How DOC Composition May Explain the Poor Correlation Between Specific Trihalomethane Formation Potential and Specific UV Absorbance

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ABSTRACT

Trihalomethane formation potential, ultra-violet light absorbance, and aromatic carbon content of dissolved organic carbon in natural water from grab sampling in watersheds across the USA and from detailed sampling in one watershed, the Sacramento-San Joaquin Delta, California, were examined in order to better understand the compositional nature of trihalomethane precursor material. Specific trihalomethane formation potential and specific ultra-violet light absorbance were not tightly correlated in either dataset, indicating that ultra-violet light absorbance cannot be used for accurate prediction of specific trihalomethane formation potential in drinking water derived from a broad spectrum of watershed types. Specific trihalomethane formation potential was not closely related to the aromatic carbon content of dissolved organic carbon isolates or to the partitioning of the dissolved organic carbon by nonionic macroporous resins, suggesting that neither of these measures are related to the compositional features of the dissolved organic carbon responsible for trihalomethane formation.

INTRODUCTION

Dissolved organic carbon (DOC) in natural water reacts to form trihalomethanes (THM) and other disinfection by-products when this water is chlorinated for use as drinking water. Aromatic-rich humic substances within the DOC have long been considered the precursors for THM, and ultra-violet (UV) absorbance measurements have been used to infer the aromatic content of natural water for the purpose of predicting THM formation (Rook, 1977; Reckhow and others, 1990). Absorbance of UV light is a standard proxy for aromatic carbon content (Traina and others, 1990; Chin and others, 1994), and along with DOC, is being considered as a surrogate measurement for trihalomethane formation potential (THMFP) that will indicate when additional water-treatment strategies are required.

In this study, we examine the relation among THMFP, UV absorbance, and aromatic carbon content of DOC in natural water from grab samples in watersheds across the USA that were collected as part of the National Water Quality Assessment (NAWQA) Program, and from detailed sampling in one watershed, the Sacramento-San Joaquin Delta, California (Delta), to better understand the compositional nature of THM precursor material. New U.S. Environmental Protection Agency (EPA) regulations that will take effect during the next several years will mandate the use of water-treatment strategies designed to lower the concentration of reactive DOC in water prior to chlorination in order to reduce THM concentrations in finished drinking water. Greater understanding of the relation between THM formation potential and compositional nature of the DOC is essential for the design of effective water-treatment strategies.

This report presents an analysis of the relations among THMFP, UV absorbance, DOC content, and percent aromaticity of DOC in samples from the Delta and NAWQA datasets. Complete data and full interpretations are reported in Fujii and others (1998), Bergamaschi and others (1999), and several forthcoming reports.

The majority of the Sacramento-San Joaquin Delta data (Twitchell Island) are compiled from a study done by the U.S. Geological Survey (USGS) in cooperation with the California Department of Water Resources Municipal Water Quality Investigation Program and as part of the USGS National Drinking Water Initiative (Fujii and others, 1998). The remaining Delta samples were collected as part of the USGS Toxic Substances Hydrology Program (Delta channel water) or the NAWQA Program (Sacramento and San Joaquin Rivers). DOC isolation and nuclear magnetic resonance characterization of the Delta channel water samples was done as part of the the USGS Toxic Substances Hydrology Program (Bergamaschi and others, 1999), and all other analyses of Delta samples were done as part of the USGS National Drinking Water Initiative. We gratefully acknowledge NAWQA Program units in Alabama, Alaska, California, Colorado, Illinois, Indiana, Louisiana, Massachusetts, Minnesota, Montana, New Jersey, New York, Ohio, Pennsylvania, South Carolina, Tennessee Texas, and Wisconson, that collected water samples for us. Analyses of the NAWQA samples were made as part of the USGS National Drinking Water Initiative, and USGS research sponsored by the EPA.

EXPERIMENTAL METHODS

The DOC present in Delta water is thought to be a mixture of river-borne DOC and DOC derived from Delta peat islands. Whole water samples were collected from the Sacramento and San Joaquin Rivers upstream of the Delta, from drainage ditches and ponds on Twitchell Island in the Delta, and from piezometers installed in two types of soil on Twitchell Island. More than 600 whole-water samples collected during a 3-year period were analyzed for DOC concentration, UV absorbance at 254 nanometers (nm), and THMFP. Measurements of DOC were made with a Shimadzu TOC-5000A total organic carbon analyzer and UV measurements were made with a Perkin-Elmer Lambda 3B ultraviolet/visible spectrophotometer using a 1-centimeter (cm) cell. (The use of trade-names in this report is for identification purposes only and does not constitute endorsement by the U.S. Geological Survey.) Aliquots of sample were reacted with chlorine to form THM using a modified version of EPA Method 510.1, following the reactivity-based dosing method (Krasner and Sclimenti, 1993; California Department of Water Resources, 1994). THM concentrations were measured using a Tekmar ALS2016 and LSC2000 purge and trap apparatus, and a Hewlett-Packard 5890 II gas chromatograph outfitted with an electron capture dectector, following a modified version of EPA Method 502.2.

To provide material for further chemical analysis, DOC was isolated from selected water samples from Twitchell Island drainage ditches and piezometers, and from main Delta flow channels. DOC was fractionated and isolated from water sample of about 140 liters using sequential XAD-8 and XAD-4 resin extractions. The XAD-8 resin retains the larger, more hydrophobic materials, including humic and fulvic acids, while the XAD-4 resin retains the smaller, more hydrophilic materials (Aiken and others, 1992). Materials are sorbed to the resins at pH 2 and then eluted at pH 13. Isolates were freeze-dried until use, and reconstituted isolates were analyzed for DOC concentration and THMFP.

Carbon-13 nuclear magnetic resonance (^{13}C-NMR) spectra for the freeze-dried DOC isolates were obtained by solid-state, cross polarization, magic angle spinning spectroscopy using a 200 megahertz Chemagnetics CMX spectrometer. We assign resonance in the region 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.

Water samples were collected at 92 sites in 18 states in conjunction with sampling by NAWQA Program. The sampling sites encompassed a wide spectrum of types of watersheds that provide water for drinking water purposes. DOC in the whole water samples was fractionated using XAD-8 resin. The XAD-8 resin retains the more hydrophobic compounds within the DOC, including the humic and and fulvic acids. Whole water, effluent from the XAD-8 resin (the unretained fraction of the DOC), and the eluate from the resin all were analyzed for DOC content, UV absorbance at 254 nm and THMFP.

RESULTS AND DISCUSSION

Whole Water

The NAWQA and Delta whole water samples show well-defined linear relations between DOC concentration and UV (fig. 1). In order to compare the two datasets, we focus on data with UV absorbance of less than 0.4 (in units of per cm), which includes all of the NAWQA samples, and all of the Sacramento and San Joaquin River samples as well as many Twitchell Island surface water samples in the Delta sample set. Linear regressions indicate both the NAWQA and Delta whole water samples form well-defined lines, as indicated by high coefficients of determination (r^2) values of 0.71 and 0.91 respectively (table 1). However, the two linear regressions yielded statistically distinct lines (t-test of difference between two slopes, $\alpha = 0.05$, P
< 0.001; Zar, 1984) for the two sets of data. The Delta samples lie on a line with shallower slope than the NAWQA samples, indicating presence of DOC with higher UV absorbance. This result is consistent with the presence of a greater proportion of peat-derived DOC in the Delta samples than in the NAWQA samples. DOC derived from reducing environments such as peat soils, generally contains a high proportion of phenolic structures (Fujii and others, 1998), and aromatic structures, including phenols, absorb UV light (Rao, 1975).

The utility of a linear regression between two water-quality variables, such as DOC and UV absorbance, to the development of water-treatment strategies, depends on how accurate a prediction of the independent variable the regression equation gives. This accuracy can be expressed as the prediction interval for the independent variable at the given confidence level ($\alpha = 0.05$ in this report). The prediction interval for the NAWQA regression is ±2.67 milligrams per liter (mg/L) DOC, whereas the prediction interval for the Delta regression is only ±1.46 mg/L DOC (table 1). All of the Delta samples lie within the prediction interval for the NAWQA samples, but the inverse is not true. Rathbun (1996) used the average percentage difference between measured and predicted values of the independent variable to assess the accuracy of prediction. Percentage difference for the Delta regression is much smaller than that for the NAWQA regression (table 1), which is in agreement with the lower prediction interval determined for the Delta regression. The larger scatter in the NAWQA data may be because that dataset includes a "national average" of watersheds. Each watershed type may have a different relation between DOC and UV absorbance, so that a national sampling represents the sum of many individual relations.

Both datasets also show linear relations between molar THMFP and UV absorbance, although the data are considerably more scattered for samples with UV less than 0.4 cm^{-1} (fig. 2). Again comparing data with UV absorbance less than 0.4 cm^{-1}, the slopes of the two regressions are significantly different (t-test of difference between two slopes, $\alpha = 0.05$, P < 0.001; Zar, 1984). The Delta samples lie on a line with shallower slope than the NAWQA samples, indicating that the excess aromatic carbon in the Delta samples is relatively unreactive with respect to THM formation during chlorination. The prediction interval is ±1.71 micromoles per liter (μmol/L) for the NAWQA samples and ±1.83 μmol/L the Delta samples, and the percentage differences are large for both (table 1), suggesting that UV absorbance alone is not a highly accurate predictor of THMFP.

Specific properties

Delta samples

In order to examine the effect of carbon composition, we use the following carbon-normalized parameters: specific trihalomethane formation potential (STHMFP), defined as millimoles (mmol) of

THM formed per mole (mol) of DOC, and specific UV absorbance (SUVA), defined as the UV absorbance divided by the DOC concentration (the units of SUVA are liters per milligram per centimeter, L/mg/cm). In the Delta samples, STHMFP ranged from 2 to 16 mmol/mol, and SUVA ranged from 0.01 to 0.09 L/mg/cm (fig. 3), indicating large variability in the reactivity and composition of the DOC. Although SUVA and STHMFP for the full range of whole water from the Delta region generally were positively correlated (fig. 3), the relation between the two parameters was not well defined, as evidenced by the very large prediction interval (STHMFP predicted to only ± 4.3 mmol/mol for a given SUVA) and small coefficient of determination ($r^2 = 0.07$) for the linear regression (table 1). The Delta results indicate that the connection between STHMFP and DOC composition is not directly related to properties measured by SUVA.

STHMFP and SUVA for water from the Sacramento and San Joaquin Rivers did show a meaningful linear relation (fig. 3) (prediction interval of ± 1.93 mmol/mol and coefficient of determination, $r^2 = 0.80$). The linear regression of STHMFP and SUVA data for the Sacramento and San Joaquin River samples yielded a percentage difference of 8.2 percent, the lowest percentage difference in the dataset, and quite comparable with percentage difference observed for samples from the Mississippi River system by Rathbun (1996). A large river system may average DOC from its entire watershed, thus obscuring the signal from DOC derived from specific sources, such as wetlands. Thus, a linear relation between STHMFP and SUVA may be an accurate enough method for predicting STHMFP for some water systems – but only for systems in which the temporal and spatial variation in DOC composition is very small because of extensive mixing of large amounts of water. However, there is no reason to expect that all such systems will show the same relation betweeen STHMFP and SUVA. Several types of organic structures that are likely to be present in the DOC pool are capable of absorbing UV light, including aromatic rings and conjugated dienes and carbonyls (Rao, 1975). Experiments on model compounds indicate high yields of THM can be produced by chlorination of aromatic structures, such as phenolic compounds, as well as nonaromatic structures, such as enolizable β-di-ketones (Larson and Weber, 1994). Not all of these nonaromatic structures are capable of absorbing UV light (Rao, 1975). No two water systems have exactly the same sources of DOC, therefore, one would expect DOC from every water system to contain a unique combination of molecular structures and thus, to have a different relation between STHMFP and SUVA.

Comparison of water samples taken from different soils and locations suggests that the lack of correlation between DOC aromaticity (as estimated by SUVA) and STHMFP may be due to the presence of an unreactive aromatic fraction in the DOC derived from peat soils. DOC derived from all of the Twitchell Island drainage and soil water samples contained more aromatic carbon than DOC derived from Sacramento and San Joaquin main stem river water samples, as indicated by the markedly higher SUVA values (t-test of differences between two means, α = 0.05, P < 0.001; Zar, 1984) (fig. 3). This result was expected, given the abundance of peat soils on Twitchell Island. Although the highest STHMFP values were measured in some Twitchell Island samples, many of the Twitchell samples have STHMFP values between 6 - 12 mmol/mol, which is indistinguishable from most of the main stem river samples (fig. 3). The mean STHMFP value for the Twitchell Island samples is statistically the same as the mean STHMFP value for the Sacramento and San Joaquin River samples (t-test of differences between two means, α = 0.05; Zar, 1984). The observation that SUVA values for the Twitchell Island samples are higher than those in the River samples, but STHMFP values are the same, suggests that some of the aromatic carbon derived from the peat soils must be unreactive.

NAWQA samples

The NAWQA whole water and fractionated samples have STHMFP values ranging from 3.9 to 16.5 mmol THM/mol DOC and SUVA values ranging from 0.007 to 0.052 L/mg/cm (fig. 4). Although STHMFP and SUVA were positively correlated (fig. 4), there was no well-defined relation as evidenced by the small coefficient of determination ($r^2 = 0.39$) and large prediction interval (± 6.4 mmol THM/mol

DOC) for the linear regression (table 1). Separation of the whole water, effluent, and eluate samples did not yield linear regressions with statistically different slopes or intercepts (t-test of difference between two slopes and two intercepts, $\alpha = 0.05$; Zar, 1984). These results indicate that the connection between STHMFP and DOC composition is not directly related to properties measured by SUVA – just as concluded from the Delta results.

DOC in the whole water, effluent, and eluate subsamples of the NAWQA samples did vary in composition. Mean SUVA and STHMFP for the effluent samples (mean = 0.025 units/mg/L, standard deviation, s = 0.010; and 6.87 mmol/mol, s = 2.19, respectively) are lower than values for the eluate samples (0.035 units/mg/L, s = 0.006; and 9.22 mmol/mol, s = 2.33, respectively) (t-test of difference between two means, a = 0.05, P < 0.001; Zar, 1984). This difference indicates that the fraction of the DOC retained by the XAD-8 resin contained slightly more aromatic carbon and was slightly more likely to form THM than the unretained fraction. However, mean SUVA and STHMFP values for the whole water and eluates, and mean STHMFP for whole water and effluents cannot be distinguished statistically (t-test of difference between two means, a = 0.05; Zar, 1984). The XAD-8 resin retained 30-75 percent of the DOC in the NAWQA whole water samples, and the eluates accounted for 20-80 percent (mean 56 percent, s = 13 percent) of the total THMFP of the whole water sample. These results suggest that the compositional properties determining retention on XAD-8 resin are only very weakly related to the compositional properties determining reactivity to form THM. The connection between the efficiency of DOC removal from water and the reactivity of the DOC removed has implications for the design of water-treatment strategies. Tests of various coagulation, flocculation, sedimentation, filtration, and adsorption methods in operating water-treatment plants and in bench-scale studies have shown that the amount of DOC removed and the amout of THM precursor carbon removed are not necessarily correlated (Lykins and Clark, 1989).

DOC isolates

DOC from a subset of the Delta samples was isolated and analyzed by ^{13}C-NMR to determine its chemical composition and aromatic carbon content. Although the isolation technique extracted only 40-80 percent of the total DOC in these samples, isolation permits analysis and direct comparison of DOC chemical composition and STHMFP. For the isolates, STHMFP ranged from 5 to 9 mmol/mol, and the percentage of aromatic carbon from 11 to 25 percent (fig. 5). The percentage of aromatic carbon and STHMFP do not show a significant relation (fig. 5) (linear regression $r^2 = 0.09$), indicating that aromatic carbon content alone does not determine the extent of THM formation.

Further evidence that aromatic carbon content does not determine THMFP is apparent when comparing XAD-8 and XAD-4 isolates. XAD-4 isolates contain only 52-82 percent of the aromatic carbon in the corresponding XAD-8 isolates (fig. 5), and should have distinctively lower STHMFP if aromatic carbon content alone determines STHMFP. However, the mean STHMFP of the XAD-4 isolates (6.48 mmol/mol; s = 1.6 mmol/mol) was 87 percent of the mean STHMFP of the XAD-8 isolates (7.43 mmol/mol; s = 1.9 mmol/mol), and the two populations were significantly different only at less than the 85 percent confidence level (t-test of difference between two means; Zar, 1984) (fig. 5). Thus, either nonaromatic carbon in the XAD-4 isolates was reactive, or some of the aromatic carbon in the XAD-8 isolates was unreactive. Since SUVA is used as a surrogate measurement of DOC aromaticity (Traina and others, 1990; Chin and others, 1994), the presence of reactive nonaromatic carbon or unreactive aromatic carbon would result in poor correlation between SUVA and STHMFP as observed in the NAWQA and Delta whole water samples.

CONCLUSIONS

1. SUVA and STHMFP in water from the NAWQA sampling and the Delta sampling are not tightly correlated, indicating that SUVA cannot be used for accurate prediction of THMFP in drinking water

derived from a broad spectrum of watershed types, and that DOC derived from different environments, such as wetlands, within the watershed has distinct composition and reactivity. However, the results from the Sacramento and San Joaquin River samples suggest that it may be possible to establish the relation between SUVA and STHMFP for specific systems.

2. STHMFP is not related to the aromatic carbon content of DOC isolates from Delta water, providing a compositional basis for the lack of correlation between SUVA and STHMFP.

3. Carbon released from Delta peat islands may contain a significant fraction of aromatic material that does not form THM upon chlorination.

4. Retention of DOC by XAD-8 resin is weakly associated with reactivity of DOC to form THM, suggesting that water treatment techniques for DOC reduction may not necessarily achieve commensurate THMFP reduction in drinking water.

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Table 1. Results of linear regressions of data for ultraviolet absorbance, dissolved organic carbon concentration, trihalomethane formation potential, specific ultraviolet absorbance, and specific trihalomethane formation potential for samples from the Sacramento-San Joaquin Delta, and the Sacramento and San Joaquin Rivers, California and from a national sampling of watersheds by the National Water Quality Assessment Program

[Equations for slope, intercept, coefficient of determination (r^2), and confidence interval for prediction of Y values at $\alpha = 0.05$ are from Zar (1984). Equation for percentage difference between measured and predicted Y values is from Rathbun (1996). Fig., figure in which data appears; NAWQA, samples national sampling of watersheds by the National Water Quality Assessment Program; Delta UV<0.4, samples from the Sacramento-San Joaquin Delta and Rivers with ultraviolet absorbance less than 0.4 cm^{-1}; Rivers, Sacramento and San Joaquin Rivers, UV; ultraviolet absorbance; DOC, dissolved organic carbon; THMFP, trihalomethane formation potential; SUVA, specific ultraviolet absorbance; STHMFP, specific trihalomethane formation potential; mg/L, milligrams per liter; µmol/L; micromoles per liter; mmol/mol, millimoles per mole]

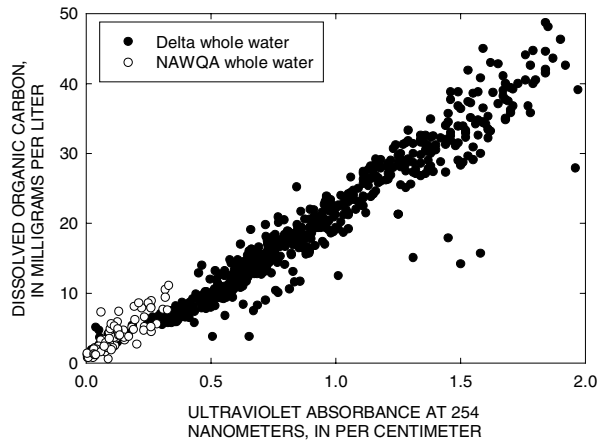| fig.	Data set	X	Y	Slope	Intercept	r^2	Percentage difference	Prediction interval
1	NAWQA	UV	DOC	24.1	1.04	0.71	31.5	2.66 mg/L
1	Delta, UV<0.4	UV	DOC	15.1	1.59	.91	13.5	1.46 mg/L
2	NAWQA	UV	THMFP	20.0	- .01	.83	21.8	1.71 µmol/L
2	Delta, UV<0.4	UV	THMFP	12.4	1.04	.73	31.5	1.83 µmol/L
3	Delta	SUVA	STHMFP	27.4	8.65	.07	11.0	4.27 mmol/mol
3	Rivers only	SUVA	STHMFP	24.9	.33	.80	8.2	1.93 mmol/mol

Figure 1. Relation between ultraviolet light absorbance at 254 nanometers and dissolved organic carbon content for whole water samples from the Sacramento-San Joaquin Delta, California and from a national sampling of watersheds the National Water Quality Assessment Program. UV absorbance measured in a 1-cm path length cell.
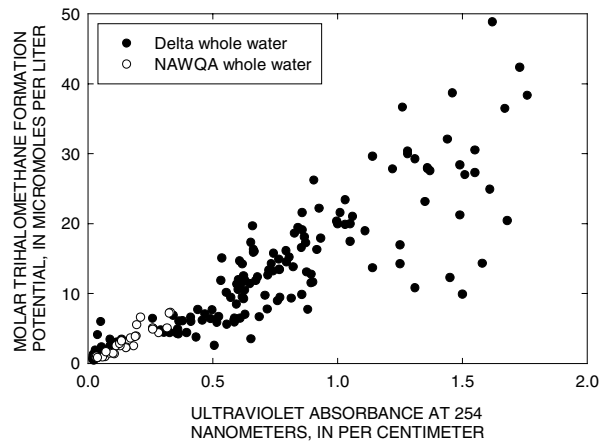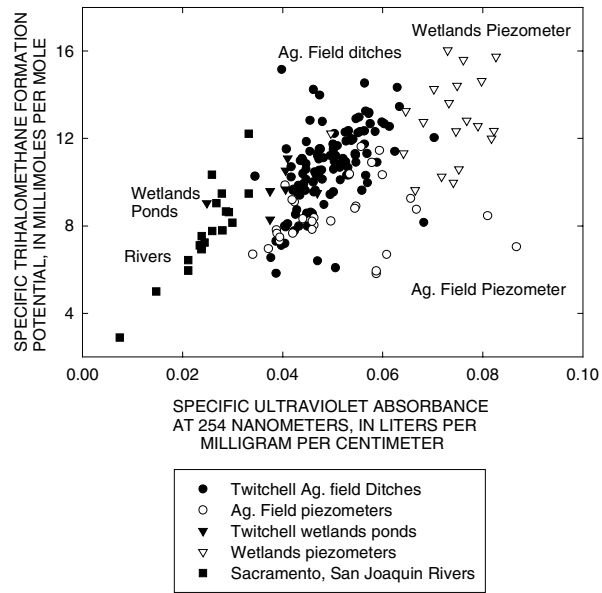

Figure 2. Relation between ultraviolet light absorbance at 254 nanometers and molar trihalomethane formation potential for whole water samples from the Sacramento-San Joaquin Delta, California and from a national sampling of watersheds the National Water Quality Assessment Program.

Figure 3. Relation between specific trihalomethane formation potential and specific ultraviolet light absorbance at 254 nanometers for whole water samples from the Sacramento-San Joaquin Delta, California the National Water Quality Assessment Program.
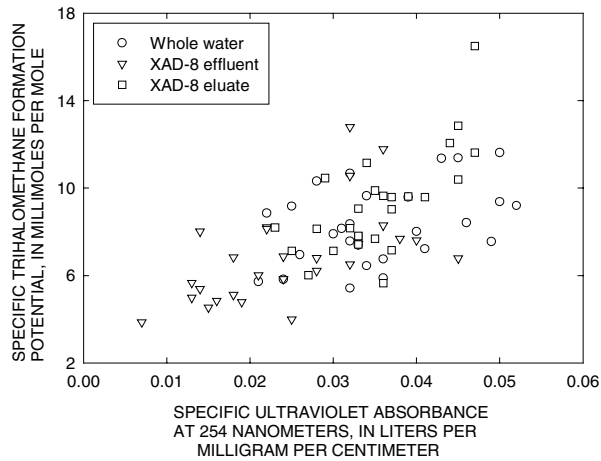
Figure 4. Relation between specific trihalomethane formation potential and specific ultraviolet light absorbance at 254 nanometers for whole water samples, XAD-8 effluents. and XAD-8 eluates from a national sampling of watersheds the National Water Quality Assessment Program.
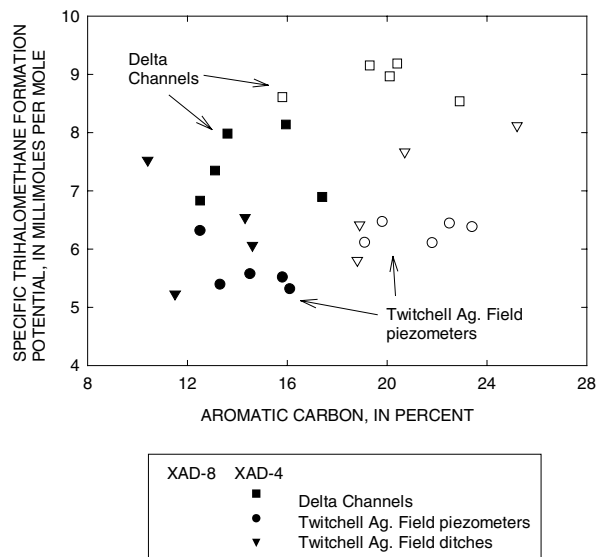

Figure 5.   Relation between specific trihalomethane formation potential and percentage of aromatic carbon for XAD-8 and XAD-4 dissolved organic carbon isolates from water samples from the Sacramento-San Joaquin Delta, California. Percentage of aromatic carbon measure by carbon-13 nuclear magnetic resonance spectroscopy.