (–sed) aged for 12 months matched that of Al-ettringite. Spectra of sediment (+amend) in seawater after 7 and 90 d had three main post-edge absorption features at 2486.0, 2492.0, and 2499.4 eV, which correspond to spectral features observed in gypsum ($\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$) (Figure 5). In contrast, the spectrum of sediment (+amend) in fresh water at 90 d lacked the post-edge absorption features associated with gypsum and was similar to the spectrum of sediment (–amend) reacted for 90 d, both of which were broadly similar to a spectrum of Fe-ettringite coprecipitated solid (Fe+cpt) studied previously (Serrano et al., 2012). In all sediment samples with and without amendment, absorption features at 2472.2-2473.5 eV below the main sulfate absorption peak indicate the presence of a minor fraction of reduced S species (Figure 5, inset). These features correspond most closely to those in pyrite (maximum absorption at 2472.2 eV) and a thiol-type species similar to S-absorption in cysteine (maximum absorption at 2473.5 eV). Among different sediment samples, different intensities of these minor adsorption features

associated with reduced S are consistent with small and variable amounts of sulfide phases such as pyrite or amorphous FeS, and variable amounts of organic matter, found in natural sediments. There is no evidence in the S XANES or in XRD data for reduction of sulfate during the course of the experiments.

3.5. Mercury L_{III} XAS

Bulk Hg XANES and EXAFS spectra of sediment (+amend) reacted in seawater for 7 and 90 d showed absorption features and inflections (observed in the first-derivative XANES spectra) similar to a spectrum of Hg(II) coprecipitated with CaO+Al₂(SO₄)₃ in synthetic seawater at high pH (Hg-Al-cpt) characterized in detail in a prior study (Serrano et al., 2012) (Figure 6). Results of shell-by-shell fits indicated a similar local environment around Hg in sediment (+amend) samples and Hg-Al-cpt (Table 5). Prior EXAFS analysis and characterizations of the Hg-Al-cpt sample showed that Hg was directly coordinated by Cl ligands only and surrounded by Hg atoms beyond the first coordination shell. The local bonding environment from EXAFS and supporting characterizations of Hg-Al-cpt were interpreted as a polynuclear chloromercury(II) salt encapsulated in ettringite particles (Serrano et al., 2012). Comparison of the EXAFS spectra of sediments aged for 7 and 90 d indicated similar backscattering amplitudes from Cl and Hg atoms at 2.51 Å and 4.14 Å, respectively, captured by the variation in N with fixed σ^2 (Table 5). Slightly stronger backscattering at longer distances from Cl at 4.24 Å, Hg at 4.46 Å, and Hg at 5.16 Å in the spectrum at 90 d compared to 7 d suggests an increase in either local structural order or particle size with longer reaction time, consistent with sample aging.

Absorption spectra of sediment (+amend) reacted in fresh water for 7 d and 90 d showed broadly similar XANES features to the seawater-reacted samples (Figure 7). However, quantitative analysis of the EXAFS spectra of fresh water samples using the same structural fit

model as the seawater samples indicated a difference in Hg coordination and lower backscattering amplitudes (lower N) from Cl and Hg shells. In addition to coordination by Cl atoms at 2.51 Å, a smaller fraction of Hg was coordinated to O, with a Hg-O distance of 2.18 Å, in fresh water sediment (+amend) samples (Table 5). This Hg-O distance is longer than those determined by EXAFS fits of reference spectra HgO(s) (2.03 Å) and Hg(II) sorbed to goethite (2.00 Å) (Serrano et al., 2012). Backscattering from Cl and Hg atoms at distances beyond the first shell were similar to those of sediment (+amend) in seawater and Hg-Al-cpt, but backscattering amplitudes were reduced in the fresh water sediment by 25% to 75%. Based on the relative fractions and peak heights of first-shell Cl or O bonded to Hg, approximately 20-25% of the total Hg present in the fresh water samples is bonded to O atoms and the remainder is bonded to Cl atoms.

4. Discussion

4.1 Mercury speciation and distribution from spectroscopy and microscopy

Results from bulk Hg L_{III} XANES and EXAFS analysis of amended sediment showed that Hg in seawater experiments was bonded only by Cl ligands and Hg in the first- and second-coordination shells at distances characteristic of a polynuclear chloromercury(II) salt, perhaps present as a nanoparticulate phase. This mechanism of Hg immobilization was characterized in our prior study of the formation of Al-ettringite-type phases from synthetic seawater solutions with trace dissolved Hg in the absence of Fe (Serrano et al., 2012). With aging from 7 to 90 d, no changes in the atomic structure around Hg were observed, but slightly stronger backscattering from atoms at greater distance from central Hg indicates an increase in atom ordering or particle size with aging time. A similar atomic configuration around Hg was observed in fresh water sediment (+amend) experiments, but for these samples, reduced amplitudes from distant Cl and

Hg atoms compared to seawater spectra indicates more disorder and/or a smaller cluster size around Hg. In addition, detection of backscattering from O atoms bonded to Hg (Hg-O = 2.18 Å) is evidence for a fraction of Hg not associated with the chloromercury fraction. Electron microprobe element mapping of a seawater sediment (+amend) sample aged for 90 d detected a diffuse distribution of Hg on gypsum particles that was not strongly correlated with any other elements (Figure 4; microprobe data were not collected on fresh water samples). This result suggests that a small fraction of Hg in the seawater sample, below detection by bulk XAS (i.e., less than ~10%), was likely present as a sorbed species rather than as the chloromercury particulate species. In fresh water samples at 7 and 90 d, the Hg-O sorbed component was present at a higher fraction, on the order of about 20-25% of total Hg in the sample, based on atom backscattering amplitudes in the bulk EXAFS spectra.

The Hg-O distance (2.18 Å) derived from EXAFS spectral fits of fresh water sediment (+amend) samples (2.18 Å) was longer than the distance obtained from the EXAFS fit of a reference spectrum of Hg(II) sorbed to goethite (2.00 Å) reported in our prior study (Serrano et al., 2012). Other EXAFS studies of Hg(II) sorption on model mineral surfaces (goethite, γ -alumina, and bayerite) derived a range of Hg-O distances from 1.99-2.07 Å (Kim et al., 2004a; Kim et al., 2004b; Slowey and Brown, 2007). Similar Hg-O distances from EXAFS analysis were reported in studies of Hg(II) addition to organic soil (Skylberg and Drott, 2010) and for Hg(II) bonded to humic acids (Hesterberg et al., 2001). However, a wide range of Hg-O distances (from 1.90 to 2.78 Å) are observed in Hg oxo-halide and oxo-sulfate compounds in which Hg is bonded in distorted oxygen-centered tetrahedra or chains (Ahmed et al., 2002; Borisov et al., 2005; Weil, 2001). Because of the covalent character of Hg bonds, Hg-O bond distances in different structural groups are strongly influenced by the presence of halide ligands,

oxyanion groups such as sulfate, and Hg-Hg pairs (Borisov et al., 2005; House et al., 1994).

Oxygen atoms bonded to Hg were detected by EXAFS only in the fresh water experiments with lower total Cl^- concentration, which may reflect the aqueous speciation of Hg in the initial reactant solutions as discussed below.

4.2 System equilibrium relationships and kinetic limitations

The uptake of Hg from solution by amended sediment can be examined in terms of bulk speciation and equilibrium driving forces, and compared with processes of cement hydration and hardening in fresh water versus seawater systems. At the initial pH of both seawater and fresh water solutions, Hg species predicted at equilibrium are Hg-Cl aqueous complexes, with the dominant complex determined by the activity of total Cl^- (Figure 8a). After 1, 7 and 30 days of reaction in fresh water solutions at a final pH of 10.5-10.7, equilibrium calculations predict $\text{Hg}(\text{OH})_2^0(\text{aq})$ as the dominant aqueous Hg species. In seawater systems with high Cl^- (~0.43 M) and a final pH of 8.5-8.7, dissolved Hg complexes with Cl^- (HgCl_3^- and HgCl_4^{2-}) are the dominant species predicted at equilibrium (Figure 8a). Characterization of Hg speciation in solid-phase sediment (+amend) samples by EXAFS showed that Hg was coordinated dominantly by Cl ligands in both seawater and fresh water experiments, and that a minor fraction of Hg was coordinated by O in fresh water solid samples. The difference in Hg coordination between aqueous and solid phases in fresh water experiments suggests that the initial Hg-Cl coordination in solution was stabilized in the cement hydration solid products and did not re-equilibrate with the final bulk solution with aging. The EXAFS results showed that Hg in the solid phase resembled a chloromercury(II) salt identical in local atomic structure to a nanoparticulate species observed in our prior study of Hg uptake from solution during the precipitation of ettringite (Serrano et al., 2012). The results suggest that the chloromercury(II) species was stabilized in

both seawater and fresh water amendment experiments, probably by an encapsulation mechanism as proposed in our previous study (Serrano et al., 2012). A fraction of Hg in the fresh water samples at higher final pH was present as an oxygen-bonded Hg-O species, most likely as a sorbed species, although bulk extractions of amended sediments did not detect a labile Hg fraction in fresh water samples.

Equilibrium calculations show that gypsum is the thermodynamically stable sulfur phase in the sediment (+amend) seawater samples at the measured final pH of the solution (Figure 8b), in agreement with S XANES and microprobe results. In fresh water experiments, ettringite was identified by XRD in a sediment (+amend) sample at 7 d (pH = 10.41). After 90 d of aging, S XANES indicated the formation of a Ca-Fe-sulfate-hydrate phase with spectral similarities to ettringite, and distinctly different from gypsum. In amendment (–sed) samples in both fresh water and seawater, formation of gypsum was observed in XRD after 7 and 30 days of reaction, but not after 90 days (pH ~12) when ettringite was present. These results are consistent with the system moving out of gypsum stability as pH increased and forming ettringite at the expense of gypsum. Therefore, the final pH of the solution in sediment (+amend) experiments (~8.5 for seawater; ~10.5 for freshwater) determined the major sulfate-bearing phases, which are in general agreement with equilibrium predictions (Figure 8b). Addition of sulfate-cement amendment raises pH and serves to encapsulate Hg as chloromercury(II) nanoparticulate species, whether the final major sulfate-bearing phase is gypsum or ettringite.

In sediment (–amend), the absence of strongly hydrating cement phases that increase pH to alkaline levels resulted in a decrease in pH from 6.3 (seawater) or 6.9 (fresh water) at 1 d to less than pH 4 at 7 and 30 d. Prior studies of Hg(II) sorption on mineral surfaces as a function of pH showed Hg desorption below pH ~5-6, with less sorption at higher Cl^- concentration and low

pH (Barrow and Cox, 1992; Bonnissel-Gissinger et al., 1999; Mangold et al., 2014; Tiffreau et al., 1995). In sediment experiments with and without amendment, Hg was generally not removed by different extraction methods targeting exchangeable, adsorbed, and organic fractions, although sediment (–amend) experiments had up to 10% of sorbed Hg associated with the exchangeable fraction (Figure 1). Therefore, Hg is strongly partitioned to solid phases from solution, both in sediment (+amend) fresh water experiments in which EXAFS indicated a fraction of sorbed Hg as a Hg-O species, and in experiments without amendment. In all sediments experiments with and without amendment, S XANES spectra were dominated by a peak from sulfate, but a small peak at lower absorption energy showed the presence of reduced S, probably associated with organic thiol (–SH) groups and/or sediment sulfide. Based on relative peak heights, the reduced S peak is on the order of 5-15% of the sulfate peak. The total S concentration in unreacted sediment was 30 mmol kg⁻¹ by bulk digestion (Table 3). If about 5-15% of total S is present as reduced S, either as sediment pyrite, FeS, or organic S, then about 1.5-4.5 mmol S kg⁻¹ sediment may be present in these forms known to strongly bind Hg (Gerbig et al., 2011; Skyllberg, 2008; Skyllberg and Drott, 2010; Slowey, 2010). Similar amounts of Hg uptake from solution were observed in fresh water experiments with and without amendment, amounting to a bulk sorbed concentration of about 4.8 mmol Hg kg⁻¹ solid after 30 d, which is slightly higher than the estimated reduced-S molar concentration in the sediment. No evidence for Hg bonding with S was detected by bulk Hg XAS in amended samples, but unamended samples were not investigated by Hg XAS. In the absence of amendment, Hg sorption and resistance to extraction may reflect relatively strong binding by reduced S species present in the marsh sediment.

5. Conclusions

The application of sulfate-cement amendments for Hg(II) immobilization in sediments is a potentially effective remediation strategy, particularly for seawater systems where high Cl^- concentrations favor encapsulation of Hg(II) as a nanoparticulate species in cement product phases. The experimental results presented here highlight the importance of initial Hg speciation and concentration of Cl^- as a complexing ligand, the rate at which cement products form, and the ability of encapsulating phases to incorporate Hg as a nanoparticulate species that is resistant to mobilization or microbial uptake. In our prior study, we noted Fe(III) hydroxide precipitation and Hg sorption during formation of cementitious products in the presence of Fe as a potentially complicating uptake mechanism in high Fe/Hg systems (Serrano et al., 2012). In this study with sediment and amendment treatment, Fe does not appear to play a major role in Hg uptake by sorption processes. Coordination of Hg by O atoms was detected by EXAFS analysis as a minor component in solid phases in fresh water sediment (+amend) experiments only, and was not correlated with higher Hg extractability from solids. The presence of reduced S species in sediments as pyrite (FeS_2), FeS, and/or thiol associated with organic matter can account for Hg sorption in the absence of amendment (Gerbig et al., 2011; Skyllberg, 2008; Skyllberg and Drott, 2010; Slowey, 2010), but we note that Hg is not necessarily stabilized against mobilization or bacterial bioavailability over longer time scales by this uptake mechanism. Given the complexity of natural systems where Hg is present, however, relative concentrations of Fe, sulfide solid phases, and organic matter may influence Hg speciation and should be considered in the choice of amendment remediation technology.

The addition of cement-type stabilization amendments may be most useful for alkaline chemical systems such as the stabilization of fly ash wastes, or sediment remediation associated

with contamination from Hg-cell chlor-alkali manufacturing facilities (Wang et al., 2012). For acidic systems, such as dredged anoxic sediments where exposure to air may promote sulfide oxidation and acidity generation, cement amendment would raise and buffer pH, favoring Hg adsorption as well as potential encapsulation. The pH of the final sediment, water, and amendment mixture is a primary factor controlling the stable assemblage of solid phases that serves to encapsulate Hg nanoparticulate species, whereas the initial solution chemistry influences Hg speciation and nanoparticulate formation. Although stabilization/solidification methods have been used for *ex situ* treatment of waste streams, they may also be economical and effective for stabilizing Hg in contaminated sediments dredged from waterways before either disposal or reuse, as well as for *in situ* applications in soils, tidal zones, or shallow water sediments. The use of molecular-scale characterizations in the development of remediation technologies is essential for identifying speciation and sequestration mechanism(s) of Hg and other toxic metals in order to evaluate long-term effectiveness. The integration of molecular information and thermodynamic constraints demonstrates the important role of pH and complexing ligands such as chloride on Hg(II) sequestration under specific conditions, which stabilize Hg in less bioavailable solid forms.

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Table 1. Chemical composition of Portland cement type 5.

Chemical composition ^a	%
SiO ₂	20.76
Al ₂ O ₃	4.25
Fe ₂ O ₃	4.00
CaO	63.98
MgO	2.35
SO ₃	2.52
Na ₂ O	0.24
K ₂ O	0.42
Loss of ignition	1.26
Free CaO	1.00
Compound composition	
C3S (Ca ₃ SiO ₅)	61.21
C2S (Ca ₂ SiO ₄)	13.34
C3A (Ca ₃ Al ₂ O ₆)	4.51
C4AF (Ca ₄ Al ₂ Fe ₂ O ₁₀)	12.16
CaSO ₄	4.29

^a Analysis report from Cemex, Inc.

Table 2. Composition of initial solutions for sorption experiments with synthetic seawater and fresh water ^a.

	Sea water (mol L ⁻¹)	Fresh water (mol L ⁻¹)
Na ⁺	0.45	0.58 x 10 ⁻³
Cl ⁻	0.43	0.56 x 10 ⁻³
K ⁺	0.01	0.086 x 10 ⁻³
Ca ²⁺	0.01	1.16 x 10 ⁻³
SO ₄ ²⁻	0.029	0.225 x 10 ⁻³
Mg ²⁺	0.059	0.237 x 10 ⁻³
Hg ^{2+ b}	4.98 x 10 ⁻⁶	4.98 x 10 ⁻⁶
Hg ^{2+ c}	250 x 10 ⁻⁶	250 x 10 ⁻⁶
pH	6.60	7.91

^a Seawater composition from (De Stefano et al., 1994).

^b Low concentration sorption experiments with amendment (no sediment).

^c High concentration sorption experiments with sediment (with and without amendment).

Table 3. Physical and chemical properties of saltwater marsh sediment^a.

Property ^b	Value
pH _w ^c	3.7 (0.14)
pH _k ^d	3.5 (0.04)
ECEC (cmol kg ⁻¹) ^e	137.77 (16.79)
Al (cmol kg ⁻¹)	6.98 (0.16)
Ca (cmol kg ⁻¹)	8.71 (1.00)
K (cmol kg ⁻¹)	7.78 (1.51)
Mg (cmol kg ⁻¹)	37.24 (1.16)
Na (cmol kg ⁻¹)	77.07 (13.28)
Total C % dws ^f	5.27 (0.05)
Hg (mmol/kg)	0.0057 (2x10 ⁻⁴)
Fe (mmol /kg)	104.58 (3.26)
S (mmol /kg)	29.82 (0.73)
Ca (mmol /kg)	47.11 (0.44)
Na (mmol /kg)	386.95 (22.53)
Al (mmol /kg)	937.41 (9.09)
Mg (mmol /kg)	277.58 (11.96)
<i>Fraction (≤2mm)</i>	
Major phases	Feldspar (Andesine) Quartz
Minor phases	Muscovite Vermiculite

^a Collected from Stege Marsh, San Francisco Bay (Richmond, CA, USA); composite sample collected from two locations.

^b Mean values and standard deviation between parenthesis (n=2); element concentrations referenced to sediment dry weight.

^c pH_w = pH measured in deionized water.

^d pH_k = pH measured in 1M KCl.

^e ECEC = Effective cation exchange capacity (centimoles charge per kg) as the sum of Ca, Mg, Na, K and Al.

^f dws: dry weight sediment.

Table 4. Mercury sorption and sediment extraction results with and without amendment ^a.

Time (days)	Initial conc. (mg L ⁻¹)	pH	Sorbed ^b		Residual ^c		Exchangeable ^d		AAO ^e		Organic ^f	
			(mg kg ⁻¹)	(%)	(mg kg ⁻¹)	(%)	(mg kg ⁻¹)	(%)	(mg kg ⁻¹)	(%)	(mg kg ⁻¹)	(%)
Seawater + Amendment (-sed)												
1	2.06	10.3	50.96	99.0	49.99 ± 14.3	98.1	0.40 ± 0.10	0.8	0.57 ± 2.8	1.1		
7	2.06	11.9	52.77	102.5	51.88 ± 11.00	98.3	0.40 ± 0.71	0.8	0.49 ± 1.4	0.9		
30	2.06	12.1	53.14	103.2	52.85 ± 1.51	99.5	0.15 ± 0.13	0.3	0.14 ± 0.08	0.3		
Seawater + Sediment (+amend)												
1	39.89	9.5	709.04	88.9	706.25 ± 6.55	99.6	0.75 ± 0.35	0.1			2.04 ± 0.83	0.3
7	50.11	8.7	968.34	96.6	967.91 ± 220.9	100.0	0.00 ± 0.00	0.0			0.43 ± 0.40	0.0
30	50.11	8.5	969.31	96.7	968.89 ± 215.8	100.0	0.20 ± 0.01	0.0			0.22 ± 0.67	0.0
Seawater + Sediment (-amend)												
1	39.89	6.3	669.11	83.9	667.87 ± 233.9	99.8	0.252 ± 0.13	0.0			0.98 ± 0.13	0.2
7	50.11	3.4	360.02	35.9	336.10 ± 453.6	93.4	23.19 ± 12.2	6.4			0.73 ± 0.41	0.2
30	50.11	3.5	286.29	28.6	257.21 ± 75.3	89.8	28.19 ± 6.7	9.9			0.89 ± 0.44	0.3
Fresh water + Amendment (-sed)												
1	0.83	11.6	20.66	99.6	19.93 ± 8.2	96.5	0.73 ± 5.76	3.5	0.40 ± 3.3	1.9		
7	0.83	11.8	20.93	100.9	20.81 ± 0.8	99.4	0.12 ± 0.04	0.6	0.24 ± 0.3	1.1		
30	0.83	12.3	21.15	101.9	21.01 ± 21.0	99.3	0.14 ± 0.19	0.7	0.17 ± 1.3	0.8		
Fresh water + Sediment (+amend)												
1	38.35	10.8	684.2	89.2	683.88 ± 1.25	100.0	0.13 ± 0.07	0.0			0.19 ± 0.22	0.0
7	48.80	10.4	927.99	95.1	927.05 ± 330	99.9	0.19 ± 0.12	0.0			0.75 ± 0.19	0.1
30	48.80	10.6	959.44	98.3	958.80 ± 51.0	99.9	0.36 ± 1.4	0.0			0.28 ± 0.32	0.0
Fresh water + Sediment (-amend)												
1	38.35	6.9	843.49	110.0	842.12 ± 55.5	99.8	0.04 ± 0.14	0.0			1.33 ± 1.29	0.2
7	48.80	3.7	959.45	98.3	953.42 ± 297.6	99.4	5.62 ± 2.8	0.6			0.41 ± 0.26	0.0
30	48.80	3.7	966.27	99.0	957.03 ± 343.5	99.0	5.88 ± 6.2	0.6			3.36 ± 0.16	0.3

^a Amendment: Portland cement + FeSO₄; ± is 95% confidence limits of the mean from replicate experiments.

^b Sorbed: Total Hg sorbed determined by the difference between initial and final solution concentrations. Concentration in solids expressed per kg total solid material and as percent (%) Hg sorbed calculated from [(Hg sorbed)/(total Hg added)*100] to show mass balance.

^c Residual: Sorbed - exchangeable - AAO - organic fractions; percent (%) normalized to total Hg sorbed and shown graphically in Fig. 1.

^d Exchangeable: Determined by extraction with 0.1 M MgCl₂.

^e AAO: 0.2 M acidic ammonium oxalate solution.

^f Organic: Determined by extraction with 0.2 M NaOH and CH₃COOH 4% (v/v).

Table 5. Results of Hg EXAFS fits ^a.

Sample	A-B	N	R (Å)	σ^2 (Å ²) ^c	ΔE_0 (Å)	χ^2
Sediment (+amend) seawater 7d	Hg-Cl	2.6	2.51 ^b	0.0043	-6.21	0.33
	Hg-Hg	3.4	4.14 ^b	0.0050		
	Hg-Cl	3.6	4.24 ^b	0.010		
	Hg-Hg	2.0	4.46 ^b	0.0043		
	Hg-Hg	1.9	5.16 ^b	0.0087		
Sediment (+amend) seawater 90d	Hg-Cl	2.8	2.51 ^b	0.0043	-6.54	0.29
	Hg-Hg	3.2	4.14 ^b	0.0050		
	Hg-Cl	4.4	4.24 ^b	0.010		
	Hg-Hg	2.9	4.46 ^b	0.0043		
	Hg-Hg	2.7	5.16 ^b	0.0087		
Sediment (+amend) fresh water 7d	Hg-O	0.7	2.18	0.003	-5.25	0.12
	Hg-Cl	1.7	2.51 ^b	0.0043		
	Hg-Hg	1.1	4.14 ^b	0.0050		
	Hg-Cl	3.1	4.24 ^b	0.010		
	Hg-Hg	1.3	4.46 ^b	0.0043		
	Hg-Hg	0.5	5.16 ^b	0.0087		
Sediment (+amend) fresh water 90 d	Hg-O	0.6	2.18	0.003	-5.95	0.15
	Hg-Cl	1.9	2.51 ^b	0.006		
	Hg-Hg	1.1	4.14 ^b	0.0043		
	Hg-Cl	3.7	4.24 ^b	0.0050		
	Hg-Hg	1.8	4.46 ^b	0.010		
	Hg-Hg	1.7	5.16 ^b	0.0043		

^a A–B is the absorber-backscatterer pair; N is the number of backscattering atoms at distance (R); σ^2 (Debye Waller term) is the absorber–backscattered mean-square relative displacement; ΔE_0 is the energy shift in the least-squares fit; χ^2 is a reduced least-squares goodness-of-fit parameter (= (F-factor)/(# of points - # of variables)); scale factor (S_0^2) fixed at 0.9.

^b Parameter fixed in least-squares fit from analysis in (Serrano et al., 2012).

^c Values for σ^2 determined from fits to reference compounds with known N (Serrano et al., 2012).

FIGURE CAPTIONS

Figure 1. Mercury sorption on and extraction from solid phases and measured solution pH as a function of reaction time in (a) seawater and (b) fresh water experiments for amendment (–sed), and sediment (±amend). Amendment: Portland cement and FeSO₄. Hg sorbed (%) is normalized to total Hg sorbed from solution where Residual = Sorbed – exchangeable – AAO – organic fractions. Inset panel shows exchangeable (0.1 M MgCl₂), AAO (0.2 M acidic ammonium oxalate solution), and organic fractions (0.2 M NaOH and CH₃COOH 4% (v/v)) of sorbed Hg (note differences in y-axis scale). Error bars: 95% confidence limits from replicate experiments; tabulated data in Table 4.

Figure 2. Powder X-ray diffractograms of amendment solid phases without sediment (–sed) reacted with fresh water or seawater at 1, 7, and 30 d.

Figure 3. Powder X-ray diffractograms of sediment with (+amend) and without (–amend) amendment reacted with fresh water at 7 d.

Figure 4. a) Scanning electron microscope image and EDS of amendment (–sed) reacted with seawater at 7 d; b) closeup of particle morphology in (a) characteristic of ettringite; c) backscattered electron microprobe image (top, left), and element fluorescence maps for Hg (top, right), Fe, Ca and S (bottom) in sediment (+amend) and reacted with seawater for 90 d.

Figure 5. Normalized sulfur K-edge XANES spectra of sediment (±amend) reacted with seawater or fresh water at 7 and 90 d compared to amendment (–sed) and reference compound spectra for gypsum (CaSO₄·2H₂O), Fe-ettringite coprecipitated solid (Fe+cpt), Al-ettringite (Ca₆Al₁₂(SO₄)₃(OH)₁₂·26H₂O), cysteine (C₃H₇NO₂S), and pyrite (FeS₂).

Figure 6. Mercury L(III)-edge normalized XANES and first-derivative spectra, and EXAFS and Fourier transforms (FT) of sediment (+amend) reacted in seawater at 7 and 90 d, compared with

Hg(II) coprecipitated with $\text{CaO}+\text{Al}_2(\text{SO}_4)_3$ in synthetic seawater at high pH (Hg_Al_cpt; see Serrano et al., 2012). Solid lines are data; dashed lines are non-linear least-squares fits; fit deconvolutions show scattering from individual absorber-backscatterer pairs (numerical results in Table 5).

Figure 7. Mercury L(III)-edge normalized XANES and first-derivative spectra, and EXAFS and Fourier transforms (FT) of sediment(+amend) reacted in fresh water at 7 and 90 d, compared with Hg(II) adsorbed on goethite (Hg/goethite) (see Serrano et al., 2012). Solid lines are data; dashed lines are non-linear least-squares fits; fit deconvolutions show scattering from individual absorber-backscatterer pairs (numerical results in Table 5).

Figure 8. a) Equilibrium aqueous speciation of Hg as a function of log activity of Cl^- ($\log a_{\text{Cl}^-}$) and pH. Initial (X's) and final (shaded bars) compositions of seawater and fresh water solutions are shown. Final Cl^- was not measured but estimated to be within one order-of-magnitude of the initial concentration; b) equilibrium distribution of solid Ca-bearing phases (shaded) and Al solid and aqueous species (dashed blue line) as a function log activity of Ca^{2+} ($\log a_{\text{Ca}^{2+}}$) and pH; X's indicate final pH and Ca^{2+} concentrations. Diagrams were calculated using the initial composition of sediment and amendment experiments in seawater or fresh water.

a) Seawater

b) Fresh water

Figure 1

Figure 2

Figure 3

a) Amend (-sed), seawater 7d

c) Sed (+ amend), seawater 90d

Scanning electron micrograph (SEM) of sediment after 90 days, showing a dense, irregular structure. A scale bar indicates 20 μm BSE 20 kV. To the right is a corresponding Hg map showing the distribution of mercury, with a color scale from blue (low) to red (high). A scale bar indicates 20 μm Hg La 20 kV.

b) Amend (-sed), seawater 7d

Figure 4

Sulfur XANES

Figure 5

Figure 6

Figure 7

Figure 8

Graphical abstract