Trihalomethane Formation Potential of Filter Isolates of Electrolyte-Extractable Soil Organic Carbon

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ABSTRACT

Certain organic C moieties of soil origin in drinking source waters of Sacramento–San Joaquin Delta (Delta) can react with chlorine to form trihalomethanes (THMs) during the disinfection process. Isolation and characterization of them and quantitation of their THM formation potential (THMFP) is necessary for developing effective strategies to reduce their influxes in Delta waters and for removing them during drinking water treatment. In this study, organic C from two Delta soils was extracted using deionized H₂O and four Na- or Ca-based electrolytes of varying electrical conductivity values. Extracts were filtered into particulate, colloidal, fine colloidal, and soluble C fractionation methods have in-nered poorly understood (Fujii et al., 1998; Fleck et al., 1999; Weishaar et al., 2003; Fleck et al., 2004), and only a small fraction of the bulk organic C may be electrolyte-extractable. The soluble organic C fraction from both soils dominated in quantity and THMFP. Electrolyte effects were cation dependent. Sodium-based electrolytes at either conductivity level did not significantly decrease extractable organic C (EOC) or THMFP compared with deionized H₂O. In contrast, Ca-based electrolytes reduced EOC and THMFP by >50% even at 1 dS m⁻¹. Further increase in Ca concentration did not significantly decrease EOC or THMFP. Most reduction in EOC and THMFP by Ca-based electrolytes occurred with the fractions other than the soluble organic C. Results suggested that under natural soil leaching and runoff conditions, the majority of THMFP is associated with organic C of <0.028 μm in diameter. Further molecular characterization of the fractions with high THMFP may help understand the nature of chlorine-reactive organic C from Delta soils.

The Sacramento–San Joaquin Delta (Delta) waterways are a major source of drinking water for >22 million residents of the State of California. Elevated organic C concentrations in Delta waters represent a serious public health concern. Organic C reacts with chlorine, a disinfectant used most by water utility operators with entitlement to Delta source waters, and forms harmful disinfection by-products (DBPs) such as trihalomethanes (THMs).

Delta peat soils are major organic C contributors to Delta waterways (Amy et al., 1990; Jassby and Cloern, 2000; Brown, 2003). Soils release organic C to the Delta through island drainage returns (Amy et al., 1990; Jassby and Cloern, 2000; Brown, 2003) and from wetlands (Brown, 2003; Fleck et al., 2004). Drainage returns from about 100,000 ha (250,000 acres) of peat soils are estimated to contribute an average of 36 Mg of organic C d⁻¹ to Delta waters (Jassby and Cloern, 2000). Large areas of Delta peat soils are being considered for conversion to wetland habitats (Fleck et al., 2004), which could further increase organic C releases to the Delta.

The peat soils, however, are not the only soils contributing organic C to Delta waterways. Mineral soils occupy >40% of the Delta area (Cosby, 1941). Although mineral soils may contribute relatively less organic C than peat soils, some mineral soils in the Delta contain elevated levels of organic C.

Studies have shown that not all organic C of soil origin in Delta waters reacts with chlorine in the same way or to the same degree (Amy et al., 1990; Fujii et al., 1998; Fram et al., 1999; Weishaar et al., 2003; Fleck et al., 2004), and only a small fraction of the bulk organic C may be reactive with chlorine to form DBPs (Rook, 1977; Owen et al., 1993; Croue et al., 2000). However, the properties of chlorine-reactive organic C from peat soils are currently poorly understood (Fujii et al., 1998; Fleck et al., 2004). Few studies have been conducted with Delta mineral soils. The differences between peat and mineral soils in composition and disinfection by-product formation potential (DBPFP), to date, have not been well characterized.

Organic C from soils may be collected from lysimeters and piezometers, or from drainage ditches and canals adjacent to the soils (Fujii et al., 1998). These approaches, however, are not preferable if variations in THMFP of soil organic C from different soil depths are of concern. An alternative and less time-consuming method is to extract organic C directly from soils sampled from the depth of interest. Preferred extractants are electrolytes that mimic the composition of the soil solution. Increases in electrolytic strength of extractants were found to decrease extractable organic C (EOC) from Delta peat soils (Chow et al., 2003). The effect of salts on organic C extractions and coagulation was found to vary with the valence of the cations present in the extractant (Ong and Bisque, 1968).

Organic C in natural waters, soil drainage, and soil extracts traditionally has been fractionated using XAD-resins for isolation and characterization of reactive organic C and THMFP (Amy et al., 1987; Aiken et al., 1992; Fujii et al., 1998). There have been known problems with the resin-based approach (Amy et al., 1987). All XAD-resin based fractionation methods have involved the use of strong acid and alkaline solutions, which may alter the properties and DBP reactivity of

Abbreviations: COC, colloidal organic carbon; DBPs, disinfection by-products; DOC, dissolved organic carbon; EOC, extractable organic carbon; FCOC, fine colloidal organic carbon; POC, particulate organic carbon; SOC, soluble organic carbon; THM, trihalomethane; THMFP, trihalomethane formation potential; TOC, total organic carbon.
organic C isolates. The XAD-resin based studies often contradicted one another on major fractions associated with the greatest THMFP (Fujii et al., 1998; Croue et al., 2000; Hwang et al., 2000; Chow et al., 2003). It is unknown if the use of strong acids and alkaline solutions contributed to such contradictions. Less destructive fractionation techniques such as filtration and ultrafiltration have been used for separation of organic C in natural waters (Kitis et al., 2002; Guo et al., 2003); these techniques need to be explored for fractionation of organic C from soils of the Delta.

Of the filtration studies conducted to date, different pore-size filters have been used. A 0.45-μm filter has been traditionally considered the cutoff point between total organic C (TOC) and dissolved organic C (DOC). It is widely believed that reactive organic C exists mostly in the dissolved phases (Owen et al., 1993). However, a pore size of 0.45 μm is large in colloidal scale. Organic C passing through a 0.45-μm filter may be further separated into heterogeneous organic fractions such as colloidal organic C (Thurman, 1985; Guo et al., 2003). Recent studies have suggested that the suspended organic C from soil extracts includes an important pool of reactive organic C (Li et al., 2003). Different organic C fractions such as particulate organic, colloidal, and dissolved organic C demonstrated different chemical properties (Guo et al., 2003). However, the THMFP of particulate organic C (POC) and colloidal organic C (COC) from Delta soils have rarely been documented.

The objectives of this study, therefore, were to (i) quantitate the EOC from two representative Delta soils using electrolytes with electrical conductivity values bracketing those of drainage waters from Delta soils, (ii) fractionate nondestructively the bulk soil EOC into isolates of homogeneous properties through filtration, and (iii) determine THMFP of different fractions to identify organic C fractions of dominant THMFP.

MATERIALS AND METHODS

Soil Sampling and Characterization

Soil samples were collected from Twitchell Island and Webb Tract in the central Delta. Sampling site coordinates were 38°07′02.3″ N lat; 121°38′20.5″ W long for Twitchell and 38°04′01.5″ N lat; 121°35′41.6″ W long for Webb. Recent surveys (USDA, 1977, 1993) classified the soil from Twitchell Island as a Scribner clay loam (Cumulic Endoaquoll), which is a mineral soil, and the soil from Webb Tract as a Rindge muck (Typic Haplosaprist), a peat soil.

At each sampling site, subsamples were collected from the surface layer between 0 and 0.3 m using an auger. Subsamples were then mixed and cleaned of rocks, undecomposed roots, and crop residue before being composited into 1-L mason jars. The soil-filled jars were then frozen in a commercial freezer with temperature set at −20°C.

Soil water content was determined by drying in an oven at 105 to 110°C until a constant weight was achieved, usually within 24 h. Specific conductivity and pH of the soils were determined from suspensions with a 1:1 soil/water ratio according to the USEPA Methods 9050 and 9045C, respectively. Soil organic C was measured by the Walkley-Black method (Nelson and Sommers, 1996). Major cations and Br− were determined by inductively coupled plasma–atomic emission spectrometry and ion exchange chromatography according to USEPA Methods 6010B and 300, respectively. Soil cation exchange capacity (CEC) was determined by mixing the soil sample with an excess of sodium acetate solution, resulting in an exchange of the added Na cations for the matrix cations. The sample was then washed with isopropyl alcohol. An ammonium acetate solution was added to replace the adsorbed Na with ammonium. The concentration of displaced Na was then determined by atomic absorption, emission spectroscopy, or equivalent means according to USEPA Method 9081.

The Rindge muck from Webb Tract contained six times more organic C than did the Scribner clay loam from Twitchell Island (Table 1). In response to this difference in organic C, CEC was also four times greater in the Scribner clay loam than in the Scribner clay loam (Table 1). Salinity of Rindge muck was five times higher than that of the Scribner clay loam, which was 2.1 and 0.4 dS m−1, respectively. Despite this salinity difference, a 1:100 soil/extractant ratio will sufficiently dilute the inherent salt effect. Extractable Br− from both soils was below the reporting limit of 0.01 g kg soil−1 (Table 1).

Organic Carbon Extraction and Operational Definitions of Carbon Fractions

Deionized H2O and electrolytes with varying concentrations of Na and Ca were used for extraction of organic C. A water purifier (Barnstead D4700 NANO PURE, Dubuque, IA) equipped with an organics removal system was used to generate deionized H2O. Organic C in deionized H2O was below the detection limit of 0.1 mg L−1, and its electrical resistance was >18 MΩ-cm. Four electrolytes, 0.005 and 0.02 M Ca solutions and 0.1 and 0.04 M Na solutions were prepared from reagent-grade CaCl2 and NaCl (Fisher Scientific, Pittsburgh, PA) and deionized H2O. The electrical conductivities were measured as 1 dS m−1 for both 0.005 M Ca and 0.01 M Na, and 4 dS m−1 for both 0.02 M Ca and 0.04 M Na. These two salinity levels were chosen because 1 and 4 dS m−1 represent the median and the highest recorded values of electrical conductivity of soil drainage waters from an agricultural field on Twitchell Island (Fujii et al., 1998).

During extraction, a 10-g soil sample (on a dry wt. basis) was weighed into a 1-L Nalgene high density polypropylene bottle and mixed with 1000 mL of deionized H2O or electrolyte. The mixture was stirred using a magnetic stirrer for 2 h at room temperature (20 ± 1°C). The mixture was then transferred to glass centrifuge tubes and centrifuged at 250 × g for 20 min. The supernatant was withdrawn and filtered through a series of mixed cellulose ester membrane filters (MF-Millipore, Bedford, MA) with four different pore sizes—1.2, 0.45, 0.1,
and 0.025 μm (Fig. 1). Each filter was rinsed with 1 L of deionized H₂O to remove residual organic contaminants before use (Karanfil et al., 2003). The supernatant was filtered through these filters in tandem. During filtration with 1.2- and 0.45-μm filters, filter fouling presented some difficulty. To avoid filter fouling, a new prerinsed filter was installed as soon as visible water pileup occurred. After each filtration, a sufficient aliquot of each filtrate was transferred to glass containers and refrigerated at 4°C for further chemical analyses. Each extraction was run in duplicate.

The entire extraction, fractionation, and operational definitions are illustrated in Fig. 1. The EOC was organic C that passed through a 1.2-μm filter, POC is organic C that passed through a 1.2-μm filter but was retained by a 0.45-μm filter, and COC included organic C that was passed through a 0.45-μm filter but retained by a 0.1-μm filter. Fine colloidal organic C (FCOC) represents organic C passed through a 0.1-μm filter but retained by a 0.025-μm filter, and SOC was organic C passed through a 0.025-μm filter. By these operational definitions, EOC contains POC, COC, FCOC, and SOC. Particulate organic C was removed when the 1.2-μm filtrates passes through a 0.45-μm filter. The 0.45-μm filtrate contained COC, FCOC, and SOC.

**Chemical Analysis**

All filtrates were analyzed for organic C and THMFP. Organic C concentration was determined by heat-promoted persulfate oxidation with an organic C analyzer (Model 1010 from O.I. Analytical, College Station, TX). A dose-based THMFP method developed by Bryte Laboratory of the California Department of Water Resources was used in this study (California Department of Water Resources, 1994). The assay was performed as follows: A water sample containing <10 mg L⁻¹ of organic C in contaminant-free, 40-mL borosilicate amber vials was spiked with sodium hypochlorite to accomplish a chlorine concentration of 120 mg L⁻¹. The spiked sample was buffered at pH 8.3 ± 0.1 by adding an aliquot of H₃BO₃ solution. Samples were then sealed without headspace and incubated for 168 h (7 d) at room temperature (20°C ± 1°C). At the end of incubation, a 150-μL 10% sodium sulfite solution was added to quench residual chlorine. Extraction and quantification of THM species were accomplished using a purge and trap condenser coupled with a Hewlett-Packard 5890 II gas chromatograph equipped with an auto injector, a capillary split/splitless inlet, and an electrical conductivity detector according to the modified USEPA Method 524.2. All THM samples were refrigerated at 4°C for no more than 2 wk before they were processed.

**RESULTS AND DISCUSSION**

**Quantities of Water-Extractable Organic Carbon and Fractions**

Quantities of H₂O-EOC in the two soils were dependent on soil organic C contents estimated by the Walkley-Black wet oxidation method. The Rindge muck had 22.9% soil organic C, and H₂O-EOC was 1.47 g C kg⁻¹ soil⁻¹, which was 0.6% of the soil organic C. The Scribner clay loam had 3.7% soil organic C, which is about one-sixth of that of Rindge muck; H₂O-EOC was 0.53 g kg⁻¹, which was 1.4% of the soil organic C. When the H₂O-EOC was fractionated, SOC and COC were the dominant fractions in both soils (Fig. 2). For the Rindge muck, SOC was 86% of the H₂O-EOC, COC was 10%, and POC and FCOC combined were 7% (insets of Fig. 2). For the Scribner clay loam, SOC was 57% of the H₂O-EOC, COC was 36%, and the other two factions combined were about 8% (insets of Fig. 2). The mineral soil, Scribner clay loam, had a much higher percentage of COC than did the Rindge muck, which suggested that a greater proportion of EOC from Scribner remained in colloidal phase. This colloidal C may be associated with mineral colloids (Laegdsmand et al., 2005; Shen, 1999), which were more abundant in the mineral soil because of its higher percentage of combined clay and silt (Table 1). The fact that discrete fractions of organic C were successfully isolated from filtrates with particle sizes <0.45 μm suggested that heterogeneous organic C fractions existed in filtrates that passed a 0.45-μm filter. The majority of H₂O-EOC remained in the filtrates that passed through the 0.025-μm filter (Fig. 2).

**Trihalomethane Formation Potential of Organic Carbon Fractions**

The THMFP of individual fractions followed patterns similar to organic C quantities for both soils. The SOC and COC combined accounted for 91 to 93% of the
total THMFP for the two soils (Fig. 3). Total THMFP of H$_2$O-EOC from the Rindge muck was 142 mg kg soil$^{-1}$, and total THMFP of H$_2$O-EOC from the Scribner clay loam was 42 mg kg soil$^{-1}$. Among the organic C fractions, SOC contributed 81 and 74% of THMFP from Rindge muck and Scribner clay loam, respectively, and THMFP from COC was 10 and 19%, respectively (insets of Fig. 3). The THMFP from either POC or FCOC was <5% of the total THMFP for both soils (Fig. 3).

The THMFP of the SOC and COC fractions differed between the two soils. In the Rindge muck, SOC accounted for 86% of total H$_2$O-EOC and 81% of THMFP. The COC was 10%, which was responsible for 11% of the THMFP (Fig. 2 and 3). The THMFP in Rindge muck was proportional to the quantity of the SOC organic fraction. In contrast, SOC accounted for only 57% of total H$_2$O-EOC in the Scribner clay loam but was responsible for 74% of the THMFP. The COC accounted for 36% of total H$_2$O-EOC and was responsible for only 19% of THMFP in the Scribner clay loam (Fig. 2 and 3).

**Electrolytes Effects on Extractable Organic Carbon**

Increases in electrical conductivity of extractants generally decreased the quantity of EOC. The magnitude of reduction, however, depended on the valence of the cation in the electrolytes and the soil type (Fig. 4). In the Rindge muck, extraction with monovalent Na-based electrolytes of 1 and 4 dS m$^{-1}$ resulted in EOC of 1.40 and 1.31 g kg soil$^{-1}$, respectively. These represented 5 and 11% reductions compared with H$_2$O-EOC (Fig. 4a). In the same soil, extraction using divalent Ca-based electrolyte with electrical conductivity of 1 and 4 dS m$^{-1}$ resulted in EOC of 0.63 and 0.60 g C kg soil$^{-1}$, respectively (Fig. 4a). This represented a reduction of >50% EOC compared with H$_2$O-EOC. The valence of the cation in the electrolytes was more relevant than the concentration or conductivity. The divalent Ca-based electrolyte with electrical conductivity of 1 dS m$^{-1}$ reduced EOC further than did Na-based electrolyte with an electrical conductivity of 4 dS m$^{-1}$ (Fig. 4a). Further increase in electrical conductivity of Ca-based electrolyte from 1 to 4 dS m$^{-1}$ did not further reduce EOC and THMFP.

Scribner clay loam was more sensitive than Rindge muck in its response to electrolytic effects. Sodium-based electrolytes with electrical conductivity of 1 and 4 dS m$^{-1}$ reduced EOC by 17 and 34%, respectively, compared with H$_2$O-EOC (Fig. 4b), which was more than twice the reduction observed in the Rindge muck. The effect of divalent Ca-based electrolytes was even greater in EOC reductions. An 87% reduction in combined EOC was observed when Ca-based electrolyte of 1 dS m$^{-1}$ was used for extraction. The only organic C fraction
remaining was the SOC, which was about 0.07 g kg⁻¹ (Fig. 4b). Further increase of Ca concentrations from 1 to 4 dS m⁻¹ did not reduce EOC (Fig. 4b).

**Electrolyte Effects on Trihalomethane Formation Potential**

Of the electrolytes examined, THMFP in the individual organic C fractions followed the same pattern as that of the size distribution of C fractions (Fig. 4 and 5). The SOC fraction produced the most THM among all fractions for both soils by all electrolytes (Fig. 5). For the Rindge muck soil, Na-based electrolytes did not change THMFP compared with deionized H₂O (Fig. 4a), which followed the same pattern as that of extractable C (Fig. 4a); THMFP did not change when Na concentrations in the Na-based electrolytes were increased from 1 to 4 dS m⁻¹ (Fig. 5a). For the Scribner clay loam, compared with deionized H₂O, Na-based electrolytes extracted less organic C as shown in the reduced sizes of the organic fractions (Fig. 4b). Consequently, THMFP of the respective organic C fractions also decreased compared with that of the fractions separated from deionized H₂O-EOC (Fig. 5b). However, the difference in THMFP between H₂O and Na-based electrolytes was not statistically significant; neither was the difference statistically significant between 1 and 4 dS m⁻¹ of Na. Contrary to monovalent Na, divalent Ca demonstrated a distinguishable effect on THMFP in both soils (Fig. 5), which was consistent with the reduction in sizes of organic C fractions (Fig. 4). For the Rindge muck soil, combined THMFP in C fractions extractable by 1 dS m⁻¹ Ca was 73 mg kg⁻¹, which was a 51% reduction compared with that from deionized H₂O-EOC (Fig. 5a). This reduction was proportional to the 50% reduction in EOC by 1 dS m⁻¹ Calcium electrolyte compared to deionized H₂O (Fig. 4a). For the Scribner clay loam, the effect of Ca on organic C removal from the solution phase and reduction in THMFP was even greater (Fig. 4b and 5b). In Ca electrolyte EOC, C and THMFP in three of the four fractions could not be quantified; SOC accounted for 100% of EOC and THMFP in Fig. 4b and 5b).

**CONCLUSION**

Two soils of contrasting texture and organic C contents were extracted using five extractants including deionized H₂O and four Na- and Ca-based electrolytes. The extractable organic C was then separated into particulate, colloidal, fine colloidal, and soluble organic C to determine THMFP. Results suggested that the electrolytes may extract between 0.6 and 1.4% of the soil organic C. For both soils, most THMFP was associated with the SOC and COC fractions. The THMFP from either POC or FCOC was small. The effect of electrolytes on organic C and THMFP differed between the organic and mineral soil. For the organic soil, monovalent Na did not significantly decrease the sizes of organic C fractions, nor did it decrease THMFP in organic C fractions compared with deionized H₂O. In contrast, divalent Ca reduced both the quantity of EOC fractions and their THMFP by about 50% compared with either deionized H₂O or monovalent Na. The effect of Ca-based electrolytes on reduction of organic C fractions and THMFP was greater in the mineral soil than in the organic soil. Results suggested that, under natural leaching and runoff conditions where electrolytes with both monovalent and divalent cations are present, the majority of THMFP are associated with the 0.025-μm filtrates regardless of the soil. Further molecular characterization of these filtrates may help understand the propensity of organic C from Delta soils to form THMs.

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