



Removal of inorganic mercury and methylmercury from surface waters following coagulation of dissolved organic matter with metal-based salts

Yumiko K. Henneberry^{a,*}, Tamara E.C. Kraus^b, Jacob A. Fleck^b, David P. Krabbenhoft^c, Philip M. Bachand^d, William R. Horwath^a

^a Department of Land, Air, and Water Resources, University of California, Davis, Davis, CA 95616, USA

^b U.S. Geological Survey, Water Science Center, 6000 J Street, Placer Hall, Sacramento, CA, 95616, USA

^c U.S. Geological Survey, Wisconsin District, 8505 Research Wy, Middleton, WI 53562, USA

^d Bachand and Associates, 2023 Regis Drive, Davis, CA 95616, USA

ARTICLE INFO

Article history:

Received 13 April 2010

Received in revised form 14 October 2010

Accepted 15 October 2010

Available online 13 November 2010

Keywords:

Mercury

Dissolved organic matter interactions

Coagulation

Ferric sulfate

Ferric chloride

Polyaluminum chloride

Water quality

ABSTRACT

The presence of inorganic mercury (IHg) and methylmercury (MeHg) in surface waters is a health concern worldwide. This study assessed the ~~removal~~ potential use of metal-based coagulants as a means to remove both dissolved IHg and MeHg from natural waters and provides information regarding the importance of Hg associations with the dissolved organic matter (DOM) fraction and metal hydroxides. Previous research indicated coagulants were not effective at removing Hg from solution; however these studies used high concentrations of Hg and did not reflect naturally occurring concentrations ~~of Hg~~. In this study, water collected from an agricultural drain in the Sacramento–San Joaquin Delta was filtered to isolate the dissolved organic matter (DOM) fraction. The DOM was then treated with a range of coagulant doses to determine the efficacy of removing all forms of Hg from solution. Three industrial-grade coagulants were tested: ferric chloride, ferric sulfate, and polyaluminum chloride. Coagulation removed up to 85% of DOM from solution. In the absence of DOM, all three coagulants released IHg into solution, however in the presence of DOM the coagulants removed up to 97% of IHg and 80% of MeHg. Results suggest that the removal of Hg is mediated by DOM-coagulant interactions. There was a preferential association of IHg with the more aromatic, higher molecular weight fraction of DOM but no such relationship was found for MeHg. This study offers new fundamental insights regarding large-scale removal of Hg at environmentally relevant ~~regarding large-scale removal of Hg at environmentally relevant~~ concentrations.

© 2010 Elsevier B.V. All rights reserved.

1. Introduction

The presence of mercury (Hg), particularly methylmercury (MeHg), in surface waters is a concern for both human and ecological health as it is a neurotoxin and can bioaccumulate in organisms to levels that adversely affect reproduction and behavior. In regions with high organic matter soils such as the Sacramento–San Joaquin Delta (Delta) in California, USA, elevated Hg concentrations in surface water is an ongoing issue concerning regulatory agencies as well as the State's intentions for ecosystem restoration (Conaway et al., 2008). As of 2007, the region has been listed as an impaired water body for Hg (CASWRCB, 2008). Major sources of Hg in the Delta include remnants

from hydraulic mining during the late 19th to mid 20th century, industrial sources as well as natural sources such as atmospheric and coastal deposition (CASWRCB, 2008; Conaway et al., 2008).

Under the current USEPA California Toxics Rule (USEPA, 1999), in freshwater systems, standards for total Hg (THg) concentrations for the protection of human and aquatic health is 249 pmol l^{-1} (50 ng l^{-1}) (USEPA, 1999). Concentrations of unfiltered THg in Delta waters typically range from below detection to 448 pmol l^{-1} (Conaway et al., 2008), which is higher than the recommended USEPA concentration. To date, there is no standard for MeHg concentrations in water. However, the USEPA's recommended human reference dose for MeHg in fish tissue is $1.5 \times 10^3 \text{ pmol g}^{-1}$ (0.3 mg kg^{-1} wet weight), while California mandates a more stringent concentration of $0.14\text{--}1.11 \text{ nmol g}^{-1}$ ($0.03\text{--}0.24 \text{ mg kg}^{-1}$) (Wood et al., 2010). Factors affecting bioaccumulation of MeHg are complex, thus the process of setting standards for surface water concentrations are still underway. In April 2010, the California Central Valley Regional Water Quality Control Board (CVRWQCB) adopted a goal of 0.3 pmol l^{-1} for unfiltered surface water MeHg in their Delta total maximum daily load (TMDL), which is awaiting Federal and State approval (Wood et al., 2010). Research into remediation

Abbreviations: DOC, dissolved organic carbon; DOM, dissolved organic matter; FC, Ferric Chloride; FS, Ferric Sulfate; MeHg, methylmercury; THg, total mercury; PAC, Polyaluminum chloride; PZC, point of zero charge; MeHg, methylmercury; S, spectral slope; S_{red}, reduced sulfur sites; SCD, Streaming current detector; SUVA, specific ultraviolet absorption.

* Corresponding author. 1111 Plant and Environmental Sciences Bldg, Dept. LAWR, University of California, Davis, Davis, CA 95616, USA. Fax: +1 530 752 1552.

E-mail address: yumberry@ucdavis.edu (Y.K. Henneberry).

strategies for Hg concentrations in the Delta, therefore, will provide managers with information pertinent to restoring the health of the region, which is one of the major goals of the California Bay Delta Authority (Conaway et al., 2008).

Although Hg is known to interact with particles in water (Choe et al., 2003), recent studies have shown that Hg in surface waters is strongly associated with dissolved organic matter (DOM) (Lamborg et al., 2003; Schuster et al., 2008). Correlations and some direct evidence suggest Hg is associated with reduced sulfur sites on DOM (Haitzer et al., 2002; Yoon et al., 2005). In systems with high concentrations of DOM such as wetlands and other peat derived water bodies, the DOM fraction plays a significant role in both IHg and MeHg concentrations (Ravichandran et al., 1998; Hill et al., 2009). Efforts to control the particulate fraction of mercury are underway; however, techniques to remove the dissolved fraction are necessary for efficient treatment. Such methods are of particular interest to areas such as California, Wisconsin, Minnesota, the North Eastern United States and Canada, and North Western Europe, where Hg concentrations are directly related to wetlands and have high proportions of Hg in the dissolved phase (St. Louis et al., 1994; Driscoll et al., 1995).

Coincidentally, DOM is also a water quality concern, as it reacts with chlorine during the water purification stage to form carcinogenic byproducts (Rostad et al., 2000). To meet drinking water regulations, drinking water treatment plants commonly remove DOM from water through coagulation with metal-based salts. The salts interact with DOM either ionically or through adsorption mechanisms, resulting in a precipitate termed floc, which is subsequently removed from solution by settling and/or filtration (Edzwald and Tobiason, 1999). Besides its use in drinking water treatment, chemical dosing has been applied broadly in natural lakes, reservoirs, storm waters and wetlands primarily to treat eutrophication. For example, Bachand et al. (Bachand et al., 2000) showed in situ coagulation implemented within storm water wetlands upstream of the Florida Everglades could effectively remove phosphorus and DOM. These techniques have also been shown to remove colloidal solids, algae, heavy metals, and bacteria (Harper et al., 1999).

Over the last 30 years, the drinking water industry has explored various techniques such as coagulation, filtration, and adsorption onto activated carbon, to remove Hg from raw water (Logsdon and Symons, 1973; Patterson, 1975; Sorg, 1979). Of these, Hg removal through the use of metal-based coagulants was examined; however, research concluded coagulants were not an effective way to remove Hg (Patterson, 1975). A majority of these results, however, were published in the mid to late 1970s through early 80s, before clean sampling and low-level analysis methods were developed (Gill and Bruland, 1990). In most instances, to produce detectable amounts of mercury, samples were spiked with Hg salts prior to coagulation creating high concentrations not present under natural conditions (Logsdon and Symons, 1973; Sorg, 1979). These previous studies that spiked water samples with excess Hg may have created Hg concentrations that exceeded the available DOM binding sites, which may explain why their results indicated coagulants were ineffective for Hg removal. Today, techniques allow for the detection of Hg and MeHg at concentrations as low as 0.2 pmol l^{-1} (0.04 ng l^{-1}), allowing the assessment of Hg removal by coagulation at concentrations relevant to environmental conditions.

The primary goal of this study was to assess whether coagulants can effectively remove both dissolved inorganic mercury (IHg) and MeHg under ambient concentrations of both Hg and DOM. Water collected from an agricultural drain in the San Francisco Bay Delta was treated with a range of coagulant doses and analyzed for IHg, MeHg and DOM concentration and composition. Three industrial-grade coagulants were examined: ferric chloride (FC), ferric sulfate (FS), and polyaluminum chloride (PAC). We anticipated that under natural conditions, any Hg associated with the fraction of DOM that reacts with coagulants would also be successfully removed from solution.

Through results of the study, we inferred possible Hg-DOM binding and removal mechanisms.

2. Materials and methods

2.1. Site description

Water samples were collected from the main drainage canal of Twitchell Island (Twitchell), a deeply (up to 10 m) subsided island located on the western portion of the San Francisco Bay Delta. Soils on the island are identified as Rindge mucky silt loam (Taxonomic Class: Euic, thermic Typic Haplosaprists), formed from tule and reed deposition (Tugel, 1993). The Island, formerly a wetland, was drained in the late 1800s for agricultural purposes to this day. Like many drained areas of the Delta, Twitchell's land surface suffers from subsidence resulting largely from oxidative loss of the peat soils; currently land-surface elevation on the island is as much as 6 m below sea level (Miller et al., 2008). To prevent the island from flooding, drainage canals transport water to the southern end of the island where a pumping station drains water into the San Joaquin River. Island drainage water returns have been estimated at $13,000 \text{ km}^3 \text{ yr}^{-1}$ for Twitchell and $530,300 \text{ km}^3 \text{ yr}^{-1}$ for most of the Delta (28). DOC concentrations in the drainage water typically range between 0.5 and 3.3 mmol l^{-1} ($6\text{--}40 \text{ mg l}^{-1}$) (Deverel et al., 2007; Kraus et al., 2008).

2.2. Sample collection

Water was collected on February 25, 2009 from Twitchell's main drain just upstream of the pumping station using trace-metal free methods (Olson and DeWild, 1999). Prior to sample collection, the main pumps were turned on for 10 min to ensure uniformity and mixing of the drain water. Water was collected from the center of the drainage channel at about 0.4 m depth using an Amazon submersible pump (ITT, White plains, NY) and high purity, plasticizer-free 1.27 cm Tygon tubing. The water was filtered during collection by passing it through a $0.2 \mu\text{m}$ in-line membrane filter (General Electric Memtrex, 25.4 cm). Samples were directly transferred into seven acid-washed 13-liter Teflon jerry cans, which were double bagged to prevent subsequent Hg contamination during storage. Water was stored in the dark at 4°C prior to experimental procedures and analyses and experiments were performed within 24 hours of sample collection.

2.3. Coagulation procedure

Three commercially available chemical coagulants were employed: ferric sulfate (FS; Kemiron Companies, Inc. Florida), ferric chloride (FC; Kemiron Companies, Inc. Florida) and polyaluminum chloride (PAC; SternPac 2300, Eaglebrook, Inc. Illinois). The amount of coagulant required to remove the maximum amount of DOC was determined using a streaming current detector (SCD; ECA 2100, Chemtrac Electronics Inc., Norcross, GA), a common method used by water utilities to determine optimal dose of coagulant. The SCD indicates the point of zero charge (PZC) has been reached, the majority of negative ions in solution, including DOC, have been removed (Dentel and Kingery, 1989).

To examine the relationship between coagulant dose and removal of DOC and Hg from solution, coagulant additions corresponding to 0%, 20%, 40%, 60%, 80% and 100% of the PZC dose for each coagulant were applied. Coagulant treatments were applied in triplicate. For each coagulant type and dose, 1 L of Twitchell water was directly poured into Teflon bottles that were rigorously cleaned in hot acid baths at the USGS Mercury Research Lab in Middleton, Wisconsin, and are suitable for low level mercury samples (for details see <http://wi.water.usgs.gov/mercury-lab/>). As the use of a standard jar tester would introduce Hg contamination, mixing occurred on magnetic stir plates using acid-cleaned, teflon stir bars. Coagulants were pipetted

into the solution and mixed at 20 rpm for 3 min and allowed to settle for one hour. After settling, samples were filtered through pre-combusted 0.3 μm ashed quartz fiber filters through using a Hg-clean filter apparatus (Advantec MFS model GF-7547 mm; Advantec MFS, Dublin, CA, USA). Samples for mercury analysis were acidified to 1% by volume by adding 4–6 ml of 6 M HCl and transferred into Hg-clean teflon containers followed by double-bagging to avoid contamination (provided by the USGS Mercury Research Laboratory located in Middleton, Wisconsin, USA).

2.4. DOC concentration and absorbance

Dissolved organic carbon (DOC) was determined by UV-persulfate digestion (Teledyne-Tekmar Phoenix 8000). To eliminate interference due to Fe(III) in absorbance (UV) measurements, 0.1 ml 3% hydroxylamine hydrochloride was added to 1 ml sample and absorbance data recorded until no further change, indicating that all of the Fe(III) had been reduced to non-interfering Fe(II) (Doane and Horwath, 2010). The absorption spectra were measured between 200 and 750 nm on filtered samples at constant temperature (25 °C) with a Cary-300 spectrophotometer using a 1 cm quartz cell and distilled water as a blank. Specific ultraviolet absorbance (SUVA), a proxy for aromaticity, was calculated by dividing absorbance at 254 nm by DOC concentration, and is reported in the units of $\text{L mg C}^{-1} \text{m}^{-1}$ (Weishaar et al., 2003). The spectral slope parameter (S) was calculated using a non-linear fit of an exponential function to the absorption spectrum over the wavelength range of 290–350 nm as described by Twardowski et al. (2004). Spectral slope serves as an indicator of DOM composition; steep spectral slopes (values close to 0.02 nm^{-1}) indicate presence of lower molecular weight compounds or decreasing aromaticity, while shallower spectral slopes (with values closer to 0.01 nm^{-1}) indicate humic-like or higher molecular weight material with higher aromatic content (Blough and del Vecchio, 2002).

2.5. Metal analysis

Total dissolved iron was determined colorimetrically with ferrozine based on the procedures described by Pullin and Cabaniss (2001) and Viollier et al. (2000). Dissolved aluminum was determined colorimetrically based on the procedures described in Pritchard (1967) and Edwards and Cresser (1983).

2.6. Mercury analysis

Total mercury (THg) and MeHg concentrations were determined on one replicate per treatment at the U.S. Geological Survey, Mercury Research Lab using USEPA and USGS approved methods. A brief description of the analytical methods is provided here, but a more complete description is available at the lab's web site (<http://wi.water.usgs.gov/mercury-lab/>). Aqueous THg concentrations on filtered samples were determined using purge and trap, and cold vapor atomic fluorescence spectrometry method (USEPA, 2002), while aqueous MeHg concentrations were analyzed using the aqueous phase methylation, gas chromatographic separation with cold vapor atomic fluorescence detection (DeWild et al., 2002). Detection limits for both THg and MeHg were 0.2 pmol l^{-1} . IHg concentrations were determined as the difference between THg and MeHg concentrations. Readers should note that the IHg species in this particular study include the colloidal fraction, inorganic Hg species that are associated with inorganic functional groups of organic ligands and inorganic ligand–Hg complexes.

When added to deionized (DI) water, the iron coagulants themselves released a substantial amount of IHg into solution (22.9 pmol l^{-1} and 26.9 pmol l^{-1} IHg per mM metal for FC and FS, respectively), while PAC did not release detectable amounts ($<0.2 \text{ pmol mmol}^{-1}$ metal). This added Hg was taken into account when calculating the removal

efficiency of Hg test solutions. Reported removal values are represented on a percent basis, assuming equal amounts of naturally occurring IHg and coagulant derived IHg were removed from solution.

3. Results and discussion

3.1. Initial water quality

The concentration of DOC in the Twitchell drainage water samples receiving no coagulant addition was $2.61 \pm 0.17 \text{ mmol l}^{-1}$ as carbon ($n=3$). This concentration falls within the range of previously reported values for Twitchell Island and other Delta island drainage waters ($0.66\text{--}3.75 \text{ mmol l}^{-1}$) (Deverel et al., 2007; Kraus et al., 2008). IHg and MeHg concentrations in the sample prior to coagulation were 8.97 and 1.20 pmol l^{-1} , respectively. These values are also similar to concentrations observed previously in the Delta region, which range from 0.75 to 7.98 pmol l^{-1} for THg and below detection to 1.32 pmol l^{-1} for MeHg (Foe, 2003; Conaway et al., 2008). Other water quality data such as pH and electrical conductivity are presented in Table 1.

3.2. Dissolved organic carbon removal

DOC removal for the two iron coagulants increased up to 80% of the PZC dose after which no significant change in DOC removal occurred ($p<0.05$), indicating maximum DOC removal was reached. Although the DOC removal curve for PAC approached a similar asymptotic response, there was still an incremental increase in DOC removal between 80% and 100% PZC, suggesting that for this coagulant maximal removal was approached but not obtained at the PZC.

Maximum percent DOC removal for each coagulant was $79.6 \pm 5.6\%$ for FC, $78.3 \pm 5.9\%$ for FS, and $67.9 \pm 6.1\%$ for PAC ($n=3$; Fig. 1). This corresponds to molar ratios of metal added to DOC removed (e.g., Fe/C) of 0.38 for FC, 0.44 for FS and 0.85 for PAC, which is in agreement with other studies (Mourad, 2008; Sieliechi et al., 2008). Overall, on a molar basis, both iron coagulants required less metal to remove a mole of carbon than did the aluminum-based coagulant.

There was a decrease in SUVA and an increase in S of the DOM remaining in solution following coagulant addition (Fig. 2), which indicates preferential removal of aromatic, high molecular weight DOM (Blough and del Vecchio, 2002; Weishaar et al., 2003). Such shifts in bulk DOM composition following coagulation have been

Table 1
Water quality characteristics upon addition of iron and aluminum-based coagulants.

Coagulant	Metal added (mmol l^{-1}) ^a	DOC remaining in solution (mmol l^{-1})	pH	EC ($\mu\text{S cm}^{-1}$)			
No addition	0.00	2.61	0.17 ^b	6.75	0.00	1.27	0.00
Ferric Chloride	0.21	1.99	0.05	6.75	0.07	1.24	0.11
	0.42	1.41	0.17	6.65	0.07	1.21	0.08
	0.63	0.79	0.13	6.25	0.21	1.28	0.10
	0.84	0.38	0.02	4.30	0.14	1.35	0.13
	1.05	0.40	0.02	3.50	0.00	1.43	0.15
Ferric Sulfate	0.20	2.00	0.06	6.90	0.00	1.23	0.11
	0.39	1.44	0.05	6.87	0.06	1.26	0.03
	0.59	0.86	0.06	5.97	0.75	1.28	0.02
	0.79	0.45	0.01	5.07	0.35	1.20	0.12
	0.98	0.43	0.01	3.70	0.00	1.26	0.01
Polyaluminum Chloride	0.32	1.98	0.34	7.23	0.21	1.17	0.09
	0.64	1.31	0.02	7.43	0.25	1.16	0.09
	0.96	0.97	0.03	7.37	0.25	1.19	0.10
	1.28	0.82	0.01	7.37	0.12	1.20	0.05
	1.61	0.72	0.00	7.23	0.35	1.23	0.07

^a For the ferric chloride and ferric sulfate coagulants, total iron was the metal analysed, while for Polyaluminum chloride, total aluminum was measured.

^b Values in italics represent standard deviation of the mean.

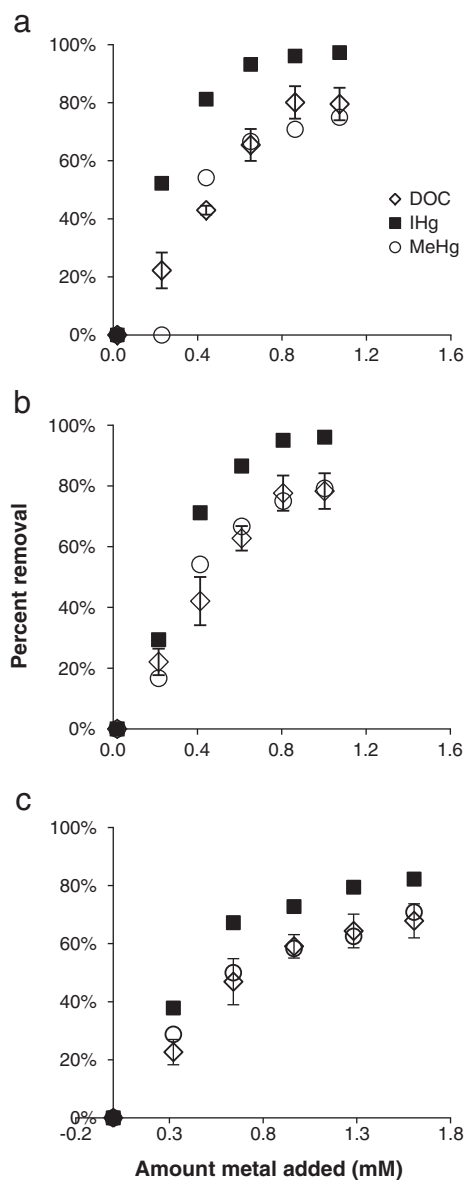


Fig. 1. Percent removal curves for concentrations of DOC, inorganic Hg (IHg), and methylmercury (MeHg) for (a) Ferric Chloride, (b) Ferric Sulfate, and (c) Polyaluminum Chloride. Error bars on DOC represent standard deviation from three replicates.

observed in previous studies (Dennett et al., 1996; Mourad, 2008). Waters with DOM having higher SUVA values have been shown to be more amenable to coagulation compared to waters with lower SUVA values (Edzwald and Tobiason, 1999).

3.3. Inorganic mercury removal

Although the FC and FS themselves released appreciable amounts of dissolved IHg when added to DI water (23.0 and 26.9 pmol IHg mmol⁻¹ Fe, respectively), when added to the drain-water sample containing DOM, dissolved IHg concentrations were lower than initial raw water concentrations, with the exception of FS at 20% of the PZC dose (Table 2). This indicates the formation of floc led to the removal of both naturally occurring IHg and that contributed by the coagulant. Highest percent removal of IHg in solution for each coagulant was 97, 96, and 84% for FC, FS, and PAC, respectively (Fig. 1). All coagulants showed a higher removal rate for

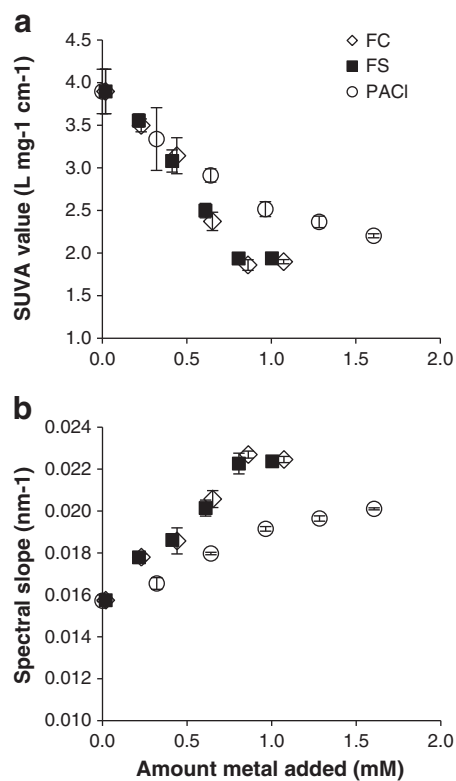


Fig. 2. Changes in (a) SUVA and (b) Spectral Slope with increasing coagulant dose for Ferric Chloride (FC), Ferric Sulfate (FS), and Polyaluminum Chloride (PACI) coagulants. Error bars represent standard deviations from three replicates.

IHg than for DOC. On a molar basis, the iron coagulants removed more IHg from solution compared to PAC.

Studies that have examined IHg solubility and complexation with minerals, including iron hydroxides, pyrite, and silica, have found various factors including pH and presence of anions such as Cl⁻ and OH⁻ greatly influence IHg adsorption in the absence of organic matter (Schuster, 1991; Gabriel and Williamson, 2004). Barrow and Cox (1992) and Walcarius et al. (2000) found that in the absence of organic matter, Hg adsorption to mineral surfaces increased with an increase in pH and decreased in the presence of Cl⁻. In addition, stability constants of Hg (II) complexes with chloride are relatively high with log K1 of 7.3 and log K2 of 14 (Table 3). These findings support our data, which show that when FC was added to DI, free IHg was released into solution. However, because FS released more IHg than FC and it is well understood that sulfate-Hg complexes have a much lower stability constant (log K = 1.3, Table 3) than chloride-Hg complexes, the presence of chloride ions may or may not explain Hg release from FC.

Studies have also shown pH plays a significant role in IHg solubility by affecting the concentration of OH⁻ groups, which in turn affect Hg speciation through hydrolysis (Schuster, 1991; Gabriel and Williamson, 2004). Hydrolyzed mercury compounds such as Hg(OH)₃ are more strongly complexed to surface of minerals compared to the Hg²⁺ ion, which predominate at a lower pH (Schuster, 1991; Walcarius et al., 2000). Both Walcarius et al. (2000) and Bower et al. (2008) found Hg(II) hydrolysis through increased pH was required for adsorption to occur on mineral surfaces. In this study, the solution pH of coagulants in DI was 2.9, 3.0, and 4.9 for FC, FS, and PAC, respectively. As hydrolysis of Hg occurs between a pH of 2 to 6 (Schuster, 1991), it is possible the predominant Hg species in these samples was Hg²⁺ and Hg²⁺ complexes, suggesting pH may be a predominant factor influencing IHg release from coagulants added to DI.

Table 2
Removal amounts for IHg and MeHg and ratios of DOC removed to Hg removed.

Coagulant	Metal added (mmol l ⁻¹)	IHg added by coagulant (pmol l ⁻¹)	Total IHg remaining in solution ^a (pmol l ⁻¹)	Ambient IHg removed (pmol l ⁻¹)	Ambient IHg removed: DOC removed (pmol:mmol)	MeHg remaining in solution (pmol l ⁻¹)	MeHg removed (pmol l ⁻¹)	MeHg removed: DOC removed (pmol:mmol)
No addition	0.00	0.00	8.97	0.00	0.00	1.20	0.00	0.00
Ferric Chloride	0.21	4.82	6.58	4.89	6.46	1.20	0.00	0.00
	0.42	9.64	3.49	7.45	6.29	0.55	0.65	0.55
	0.63	14.46	1.60	8.55	4.30	0.40	0.80	0.40
	0.84	19.28	1.10	8.82	3.71	0.35	0.85	0.36
	1.05	24.10	0.90	8.92	3.77	0.30	0.90	0.38
Ferric Sulfate	0.20	5.28	10.07	2.69	3.71	1.00	0.20	0.28
	0.39	10.56	5.63	6.49	4.64	0.55	0.65	0.46
	0.59	15.84	3.34	7.91	4.28	0.40	0.80	0.43
	0.79	21.12	1.50	8.69	3.73	0.30	0.90	0.39
	0.98	26.40	1.40	8.77	3.74	0.25	0.95	0.40
Polyaluminum Chloride	0.32	0.00	5.58	3.39	3.37	0.85	0.34	0.34
	0.64	0.00	2.94	6.03	4.02	0.60	0.60	0.40
	0.96	0.00	2.44	6.53	3.63	0.50	0.70	0.39
	1.28	0.00	1.84	7.13	3.64	0.45	0.75	0.38
	1.61	0.00	1.60	7.38	3.57	0.35	0.85	0.41

^a Includes both IHg released by coagulant and IHg present in the drainwater.

Although the final solution pH at the maximum coagulant dose was below 4 for both iron coagulants, a continuous decrease in dissolved IHg with increasing coagulant dose was observed. This phenomenon may be explained by the presence of DOM, which has been shown to strongly complex IHg, and thereby strongly affect the resulting Hg concentrations in solution (Ravichandran, 2004; Schuster et al., 2008). Experimental log K values have shown organic carbon–Hg constants to be substantially higher than those for Cl–Hg and OH–Hg complexes and other competing ligands that complex with organic matter (Tables 3 and 4). Of the various organic functional groups, those containing reduced sulfur (e.g. thiol and cystine groups) have been found to govern this strong association between Hg and DOC (Schuster, 1991; Skyllberg et al., 2006). Using calculations from Ravichandran (2004), which assumes that total sulfur sites make up 1% of DOM (by weight) and that reduced sulfur sites (S_{red}) make up 20% of these sulfur sites (Xia et al., 1998), a DOC concentration of 2.61 mmol l⁻¹ (the concentration of Twitchell water sampled for this study) would provide about 4×10^{-3} mmol l⁻¹ of S_{red} for Hg complexation. Assuming an IHg concentration of 9 pmol l⁻¹, which takes into account both the IHg contributed by the highest doses of iron coagulants and naturally occurring IHg, this is an estimated 10^6

excess of reduced-sulfur containing DOM binding sites that IHg could potentially complex with.

The ratio of DOM to Hg has also been found to influence Hg–DOM interactions. Haitzer et al. (2002) found stability constants will vary depending on the Hg to DOC ratio due to the availability of thiol bonds. They found at Hg to DOM ratios less than 120 nmol Hg mmol⁻¹ DOC, Hg was strongly bound to available thiol groups on the DOM. At higher Hg to DOM ratios the excess Hg bound to carboxyl groups with lower bond strength, resulting in lower log K values. The ratio of Hg to DOC in Twitchell water is 13.1 pmol Hg mmol⁻¹ DOC, which is far below the 120 nmol of Hg mmol⁻¹ DOC S_{red} saturation point reported by Haitzer et al. (2002). This indicates a majority if not all the bonds between Hg and DOC in this system are strong bonds between reduced sulfur groups and Hg. The much lower average THg removal efficiencies of 35% reported by some authors in earlier studies (Logsdon and Symons, 1973; Sorg, 1979) may be attributed to the fact that they spiked their system with unnaturally high Hg concentrations (10–50,000 nmol l⁻¹), which most likely saturated the available S_{red} sites. Although DOC concentrations were not reported in these studies, if we consider a DOC concentration of 5 mg l⁻¹ (0.416 mmol DOC l⁻¹), this would result in an Hg to DOC

Table 3
Stability constants of various ligands with Hg.

Ligand	pH	Ionic strength (M)	T (°C)	log K ₁ ^{a1}	log K ₂ ^b	Reference
Cl	n/a ^c	0.5	25	7.3	14	Ravichandran (2004)
SO ₄	n/a	0.5	25	1.3	n/a	Ravichandran (2004)
OH	n/a	0.5	25	10.6	21.8	Ravichandran (2004)
EDTA	n/a	0.5	25	20.1	n/a	Ravichandran (2004)
Cysteine	n/a	0.1	25	14.4	n/a	Ravichandran (2004)
Thisalicylic acid	n/a	0.1	25	25.7	n/a	Ravichandran (2004)
Fawn Lake Humic Acid	6.5	0.001	n/a	12.11	12.7	Hintelmann et al. (1995)
Estuarine and Coastal DOC	7–9	0.1	n/a	20–28	n/a	Han and Gill (2005)

^a K₁ is derived from the reaction between Hg and ligand (L) of the HgL type: [Hg²⁺] + [Ln⁻] ↔ [HgL]ⁿ⁺².

^b K₂ is derived from the secondary reaction of HgL₂: [Hg²⁺] + [2Ln⁻] ↔ [HgL₂]ⁿ⁺².

^c n/a indicates unavailable data.

Table 4

Comparison of various stability constants of metal complexes with organic matter. Abbreviation of elements: Cu = copper, Zn = zinc, Mn = manganese, Cd = cadmium, Hg = mercury.

Complex	pH	Ionic Strength (M)	T (°C)	log K	Reference
Cu–COOH	4.5	0.01	n/a	4.5	Karlsson et al. (2008)
Zn(II)-coastal sedimentary fulvic acids	8.0	0.01	20	4.86–6.36	Hirata (1981)
Mn(II)-coastal sedimentary fulvic acids	8.0	0.01	20	3.8–5.30	Hirata (1981)
Cu–Bog water	n/a ^a	0.1	25	3.63–4.10	Lövgren and Sjöberg (1989)
Cd–Bog water	n/a	0.1	25	2.8–10.3	Lövgren and Sjöberg (1989)
Hg–Bog water	n/a	0.1	25	4.4–10.37	Lövgren and Sjöberg (1989)
Hg–Organic matter isolates from Florida Everglades	6.0	0.04	n/a	10.6–11.8	Benoit et al. (2001)

^a n/a indicates unavailable data.

ratio of 0.024–0.120 mmol Hg mmol⁻¹ DOC, the upper limit far exceeding the strong binding limit reported by Haitzer et al. (2002).

The similarities between the curvilinear shape of the DOC and Hg removal curves support the hypothesis that Hg is associated with DOM (Fig. 1). Percentage removal rates of IHg exceeded that of DOC for all three coagulants (Fig. 1). In addition, the ratios of IHg to DOC removed are generally higher at lower coagulant doses (Table 2), suggesting that the fraction of the DOM pool which is removed from solution at lower coagulant doses has a higher affinity for IHg than the fraction removed at higher doses. These factors, along with the coincident removal of both IHg and the fraction of DOM with higher SUVA and S values from solution, suggests there is preferential association of IHg with more aromatic, larger molecular weight DOM. In support of the findings above, studies have found a relationship between the presence of aromatic DOM and dissolved Hg (Aiken et al., 2003; Dittman et al., 2009).

3.4. Methylmercury removal

Coagulants did not release detectable amounts of MeHg into solution (<0.19 pmol l⁻¹); hence, the experimental results from all three coagulants reflect interactions of naturally occurring MeHg with the coagulant. Coagulant additions decreased MeHg concentrations up to 77, 81, and 73% for FC, FS, and PAC, respectively (Fig. 1). The lower removal rate of MeHg compared to IHg is expected and consistent showing lower distribution coefficients (K_d's) for MeHg metal interactions (Pasquale et al., 2009). At all coagulant doses, the percent removal of MeHg was very similar to that of DOC.

In general, as with IHg, factors such as pH and presence of hydroxides have been found to govern MeHg solubility and its association with DOM (Schuster et al., 2008). Detailed studies that investigate the nature of DOM and its complexation with MeHg however, are lacking. Studies have found sorption of MeHg to humic acids decrease with a decrease in pH (Amirbahman et al., 2002). In addition, like IHg, sorption of dissolved MeHg is tightly correlated with S_{red} on DOM (Skylberg et al., 2006). There are direct observations, however, that only particular fractions of sulfur bind to MeHg (Yoon et al., 2005). Yoon et al. (2005) found MeHg to first bind to thiol groups then to carboxylic functional groups of soil humic acids rather than other reduced sulfur groups. Although this study did not look at the hydrophobic fraction, it is noteworthy that authors have reported that MeHg can bind to mineral surfaces including goethite, and have even detected adsorption beyond the saturation point of these minerals, suggesting potential hydrophobic interactions with MeHg (Desauziers et al., 1997).

Our results showed percent removal of MeHg was very similar to DOC for all rates of coagulant addition, suggesting that MeHg is not preferentially associated with the fraction of DOM with high SUVA and low S values. This is in contrast to IHg, which showed higher removal rates than DOC in these fractions. Similar ratios of DOC:MeHg removed at all coagulant doses also suggests MeHg is not associated with the specific fraction of the DOC pool that is removed by coagulation.

4. Implications and future work

Results suggest that coagulation can effectively remove environmentally relevant concentrations of dissolved Hg from solution in the presence of DOM, which indicate coagulants may be a viable method for the removal of both dissolved IHg and MeHg from solution. As Delta waters frequently exceed the EPA toxics limit of 249 pmol l⁻¹ for unfiltered THg (Conaway et al., 2008), techniques to control the concentrations of IHg and MeHg would benefit water treatment systems. However, before coagulation can be used as a technique to ameliorate aqueous Hg concentrations in natural systems, additional research is needed to ensure the effectiveness and feasibility of this approach. This is particularly the case if the floc is to be left in the

environment, such as in constructed wetlands used as floc settling basins. More research will be needed to determine whether the floc can be safely retained on-site or whether it must be removed and disposed of off-site.

Further study to determine the character of DOM that is removed by coagulation and its association with both IHg and MeHg is also needed. This type of research should address the interaction between the different Hg species and the fraction of DOM that is not amenable to coagulation, as this pool of Hg may represent the potentially bioavailable fraction susceptible to methylation and subsequent bioaccumulation in organisms.

In addition, potential biogeochemical effects resulting from coagulation should be considered. For example, changes in solution pH or release of various ions into solution (e.g. iron, aluminum, chloride, and sulfate) could influence the surrounding environment and ecosystems downstream, as well as floc stability. There are also ecotoxicity effects from the presence of the metal hydroxide–Hg complex itself, as it may stimulate biota such as iron and sulfate reducing microbes, enhancing Hg methylation. Understanding these processes will determine whether use of coagulants to remove Hg can be used to reduce surface water Hg concentrations, or even be used to prevent release of Hg from sediments.

Acknowledgments

This work was funded by the California Department of Water Resource (Agreement #v4600003886). We would like to thank John DeWild, Tad Doane, William Kerlin, and Yan Liang for their assistance with laboratory analyses. In addition, we would like to express our appreciation to Kemiron, Inc, particularly Fred Sims, for providing us with coagulant samples and correspondence.

References

- Aiken G, Haitzer M, Ryan JN, Nagy K. Interactions between dissolved organic matter and mercury in the Florida Everglades. *J Phys IV* 2003;107:29–32.
- Amirbahman A, Reid AL, Haines TA, Kahl JS, Arnold C. Association of methylmercury with dissolved humic acids. *Environ Sci Technol* 2002;36:690–5.
- Bachand PAM, Richardson CJ, Vaithyanathan P. Phase II Low Intensity Chemical Dosing (LCD): Development of Management Practices; 2000. December.
- Barrow NJ, Cox VC. The effects of pH and chloride concentration on mercury sorption. 2. By a soil. *J Soil Sci* 1992;43:305–12.
- Benoit JM, Mason RP, Gilmour CC, Aiken GR. Constants for mercury binding by dissolved organic matter isolates from the Florida Everglades. *Geochim Cosmochim Acta* 2001;65:4445–51.
- Blough N, del Vecchio R. Chromophoric DOM in the coastal environment. In: Hansell D, editor. Carlson, editors. *Biogeochemistry of marine dissolved organic matter*. San Diego, CA: Academic; 2002. p. 509–46.
- Bower J, Savage KS, Weinman B, Barnett MO, Hamilton WP, Harper WF. Immobilization of mercury by pyrite (FeS₂). *Environ Pollut* 2008;156:504–14.
- CASWRCB. Section 303(d): List of Water Quality Limited Segments. Environmental Protection Agency; 2008.
- Choe K-Y, Gill GA, Lehman R. Distribution of Particulate, Colloidal, and Dissolved Mercury in San Francisco Bay Estuary. 1. Total Mercury. *Limnol Oceanogr* 2003;48:1535–46.
- Conaway CH, Black FJ, Grieb TM, Roy S, Flegal AR. Mercury in the San Francisco estuary. *Rev Environ Contam Toxicol* 2008;vol. 194:29–54.
- Dennett KE, Amirbahman A, Moran TF, Gould JP. Coagulation: Its effect on organic matter. *J Am Water Works Assn* 1996;88:129–42.
- Dentel SK, Kingery KM. Using Streaming Current Detectors in Water Treatment. *J Am Water Works Assn* 1989;81:85–94.
- Desauziers V, Castre N, LeCloirec P. Sorption of methylmercury by clays and mineral oxides. *Environ Technol* 1997;18:1009–18.
- Deverel SJ, Leighton DA, Finlay MA. Processes affecting agricultural drainwater quality and organic carbon loads in California's Sacramento–San Joaquin Delta. *San Francisco Estuary and Watershed Science*, 5 ; 2007. Article 2.
- DeWild JF, Olson ML, Olun S. Determination of methylmercury by aqueous phase ethylation, followed by gas chromatographic separation with cold vapor atomic fluorescence detection. Open File Report. United States Geological Survey; 2002. 01–445.
- Dittman JA, Shanley JB, Driscoll CT, Aiken GR, Chalmers AT, Towse JE. Ultraviolet absorbance as a proxy for total dissolved mercury in streams. *Environ Pollut* 2009;157:1953–6.
- Doane TA, Horwath WR. Eliminating interference from iron (III) for ultraviolet absorbance measurements of dissolved organic matter. *Chemosphere* 2010;78:1409–15.

- Driscoll CT, Blette V, Yan C, Schofield CL, Munson R, Holsapple J. The role of dissolved organic carbon in the chemistry and bioavailability of mercury in remote Adirondack lakes. *Water Air Soil Pollut* 1995;80:499–508.
- Edwards AC, Cresser MS. An improved, automated xylenol orange method for the colorimetric determination of aluminum. *Talanta* 1983;30:702–4.
- Edzwald JK, Tobiason JE. Enhanced coagulation: US requirements and a broader view. *Water Sci Technol* 1999;40:63–70.
- Foe C. Mercury mass balance for the freshwater Sacramento–San Joaquin Bay-Delta Estuary (Task 1A). Sacramento, CA: Central Valley Regional Water Quality Control Board; 2003. September.
- Gabriel MC, Williamson DG. Principal biogeochemical factors affecting the speciation and transport of mercury through the terrestrial environment. *Environ Geochem Health* 2004;26:421–34.
- Gill GA, Bruland KW. Mercury speciation in surface fresh-water systems in California and other areas. *Environ Sci Technol* 1990;24:1392–400.
- Haitzer M, Aiken GR, Ryan JN. Binding of mercury(II) to dissolved organic matter: the role of the mercury-to-DOM concentration ratio. *Environ Sci Technol* 2002;36:3564–70.
- Han SH, Gill GA. Determination of mercury complexation in coastal and estuarine waters using competitive ligand exchange method. *Environ Sci Technol* 2005;39:6607–15.
- Harper HH, Herr JL, Livingston EH. Chapter 9: Alum Treatment of Stormwater: The First Ten Years. In: James W, editor. *New Applications in Modeling Urban Water Systems*. Canada: CHI Guelph; 1999.
- Hill JR, O'Driscoll NJ, Lean DRS. Size distribution of methylmercury associated with particulate and dissolved organic matter in freshwaters. *Sci Total Environ* 2009;408:408–14.
- Hintelmann H, Welbourn PM, Evans RD. Binding of methylmercury compounds by humic and fulvic-acids. *Water Air Soil Pollut* 1995;80:1031–4.
- Hirata S. Stability constants for the complexes of transition-metal ions with fulvic and humic acids in sediments measured by gel filtration. *Talanta* 1981;28:809–15.
- Karlssoon T, Elgh-Dalgren K, Skyllberg U. Modeling copper(II) complexation in a peat soil based on spectroscopic structural information. *Soil Sci Soc Am J* 2008;72:1286–91.
- Kraus TEC, Bergamaschi BA, Hernes PJ, Spencer RGM, Stepanauskas R, Kendall C, et al. Assessing the contribution of wetlands and subsided islands to dissolved organic matter and disinfection byproduct precursors in the Sacramento–San Joaquin River Delta: a geochemical approach. *Org Geochem* 2008;39:1302–18.
- Lamborg CH, Tseng CM, Fitzgerald WF, Balcom PH, Hammerschmidt CR. Determination of the mercury complexation characteristics of dissolved organic matter in natural waters with “reducible Hg” titrations. *Environ Sci Technol* 2003;37:3316–22.
- Logsdon GS, Symons JM. Mercury removal by conventional water-treatment techniques. *J Am Water Work Assoc* 1973;65:554–62.
- Lövgren L, Sjöberg S. Equilibrium approaches to natural water systems-7. Complexation reactions of copper(II), cadmium(II) and mercury(II) with dissolved organic matter in a concentrated bog-water. *Water Res* 1989;23:327–32.
- Miller RL, Fram MS, Fujii R, Wheeler G. Subsidence reversal in a re-established wetland in the Sacramento–San Joaquin Delta, California, USA. *San Francisco Estuary and Watershed Science*, 6. ; 2008. Article 1.
- Mourad DM. Investigating the use of coagulation seasonally to reduce DOC and DBP precursor loads from subsided islands in the Sacramento–San Joaquin Delta, CA. *Soils and Biogeochemistry*. Davis, CA: University of California, Davis; 2008.
- Olson ML, DeWild JF. Techniques for the collection and species specific analysis of low levels of mercury in water, sediment, and biota. *United States Geological Survey*; 1999. 99-4018-B.
- Pasquale MMD, Lutz MA, Brigham ME, Krabbenhoft DP, Aiken GR, Orem WH, et al. Mercury cycling in stream ecosystems. 2. Benthic methylmercury production and bed sediment–pore water partitioning. *Environ Sci Technol* 2009;43:2726–32.
- Patterson JW. *Wastewater Treatment Technology*. Treatment technology for mercury. Ann Arbor, MI: Ann Arbor Science; 1975. p. 147–60.
- Pritchard DT. Spectrophotometric determination of aluminum in soil extracts with xylenol orange. *Analyst* 1967;92:103–6.
- Pullin MJ, Cabaniss SE. Colorimetric flow-injection analysis of dissolved iron in high DOC waters. *Water Res* 2001;35:363–72.
- Ravichandran M. Interactions between mercury and dissolved organic matter – a review. *Chemosphere* 2004;55:319–31.
- Ravichandran M, Aiken GR, Reddy MM, Ryan JN. Enhanced dissolution of cinnabar (mercuric sulfide) by dissolved organic matter isolated from the Florida Everglades. *Environ Sci Technol* 1998;32:3305–11.
- Rostad CE, Martin BS, Barber LB, Leenheer JA, Daniel SR. Effect of a constructed wetland on disinfection byproducts: removal processes and production of precursors. *Environ Sci Technol* 2000;34:2703–10.
- Schuster E. The Behavior of Mercury in the Soil with Special Emphasis on Complexation and Adsorption Processes – a Review of the Literature. *Water Air Soil Pollut* 1991;56:667–80.
- Schuster PF, Shanley JB, Marvin-Dipasquale M, Reddy MM, Aiken GR, Roth DA, et al. Mercury and organic carbon dynamics during runoff episodes from a northeastern USA watershed. *Water Air Soil Pollut* 2008;187:89–108.
- Sieliechi JM, Lartiges BS, Kayem GJ, Hupont S, Frochot C, Thieme J, et al. Changes in humic acid conformation during coagulation with ferric chloride: implications for drinking water treatment. *Water Res* 2008;42:2111–23.
- Skyllberg U, Bloom PR, Qian J, Lin CM, Bleam WF. Complexation of mercury(II) in soil organic matter: EXAFS evidence for linear two-coordination with reduced sulfur groups. *Environ Sci Technol* 2006;40:4174–80.
- Sorg TJ. Treatment technology to meet the interim primary drinking water regulations for organics 4. *J Am Water Works Assn* 1979;71:454–66.
- St. Louis VL, Rudd JWM, Kelly CA, Beaty KG, Bloom NS, Flett RJ. Importance of wetlands as sources of methylmercury to boreal forest ecosystems. *Can J Fish Aquat Sci* 1994;51:1065–76.
- Tugel AJ. *Soil survey of Sacramento County; California*. Washington DC: USDA Soil Conservation Service; 1993.
- Twardowski MS, Boss E, Sullivan JM, Donaghay PL. Modeling the spectral shape of absorption by chromophoric dissolved organic matter. *Mar Chem* 2004;89:69–88.
- USEPA. National recommended water quality criteria—correction. Washington, D.C.: US Environmental Protection Agency, Office of Water; 1999. April. 822-Z-99-001.
- USEPA. Mercury in water by oxidation, purge and trap, and cold vapor atomic fluorescence spectrometry. Environmental Protection Agency, Office of Water; 2002. August.
- Viollier E, Inglett PW, Hunter K, Roychoudhury AN, Van Cappellen P. The ferrozine method revisited: Fe(II)/Fe(III) determination in natural waters. *Appl Geochem* 2000;15:785–90.
- Walcarius A, Devoy J, Bessiere J. Silica-modified electrode for the selective detection of mercury. *J Solid State Electrochem* 2000;4:330–6.
- Weishaar JL, Aiken GR, Bergamaschi BA, Fram MS, Fujii R, Mopper K. Evaluation of specific ultraviolet absorbance as an indicator of the chemical composition and reactivity of dissolved organic carbon. *Environ Sci Technol* 2003;37:4702–8.
- Wood M, Cooke J, Morris P, Louis S. Amendments to the water quality control plan for the Sacramento and San Joaquin river basins for the control of methylmercury and total mercury in the Sacramento–San Joaquin Delta estuary. Rancho Cordova, CA; 2010.
- Xia K, Weesner F, Bleam WF, Bloom PR, Skyllberg UL, Helmke PA. XANES studies of oxidation states of sulfur in aquatic and soil humic substances. *Soil Sci Soc Am J* 1998;62:1240–6.
- Yoon SJ, Diener LM, Bloom PR, Nater EA, Bleam WF. X-ray absorption studies of CH₃Hg⁺-binding sites in humic substances. *Geochim Cosmochim Acta* 2005;69:1111–21.