Trihalomethane Reactivity of Water- and Sodium Hydroxide–Extractable Organic Carbon Fractions from Peat Soils

Alex T. Chow, Fengmao Guo,* Suduan Gao, and Richard S. Breuer

ABSTRACT

Certain organic carbon moieties in drinking source waters of the Sacramento–San Joaquin Delta can react with chlorine during disinfection to form potentially carcinogenic and mutagenic trihalomethanes. The properties of reactive organic carbon in Delta waters, particularly those of soil origin, have been poorly understood. This study attempts to characterize trihalomethane reactivity of soil organic carbon from three representative Delta peat soils. Soil organic carbon was extracted from all three soils with either deionized H2O or 0.1 M NaOH and sequentially separated into humic acids, fulvic acids, and nonhumic substances for quantitation of trihalomethane formation potential. Water-extractable organic carbon represented only 0.4 to 0.7% of total soil organic carbon, whereas NaOH extracted 38 to 51% of total soil organic carbon. The sizes and specific trihalomethane formation potential (STHMFP) of individual organic carbon fractions differed with extractants. Fulvic acids were the largest fraction in H2O-extractable organic carbon, whereas humic acids were the largest fraction in NaOH-extractable organic carbon. Among the fractions derived from H2O-extractable organic carbon, fulvic acids had the greatest specific ultraviolet absorbance and STHMFP and had the majority of reactive organic carbon. Among the fractions from NaOH-extractable organic carbon, humic acids and fulvic acids had similar STHMFP and, thus, were equally reactive. Humic acids were associated with the majority of trihalomethane reactivity of NaOH-extractable organic carbon. The nonhumic substances were less reactive than either humic acids or fulvic acids regardless of extractants. Specific ultraviolet absorbance was not a good predictor of trihalomethane reactivity of organic carbon fractions separated from the soils.

Waters within the complex channels and rivers of the Sacramento–San Joaquin Delta are a major source of drinking water for more than 22 million people in California. Delta source waters, however, contain elevated concentrations of organic carbon (California Department of Water Resources, 2003), which may react with chlorine, a common disinfectant, to form carcinogenic and mutagenic disinfection by-products (DBPs) during the disinfection process (Christman et al., 1983; Norwood et al., 1987; Rook, 1977). Organic carbon levels in Delta source waters are so elevated that removal of organic carbon is often required before disinfection can proceed.

Studies have shown that a considerable portion of organic carbon in Delta source waters originates from Delta island peat soils through drainage returns (Amy et al., 1990; Fujii et al., 1998; Jassby and Cloern, 2000; Brown, 2003) or wetlands where soil organic carbon is in direct contact with the water (Fleck et al., 2004). A recent 3-yr grab sampling study found that total organic carbon (TOC) in a drainage canal at Twitchell Island within the Delta ranged from 9.0 to 44.5 mg L\(^{-1}\) (California Department of Water Resources, 2003); TOC concentrations above 100 mg L\(^{-1}\) have also been reported in soil leachates at the same island (Fujii et al., 1998). Drainage waters with such elevated levels of organic carbon are pumped into Delta waterways daily. A proposal to improve the Delta’s ecological health recommends converting tens of thousands of hectares of Delta agricultural land to wetland habitats (Fleck et al., 2004). When this proposal is implemented, soil contribution of organic carbon to Delta waters might increase due to Delta water’s direct contact with peat soils. For one gram of dry peat soil, as much as 1.5 mg C may become soluble when the soil is in direct contact with the water (Chow et al., 2003).

Not all organic carbon of soil origin reacts with chlorine in the same way or to the same degree (Fujii et al., 1998; Fleck et al., 2004), and only a relatively small fraction of the bulk organic carbon may be reactive with chlorine to form DBPs (Rook, 1977). Early studies considered aromatic organic carbon moieties to be the reactive organic carbon (Rook, 1977; Amy et al., 1990; Krasner et al., 1996; Reckhow et al., 1990; Owen et al., 1993). Recent studies, however, found that organic carbon aromaticity alone cannot fully explain or predict DBP reactivity (Fujii et al., 1998; Fleck et al., 2004). To date the molecular nature of reactive organic carbon in Delta waters remains poorly characterized. Further studies on DBP reactivity of organic carbon in Delta waters including those of peat soil origin are necessary (Fujii et al., 1998; Fleck et al., 2004).

Reliable characterization of reactive organic carbon from peat soils requires extraction, isolation, and concentration of the reactive organic carbon from the soil. Soil organic carbon is a complex mixture and mostly in the form of humic substances, which is usually extracted with dilute alkaline solutions such as 0.1 M NaOH (Stevenson, 1994; Swift, 1996). Although alkaline solutions are widely used and effective in dissolving humic substances from soils, this approach has been questioned

Abbreviations: DBP, disinfection by-product; STHMFP, specific trihalomethane formation potential; SUVA, specific ultraviolet absorbance; THM, trihalomethane; THMFP, trihalomethane formation potential; TOC, total organic carbon; UVA, ultraviolet absorbance.
in the literature (Stevenson, 1994; Swift, 1996; Pokorna et al., 2001). The primary concern is the possibility of chemical alteration of the organic carbon moieties, resulting in artifact formation during the extraction process (Swift, 1996). Therefore, a less destructive reagent, NaOH before acidic precipitation (Stevenson, 1994; Swift, 1996; Mace et al., 2001). The primary concern is the possibility of chemical alteration of the organic carbon moieties, resulting in artifact formation during the extraction process (Swift, 1996). Therefore, a less destructive reagent, NaOH before acidic precipitation (Stevenson, 1994; Swift, 1996; Mace et al., 2001).

Isolation and concentration of reactive organic carbon may be accomplished by fractionation of the bulk soil organic carbon into relatively more molecularly homogeneous isolates such as humic acids and fulvic acids (Aiken, 1985; Swift, 1996). Humic acids are isolated by precipitation at pH 1, whereas aquatic humic acids are eluted and isolated from XAD-8 resins with 0.1 M NaOH before acidic precipitation (Stevenson, 1994; Aiken, 1985; Swift, 1996; Mace et al., 2001).

Although H2O and NaOH are common extractants for dissolving organic carbon from soils and other environmental media, few studies have been conducted to combine these extractants with common isolation procedures such as XAD resins commonly used in the water industry for direct evaluation of DBP reactivity of organic carbon from soils. A study is thus warranted to evaluate the differences and adequacy of both extractants for characterizing DBP precursors in Delta peat soils.

One study employed this integrated approach and examined trihalomethane (THM) reactivity of organic carbon from leaf mold (Ishikawa et al., 1984); results suggested that NaOH-extractable humic substances form less THM during chlorination than do H2O-extractable humic substances. The objectives of this study were to (i) extract bulk soil organic carbon from representative peat soils of the Delta with H2O and NaOH and compare the THM reactivity of organic carbon by both extracts and (ii) sequentially fractionate bulk soil organic carbon into humic acids, fulvic acids, and nonhumic substances for examination of THM reactivity.

MATERIALS AND METHODS

Soil Sampling and Characterization

Soil samples were collected from three Delta islands—Bacon, Bouldin, and Webb Tract. The soil from Bacon Island is classified as a Kingile–Ryde Complex, which will be referred to as Bacon Complex. The soils from Bouldin Island and Webb Tract are both classified as Rindge Muck and will be referred to as Bouldin Muck and Webb Muck, respectively. These soils represent major organic peat soils in the Delta. Taxonomic information and basic properties are presented in Table 1.

Subsamples were taken with an auger at each site from the top layer between 0 and 0.3 m. Subsamples were then mixed, cleaned of rocks, undecomposed roots, and crop residue before samples were 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 accomplished, usually within 24 h. Soil specific conductivity and pH were determined from a suspension with a 1:1 soil to water ratio according to USEPA Methods 9080 and 9045C, respectively. Total soil organic carbon was measured by the Walkley–Black method (Nelson and Sommers, 1996). Major cations and anions 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 sodium cations for the matrix 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 then determined by atomic absorption, emission spectrometry, or equivalent means according to USEPA Method 9081.

All three soils are considered loam soils, but they have textural differences (Table 1). The Bacon Complex contains the most clay among the three soils; the Rindge Muck soils are both dominated by sand and silt fractions. The Rindge Muck soils contain twice as much soil organic carbon as the Bacon Complex. The Webb Muck soil had the highest salinity as shown by its specific conductivity and K, Na, and Ca contents. Webb Tract has been irrigated with mostly San Joaquin River water, which contains higher salinity than waters from the Old/Middle and Mokelumne Rivers, which are used to irrigate the other two soils. Although soil specific conductivities differed, which may affect leaching of organic carbon (Chow et al., 2003), a small soil to extractant ratio used in this study (1:100) should dilute the salt sufficiently to minimize the effect on leaching of organic carbon. Bromide was below the detection limit of 0.01 mg g⁻¹ soil; brominated THM species were not quantifiable due to a small soil to extractant ratio.

**Extraction and Fractionation of Soil Organic Carbon**

Organic carbon from each soil was extracted by H2O and NaOH separately. Deionized water with electrical resistance

<table>
<thead>
<tr>
<th>Soil property</th>
<th>Bacon Complex (Terric Medisparist–Cumulic Haplauquoll)</th>
<th>Bouldin Muck (Typic Medisparist)</th>
<th>Webb Tract (Typic Haplosaprist)</th>
</tr>
</thead>
<tbody>
<tr>
<td>pH</td>
<td>5.85</td>
<td>5.31</td>
<td>5.25</td>
</tr>
<tr>
<td>Specific conductivity, μhos cm⁻¹</td>
<td>830</td>
<td>860</td>
<td>2100</td>
</tr>
<tr>
<td>Total soil organic carbon, %</td>
<td>9.9</td>
<td>18.8</td>
<td>22.7</td>
</tr>
<tr>
<td>Na, g kg⁻¹</td>
<td>0.27</td>
<td>0.13</td>
<td>0.68</td>
</tr>
<tr>
<td>K, g kg⁻¹</td>
<td>1.99</td>
<td>0.84</td>
<td>0.41</td>
</tr>
<tr>
<td>Ca, g kg⁻¹</td>
<td>6.63</td>
<td>9.10</td>
<td>15.24</td>
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<td>Mg, g kg⁻¹</td>
<td>4.24</td>
<td>3.47</td>
<td>3.50</td>
</tr>
<tr>
<td>Br, g kg⁻¹</td>
<td>&lt;0.01</td>
<td>&lt;0.01</td>
<td>&lt;0.01</td>
</tr>
<tr>
<td>Cation exchange capacity, meq kg⁻¹</td>
<td>4.1</td>
<td>4.5</td>
<td>14.9</td>
</tr>
<tr>
<td>Sand, %</td>
<td>37.4</td>
<td>53.2</td>
<td>51.2</td>
</tr>
<tr>
<td>Silt, %</td>
<td>31.0</td>
<td>36.3</td>
<td>34.7</td>
</tr>
<tr>
<td>Clay, %</td>
<td>31.6</td>
<td>10.5</td>
<td>14.1</td>
</tr>
</tbody>
</table>
RESULTS AND DISCUSSION

Quantity and Composition of Whole Extracts

The quantities of extractable organic carbon differed between the two extractants and among soils. Water-extractable organic carbon in the whole extracts of the three soils ranged from 0.5 to 1.5 mg g\(^{-1}\) soil, which represents from 0.4 to 0.7% of total soil organic carbon estimated by the Walkley–Black method (Table 2). In contrast, NaOH-extractable organic carbon was 79 to 101 times greater than H\(_2\)O-extractable organic carbon (Table 2). The NaOH-extractable soil organic carbon ranged from 42.5 to 116.5 mg g\(^{-1}\) soil, which represented 38 to 51% of total soil organic carbon.

Relative percentages of H\(_2\)O- and NaOH-extractable organic carbon differed among the three soils (Table 2). Bacon Complex had the lowest total soil organic carbon among the three soils, but its relative percentages of both H\(_2\)O- and NaOH-extractable organic carbon to total soil organic carbon was second among the soils. The smallest relative percentage was found with the Bouldin Muck (Table 2). Clay content in Bouldin Muck was the lowest of the three soils (Table 1). The differences in clay contents and soil organic carbon collectively may have
caused the differences in relative percentages of H₂O-
and NaOH-extractable organic carbon of the three soils.

Organic carbon recovered by the two extractants dif-
fered widely in their compositions (Fig. 2). The H₂O
whole extract was dominated by fulvic acids, which con-
stituted about 50% of extractable organic carbon; humic
acids and nonhumic substances ranged from 25 to 35%
depending on the soils. With the Bacon Complex, the
percentage of humic acids was more than 10% greater
than that of nonhumic substances. With both Bouldin
and Webb Muck soils, percentages of nonhumic sub-
stances were about 5% greater than that of humic acids
(Fig. 2). In contrast, nearly 80% of organic carbon was
humic acids in the NaOH whole extract; fulvic acids
and nonhumic substances each represented about 10%
of NaOH-extractable organic carbon. The percentages
of fulvic acids and nonhumic substances were about the
same in all three soils (Fig. 2).

Ultraviolet Absorbance and Trihalomethane
Reactivity of Whole Extracts

Both H₂O and NaOH whole extracts were examined
for UVA and THMFP. The UVA at a wavelength of
254 nm normalized on the carbon basis, or specific UVA
(SUVA), may be indicative of the abundance of aro-
matic organic carbon (Traina et al., 1990; Novak et al.,
1992; Krasner et al., 1996; Fujii et al., 1998; Korshin et al.,
1999; Li et al., 2000). Likewise, THM reactivity of or-
ganic carbon may be expressed as THMFP normalized
on a per carbon basis, which is referred to as specific
THMFP (STHMFP).

On average, SUVA of the H₂O whole extract was ap-
proximately 14% lower than that of the NaOH whole
extract (Fig. 3), and this difference was statistically sig-
ificant \( p = 0.001 \). This suggests that aromatic organic
substances are significantly more abundant in NaOH
whole extracts than in H₂O whole extracts. Aromatic
organic carbon molecules have been implicated as the primary reactive organic carbon (Boyce and Hornig, 1983; Christman et al., 1983; Norwood et al., 1987). Results suggested that STHMFP of NaOH whole extracts on average were 29% greater than that of the H₂O whole extracts (Fig. 3), which is also statistically significant ($p < 0.001$).

Results also indicated that humic acids of NaOH whole extracts may be more abundant in aromatic organic carbon. The higher SUVA (Fig. 3a) and STHMFP (Fig. 3b) in NaOH whole extracts compared with H₂O whole extracts may be attributed to a higher percentage of humic acids in the whole NaOH extracts (Fig. 2).

The pattern of STHMFP for the H₂O whole extracts of the three soils (Fig. 3b) appeared to be consistent with the pattern of relative percentages of humic acids to extractable organic carbon (Fig. 2). Phenolic and aromatic carbon, which are main moieties of humic acids, have been implicated as reactive sites for THM formation (Boyce and Hornig, 1983; Christman et al., 1983; Norwood et al., 1987). However, recent studies did not indicate a strong correlation between aromaticity and THM reactivity (Fujii et al., 1998; Fleck et al., 2004). More extensive studies involving more soils may be needed to reach a more definitive conclusion that humic acids are, indeed, more abundant in reactive organic carbon.

**Ultraviolet Absorbance and Trihalomethane Formation Potential of Organic Carbon Fractions**

Compared with whole extracts, SUVA of the individual fractions, humic acids, fulvic acids, and nonhumic substances varied with extractants (Fig. 4). Of the fractions separated from H₂O extracts of all three soils, average SUVA of fulvic acids was significantly higher than those of humic acids ($p = 0.0001$) and nonhumic substances ($p < 0.0001$). No significant difference ($p = 0.713$) was found between average SUVA of humic acids and nonhumic substances. Among the fractions from NaOH extracts of the three soils, humic acids had the greatest average SUVA, followed by fulvic acids and nonhumic substances (Fig. 4). The differences in average SUVA among the three individual fractions were all highly significant with $p < 0.0001$.

Some differences were found among soils. For the humic acids, SUVA of Bacon Complex was the greatest among the soils; SUVA of Webb Muck was the smallest (Fig. 4a). For the fulvic acids fraction, the lowest SUVA was found in the Bouldin Muck; SUVA was similar in Bacon Complex and Webb Muck was similar (Fig. 4b). No difference was found in SUVA of the nonhumic substance fraction from the soils (Fig. 4c).

The STHMFP of individual fractions also varied with extractants and soil. For the fractions derived from H₂O extracts, the pattern of STHMFP followed that of SUVA of the H₂O extracts (Fig. 4). Average STHMFP of fulvic acids was significantly higher than those of humic acids ($p = 0.001$) and nonhumic substances ($p = 0.0063$), but no significant difference in average STHMFP was found between humic acids and nonhumic substances ($p = 0.4673$). For NaOH fractions, however, the pattern of STHMFP was different from that of SUVA of NaOH fractions. Average STHMFP was 138.9 and 126.3 µg mg⁻¹ C for fulvic acids and humic acids, respectively, which were not significantly different ($p = 0.5014$), indicating similar THM reactivity for both humic and fulvic acids (Fig. 4). Average STHMFP of both fulvic and humic acids was significantly higher than that of nonhumic substances ($p = 0.0001$).

The STHMFP of the fractions among soils also differed. The pattern of STHMFP of humic acids was the same in both H₂O and NaOH extracts. The STHMFP of humic acids from Bacon Complex was the greatest among all soils, and STHMFP of humic acids from Webb Muck
was the lowest of all fractions (Fig. 4b). The STHMFP of both fulvic acids and nonhumic substances was similar from both H₂O and NaOH extracts (Fig. 4d and 4f). For both fractions from both H₂O and NaOH extracts, STHMFP of Bacon Complex was higher than those of Bouldin and Webb Muck; the STHMFP of both fulvic acids and nonhumic substances was similar (Fig. 4d and 4f).

For each organic carbon fraction, differences were also found between the two extractants (Fig. 4). The SUVA and STHMFP of humic acids of the NaOH-extractable organic carbon were significantly higher than those of the H₂O-extractable (Fig. 4a and 4b). The opposite was observed for the nonhumic fraction (Fig. 4c and 4f). The SUVA and STHMFP of the nonhumic fraction were 23 and 35% greater, respectively, in the H₂O-extractable...
carbon than in the NaOH-extractable organic carbon. Unlike the humic acids and nonhumic substances, no distinguishable differences in STHMFP were observed for fulvic acids between H$_2$O and NaOH (Fig. 4d), despite the fact that average SUVA of fulvic acids from H$_2$O extract was 12% greater than that from the NaOH extract ($p = 0.001$).

Despite differences among soils, the data suggested that reactivity of the fractions varied with extractants. For H$_2$O extracts, the fulvic acids were the most reactive fraction, followed by humic acids and nonhumic substances (Fig. 4b, 4d, and 4f). Considering the size of the fulvic fraction (Fig. 2), the fulvic acids contain most of the THM reactivity in H$_2$O-extractable soil organic carbon from all three soils. For NaOH extracts, fulvic acids and humic acids were equally reactive, and both were more reactive than nonhumic substances as indicated by STHMFP. Because humic acids dominate in size in NaOH-extractable organic carbon (Fig. 2), they contain most of the THM reactivity in NaOH-extractable soil organic carbon from all three soils.

The data indicated that SUVA patterns of the organic carbon fractions from H$_2$O extracts were consistent with those of their STHMFP, but were inconsistent with STHMFP patterns of the fractions from NaOH extracts. This suggested that SUVA did not predict reactivity of the fractions accurately in NaOH extracts. This confirmed findings from a few recent studies involving natural waters and wetland organic carbon isolates (Fujii et al., 1998; Fram et al., 1999; Weishaar et al., 2003; Fleck et al., 2004). The SUVA was strongly correlated with percent aromaticity as determined by $^{13}$C NMR for 13 organic matter isolates from a variety of aquatic environments, but SUVA failed to accurately predict THM reactivity of organic carbon (Weishaar et al., 2003). Fleck et al. (2004) observed similar findings with organic carbon from wetlands.

**CONCLUSIONS**

Organic carbon from three peat soils was extracted by H$_2$O and NaOH. Water- and NaOH-extractable organic carbon was sequentially fractionated into three relatively homogeneous fractions—humic acids, fulvic acids, and nonhumic substances. Results showed that, on average, the quantity of H$_2$O-extractable organic carbon was much smaller than NaOH-extractable organic carbon from the three soils. Water-extractable organic carbon was dominated by fulvic acids; humic acids and nonhumic substances were similar in quantities and varied with soil. The NaOH-extractable organic carbon was dominated by humic acids, followed by fulvic acids and nonhumic substances in roughly equal amounts. The SUVA was not a good predictor of STHMFP for the whole H$_2$O and NaOH extracts nor for the organic carbon fractions separated from the NaOH extract. The SUVA and STHMFP of organic carbon fractions varied with extractants. Among the fractions separated from H$_2$O-extractable carbon, fulvic acids had the greatest SUVA and STHMFP for all soils. In contrast, among fractions derived from NaOH-extractable carbon, humic acids had the greatest SUVA; STHMFP of both humic acids and fulvic acids were similar. The SUVA and STHMFP of nonhumic substances were smaller than those of either humic acids or fulvic acids. For H$_2$O-extractable soil organic carbon, the majority of reactive organic carbon was found in the fulvic acids fraction because that fraction was much greater in quantity and had the greatest STHMFP among all fractions. For NaOH-extractable soil organic carbon, however, the humic acids dominated in size and the STHMFP was as great as that of fulvic acids.

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