

# Investigating the Temporal Effects of Metal-Based Coagulants to Remove Mercury from Solution in the Presence of Dissolved Organic Matter

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**Abstract** The presence of mercury (Hg), particularly methylmercury (MeHg), is a concern for both human and ecological health as MeHg is a neurotoxin and can bioaccumulate to lethal levels in upper trophic level organisms. Recent research has demonstrated that coagulation with metal-based salts can effectively remove both inorganic mercury (IHg) and MeHg from solution through association with dissolved organic matter (DOM) and subsequent flocculation and precipitation. In this study, we sought to further examine interactions between Hg and DOM and the resulting organo-metallic precipitate (floc) to assess if (1) newly added IHg could be removed to the same extent as ambient IHg or whether the association between IHg and DOM requires time, and (2) once formed, if the floc has the capacity to remove additional Hg from solution. Agricultural drainage

water samples containing ambient concentrations of both DOM and IHg were spiked with a traceable amount of isotopically enriched IHg and dosed with ferric sulfate after 0, 1, 5, and 30 days. Both ambient and newly added IHg were removed within hours, with 69–79 % removed. To a separate sample set, isotopically enriched IHg was added to solution after floc had formed. Under those conditions, 81–95 % of newly added Hg was removed even at Hg concentrations 1000-fold higher than ambient levels. Results of this study indicate coagulation with ferric sulfate effectively removes both ambient and newly added IHg entering a system and suggests rapid association between IHg and DOM. This work also provides new information regarding the ability of floc to remove additional Hg from solution even after it has formed.

**Keywords** Coagulation · Methylmercury · Ferric sulfate · Dissolved organic matter · Flocculation

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## Introduction

Although organic matter and mercury (Hg) exist naturally in water, both constituents have become identified as human health concerns. Mercury, particularly methylmercury (MeHg), in aquatic systems can bioaccumulate to lethal levels in upper trophic level organisms (Mergler et al. 2007; Crump and Trudeau 2009). Organic material—particularly dissolved organic matter (DOM)—is also a concern in potable water supplies, as a fraction reacts during the disinfection process to form halogenated, carcinogenic by-products, such as trihalomethanes and haloacetic acids (Richardson et al. 2007). In the past decade, there has been a growing recognition of the strong association between dissolved Hg and DOM (Ravichandran 2004; Aiken et al. 2003; Haitzer et al. 2002),

which suggests that approaches targeting DOM removal may concomitantly remove Hg.

Rivers and wetlands are a natural source of DOM; however, agricultural drainage and re-flooding of organic rich soils, such as peat, export water with high concentrations of DOM, which is a concern for drinking water quality (Aitkenhead-Peterson et al. 2002; Chow et al. 2006; O'Geen et al. 2010). Elevated Hg concentrations in the Sacramento-San Joaquin Delta (Delta) in California, USA, is an ongoing issue concerning regulatory agencies as well as the State's intentions for ecosystem restoration (Conaway et al. 2008). In 2011, regulations for total maximum daily loads (TMDL) of both Hg and MeHg were put in place by the Central Valley Regional Water Quality Control Board in California (CVRWQCB 2010). This TMDL necessitates the development of effective management strategies that will reduce MeHg export from both point and non-point sources, including agricultural lands and wetlands. The in situ application of metal-based coagulants has been identified as a potential management practice to remove Hg prior to discharge; however, one that requires further investigation (McCord and Heim 2015).

In a prior study Henneberry et al. (2011) found that coagulation with metal-based salts, a method conventionally used to remove particulates and dissolved impurities from drinking water, not only effectively removed DOM, but also removed total Hg at naturally occurring levels (9.0 and 1.2 pmol L<sup>-1</sup> for IHg and MeHg, respectively). Up to 97 % of dissolved inorganic Hg (IHg) and 80 % of methylmercury (MeHg) were removed from agricultural drainage waters using both iron (Fe)- and aluminum (Al)-based coagulants at levels commonly applied in the water treatment industry. The authors concluded the particularly effective removal of dissolved IHg was most likely due to its association with the higher molecular weight, aromatic fraction of DOM, which has been shown to be more amenable to coagulation compared to other DOM fractions (Dempsey et al. 1984; Henneberry et al. 2011). The aromatic fraction of DOM, in turn, contains a higher concentration of reduced sulfur sites, which have been shown to be largely responsible for Hg-DOM interactions (Aiken et al. 2003; Ravichandran 2004).

Although successful total Hg and DOM removal was demonstrated in the prior study, only native Hg was used. Removal of non-native, newly added IHg is particularly important in light of studies that suggest new sources of IHg entering the water column from terrestrial and atmospheric sources are more prone to methylation and thus impact bioaccumulation (Hintelmann et al. 2000; Harris et al. 2007; Jonsson et al. 2014). Because past research has suggested newly added IHg does not instantaneously reach equilibrium with the naturally occurring organic matter in water (Benoit et al. 2001; Black et al. 2007; Miller et al. 2009), an important question is whether coagulants will

also remove new IHg entering the system in the form of atmospheric deposition and external runoff. This is particularly important in light of studies that suggest new sources of Hg entering the water column from terrestrial and atmospheric sources are more prone to methylation and thus impact bioaccumulation (Hintelmann et al. 2000; Harris et al. 2007; Jonsson et al. 2014).

Prior studies observed equilibration times between DOM and newly added IHg ranging from 4 h to over 3 days (Benoit et al. 2001; Black et al. 2007; Miller et al. 2009). Although most studies found IHg and DOM to reach equilibrium within 24 h, these only examined bulk DOM-IHg dynamics. In contrast, studies that assessed Hg associations with different fractions of DOM observed longer equilibration times. For example, Babiarez et al. (2003) found that even after 3 days, newly added isotopic IHg was not uniformly distributed among the various size fractions of DOM, while the colloidal phase (<0.4 μm–10 kDa) played an important role in IHg-DOM fractionation.

In this study, we sought to further examine the interaction between IHg and DOM and the fate of the resulting organo-metallic precipitate (floc). Our hypotheses were that, (1) newly added IHg could be removed by flocculation to the same extent as ambient IHg; however, (2) the association between newly added IHg and DOM would not be instantaneous and thus percent removal of IHg would increase over time, and (3) once formed, floc has the capacity to remove additional IHg from solution. In the first study, isotopically enriched IHg (<sup>200</sup>Hg) was added to agricultural drainage water to represent "new" IHg sources. These samples were then coagulated with ferric sulfate (FS) at various times over 30 days to observe potential changes in amended IHg removal. In the second study, isotopically enriched IHg was added to solution after the floc had formed and sampled at similar time periods to determine whether newly added IHg could become associated with the organo-metal precipitate, and whether there was a temporal component to this interaction.

## Materials and Methods

Two studies were conducted simultaneously to allow for overlap of some sample analyses such as dissolved organic carbon (DOC) and IHg concentrations in initial water samples, DI controls, and coagulants. The first study examined the temporal association of IHg with DOM over a 30-day period by assessing the incorporation of newly added, isotopically labeled IHg into the DOM pool removed from solution through coagulation. The second study observed the capacity of the Fe-DOM precipitate to adsorb additional IHg after floc formation, also over a 30-day incubation period. The range of sampling periods was chosen to capture the variation in equilibrium times

noted from other studies (Benoit et al. 2001; Black et al. 2007; Miller et al. 2009) and additional time to document whether any further changes in dissolved IHg concentrations occurred.

### Sample Collection

Water was collected from an agricultural drain receiving rice field runoff on September 15, 2010, from Twitchell Island (38°06'40"N, -121°39'38"W) receiving rice field runoff. Twitchell Island is located on the western portion of the San Francisco Bay Delta in California (USA). Soils on the island are identified as Ringe mucky silt loam (Taxonomic Class: Euic, thermic Typic Haplosaprists), formed predominantly from tule and reed deposition (Tugel 1993). In the late 1800s the area, formerly a vast freshwater tidal wetland, was drained for agricultural purposes leading to significant land surface subsidence due to oxidative loss of the peat soils (Miller et al. 2008). To keep the leveed islands, now below sea level, from re-flooding, water is continually pumped off of the island with a system of drainage ditches into surrounding Bay Delta waterways. Current land uses on the island include rice farming, livestock pasture, and constructed wetlands. DOC concentrations of Twitchell Island drainage water typically range between 0.5 and 7.5 mol-C L<sup>-1</sup> (Deverel et al. 2007; Kraus et al. 2008).

Water samples were collected using an Amazon submersible pump and high purity, plasticizer-free 1.27 cm Tygon tubing. The water was filtered directly in the field through a 0.2 µm in-line membrane filter into four acid-washed 13-L Teflon jerry cans, which were double bagged to prevent Hg contamination. In the laboratory, water was stored at 4 °C until it was transferred to smaller acid-washed Teflon containers, frozen, and then freeze-dried over a course of 3 months. During storage and prior to freeze drying, DOC concentration, and absorbance at 254 nm did not change. Once freeze-dried, samples were stored in the dark at room temperature.

### Sample Preparation

Approximately 2.2 g of the freeze-dried material was re-dissolved in 10 L of deionized (DI) water. The solution was stirred for 1 h and filtered through pre-combusted 0.3 µm ashed quartz fiber filters (Advantec MFS, Dublin, CA, USA) using a Hg-clean filter apparatus to remove any particulate material. Ultra clean handling protocols were followed throughout the entire procedure, including equipment cleaning, sample collection, experimental manipulation, and analysis (Gill and Fitzgerald 1985).

A 2.7 mol L<sup>-1</sup> ferric sulfate solution (coagulant) was made by mixing reagent grade ferric sulfate powder

(Spectrum chemicals) in Hg-clean 6 mol L<sup>-1</sup> H<sub>2</sub>SO<sub>4</sub>, provided by the U.S. Geological Survey Mercury Research Laboratory (USGS MRL, Middleton, WI, USA). The amount of coagulant required to remove the maximum amount of DOC was determined using a streaming current detector (SCD), a common method used by water utilities to determine coagulant dosing requirements. The SCD measures the electrical charge on colloids present in water to indicate the extent of destabilization (Dentel and Kingery 1989). Optimal dose is reached when the SCD indicates a neutral solution charge. For this study, a final solution concentration of 0.06 mol L<sup>-1</sup> of Fe as coagulant was added, which removed 36 % of the DOC. This coagulant dose was chosen as prior studies demonstrated significant amounts of inorganic Hg were removed at this level of DOC removal (Henneberry et al. 2011).

The IHg spike, used in these studies to represent new IHg entering surface water, was provided by the USGS MRL as a concentrated stock solution of 19.04 nmol L<sup>-1</sup> <sup>200</sup>Hg (96.41 % enrichment purity). Samples were transferred to Teflon bottles, immediately preserved by acidification by adding high purity hydrochloric acid to 0.5 % (v/v), and kept in the dark at room temperature until analysis. All samples for IHg analysis were analyzed at the USGS MRL.

### Solution Analyses

Dissolved organic carbon concentration, used as a proxy for DOM concentration, was determined by UV-persulfate digestion (Teledyne-Tekmar Phoenix 8000) and is reported in mg-C L<sup>-1</sup>. The absorption at 254 nm was measured 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. To eliminate interference due to Fe(III) in absorbance measurements, 0.1 mL 3 % hydroxylamine hydrochloride was added to 1 mL of sample and absorbance data recorded until no further change, indicating all Fe(III) had been reduced to non-interfering Fe(II) (Doane and Horwath 2010). 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 L mg-C L<sup>-1</sup> m<sup>-1</sup> (Weishaar et al. 2003). Total dissolved Fe was determined colorimetrically with ferrozine based on the procedures described by Pullin and Cabaniss (2001) and Viollier et al. (2000).

Ambient mercury (ambient IHg) concentrations were determined using USEPA and USGS approved methods. Aqueous ambient IHg concentrations on filtered samples were determined using the purge and trap, cold vapor atomic fluorescence spectrometry method (US EPA 2002). Isotopic Hg was determined using the ICP-MS method, as described in Babiarez et al. (2003). The minimum detection

limit (MDL) for both total Hg (THg) and isotopic IHg was  $0.2 \text{ pmol L}^{-1}$  ( $0.04 \text{ ng Hg/L}$ ). A more complete description of the analytical methods is available at <http://wi.water.usgs.gov/mercury-lab>.

When added to deionized water, the coagulant and NaOH themselves released  $7.4$  and  $0.6 \text{ nmol L}^{-1}$  of total Hg, respectively. However, because concentrations of  $^{200}\text{Hg}$  in the coagulant and NaOH solutions were below the detection limit ( $1.0 \times 10^{-4} \text{ nmol L}^{-1}$ ), we assumed there were negligible contributions of  $^{200}\text{Hg}$  from these sources. Thus, the Hg added from the coagulant and NaOH was taken into account only when calculating the removal efficiency of total ambient IHg in the test solutions.

### Study 1: Effect of Time on Hg-DOM Interactions and Removal by Coagulation

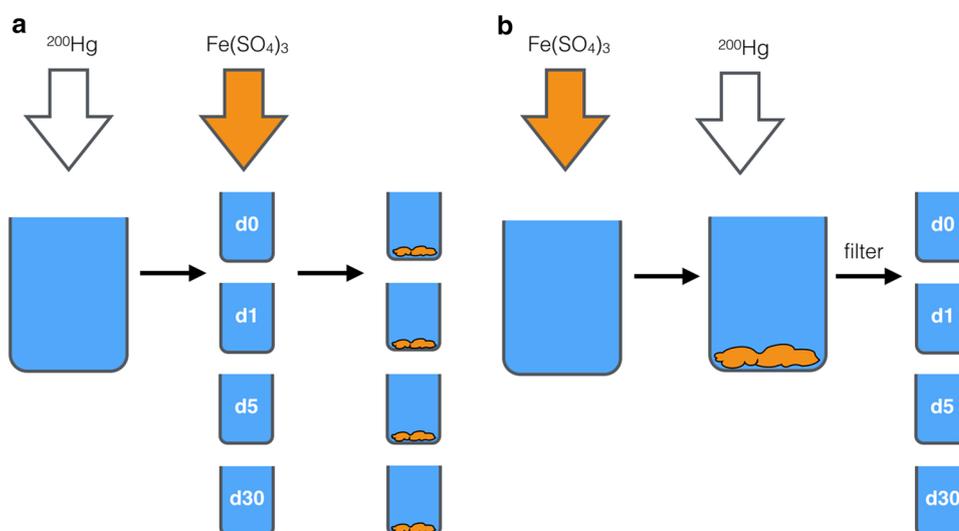
Solution from the same master “batch” of reconstituted freeze-dried Twitchell DOM was used for all studies to assure consistency across treatments. The first study was conducted in triplicate: three 3-L, Hg-clean Teflon bottles each received 2 L of the reconstituted Twitchell DOM. Each bottle was then spiked with  $^{200}\text{Hg}$  to a final concentration of  $0.02 \text{ nmol L}^{-1}$ . At the specified incubation times (2–3 h (0 day), 1 day, 5, 30 days), 500 mL aliquots were taken from each of the three bottles, transferred to Polyethylene Terephthalate Glycol bottles (Nalgene) and  $0.03 \text{ mol}$  of Fe as coagulant was pipetted into the solutions while being stirred at 20 rpm for 3 min (Fig. 1). The pH was adjusted to a final value of  $6.5 \pm 0.1$  through drop-wise addition of  $6 \text{ mol L}^{-1}$  NaOH. This pH represents average values found for drainage water from the area (Mourad 2003; Henneberry et al. 2011). Each aliquot was analyzed for the constituents described below, with the exception of IHg which, due to the high cost associated with IHg analyses, was analyzed in two of three duplicates.

A set of samples consisting of reconstituted Twitchell DOM with the  $^{200}\text{Hg}$  spike but no addition of coagulant was used as a control to determine potential adsorption of Hg to the container and loss through volatilization over the 30-day incubation. These samples were treated in the same manner as the treatment samples. Negligible adsorption was assumed as these samples showed minimal loss over 30 days ( $<5\%$  for  $^{200}\text{Hg}$ ,  $<8\%$  for ambient Hg).

### Study 2: Removal of Newly Added Hg by Organo-Metallic Precipitate

The second study was conducted by sampling in duplicate, with the exception of the higher dose of  $^{200}\text{Hg}$  (see below). As in the first study, 3 L acid-washed Hg-free Teflon bottles were filled with 2 L of reconstituted Twitchell DOM but not spiked with isotopic IHg until after the coagulation treatment was applied. All samples received the iron sulfate coagulant on day 0 using the methods described above, including pH adjustment. After allowing the coagulated material to settle for 1 h, the treatments were then spiked with two different concentrations of  $^{200}\text{Hg}$ :  $0.04 \text{ nmol L}^{-1}$ , representing 200 times the amount of naturally occurring  $^{200}\text{Hg}$  and  $1.05 \text{ nmol L}^{-1}$ , representing  $7 \times 10^3$  times the amount of naturally occurring  $^{200}\text{Hg}$ . Following the same incubation times as the above study (2–3 h (0 day), 1 day, 5, and 30 days), 500 mL from each bottle was filtered through ashed  $0.3 \mu\text{m}$  filters using a Hg-clean filtration device (Fig. 1). Treatments which received the  $0.04 \text{ nmol L}^{-1}$  spike were applied in duplicate, while the sample spiked with  $1.05 \text{ nmol L}^{-1}$   $^{200}\text{Hg}$  was only analyzed on day 30 and not replicated due to sample number constraints.

**Fig. 1** Schematic of the two studies: **a** study 1, **b** study 2. The control treatments did not receive isotopic Hg. d = day, d0 = 2–3 h post coagulant addition



### Statistical Analysis

For both studies, statistical analyses were performed using R software (version 2.10.1). Statistical differences between ambient and newly added IHg removal by coagulation were determined using the Welch two sample *t* test. Analysis of variance was run using time as the independent factor to determine differences between DOC concentrations, and SUVA over the 30 day sampling period, while one-way ANOVA using the Welch correction was applied to both IHg and <sup>200</sup>Hg. Data met the assumptions for each respective statistical test applied. Differences were considered significant, if *p* values were less than 0.05.

### Results and Discussion

#### Initial Water Quality

The reconstituted, freeze-dried Twitchell DOM had an initial DOC concentration of 1.58 mol-C L<sup>-1</sup> (18.9 mg-C L<sup>-1</sup>) and a SUVA value of 3.48 L mg-C<sup>-1</sup> m<sup>-1</sup>, which falls within the natural range of values found in water collected from Twitchell Island (Deverel et al. 2007; Kraus et al. 2008; Mourad 2003; Table 1). The total Hg concentration in filtered solution was 6.5 × 10<sup>-3</sup> nmol L<sup>-1</sup> (1.3 ng L<sup>-1</sup>), giving a Hg:DOC ratio of 4.10 × 10<sup>-3</sup> nmol Hg per mmol DOC, which is comparable to a previous study using water collected from a similar location (Henneberry et al. 2011). Other water quality parameters such as total Fe and pH also reflect average conditions found in the area (Henneberry 2012; Table 1).

#### Solution Chemistry Over Time

There was no significant difference in total dissolved Fe concentration nor pH over time for Study 1 (pH *p*-value = 0.17, Fe *p*-value = 0.05, Table 1). In contrast, in Study 2 where the coagulant was added at the beginning of the experiment and was present in the sample throughout the experiment, there was a significant decrease in total dissolved Fe by 25 % (*p*-value <0.001) over the 30 day period. This decrease was presumably due to the measured increase in pH from about 6.5 to 7.8 during the incubation, which may have promoted further hydrolysis of dissolved Fe (Stumm and Morgan 1996). However, the decrease in Fe concentration which occurred during the 30 day incubation did not significantly alter either DOC concentrations or SUVA values (see below).

**Table 1** Water quality characteristics following coagulation and filtration

| Sample treatment    | Day | DOC remaining in solution (mmol L <sup>-1</sup> ) | SD   | FeT remaining in solution (mmol L <sup>-1</sup> ) | SD       | pH   | SD   | EC (cm <sup>-1</sup> ) | SD    | SUVA (L mg <sup>-1</sup> cm <sup>-1</sup> ) | SD   | Ambient Hg (nmol L <sup>-1</sup> ) | SD       | <sup>200</sup> Hg (nmol L <sup>-1</sup> ) | SD       |
|---------------------|-----|---|------|---|----------|------|------|------------------------|-------|---|------|------------------------------------|----------|---|----------|
| <b>Experiment 1</b> |     |   |      |   |          |      |      |                        |       |   |      |                                    |          |   |          |
| Control             | -   | 1.58  | 0.10 | 0.12  | 0        | 6.91 | 0.02 | -                      | -     | 3.48  | 0    | 1.3E-03                            | 0        | 0.03E-03                                  | -        |
| Coagulated water    | 0   | 0.98  | 0.02 | 1.09E-03  | 9.81E-04 | 6.82 | 0.20 | 327.77                 | 6.66  | 3.01  | 0.03 | 5.22E-03                           | 1.06E-03 | 4.25E-03                                  | 7.78E-04 |
|                     | 1   | 0.98  | 0.07 | 2.79E-03  | 1.99E-04 | 5.42 | 2.28 | 336.50                 | 3.54  | 3.10  | 0.05 | 4.59E-03                           | 5.64E-04 | 4.23E-03                                  | 5.30E-04 |
|                     | 5   | 0.92  | 0.03 | 3.89E-03  | 7.34E-04 | 6.54 | 0.10 | 335.00                 | 4.58  | 3.22  | 0.03 | 5.48E-03                           | -        | 4.95E-03                                  | 7.07E-05 |
|                     | 30  | 0.93  | 0.06 | 3.81E-03  | 1.89E-03 | 6.9  | 0.20 | 430.67                 | 49.90 | 3.27  | 0.13 | 4.04E-03                           | 2.82E-04 | 3.48E-03                                  | 3.89E-05 |
| <b>Experiment 2</b> |     |   |      |   |          |      |      |                        |       |   |      |                                    |          |   |          |
| Coagulated water    | 0   | 1.00  | 0.03 | 2.56E-03  | 2.08E-03 | 6.53 | 0.11 | 335.00                 | 16.97 | 3.21  | 0.18 | 4.84E-03                           | 1.62E-03 | 4.04E-03                                  | 5.68E-03 |
|                     | 1   | 0.53  | -    | 1.63E-03  | -        | 6.17 | -    | 339.00                 | -     | 3.08  | -    | 5.98E-03                           | -        | 6.00E-03                                  | -        |
|                     | 5   | 1.03  | 0.01 | 1.47E-02  | 5.52E-03 | 6.80 | 0.12 | 328.00                 | 5.66  | 3.74  | 0.29 | 5.48E-03                           | 7.05E-04 | 6.75E-03                                  | 3.54E-04 |
|                     | 30  | 0.99  | 0.01 | 1.09E-03  | 4.75E-03 | 7.84 | 0.11 | 553.00                 | 27.58 | 3.34  | 0.09 | 7.98E-03                           | 7.76E-03 | 1.73E-03                                  | 2.37E-03 |
| Spiked sample       | 30  | 0.93  | -    | 1.19E-03  | -        | 7.73 | -    | 544.00                 | -     | 3.33  | -    | 1.79E-02                           | -        | 1.65E-01                                  | -        |

Values in italics are standard deviations

DOC dissolved organic carbon, FeT total iron, EC electrical conductivity, SUVA specific UV absorbance (average ± SD), SD standard deviation

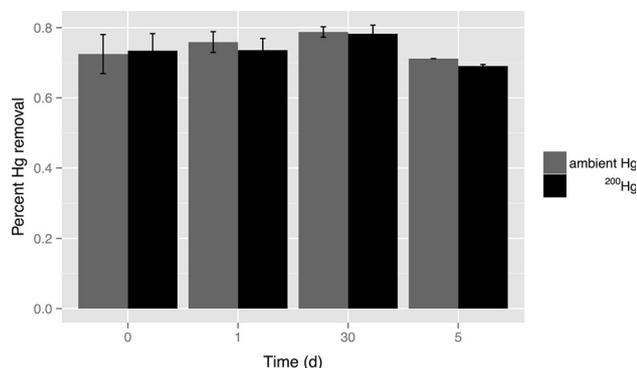
## DOC Concentration and Quality Following Coagulation

For both Study 1 and Study 2, coagulation at the rate of 1.0 mol Fe: $5.0 \times 10^{-3}$  mol DOC removed on average  $36 \pm 2$  % of the initial DOC in solution, with no significant effect of time on the percent DOC removed ( $p$ -value = 0.33, Table 1). Following coagulation, SUVA values decreased from 3.5 to 3.0, indicating preferential removal of the more aromatic, high molecular weight DOM (Blough and Del Vecchio 2002; Weishaar et al. 2003); this decrease has been documented in prior studies on these waters (Mourad 2003; Henneberry et al. 2011, 2012). Although measured SUVA values increased slightly for both studies over the course of 30 days (Table 1), changes were less than 10 %, so the values were considered negligible considering the errors associated with both DOC and absorbance measurements.

### IHg Concentrations: Study 1

Following addition of the  $^{200}\text{Hg}$  spike, there was no significant effect of time (0, 1, 5, 30 days) on ambient IHg removal by coagulation ( $p$ -value = 0.47, Fig. 2). Taking all time points into account, average percent removal of ambient dissolved IHg through coagulation was  $75 \pm 3$  % ( $n = 8$ ). This percent removal is comparable to a previous experiment using a similar dose of  $\text{Fe}_2(\text{SO}_4)_3$  (Henneberry et al. 2011).

Similarly, percent removal of the  $^{200}\text{Hg}$  spike did not differ significantly over time ( $p$ -value = 0.17) which indicates the association between new IHg (in the form of  $^{200}\text{Hg}$  spiked into the water column on day 0) and DOM occurred in a matter of minutes to hours. Removal of new IHg did not differ significantly from that of ambient IHg ( $p$ -value = 0.11), with  $74 \pm 4$  % ( $n = 8$ ) average percent removal across all time points. These results demonstrate



**Fig. 2** Percent removal of spike Hg and ambient Hg for study 1 over course of experimental period. ( $n = 2$ ). Error bars represent standard deviation from the mean

that a large fraction of incoming IHg to the aquatic environment can be removed immediately even when the concentration of coagulant does not remove the maximum amount of DOM.

There are two possible mechanisms of dissolved IHg removal through addition of Fe coagulant: direct removal of IHg through complexation/adsorption to the various Fe species formed through the addition of coagulant, or indirect removal of IHg through its complexation with DOM and subsequent removal of DOM via coagulation. The hydrolysis of IHg occurs between a pH of 2–6 (Schuster 1991). At the near neutral pH of our system, the most likely IHg species present would be Hg hydroxide,  $\text{Hg}(\text{OH})_2$ . Similarly, Fe species at this pH range would also include various soluble hydrolysis species such as  $\text{Fe}(\text{OH})_2$  and both soluble and amorphous  $\text{Fe}(\text{OH})_3$  (Jiang 2001). However, as the presence of the  $\text{OH}^-$  ion has been found to be very important in IHg-metal complexation (Forbes et al. 1974; Gabriel and Williamson 2004); IHg would most likely be complexed with fully hydrolyzed Fe species such as  $\text{Fe}(\text{OH})_3$  and amorphous Fe hydroxide ( $\text{Fe}(\text{OH})_3(\text{am})$ ). These complexation mechanisms would most likely involve a bridge between the oxide surface of the Fe species and Hg (Forbes et al. 1974; Tiffreau et al. 1995).

In natural systems, however, THg is highly correlated with the presence of DOM (Aiken et al. 2001; Ravichandran 2004; Dittman et al. 2009). In particular, the aromatic, larger molecular weight fraction of DOM, which contains a higher proportion of reduced sulfur rich functional groups (e.g., thiol and cysteine groups), has been found to strongly complex with IHg (Schuster 1991; Skyllberg et al. 2006). Henneberry et al. (2011) found that upon coagulation with metal-based salts, a majority of the IHg removed was strongly linked with the DOM pool that was removed at lower coagulant dose, which is composed of more aromatic, larger molecular weight compounds (Dempsey et al. 1984; Edzwald and Tobiason 1999). Thus, by removing this DOM pool from solution, coagulants may also effectively remove the strongly DOM-associated IHg fraction.

For the newly added spiked IHg, both direct and indirect mechanisms may have taken place although past studies conducted on the adsorption of IHg in the presence of both DOM and Fe hydroxide species have found the IHg-DOM interaction to predominate. Feyte et al. (2010) found IHg in lake sediment containing iron oxyhydroxides to be preferentially associated with humic substances. In addition, Bäckström et al. (2003) observed that in the presence of fulvic acid the adsorption of IHg to goethite was enhanced. The authors attributed this to the association of Hg to the fulvic acids, most likely with the reduced sulfur sites.

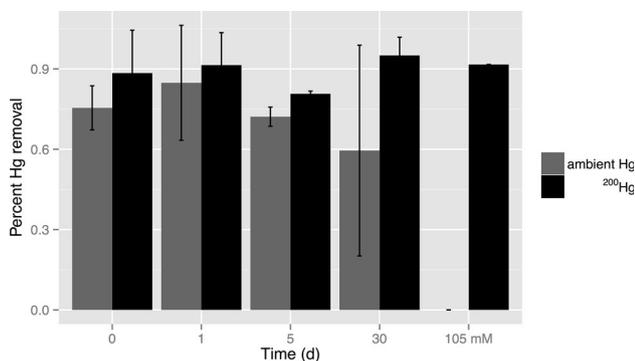
If complexation of IHg with the fraction of DOM most amenable to coagulation is a predominant mechanism, results suggest that the equilibrium period between

incoming IHg and this DOM fraction takes less than 3 h. However, as only 36 % of the DOM was removed in this case, it is difficult to say how the new Hg that was not removed via coagulation ( $\sim 25\%$ ) interacted with this remaining fraction of DOM.

### Hg Concentrations: Study 2

Results from Study 2 indicate that once formed, the DOM-Fe floc has the capacity to remove additional IHg from solution even at high concentrations (up to 200 to  $7 \times 10^3$  times that of ambient levels), and that this removal occurs rapidly ( $<3$  h). As was observed in Study 1, there were no significant changes in solution IHg concentration between day 0 and day 30 ( $p$ -value = 0.1), which indicates there was no release of IHg from the flocculate over time. Average percent removal of newly added IHg was  $89 \pm 6\%$  (Fig. 3). The sample that received the highest dose of new IHg ( $1.04 \text{ nmol L}^{-1}$ ) resulted in a similar percent loss of IHg from solution (84 %) compared to samples spiked with  $0.04 \text{ nmol L}^{-1}$  (Fig. 3).

Percent removal of both ambient and new IHg is significantly higher in Study 2, when the IHg spike was added following floc formation compared to Study 1 and when it was added prior to floc formation ( $p$ -value = 0.01). Further studies which investigate the mechanism behind this difference are needed. However, not only was 10 % more newly added IHg removed when floc was already present than when new IHg was added prior to coagulation, but also there was no indication that saturation of the floc was reached even when IHg concentrations  $7 \times 10^3$  times the ambient was added, as IHg removal rates remained relatively constant regardless of spike Hg concentration. This phenomenon may be attributed to the fact that there is still an excess of reduced sulfur sites available on the DOM within the floc (Bäckström et al. 2003) and as with Study 1



**Fig. 3** Percent removal of spike Hg and ambient Hg for Study 2 over course of experimental period. ( $n = 2$  except for d1, d30 and  $30\times$  spike where  $n = 1$ ). Error bars represent standard deviation from the mean

potential interactions between the Fe hydroxide on the surface of the floc and Hg. However, studies have noted changes in binding capacity of minerals with IHg under different water quality conditions such as varying pH and presence of anions such as  $\text{Cl}^-$  and  $\text{OH}^-$  (Schuster 1991; Walcarius et al. 2000; Gabriel and Williamson 2004). The effects of these factors as well as potential long-term changes to the physical and chemical structure of the floc material that may take place in natural environments should be taken into consideration when attempting large-scale applications of this Hg removal method.

### Conclusions and Future Implications

Results of this study indicate that coagulation not only removes ambient Hg from solution, but that it also effectively removes newly added inorganic IHg from solution and confirms prior studies which suggest a preferential association between IHg and high SUVA DOM. We saw no effect of incubation time on the percent removal of the newly added IHg, suggesting IHg-DOM associations occur very rapidly. Data from this research offers new insights into the relationship between DOM and new IHg entering a system in comparison to ambient IHg. In addition, this study provides new information on the effectiveness of coagulants in removing IHg from solution, both during floc formation and after the flocculate has formed. Such insights into IHg removal will help managers determine if in situ coagulation can be effectively implemented to reduce MeHg formation and export.

In this study, we applied a coagulant dose that led to less than 40 % removal of the total DOM pool, yet greater than 75 % removal of IHg. Based on the change in SUVA values and on prior studies (Dempsey et al. 1984; Henneberry et al. 2011), we can assume that the DOM removed at this rate comprised the more aromatic, high molecular weight fraction, and not the more aliphatic, low molecular weight DOM fraction which requires higher coagulant dose to remove. Prior studies using water collected from the same location showed that higher doses of coagulant can remove larger amounts (up to 80 %) of the DOM (Mourad 2003; Henneberry et al. 2011). To examine whether the pool of newly added IHg and the DOM fraction that was not coagulated in this study are in equilibrium with each other, future studies should employ variable and higher doses of coagulant.

A very significant finding is that once formed, the DOM-Fe floc is able to further adsorb newly added IHg from solution, which suggests the floc may serve as a sink for dissolved IHg. Such information offers insight into various alternative uses for floc rather than disposal in a landfill. For example, floc could be added to a wetland or a

wastewater treatment pond as an amendment to adsorb excess IHg (Henneberry et al. 2012), although studies should be conducted to determine the maximum adsorption capacity of the Fe-DOM floc. Removal of MeHg by floc may differ, however, as this species of Hg was not found to be associated with a particular fraction of DOM (Henneberry et al. 2011). Future studies should incorporate the use of isotopically labeled MeHg to look at potential interactions between this more bioavailable form of Hg and the DOM-floc system. Another interesting research topic would be to determine how an influx of new DOM species, such as from plant exudates, would affect the Hg complexed with the floc. For example, the more aliphatic DOM associated with the floc could potentially be replaced by the new, higher molecular weight, and aromatic DOM rich in carboxylic groups. Such interactions could in turn further increase the floc's capacity to adsorb Hg by increasing the number of reactive sites. Alternatively, this new incoming DOM could contain stronger binding sites and transfer the IHg associated with the floc back into solution. Such investigations would enhance our knowledge regarding the feasibility of using coagulants in a dynamic wetland system to remove both ambient and newly amended Hg perhaps from both solution and sediment.

We also would like to recognize that more research must be conducted to ensure that the floc system is stable in terms of Hg and DOM release under natural conditions. This is of particular concern if the floc is to be retained in constructed wetlands used as settling basins (McCord and Heim 2015). Henneberry et al. (2012) examined the stability of floc, defined as its capacity to retain DOC, under abiotic reducing conditions and found that the floc was indeed stable, as no DOC was released and no changes in floc structure were observed. However, the question of whether the floc that forms following coagulation can remain in the environment, or should be removed by collection in settling basins, will be investigated as part of ongoing studies, and likely will need to be addressed on a site-specific basis. Future studies should involve both dynamic and biotic environments involving the presence of plants and microbes, as well as various hydrologic regimes and variable redox conditions.

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