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## Size and XAD fractionations of trihalomethane precursors from soils

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### Abstract

Soil organic matter is an important source of allochthonous dissolved organic matter inputs to the Sacramento–San Joaquin Delta waterways, which is a drinking water source for 22 million people in California, USA. Knowledge of trihalomethane (THM) formation potential of soil-derived organic carbon is important for developing effective strategies for organic carbon removal in drinking water treatment. In this study, soil organic carbon was extracted with electrolytes (deionized H<sub>2</sub>O and Na- or Ca-based electrolytes) of electrical conductivity bracketing those found in Delta leaching and runoff conditions. The extracts were physically and chemically separated into different fractions: colloidal organic carbon (0.45–0.1 μm), fine colloidal organic carbon (0.1–0.025 μm), and dissolved organic carbon (DOC) (<0.025 μm); hydrophobic acid (HPOA), transphilic acid, and hydrophilic acid. Two representative Delta soils, Rindge Muck (a peat soil) and Scribner Clay Loam (a mineral soil) were examined. Results showed that less than 2% of soil organic carbon was electrolyte-extractable and heterogeneous organic fractions with distinct THM reactivity existed. Regardless of soil and electrolytes, DOC and HPOA fractions were dominant in terms of total concentration and THMFP. The amounts of extractable organic carbon and THMFP were dependent on the cation and to a lesser extent on electrical conductivity of electrolytes. Along with our previous study on temperature and moisture effects on DOC production, we propose a conceptual model to describe the impacts of agricultural practices on DOC production in the Delta. DOC is mainly produced in the surface peat soils during the summer and is immobilized by accumulated salt in the soils. DOC is leached from soils to drainage ditches and finally to the Delta channels during winter salt leaching practices.

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**Keywords:** Colloidal organic carbon; Dissolved organic carbon; Peat soil; Sacramento–San Joaquin Delta; Salt effects

**Abbreviations:** COC, colloidal organic carbon; DBPs, disinfection byproducts; DOC, dissolved organic carbon; FCOC, fine colloidal organic carbon; HPIA, hydrophilic acid; HPOA, hydrophobic acid; HPON, hydrophobic neutral; SOC, soil organic carbon; THM, trihalomethanes; TPHA, transphilic acid; TPHN, transphilic neutral; THMFP, trihalomethane formational potential; WEOC, water extractable organic carbon.

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## 1. Introduction

The Sacramento–San Joaquin Delta (the Delta) waterways are a major source of drinking water for more than 22 million residents of California. Elevated organic carbon concentrations in Delta waters represent a public health concern. Organic carbon reacts with chlorine, a disinfectant used by most water utilities with entitlement to Delta source waters, and forms harmful disinfection byproducts (DBPs), such as trihalomethanes (THMs) (Rook, 1977). Peat soil in the Delta is considered as one of the major organic carbon contributors to Delta waterways through agricultural drainage returns and wetlands outflows (Amy et al., 1990; Jassby and Cloern, 2000; Brown, 2003). Drainage return from about 250,000 acres of peat soils was estimated to contribute an average of 36 Mg of total organic carbon per day (Jassby and Cloern, 2000). Large areas of Delta peat soil are being considered for conversion to wetland habitats (Fleck et al., 2004), which could substantially increase organic carbon releases to Delta waterways.

Organic carbon that potentially leaches from soil can be collected through installing lysimeters or piezometers at different soil depths. In spite of the advantages in obtaining information about the seasonal variations in organic carbon, results of field studies highly depend on hydrological and environmental conditions and data interpretation is difficult. In addition, subirrigation and salt leaching cause large variations in soil salinity and sodicity, which can change the composition of organic carbon in soil water (Chow et al., 2003). Fractions of soil organic carbon that are coagulated in high salinity condition may not be collected in field studies. Thus, laboratory controlled extraction appears to be an alternative way to isolate dissolved organic carbon directly from soils sampled from the depth of interest.

Not all organic carbon from Delta soils reacts with chlorine in the same way or to the same degree (Fujii et al., 1998; Fleck et al., 2004), and only a small fraction of the bulk organic carbon may be reactive with chlorine to form DBPs (Owen et al., 1993; Croue et al., 2000). Knowledge of the reactive fractions of soil-derived organic carbon is important for water utilities to develop effective treatment strategies for organic carbon removal. Although studies have been conducted on the DBPs reactivity of organic carbon in peat soil (Amy et al., 1990; Fujii et al., 1998; Chow et al., 2003), to date the properties of the reactive organic carbon fractions are poorly understood (Chow et al., submitted for publication).

Inconsistent results for DBP reactivity of organic carbon from different water bodies were observed (Chow et al., submitted for publication). A potential explanation is the use of a 0.45  $\mu\text{m}$  filter for isolating dissolved organic carbon (DOC). A conventionally used 0.45  $\mu\text{m}$  pore size filter is relatively large on a colloidal scale

and water passing through a 0.45  $\mu\text{m}$  filter may contain heterogeneous organic fractions including colloidal organic carbon (COC) (Thurman, 1985; Guo et al., 2003; Chow et al., 2005). A study examining Delta agricultural drainage showed that the most reactive organic carbon had an apparent molecular weight of 1000–5000 Da (Amy et al., 1990). Thus, the 0.45  $\mu\text{m}$  filtrate may contain a significant portion of organic carbon that is not reactive during chlorination. In addition, a recent study showed that DOC from agricultural drainage in the Delta has the lowest propensity to form THM compared to other natural waters, even though it contained the highest aromatic carbon content (Bergamaschi et al., 1999). These results demonstrate the need to estimate the abundance of THM precursors in Delta soils.

Reclamation activities for agriculture over the last 100 years caused land subsidence and significantly reduced the area of peat soil in the Delta (CDWR, 1994; Deverel and Rojstaczer, 1996). A soil survey in 1941 showed that mineral soils covered more than 40% of the Delta (Cosby, 1941). Definitely, this number must be higher nowadays with intensive agricultural uses in the last 60 years. Few, if any, studies examined organic carbon from mineral soils in the Delta. In addition, current agricultural practices, which include intensive summer subirrigation and winter leaching, significantly affect soil salinity, soil–water composition, and soil respiration (CDWR, 1994). Our previous study showed that an increase in salinity or a decrease in sodicity decreased the concentration of DOC in the soil–water from agricultural peat soils (Chow et al., 2003). In addition, a two-year field study conducted by the US Geological Survey indicated that water from the subsurface-reduced soil layer had a higher DOC concentration and a higher specific UV absorbance at 254 nm ( $\text{SUVA}_{254}$ ) than that of the surface-oxidized layer (Fujii et al., 1998). However, our salinity extraction study showed that surface-oxidized soil contained higher DOC and the DOC had higher  $\text{SUVA}_{254}$ . The specific process causing higher concentrations of DOC in the subsurface-reduced soil layer is not clearly known.

Chemical, biological and hydrological activities could affect DOC production in the Delta. The DOC production mechanism associated with the summer irrigation and winter leaching practices has not been described in detail. In addition to examining the chemical properties and THM reactivity of organic carbon fractions, we synthesized and integrated the results of current and previous studies (CDWR, 1994; Fujii et al., 1998; Chow et al., 2003; Chow et al., in press; Thibodeaux and Aguilar, 2005) to develop a conceptual model for describing the DOC production mechanism in Delta agricultural fields. Our objective was to understand salt effects on organic carbon and THM precursors leaching from representative Delta soils.

## 2. Materials and methods

### 2.1. Soil sampling and characterization

Soil samples were collected from Twitchell Island and Webb Tract in the central Delta. Sampling site coordinates were N38°07'02.3", W121°38'20.5" and N38°04'01.5", W121°35'41.6" for Twitchell and Webb, respectively. Soil surveys (USDA, 1977; USDA, 1993) classified the soil from Twitchell Island as a Scribner Clay Loam (Cumulic Endoaquoll), and the soil from Webb Tract as a Rindge Muck (Typic Haplosaprist). These soils represent major peat and mineral soils in the Delta. At each sampling site, subsamples were taken from the surface layer between 0 and 0.3 m using an auger. Subsamples were mixed and cleaned of rocks, undecomposed roots, and crop residue before being composited into 1-liter Mason jars. The soil-filled jars were frozen in a commercial freezer (−20 °C). Soil–water content was determined by drying at 105–110 °C until a constant weight was achieved, usually within 24 h. Specific conductivity and pH of soils were determined from suspension with a 1:1 soil:water ratio according to US Environmental Protection Agency (EPA) Methods 9050 and 9045C, respectively. Soil organic carbon was measured by the Walkley–Black Method. Major cations and bromide (Br) were determined by inductively coupled plasma-atomic emission spectrometry and ion exchange chromatography, according to EPA 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 exchange of sodium for the adsorbed cations. The sample was then washed with isopropyl alcohol. An ammonium acetate solution was added to replace the adsorbed sodium with ammonium. The concentration of displaced sodium was determined by atomic absorption, emission spectroscopy, or equivalent means according to EPA Method 9081.

The Rindge Muck from Webb Tract contains six times more organic carbon than the Scribner Clay Loam from Twitchell Island (Table 1). In response to this difference in organic carbon, CEC was also four times greater in the Rindge Muck than in the Scribner Clay Loam. Salinity of Rindge Muck was five times higher than the Scribner Clay Loam, which was 2.1 and 0.4 dS m<sup>−1</sup>, respectively. Despite this salinity difference, a 1:100 soil:extractant ratio sufficiently diluted the inherent salt effect. Extractable bromide from both soils was below the reporting limit of 0.01 mg g<sup>−1</sup> (Table 1).

### 2.2. Organic carbon extraction and operational definitions of carbon fractions

Deionized H<sub>2</sub>O and electrolytes with varying concentrations of Na and Ca were used for extraction of organic carbon. A water purifier (Barnstead D4700

Table 1

Properties of two representative soils of the Sacramento-San Joaquin Delta

Property	Scribner Clay Loam (Cumulic Endoaquoll)	Rindge Muck (Typic Haplosaprist)
pH	6.41	5.25
Electrical conductivity, dS m <sup>−1</sup>	0.35	2.10
Soil organic carbon, %	3.7	22.9
Br, mg g <sup>−1</sup>	<0.01	<0.01
Na, mg g <sup>−1</sup>	0.22	0.68
K, mg g <sup>−1</sup>	0.92	0.41
Ca, mg g <sup>−1</sup>	4.87	15.24
Mg, mg g <sup>−1</sup>	6.72	3.50
Soil CEC, meq 100 g <sup>−1</sup>	36.6	148.7
Sand, %	48.1	51.2
Silt, %	41.8	34.7
Clay, %	10.1	14.1

NANO PURE, Dubuque, IA) equipped with an organics removal system was used to generate deionized H<sub>2</sub>O. Organic carbon in deionized H<sub>2</sub>O was below the detection limit of 0.1 mg l<sup>−1</sup>, and its electrical resistance was greater than 18 MΩ cm. Four electrolytes, 0.005 M and 0.02 M Ca solutions and 0.01 M and 0.04 M Na solutions, were prepared from reagent grade CaCl<sub>2</sub> and NaCl (Fisher Scientific, Pittsburgh, PA). The electrical conductivities were measured as 1 dS m<sup>−1</sup> for both 0.005 M Ca and 0.01 M Na, and 4 dS m<sup>−1</sup> for the 0.02 M Ca and 0.04 M Na. These two salinity levels were chosen because 1 and 4 dS m<sup>−1</sup> represent the median and the highest recorded values of electrical conductivity in peat soils from Twitchell Island (Fujii et al., 1998).

During extraction, a 10-g soil sample (on a dry basis) was weighed into a 1-liter Nalgene® high density polypropylene bottle and mixed with 1000 ml of deionized H<sub>2</sub>O or electrolyte. The mixture was stirred using a magnetic stirrer for 2 h at room temperature (20 ± 2 °C). The mixture was then transferred to a glass centrifuge tube and centrifuged at 250g relative centrifugal force for 20 min. The supernatant was withdrawn and filtered through a series of mixed cellulose ester membrane filters (MF-Millipore, Bedford, MA) with three different pore sizes—0.45, 0.1, and 0.025 μm. Each filter was rinsed with 1000 ml of deionized H<sub>2</sub>O to remove residual organic contaminants before use. The supernatant was filtered through these filters in tandem. During filtration with 0.45 μm filters, filter fouling presented some difficulty. To avoid filter fouling, a new pre-rinsed 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.

In this study, water extractable organic carbon (WEOC) was organic carbon that passed through a 0.45  $\mu\text{m}$  filter. COC included organic carbon that passed through a 0.45  $\mu\text{m}$  filter but was retained by a 0.1  $\mu\text{m}$  filter. Fine colloidal organic carbon (FCOC) represented organic carbon that passed through a 0.1  $\mu\text{m}$  filter but was retained by a 0.025  $\mu\text{m}$  filter. DOC was organic carbon that passed through a 0.025  $\mu\text{m}$  filter. By these operational definitions, WEOC contained COC, FCOC, and DOC. Quantification of organic carbon and THMFP for fractions retained by a given filter was by difference.

In addition, 0.45  $\mu\text{m}$  filtrates of all extracts were further characterized by XAD-fractionation. In the XAD-fractionation (Aiken et al., 1992), 20 ml capacity columns were used and these columns processed sample volumes of 1000 ml with a WEOC concentration of no greater than 20  $\text{mg l}^{-1}$  for maximum adsorption efficiency. The samples were acidified to pH 2 by the addition of 12.1 M HCl. After acidification, the samples were passed through the XAD-8 column, and the effluent was collected in an Erlenmeyer flask. The XAD-8 effluent was then run through a XAD-4 column and the effluent collected in an Erlenmeyer flask. These samples were run through both columns at a rate of 4  $\text{ml min}^{-1}$ . After all the samples were run through the columns, each column was separately back eluted with 100 ml of 0.1 M NaOH at a rate of 2  $\text{ml min}^{-1}$ . The eluates were collected in volumetric flasks and acidified to pH 2 with 12.1 M HCl. The eluate from XAD-8 is defined as hydrophobic acid (HPOA) and the eluate from XAD-4 is defined as transphilic acid (TPHA). The hydrophobic neutral (HPON) and transphilic neutral (TPHN) fractions are those compounds that adsorb onto XAD-8 and XAD-4 resins, respectively, but are not dissolved during back elution with NaOH. The hydrophilic acid (HPIA) fraction is the carbon in the XAD-4 effluent.

### 2.3. Chemical analysis

All filtrates, eluates and effluents from XAD columns were analyzed for organic carbon and THMFP. Organic carbon was determined by heat-promoted persulfate oxidation with a total organic carbon 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 (CDWR, 1994). Samples for THMFP were chlorinated with a freshly prepared  $\text{NaOCl}/\text{H}_3\text{BO}_3$  buffer with pH  $8.3 \pm 0.1$ . A fixed chlorine dosage ( $120 \text{ mg l}^{-1}$ ) was added into each sample with less than  $10 \text{ mg l}^{-1}$  of organic carbon. Excess chlorine was applied in the formation test to assure reactivity with all reactive sites. Samples were stored in contaminant-free, 40-ml borosilicate amber vials and sealed without headspace. The vials were incubated for 7 days at room temperature ( $20 \pm 2^\circ\text{C}$ ), followed by adding

150  $\mu\text{l}$  10% sodium sulfite solution 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 (modified EPA Method 524.2). All THM samples were refrigerated at  $4^\circ\text{C}$  for no more than 2 weeks before they were processed.

## 3. Results and discussion

### 3.1. Distribution of organic carbon fractions

Experimental results indicated that only a small fraction of soil organic carbon (SOC) was water extractable. The Scribner Clay Loam contained a total of 37  $\text{mg-SOC g-soil}^{-1}$  (3.7%), of which only 14  $\text{mg-C g-SOC}^{-1}$  (1.4%) was water extractable (Figs. 1 and 2). Similarly, only 6  $\text{mg-C g-SOC}^{-1}$  (0.6%) was extracted from the Rindge Muck, although it contained a total of 230  $\text{mg-SOC g-soil}^{-1}$  (23%), five times more than the Clay Loam. Yields of WEOC were similar to a leaching study mentioned in Aguilar and Thibodeaux (2005), in which 4.4%, 0.48%, and 0.45% carbon were released from soils with 0.65%, 10% and 19% carbon contents, respectively. Except for the quick release fraction contained in the carbon bed, most of DOC released in peat soil is a microbially driven process and only a small fraction of the SOC will be released over time, as the “tea bag” type release process (Aguilar and Thibodeaux, 2005; Thibodeaux and Aguilar, 2005). Thus, this extraction process using deionized water should contain the quick release fraction and represents the soil–water in the field. More organic carbon was extracted from SOC in the Clay Loam than from SOC in Rindge Muck, indicating that SOC in the Clay Loam was more water soluble than that of Rindge Muck.

When WEOC was physically fractionated, DOC and COC were the dominant fractions in both soils (Fig. 1). DOC, COC, FCOC comprised 87%, 11%, and 2% of the WEOC in the Rindge Muck extracts and 60%, 38%, and 2% of the WEOC in the Clay Loam extracts, respectively. A higher percentage of COC in Scribner Clay Loam suggested that a greater proportion of WEOC remained in the colloidal phase. This colloidal carbon may be associated with silt and clay colloids abundant in mineral soils (Shen, 1999a,b; Laegdsmand et al., 2005) (Table 1). The existence of a higher portion of COC may cause membrane fouling in water treatment (Kwon et al., 2005). WEOC was chemically fractionated into five operational fractions: HPOA, HPON, TPHA, TPHN, and HPIA (Fig. 2). More than half of WEOC was HPOA in both soils. TPHA and HPIA were relatively minor, ranging from 16% to 24%. The sums of

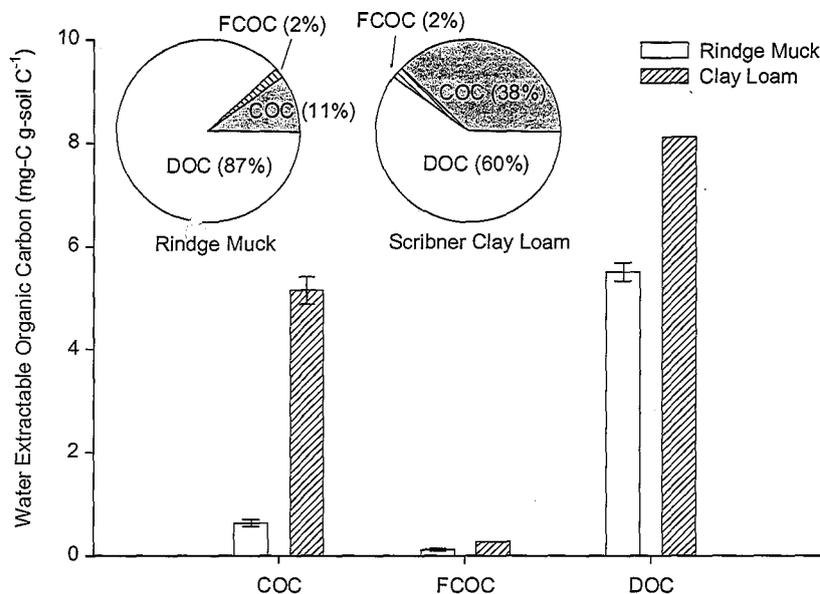


Fig. 1. Size fractionation of WEOC from Rindge Muck and Clay Loam. The two pie diagrams indicate the distributions of carbon fractions in the water extracts. COC, FCOC, and DOC are abbreviations of colloidal, fine colloidal, and dissolved organic carbon, respectively.

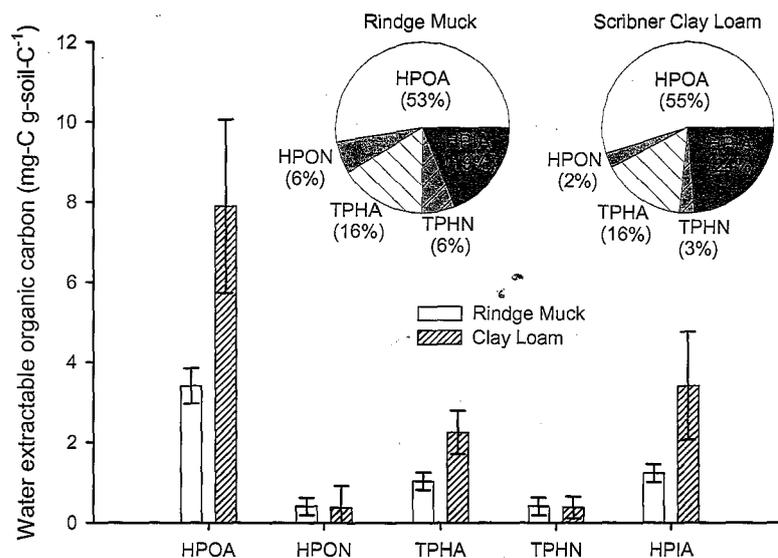


Fig. 2. XAD fractionation of WEOC from Rindge Muck and Clay Loam. The two pie diagrams indicate the distributions of carbon fractions in the water extracts. HPOA, HPON, TPHA, TPHN, and HPIA are abbreviations of hydrophobic acid, hydrophobic neutral, transphilic acid, transphilic neutral, and hydrophilic acid, respectively.

HPON and TPIN were less than 10%. The distributions of chemical fractions in water extracts from both soils appeared similar to each other, in spite of the difference in COC content. Organic carbon sorption on mineral soils is largely due to ligand exchange between organic

carbon and hydroxyl groups on soil mineral surfaces (Shen, 1999a). Acid and base manipulation during XAD fractionation may disrupt this linkage and homogenize the physically separated organic carbon fractions.

### 3.2. Trihalomethane formation of organic carbon fractions

The amount of THM formation is basically proportional to the concentration of dissolved organic matter in water (Rook, 1977). The amount of THM precursor in a soil should be proportional to its SOC content. The results of our THM formation potential (THMFP) test were consistent with this assumption and showed that Rindge Muck had contained  $14 \mu\text{g-C g-soil}^{-1}$  that formed THM under chlorination, whereas the Clay Loam only contained  $4 \mu\text{g-C g-soil}^{-1}$ . Among the carbon fractions, DOC and COC were the major reactive fractions for THMFP, contributing 85% and 11%, and 78% and 20% from Rindge Muck and Scribner Clay Loam, respectively (Fig. 3). FCOC produced insignificant amount of THM. However, the reactivity of DOC and COC in forming THM differed between the two soils. In the Rindge Muck, DOC and COC accounted for 87% and 11% of WEOC (Fig. 1), respectively, which were equivalent to the portions of

THMFP in extracts (85% and 11%). In contrast, DOC accounted for only 60% of total WEOC in the Scribner Clay Loam but was responsible for 78% of the THMFP. Meanwhile, COC accounted for 38% of total WEOC and was responsible for only 20% of THMFP (Fig. 3). The results suggested that reactivity of DOC and COC were similar in Rindge Muck, but DOC was more reactive than COC in the Scribner Clay Loam. In chemical fractions, HPOA was the major fraction that contributed THM formation, corresponding to 66% and 79% of total THMFP in extracts. All other fractions were relatively minor and accounted for about 10% each. Also, HPOA in both soils extracts accounted for about 50% of WEOC, but it produced over 65% of THM in the extracts, suggesting that this fraction may have a higher reactivity in THM formation.

To determine the reactivity of each carbon fraction, we calculated the specific THMFP (STHMFP), which is equal to THMFP divided by the organic carbon concentration. The STHMFP of COC, FCOC, and DOC

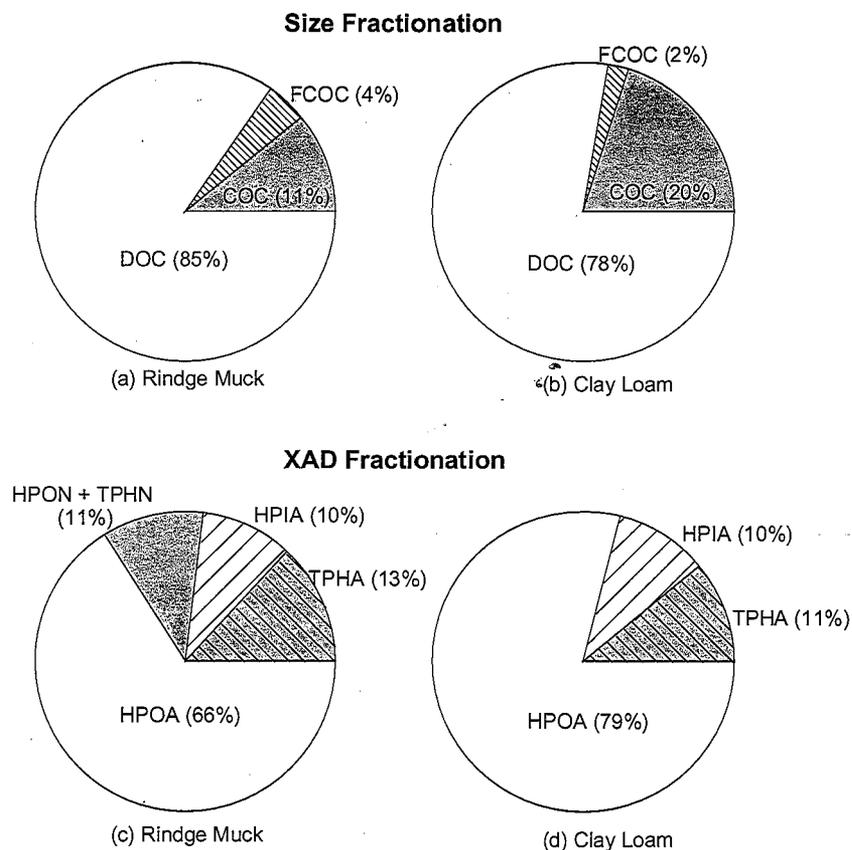


Fig. 3. Distributions of carbon fractions in THM formation. (a, b) COC, FCOC, and DOC are abbreviations of colloidal, fine colloidal, and dissolved organic carbon, respectively. (c, d) HPOA, HPON, TPHA, TPHN, and HPIA are abbreviations of hydrophobic acid, hydrophobic neutral, transphilic acid, transphilic neutral, and hydrophilic acid, respectively.

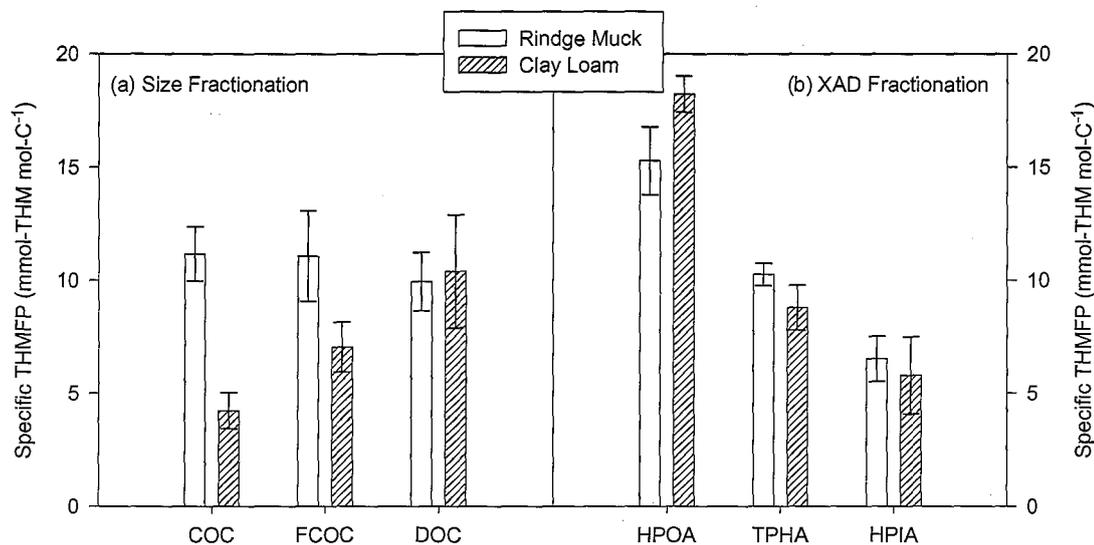


Fig. 4. Specific THM formation potential of WEOC fractions. (a) COC, FCOC, and DOC are abbreviations of colloidal, fine colloidal, and dissolved organic carbon, respectively. (b) HPOA, TPHA, and HPIA are abbreviations of hydrophobic acid, transphilic acid, and hydrophilic acid, respectively.

from Rindge Muck extracts had an average of 10, 11, and 11 mmol-THM mol-C<sup>-1</sup>, respectively, whereas the STHMFP from Clay Loam extracts had an average of 4, 7 and 10 mmol-THM mol-C<sup>-1</sup> (Fig. 4). In other words, about 10–11 carbon atoms per 1000 carbon atom in the DOC fraction react to form THM. Results fall in the middle of the range of many other THM studies of natural waters (STHMFP = 3–20 mmol-C mol-C<sup>-1</sup>, 168 h contact time, pH 8.3, and residual chlorine 2–4 mg l<sup>-1</sup>) (Fram et al., 1999). Differences in STHMFP were not significant ( $p > 0.05$ ) among fractions in Rindge Muck extracts, but were significant ( $p < 0.05$ ) in Clay Loam extracts. Also, the STHMFP of DOC was not significantly different between soils ( $p > 0.05$ ). We speculate that some of the reactive functional groups in COC and FCOC were protected by colloids during chlorination. In chemical fractions, HPOA had the highest STHMFP and an average of 15 and 18 mmol-THM mol-C<sup>-1</sup> for Rindge Muck and Clay Loam, respectively (Fig. 4). The STHMFP of TPHA and HPIA from Rindge Muck extracts had an average of 10 and 7 mmol-THM mol-C<sup>-1</sup>; the STHMFP of TPHA and HPIA from Clay Loam extracts had an average of 9 and 6 mmol-THM mol-C<sup>-1</sup>, respectively. The reactivity of organic carbon fractions from the two soils were not significantly different ( $p > 0.05$ ). However, the reactivity of HPOA from the two soils were significantly higher than all other fractions ( $p < 0.05$ ), indicating that this fraction contained more THM precursor. Our results followed the trend of relative reactivity among fractions found in other studies: HPOA > TPHA > HPIA (Owen et al., 1993; Croue et al., 2000; Kitis et al., 2002).

### 3.3. Salt effects on the distribution of organic carbon fractions

Different electrolytes used as extractants did not affect the distribution of size fractions in Rindge Muck extracts (Fig. 5). However, previous studies (Kalbitz et al., 2000; Chow et al., 2003) and results of this study showed that an increase in electrical conductivity of extractants or using divalent cations in extractants generally decreased the quantity of WEOC. The extraction with monovalent Na-based electrolytes of 1–4 dS m<sup>-1</sup> resulted in a 5% and 11% reduction in WEOC compared to deionized water extracts. Extraction with divalent Ca-based electrolyte with electrical conductivity of 1 and 4 dS m<sup>-1</sup> resulted in more than a 50% reduction in WEOC. However, DOC was the dominant fraction in all extracts. More than 80% of WEOC was DOC and other fractions were generally less than 10%. Moreover, the addition of electrolyte in extracting solutions only slightly altered the chemical compositions of WEOC. HPOA in the deionized water extract was about 53%. Extractions with Na-based electrolytes with electrical conductivity of 1 and 4 dS m<sup>-1</sup> resulted in an increase in HPOA to 61% and 67% of total WEOC, respectively (Fig. 6). These increases were significant ( $p < 0.05$ ). In contrast, the application of Ca-based electrolytes slightly reduce HPOA in extracts with an average of 45% and 52% in 1 and 4 dS m<sup>-1</sup> Ca<sub>2</sub> extracts, respectively. The differences between water and Ca extracts were not significant ( $p > 0.05$ ). All other fractions appeared relatively stable with no statistical differences between extracts. Results showed that the application

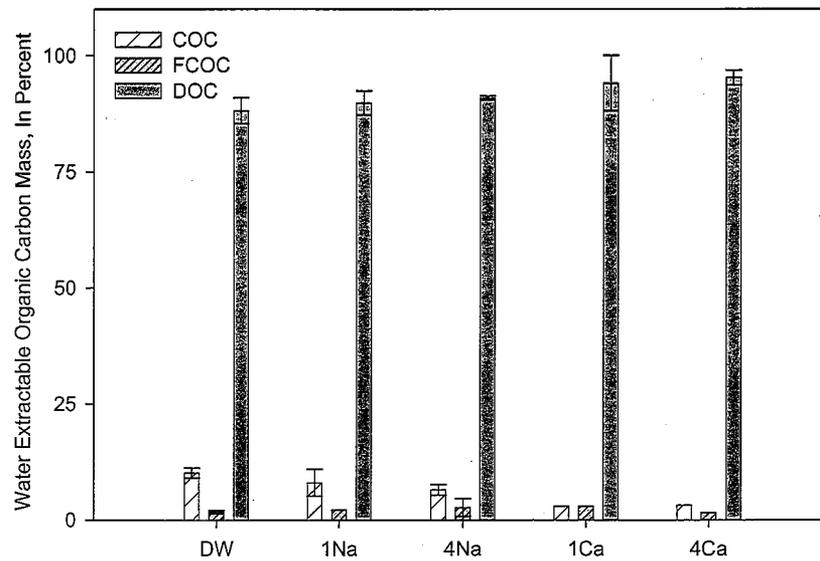


Fig. 5. Salt effects on the distribution of size fractions. DW represents deionized water. 1Na and 4Na represents Na-based electrolytes with electrical conductivity of 1 and 4  $\text{dS m}^{-1}$ , respectively. 1Ca and 4Ca indicate Ca-based electrolytes with electrical conductivity of 1 and 4  $\text{dS m}^{-1}$ , respectively.

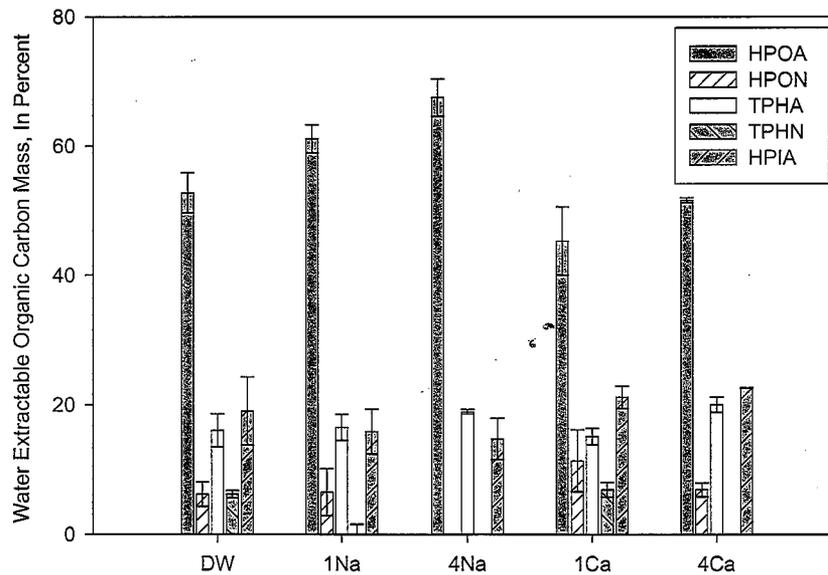


Fig. 6. Salt effects on the distribution of XAD fractions. DW represents deionized water. 1Na and 4Na represents Na-based electrolytes with electrical conductivity of 1 and 4  $\text{dS m}^{-1}$ , respectively. 1Ca and 4Ca indicate Ca-based electrolytes with electrical conductivity of 1 and 4  $\text{dS m}^{-1}$ , respectively.

of electrolyte reduced WEOC from soils, did not alter the distribution of size fractions, and slightly altered the distribution of chemical fractions.

Soil salinity can affect the fate of DOC in soils. Changes in soil salinity can potentially affect the structure of soil organic matter and possibly change the con-

centration of DOC in drainage water. Several studies have shown that there is an inverse relationship between leached DOC and ionic strength of soil solutions (Evans et al., 1988; Kalbitz et al., 2000). In the Sacramento–San Joaquin Delta, DOC in soil water and drainage varies with seasons. The highest concentrations of DOC were

recorded in summer and winter. Soil salinity and sodicity increase in the summer due to evapoconcentration of soil–water from evaporation and transpiration by crop plants, whereas soil salinity and sodicity decrease in winter due to salt leaching. We believe that the production and fate of DOC in the agricultural fields are controlled by soil salinity along with soil microbial activity. Based on the results of this study and other studies examining temperature, water content, salinity and sodicity effects on DOC productions (Fujii et al., 1998; Chow et al., 2003; Aguilar and Thibodeaux, 2005; Chow et al., in press; Thibodeaux and Aguilar, 2005), a conceptual

model to describe possible mechanisms of DOC production associated with agricultural practices in the Delta is proposed (Fig. 7).

We consider an agricultural field after winter flooding in April as the starting point (Fig. 7a). The salinity levels and DOC concentrations are low following salts and DOC flushing throughout the winter. In summer, intensive irrigation and high temperatures drastically alter the soil-water content. Subirrigation raises the water table near the surface and creates short-term flooded environments. High temperature in summer and flooded conditions could promote microbial activity

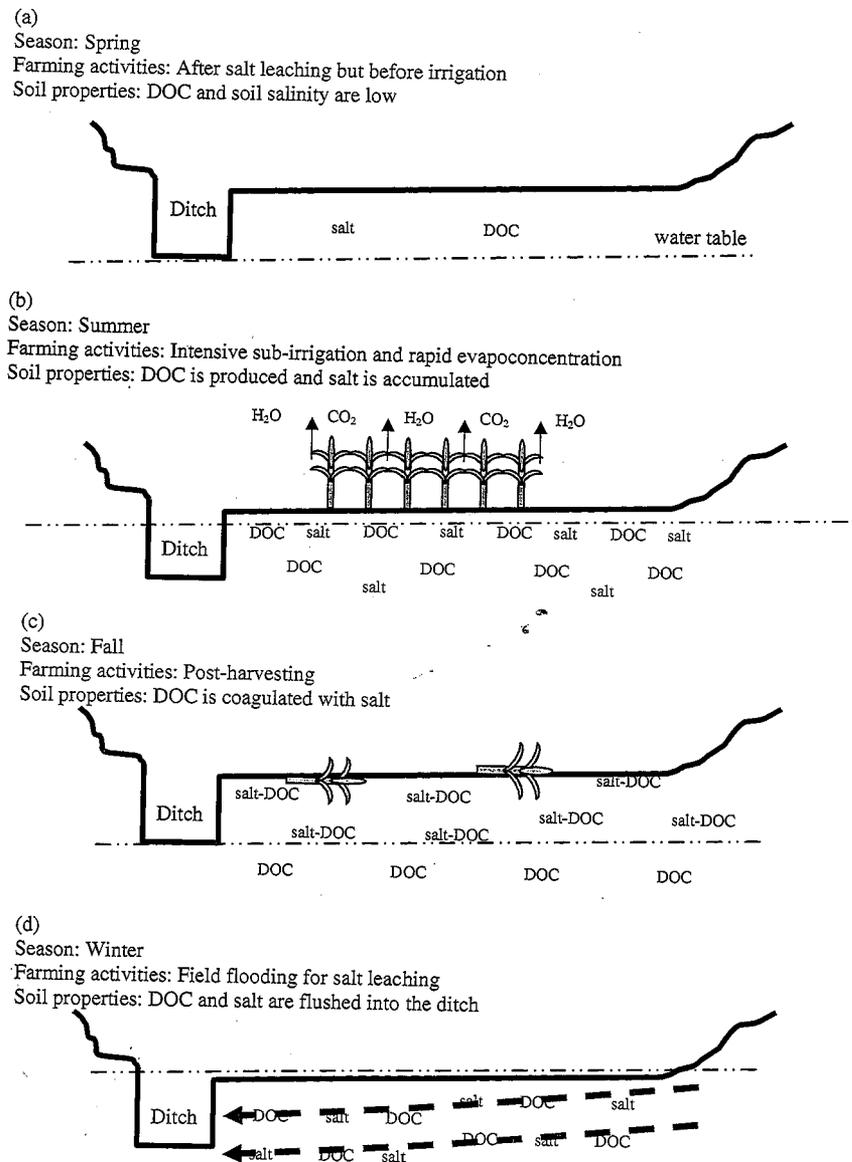


Fig. 7. A conceptual model for describing DOC dynamics in an agricultural field in the Sacramento–San Joaquin Delta.

and produce a significant amount of DOC (Fig. 7b). Labile DOC will be mineralized to  $\text{CO}_2$ , but DOC with refractory structures such as aromatic and lignin structures that are not degradable in a short period of time are retained in the field (Zsolnay and Steindl, 1991). The retained aromatic DOC may increase the aromaticity of the soil–water. When the water table is lowered after subirrigation practices, part of this DOC will leach to the subsurface layer. The migration of DOC from the upper to the lower soil zone may explain the higher concentrations of DOC and aromaticity in the lower reduced soil zone of a field study (Fujii et al., 1998). Furthermore, dry conditions in the surface soil rapidly develop after the water table is lowered. High temperature causes evapoconcentration of soil water such that a large amount of salt accumulates in the surface soil. As soil salinity increases, DOC flocculates with cations (e.g.,  $\text{Ca}^{2+}$  and  $\text{Mg}^{2+}$ ) and become inaccessible to microorganisms.

In fall and winter, significant amounts of DOC and salt are accumulated (Fig. 7c). After harvesting, additional C inputs from plant and crop debris are added to the surface layer of soil. Salt leaching practices and precipitation introduce low salinity water and the field is flooded. As a result, further DOC can be produced under flooding conditions, and coagulated SOC could be dispersed and DOC released to soil water. Low winter temperature and anaerobic conditions may slow C mineralization and DOC is accumulated in the field. As the field is drained, DOC and salt could be leached to drain ditches and eventually flushed to Delta channels (Fig. 7d). After the field is flooded and drained, both soil salinity and DOC concentrations decrease. Then, the field will be ready for the next summer's irrigation periods (Fig. 7a). This farming cycle, summer irrigation and winter flooding, occurs every year, and it significantly alters the physical, chemical and biological properties of peat soils in the Delta. These cyclical changes affect the availability, production and quality of DOC in soils. Although complex hydrologic conditions prevail, the proposed conceptual model helps to explain DOC production processes associated with current agricultural practices in the Sacramento–San Joaquin Delta.

#### 4. Conclusion

Two soils (peat and mineral soils) of contrasting texture and organic carbon contents were extracted with deionized  $\text{H}_2\text{O}$  and four electrolytes ( $\text{Na}^+$  and  $\text{Ca}^{2+}$ ). Water extractable organic carbon was fractionated by different pore size filters into COC, FCOC, and DOC and fractionated by XAD resins into HPOA, TPHA, and HPIA. Results suggested that reactivity of DOC and COC from the Rindge Muck were the same, but DOC was more reactive than COC from Scribner

Clay Loam. HPOA from both soils had the highest reactivity in forming THM compared to other chemical fractions. The effect of electrolytes on the distribution of organic carbon fractions is minimal, although the presence of divalent Ca can significantly reduce the amount of WEOC from soils. Results suggested that, under natural leaching and runoff conditions where electrolytes with both monovalent and divalent cations are present, the DOC fraction ( $0.025 \mu\text{m}$  or smaller) and HPOA fraction are the most reactive THM precursors.

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