

# The Carbon Isotopic Composition of Trihalomethanes Formed from Chemically Distinct Dissolved Organic Carbon Isolates from the Sacramento-San Joaquin River Delta, California, USA.

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## ABSTRACT

Dissolved hydrophobic and hydrophilic acids were isolated from samples collected at five channel sites within the Sacramento-San Joaquin Rivers and Delta, California, USA, and from a peat island agricultural drain to examine the relationship between the chemical composition of dissolved organic carbon and the formation of trihalomethane, and to test whether peat island-derived dissolved organic carbon contributed substantially to reactivity. The chemical composition of the isolates was quite variable, as indicated by significant differences in carbon-13 nuclear magnetic resonance spectra and carbon to nitrogen concentrations ratios, though the variability was not consistent with simple mixing of river- and peat-derived dissolved organic carbon. The lowest propensity to form trihalomethane observed was in the peat island agricultural drain sample, suggesting the addition of peat island waters into Delta channels did not increase the amount of trihalomethane formed from channel water dissolved organic carbon. Changes in the chemical and isotopic composition of the isolates suggest the source of the trihalomethane precursors was different among samples and between isolates. The carbon isotopic composition of the trihalomethane formed from the isolates generally tracked the carbon isotopic composition of the isolates themselves, but variability in the carbon isotopic composition of the trihalomethane was higher.

## INTRODUCTION

Dissolved organic carbon (DOC) present in source water for drinking water forms a variety of disinfection byproducts when chlorinated during treatment (Rook, 1974). Some of these byproducts are known to be carcinogenic, and the final concentrations are regulated in finished drinking water (U.S. Environmental Protection Agency, 1994). The largest class of these byproducts is trihalomethane (THM), which is comprised of the sum of chloroform, and bromodichloromethane, dibromochloromethane, and bromoform. The environmental factors determining the extent to which a particular source water forms THM upon chlorination are the concentration of bromide, the amount of DOC present in the source water, and the molar reactivity of the DOC with respect to

THM formation (Reckhow and others, 1990). It is commonly held that the predominant pathway for THM formation is by reaction of chlorine with aromatic structures present in dissolved humic material (Reckhow and others, 1990). However, available data show no simple molar relation between ultraviolet (UV) absorbance at 254 nanometers, the common surrogate for DOC aromaticity, and the amount of THM formed upon chlorination of waters from the Sacramento-San Joaquin Delta (Delta) (Fujii and others, 1998). Thus, the amount of THM formed upon chlorination of any given water must depend on the composition as well as the concentration of the DOC.

THM formation is of particular concern for managers of the water-treatment facilities that

supply drinking water, originating in the tidal reaches of the Delta, to 22 million people. The Delta is a region largely composed of below-sea-level, peat-rich islands maintained in agricultural production by a network of levees and pumps (California Department of Water Resources 1993). It is commonly believed that the DOC content and composition of river water changes as it flows through the Delta before being diverted into the California Aqueduct system for use as drinking water in southern California (California Department of Water Resources 1990, 1994a; Fujii and others 1998). The changes are thought to result from the addition of water that is high in DOC because this water drains peat-rich Delta islands. High DOC concentrations in Delta water combined with high bromide levels from tidal mixing of brackish water frequently results in source water that potentially forms THM in excess of regulated levels upon chlorination (California Department of Water Resources 1990, 1994a; Fujii and others, 1998).

The purpose of this study is to investigate the relationship between biogeochemical processes in the Delta, composition of the DOC, and the molar capacity of DOC to form THM by examining the chemical and isotopic variability in DOC isolates from water samples collected in the rivers and Delta. This report presents the data obtained in this study and a discussion of the results. Based on the chemical and isotopic variability of the DOC isolates, we conclude that the DOC in Delta channel water does not represent a simple mixture of river- and peat-derived DOC, and that the THM formation potential of Delta water is not increased by addition of peat-island drainage waters. Based on the variability in the carbon isotopic composition of THM formed upon chlorination of the DOC isolates, we conclude that THM precursors in various fractions of the DOC are different, and that in-channel processes may contribute to the observed variability in the composition of the DOC. This study was done as part of the USGS Toxic Substances Hydrology Program and the USGS National Drinking Water Initiative.

## EXPERIMENTAL METHODS

Samples of about 140 liters (L) were collected by pump from below the surface, near mid-channel at five sites in the Sacramento and San Joaquin Rivers and main Delta flow channels. Additionally, an agricultural drainage water sample was collected from a drainage ditch on Twitchell Island. The experimental design used the

Sacramento and San Joaquin Rivers and the Twitchell Island Drainage samples, respectively, as representatives of upland river and Delta island sources of DOC transported to Delta channel water. The Old River and Middle River sites are located within the Delta and represent a mixture of riverine DOC and DOC added or modified within the Delta. The Export site is located just upstream of the facility that pumps water from the Delta into the California Aqueduct, and other drinking-water supply aqueducts.

Analytical methods are described in detail elsewhere (Bergamaschi and others, in press). Briefly, DOC was isolated and concentrated from the water samples by sequential extraction on nonionic macroporous resins (XAD-8 and XAD-4; Aiken and others, 1992). Materials eluted with base from the XAD-8 and XAD-4 resins are termed hydrophobic acids (HPoA) and hydrophilic acids (HPiA), respectively. DOC measurements were made with a Shimadzu TOC-5000A total organic carbon analyzer. (The use of trade names in this report is for identification purposes only and does not constitute endorsement by the U. S. Geological Survey.) Elemental composition was determined using a Perkin-Elmer 2400 Series II CHNS/O analyzer. UV measurements were made on filtered samples in a PE Lambda 3B UV/VIS spectrophotometer using a 1 centimeter (cm) cell.

Nuclear magnetic resonance (NMR) spectra for the DOC isolates were obtained by carbon-13 solid-state, cross polarization, magic angle spinning spectroscopy ( $^{13}\text{C}$ -CPMAS) using a 200 megahertz Chemagnetics CMX spectrometer with a 7.5 millimeter diameter probe. The spinning rate was 5,000 hertz, the pulse delay was 1 second, the pulse width was 4.5 microseconds for the 90° pulse, and contact times were 1 milliseconds in duration. Data were collected over approximately 2000 transients, and a line broadening of 100 hertz was applied in Fourier transformation of the free induction decay data. We assign resonance in the regions 0-60 parts per million (ppm) as aliphatic, 60-90 ppm as heteroaliphatic, 90-110 ppm as anomeric, 110-160 ppm as aromatic, and 160-190 as carboxylic. Integrated areas in these regions were normalized to the aggregate area and the proportion of each functional assignment expressed as a percentage of the whole.

Aliquots of the reconstituted XAD isolates were reacted with chlorine to form THM using a modified version of U.S. Environmental Protection

Agency (EPA) Method 510.1, following the reactivity-based dosing method (Krasner and Scilimenti, 1993; California Department of Water Resources, 1994b). THM concentrations were measured using a Tekmar ALS2016 and LSC200 purge and trap, and a Hewlett-Packard 5890 II gas chromatograph with an electron capture detector, following a modified version of U.S. EPA Method 502.2. Results are reported as millimoles of THM formed per mole carbon (mmol/mol). Carbon isotopic ratios of THM were measured using purge and trap introduction into a gas chromatograph coupled with a combustion furnace and a Micromass Optima continuous flow stable-isotope mass spectrometer. Results are reported in standard  $\delta$  notation, where  $\delta^{13}\text{C} = 1000 * [(\frac{^{13}\text{C}}{^{12}\text{C}})_{\text{sample}} - (\frac{^{13}\text{C}}{^{12}\text{C}})_{\text{std}}] / (\frac{^{13}\text{C}}{^{12}\text{C}})_{\text{std}}$  and V-PDB is the C standard, and atmospheric nitrogen is the N standard.

Mean deviation between replicate THM isotopic measurements was 0.30 per mil (‰) (standard deviation=0.2 ‰). Replicate analyses for isolate samples were within 0.05‰ for  $\delta^{13}\text{C}$  and 0.2‰ for  $\delta^{15}\text{N}$ . All replicate sample analyses were within 1% for concentrations of C and N.

## RESULTS

### Whole Water

The DOC content of Delta water is a concern for municipalities using the Delta as a source for drinking water. In this study, DOC concentrations in Delta water varied over a relatively narrow range, from 4.4 milligrams per liter of carbon (mg/L C) for the Old River sample,

**Table 1.** Dissolved organic carbon content and specific ultraviolet absorbance at 254 nanometers of whole water samples from locations in the Sacramento-San Joaquin Delta, California, USA

[Dissolved organic carbon (DOC) concentrations reported in milligrams of carbon per liter of water (mg/L C); specific ultraviolet absorbance at 254 nanometers (SUVA) reported in absorbance units per milligram of carbon per liter of water (abs/mg/L). UV absorbance measurements made in a 1 centimeter cell]

Sample	DOC (mg/L)	SUVA (abs/mg/L)
Sacramento River	3.7	0.015
San Joaquin River	4.2	.032
Twitchell Is. Drainage	17.1	.049
Middle River	6.1	.028
Old River	4.4	.042
Export	4.6	.038

to 6.1 mg/L C for the Middle River sample (table 1). The DOC concentration of the Export sample was 4.6 mg/L C, and the San Joaquin River sample had a DOC content of 4.2 mg/L C. For these samples, therefore, the water did not become appreciably elevated in DOC content by passage through the Delta, even though the Twitchell Island Drainage sample possessed a high DOC concentration of 17.1 mg/L C.

UV absorbance at 254 nm is a common parameter used to infer the amount of humic material in river waters, and predict the amount of THM likely formed during water-treatment. The carbon-normalized UV absorbance (SUVA) is used to compare water with different DOC contents to infer the proportion of aromatic humic material within the DOC pool. SUVA varied by less than a factor of two within the study (table 1), with the Delta sample yielding 0.028 and 0.042 absorbance units per centimeter per milligram per liter of carbon (abs/mg/L) at Middle River and Old River respectively. The Drainage water sample, as expected, had the highest SUVA (0.049 abs/mg/L), indicating a higher aromatic content. The San Joaquin River sample SUVA value, 0.032 abs/mg/L, was between those of the two Delta channel samples, and lower than the

**Table 2.** Carbon and nitrogen isotopic compositions, carbon-nitrogen ratios, and specific trihalomethane formation potentials of the hydrophobic and hydrophilic acid fractions of isolated dissolved organic carbon, and carbon isotopic compositions of trihalomethane formed upon chlorination of these dissolved organic carbon isolates from water samples from locations in the Sacramento-San Joaquin Delta

[HPoA, hydrophobic acid fraction; HPiA, hydrophilic acid fraction; carbon (C) and nitrogen (N) isotopic ratios reported as permil relative to standards (‰); subscript BULK refers to the solid isolate material; subscript THM refers to the trihalomethane; carbon to nitrogen ratio (C:N) reported in molar units; STHMFP, specific trihalomethane formation potential reported in millimole trihalomethane per mole dissolved organic carbon (mmol THM/mol DOC); na, not analyzed]

Sample	$\delta^{13}\text{C}_{\text{BULK}}$ (‰)	$\delta^{13}\text{C}_{\text{THM}}$ (‰)	$\Delta\delta^{13}\text{C}_{\text{BULK-THM}}$ (‰)	$\delta^{15}\text{N}_{\text{BULK}}$ (‰)	C:N (molar)	STHMFP (mmol THM/ mol DOC)
HPoA Isolate						
Sacramento River	-27.1	-31.1	4.0	1.7	31	9.7
San Joaquin River	-26.9	-31.3	4.4	0.4	52	9.0
Twitchell Is. Drainage	-27.1	-31.5	4.5	-1.7	31	8.5
Middle River	-26.7	-31.3	4.6	.9	33	9.2
Old River	-26.9	-32.0	5.1	2.7	30	9.2
Export	-26.5	-29.6	3.1	.8	62	8.6
HPiA Isolate						
Sacramento River	na	na	na	na	na	na
San Joaquin River	-25.8	-30.3	4.5	3.0	33	8.0
Twitchell Is. Drainage	-26.5	-31.0	4.5	.2	25	6.9
Middle River	-25.8	-30.4	4.6	.8	23	6.9
Old River	-25.7	-30.5	4.8	1.3	24	8.2
Export	-25.9	-30.3	4.4	9.7	35	7.4

Export sample (0.038 abs/mg/L), suggesting that the DOC may have increased in UV absorbance and aromatic humic content during passage through the Delta.

### Dissolved Organic Carbon Isolates

Carbon to nitrogen ratio measurements (C:N) of HPoA and HPiA isolates in this study revealed that the DOC isolates were universally low in N. HPiA C/N values ranged from 23 in the Middle River sample, to 35 in the Export sample (table 2). HPoA C/N values were more depleted in N than their HPiA counterparts, ranging from 30 in the Old River sample to 62 in the Export sample. The highest values were observed in samples from San Joaquin River and the Export site. C:N can be

indicative of the diagenetic state and source of DOC because terrestrial plants generally have C:N greater than 15 while planktonic algae have C:N about 6.5 (Hedges and others, 1988a), and diagenesis of organic matter generally results in increasing C:N (Hedges and others, 1988b).

The  $\delta^{13}\text{C}_{\text{BULK}}$  values of each type of isolate varied only slightly among the six samples, but the HPoA and HPiA isolates were distinctly different from each other (t-test of difference between two means,  $\alpha = 0.05$ ,  $P < 0.001$ ; Zar, 1984) (fig. 1; table 2). The  $\delta^{13}\text{C}_{\text{BULK}}$  of the HPiA isolates averaged -25.9 ‰, while HPoA isolates, averaging -26.9 ‰, were 1‰ lighter. The lighter  $\delta^{13}\text{C}_{\text{BULK}}$  value for HPoA isolates may be a result of the higher aromatic carbon content: lignin, the

**Table 3.** Percentages of carboxylic, aromatic, anomeric, heteroaliphatic, and aliphatic carbon in the hydrophobic and hydrophilic acid fractions of isolated dissolved organic carbon from water samples from locations in the Sacramento-San Joaquin Delta as determined by carbon-13 nuclear magnetic resonance spectroscopy

[Values reported as percentages. HPoA, hydrophobic acid fraction; HPiA, hydrophilic acid fraction. Sacramento River isolates were not analyzed]

Sample	Carboxylic	Aromatic	Anomeric	Heteroaliphatic	Aliphatic
HPoA Isolate					
San Joaquin River	13	21	9	21	36
Twitchell Is. Drainage	15	25	7	18	35
Middle River	14	21	9	20	37
Old River	13	21	10	21	36
Export	12	16	8	19	44
HPiA Isolate					
San Joaquin River	13	14	8	24	40
Twitchell Is. Drainage	18	18	8	22	34
Middle River	17	13	9	26	35
Old River	16	12	9	25	38
Export	17	13	10	23	38

putative primary precursor for aromatic moieties in humic materials, is isotopically lighter than bulk humic material by about 2 ‰ (Benner and others, 1987). The variability in  $\delta^{13}\text{C}_{\text{BULK}}$  values of the isolates among sites may reflect small variations in the sources of the DOC. The lightest isotopic ratios for both the HPoA and HPiA isolates were observed in the Twitchell Island Drainage sample. The peat soils were formed largely from the decayed remains of *Scirpus*, a C-3 marsh plant endemic to the Delta prior to cultivation of this area by man in the mid 19th century (Mason, 1957; Atwater, 1980; Fujii and others, 1998). The Export sample HPoA isolate  $\delta^{13}\text{C}_{\text{BULK}}$  value was heavier than average, perhaps indicative of the contribution of small amounts of heavier, algal- or C-4 plant-derived carbon.

The  $\delta^{15}\text{N}_{\text{BULK}}$  values of HPoA and HPiA isolates varied considerably, ranging over 10 ‰ between samples, in contrast to the  $\delta^{13}\text{C}_{\text{BULK}}$  results (table 2). The Export sample HPiA isolate exhibited the highest  $\delta^{15}\text{N}$  value (9.7 ‰), while the HPoA isolate from the Twitchell Island Drainage sample exhibited the lowest value (-1.7 ‰).

$\delta^{15}\text{N}_{\text{BULK}}$  values did not vary systematically among

the samples from the six sites nor between the HPiA and HPoA isolates. The Export sample, however, exhibited a nearly 9 ‰ difference between HPoA and HPiA isolates, indicating distinct sources for the organic nitrogen found in each isolate.

$^{13}\text{C}$ -CPMAS NMR analysis of the isolate samples yielded information about the distribution of functional groups within the bulk material, and provided a basis for comparison of the compositional differences between isolates and among samples. As expected, the aromatic carbon content of the HPoA isolates, which averaged 21%, was distinctly higher than the higher aromatic carbon content of the HPiA isolates, which averaged only 14% (t-test of difference between two means,  $\alpha = 0.05$ ,  $P < 0.001$ ; Zar, 1984) (fig. 1; table 3). The HPiA isolates were relatively enriched in heteroaliphatic and carboxylic carbon compared to the HPoA isolates (table 3). The enrichment in heteroaliphatic and carboxylic carbon, and depletion in aromatic carbon in the HPiA, compared with the HPoA isolate, may indicate that the HPiA material is more degraded.

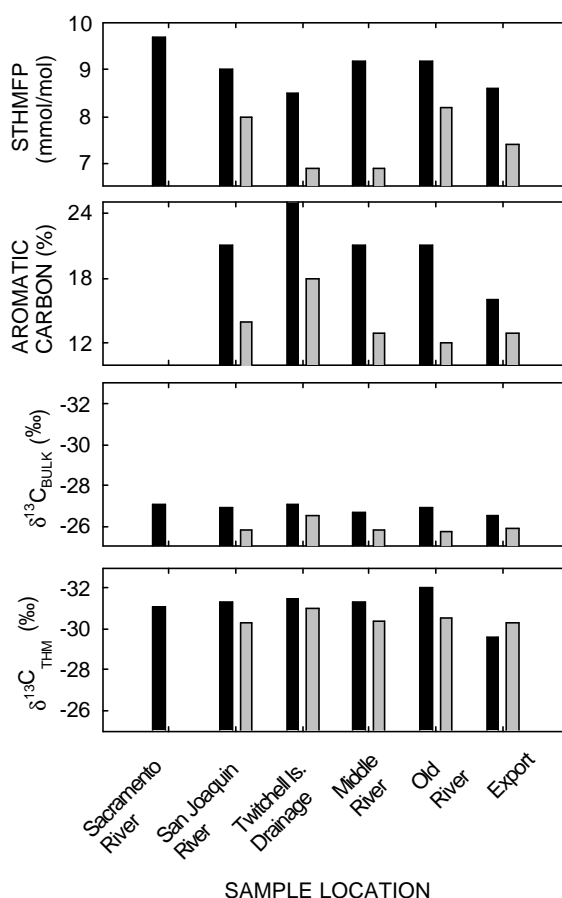
The highest proportions of aromatic and carboxylic carbon for both the HPoA and HPiA isolates were found in isolates from the Twitchell Island Drainage sample (table 3). This result is consistent with a peat origin for the material, as peats in other environments have been shown to be enriched in aromatic and carboxylic carbon (Spiker and Hatcher, 1988). Despite the high aromatic carbon content of DOC derived from the Delta islands, the Delta channel samples from Old River and Middle River did not contain higher proportions of aromatic carbon than the San Joaquin River sample. This result indicates that either DOC derived from the peat islands may not be a substantial contributor to the bulk DOC in the channel waters, or that the aromatic carbon may be degraded by the time it reaches the channels.

The Export sample HPoA isolate was distinctive; it contained more aliphatic and less aromatic carbon than all of the other isolates. This chemical difference may result from the addition of algal-, agricultural-, or sewage-derived organic material to the water, or from in-channel degradation of organic material.

## Trihalomethanes

The specific trihalomethane formation potential (STHMFP) is a measure of the potential of the organic material in the DOC isolates to form THM when treated with chlorine. The reactivity of the HPoA isolates averaged 1.5 millimoles THM per mole DOC (mmol/mol) higher than that of the HPiA isolates (t-test of difference between two means,  $\alpha = 0.05$ ,  $P = 0.003$ ; Zar, 1984) (table 2; fig. 1). STHMFP values of the HPoA isolates ranged from 8.5 to 9.7 mmol/mol (average = 9.0 mmol/mol) while the STHMFP values of the HPiA isolates were more variable, ranging from 6.9 to 8.2 mmol/mol (average = 7.5 mmol/mol). Surprisingly, the HPoA and HPiA isolates from the Twitchell Island Drainage sample exhibited the lowest reactivity, forming 8.5 and 6.9 mmol/mol, respectively. The fact that the Twitchell Island Drainage isolates were the least reactive is curious in view of the fact that they were the most aromatic of the isolates (table 3), and aromatic structures are the putative precursors for THM compounds.

**Figure 1.** Specific trihalomethane formation potential, percentage aromatic carbon, and carbon



isotopic compositions of solid material and trihalomethanes formed upon chlorination for the hydrophobic (dark bars) and hydrophilic (light bars) acid fractions of isolated dissolved organic carbon from water samples from locations in the Sacramento-San Joaquin Delta (data from tables 2 and 3).

$\delta^{13}C_{THM}$  values of the THM formed from the isolates averaged 4.4 ‰ lighter than that of the bulk material (table 2; fig. 1), which is similar to the average difference of 3.5 ‰ found for 60 other samples of DOC isolates (Bergamaschi and others, in press). The average  $\delta^{13}C_{THM}$  formed from the HPoA isolates was 0.6 ‰ lighter than that from the HPiA isolates, but this difference was not statistically significant (t-test of difference between two means,  $\alpha = 0.05$ ; Zar, 1984). The carbon isotopic fractionations observed between HPoA and HPiA isolates, between THM derived from HPoA and HPiA isolates, and between THM and bulk materials suggest strong intermolecular differences within the DOC. Different compounds within the DOC carry distinct  $\delta^{13}C$  values, and the chlorination reactions are highly selective in which compounds are attacked and broken down to form

THM (Bergamaschi and others, in press; Fram and others, 1998). The THM formation reactions occur preferentially on isotopically lighter compounds within the DOC.

The difference between the  $\delta^{13}\text{C}_{\text{THM}}$  and  $\delta^{13}\text{C}_{\text{BULK}}$  (defined as  $\Delta\delta^{13}\text{C}_{\text{BULK-THM}}$ ) does vary among the six samples, which may reflect distinct sources or diagenetic histories of the THM precursors in them. HPiA isolate  $\Delta\delta^{13}\text{C}_{\text{BULK-THM}}$  values ranged from 4.4 to 4.8 ‰, and HPoA  $\Delta\delta^{13}\text{C}_{\text{BULK-THM}}$  values ranged from 3.1 to 5.1 ‰ (table 2). The highest values for both isolates were in the Old River sample, while the lowest values for both isolates were in the Export sample. The  $\Delta\delta^{13}\text{C}_{\text{BULK-THM}}$  values for Twitchell Island Drainage and San Joaquin River samples were similar, and averaged 4.5‰ for both the HPoA and HPiA isolates. The Export sample had the greatest difference between values (1.3 ‰) for the HPoA and HPiA isolates.

## DISCUSSION

### Mixing and In-Channel Processes

The results presented here are in disagreement with the general view that the DOC in Delta channel waters represents conservative mixing between riverine and peat island-derived DOC. This simple scenario does not fully account for the chemical variability among samples in this study. No systematic differences were observed between the Sacramento and San Joaquin River samples and the Old River, Middle River, and Export site Delta channel samples in DOC content, proportion of aromatic carbon, C:N,  $\delta^{15}\text{N}_{\text{BULK}}$ , STHMFP,  $\delta^{13}\text{C}_{\text{BULK}}$ , or  $\delta^{13}\text{C}_{\text{THM}}$ . The compositions of the Old River, Middle River, and Export site Delta channel samples cannot be accounted for by combinations of the Sacramento River, San Joaquin River, and Twitchell Island Drainage samples (tables 1-3; fig. 1). C:N,  $\delta^{13}\text{C}_{\text{BULK}}$ ,  $\delta^{15}\text{N}_{\text{BULK}}$ , and  $^{13}\text{C}$ -NMR measurements of the isolates indicate substantial differences in DOC source and composition, and differences among HPoA and HPiA fractions of the DOC isolates.

The Export sample was chemically quite distinct from other samples in the study, suggesting that in-channel processes may be more influential

than previously thought in determining the DOC content, composition, and THMFP of Delta channel waters. Although the Export sample was relatively high in UV absorbance (table 1), the isolates had relatively low proportions of aromatic and high proportions of aliphatic carbon (table 3). The  $\delta^{13}\text{C}_{\text{BULK}}$  of the Export sample HPoA isolate, and the  $\delta^{15}\text{N}_{\text{BULK}}$  of the Export HPiA isolate, were the heaviest C and N isotopic values measured, respectively, and the  $\delta^{13}\text{C}_{\text{THM}}$  of the THM formed from Export sample HPoA isolate was 1.5 ‰ heavier than the average (table 2). These results suggest that material with a heavier isotopic composition had influenced the Export. Possible sources for this material include: algal, sewage, or agricultural source. The high C:N values for the isolates (table 2), however, suggest fresh algal or sewage material was not the source of the heavier carbon.

### Specific Trihalomethane Formation Potential and Carbon Aromaticity

The results presented here are in disagreement with the generally held view that aromatic carbon content of Delta water determines its STHMFP (California Department of Water Resources, 1994a). The Twitchell Island Drainage sample, with the highest aromatic carbon content had the lowest STHMFP, while the HPoA isolate of the Export sample had the lowest aromatic content, but higher STHMFP (table 2; fig. 1). This decoupling between aromatic carbon content and THMFP was the probable cause for the general failure of UV absorbance 254 nm to predict STHMFP in Delta water (Fujii and others, 1998). Another indication that aromatic carbon content does not determine STHMFP in these samples is the difference between HPoA and HPiA isolates. HPiA isolates contained 33 percent less aromatic carbon than the HPoA isolates, and HPiA isolates also were less likely to form THM on chlorination. However, STHMFP of HPiA was only 16 percent less than STHMFP of HPoA isolates, or only about half the decrease expected based on the difference in aromatic carbon content.

One possible explanation for why these samples do not react to form THM in expected molar ratios may be related to the differences in the  $\Delta\delta^{13}\text{C}_{\text{BULK-THM}}$  values between the samples. We have previously found isotopically distinct pools of organic material within isolates that react to form

THM at different rates, the combination of which determines the final  $\delta^{13}\text{C}_{\text{THM}}$  and the  $\Delta\delta^{13}\text{C}_{\text{BULK-THM}}$  values (Fram and others, 1998).  $\Delta\delta^{13}\text{C}_{\text{BULK-THM}}$  results from fresh plant decoctions suggest that the THM precursors removed during diagenesis are isotopically the lightest precursors, so that diagenesis yields residual samples with lower  $\Delta\delta^{13}\text{C}_{\text{BULK-THM}}$  values (Bergamaschi and others, in press). The reactivity of organic compounds to diagenesis and chlorination are not likely related to the aromaticity of the carbon in the same way. Thus, in samples of various diagenetic maturities, as indicated by the  $\Delta\delta^{13}\text{C}_{\text{BULK-THM}}$ , a correlation between aromatic carbon content and STHMFP would not be expected.

## CONCLUSIONS

1. The variability in chemical composition of the Delta channel water isolates, as indicated by significant differences in  $^{13}\text{C}$  CPMAS NMR spectra and C:N measurements, was not consistent with simple mixing of river- and peat-derived DOC.

2. For these samples, there was no significant increase in DOC concentration, or STHMFP and aromatic carbon content of DOC isolates between the Sacramento and San Joaquin River samples and the Delta channel samples (Old River, Middle River, and Export), even though SUVA did increase. These results indicate that changes in UV absorbance may be decoupled from THMFP and aromatic carbon contents in this environment.

3. The lowest STHMFP observed was in the peat island agricultural drainage sample, even though this sample had the highest SUVA and aromatic carbon content, suggesting that the addition of peat island waters into Delta channels will not increase the channel water STHMFP.

4. The higher aromatic carbon content and STHMFP of the HPoA isolates, and lower  $\delta^{13}\text{C}$  value of THM formed from the HPoA isolates suggests that THM have different chemical sources in HPoA and HPiA isolates.

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