Science of the Total Environment 409 (2011) 631–637

Contents lists available at ScienceDirect

Science of the Total Environment

journal homepage: www.elsevier.com/locate/scitotenv

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

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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.

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 1.5×10^3 pmol g^{-1} (0.3 mg kg^{-1} wet weight), while California mandates a more stringent concentration of 0.14–1.11 nmol g^{-1} (0.03–0.24 mg kg^{-1}) (Wood et al., 2010). Factors affecting bioaccummulation 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

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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.

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doi:10.1016/j.scitotenv.2010.10.030

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 $km^3 yr^{-1}$ for Twitchell and 530,300 $km^3 yr^{-1}$ for most of the Delta (28). DOC concentrations in the drainage water typically range between 0.5 and 3.3 mmol l^{-1} (6–40 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 μm 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