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HOW DOC COMPOSITION MAY EXPLAIN THE POOR CORRELATION BETWEEN SPECIFIC TRIHALOMETHANE FORMATION POTENTIAL AND UV ABSORBANCE IN WATERS FROM THE SACRAMENTO-SAN JOAQUIN DELTA, CALIFORNIA, USA

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Dissolved organic carbon (DOC) in natural waters reacts to form trihalomethanes (THM) and other disinfection by-products when natural waters are 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 waters for the purpose of predicting THM formation (e.g. refs. 1, 2). In this study, we critically examine the relationship between UV absorbance, aromaticity and THM formation potential in natural waters from the Sacramento-San Joaquin Delta (Delta) to better understand the compositional nature of THM precursor material. New U.S. Environmental Protection Agency regulations to take effect during the next several years will mandate the use of treatment strategies designed to lower DOC concentrations in order to reduce THM concentrations in treated drinking water. Consequently, a full understanding of the relationship between THM formation potential and compositional nature of the DOC is essential.

The DOC present in Delta waters 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 different soil types on Twitchell Island. Over 600 samples collected over a 3 year period were analyzed for DOC concentration, UV absorbance at 254 nm, and trihalomethane formation potential (THMFP) (ref. 3). UV absorbance at 254 nm is a standard proxy for aromatic carbon content, and along with DOC, is under consideration as a THMFP surrogate measurement to indicate when additional water treatment strategies are required. To provide material for further chemical analysis, DOC was isolated from selected water samples collected from the Twitchell Island drainage ditches and piezometers, and from the main flow channels through the Delta. DOC was fractionated and isolated 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 material (ref. 4). Reconstituted isolates were analyzed for DOC concentration, UV absorbance, and THMFP.

For the large number of whole water samples within this study, there was a correlation between DOC concentration and UV absorbance ($r^2 = 0.92$; Figure 1), and between UV absorbance and THMFP ($r^2 = 0.89$; Figure 2). However, these correlations do not speak to the relationship between composition and reactivity of the DOC. In order to look at the effect of carbon composition, we use the following carbon-normalized parameters: specific trihalomethane formation potential (STHMFP), defined as millimoles of THM formed per mole of DOC, and specific UV absorbance (SUVA) defined as absorbance per mole of DOC. STHMFP varied from 2 to 16 %, and SUVA varied from 0.1 to 1.1 units (Figure 3), indicating large differences in the reactivity and composition of the DOC. Moreover, there was no significant correlation ($r^2 = 0.35$) found between SUVA and STHMFP for the full range of waters from the Delta region (Figure 3). However, whole water samples from the Sacramento and San Joaquin Rivers do show a linear correlation ($r^2 = 0.80$) between STHMFP and SUVA (Figure 3), consistent with results for other

large river systems (e.g. ref. 5). Large river systems may swamp out the signal from DOC derived from specific sources, such as wetlands. The Delta results indicate that the connection between STHMFP and DOC composition is not directly related to properties measured by SUVA.

DOC from a subset of the Delta samples was isolated and analyzed by ^{13}C -CP/MAS-NMR to determine their chemical composition and aromatic carbon content. Although the isolation technique extracts only 40-80% of the total DOC, isolation permits analysis and direct comparison of DOC chemical composition and STHMFP. STHMFP for the isolates ranged from 5 to 9 mmol/mol, and the percentage of aromatic carbon from 11 to 25% (Figure 4). STHMFP and percentage of aromatic carbon were not found to be significantly correlated ($r^2 = 0.09$; Figure 4), 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% of the aromatic carbon in the corresponding XAD-8 isolates (Figure 4), and should have distinctively lower STHMFP if aromatic carbon content alone determines STHMFP. However, the mean STHMFP of the XAD-4 isolates (6.4 mmol/mol; $\sigma = 1.0$) was 87% of the mean STHMFP of the XAD-8 isolates (7.43 mmol/mol; $\sigma = 1.3$), and the two means were not significantly different (Figure 4). Either non-aromatic carbon in the XAD-4 isolates was reactive, or some of the aromatic carbon in the XAD-8 isolates was non-reactive. Because SUVA is used as a surrogate measurement of DOC aromaticity, this result also explains the lack of correlation between SUVA and STHMFP observed for the whole water samples.

Comparison of samples taken in different soils and locations suggests the lack of correlation between DOC aromaticity and STHMFP may be due to the presence of an unreactive aromatic fraction within DOC derived from peat soils. Waters from piezometers installed in an organic mineral soil (10-15% organic matter) in an experimental wetland have higher STHMFP, but similar SUVA to waters from piezometers in a peat soil (40-80% organic matter) in an agricultural field (Figure 3). This result requires that either the wetlands contribute highly reactive, non-aromatic carbon (ref. 6), or the peat soils contribute non-reactive, aromatic carbon to the soil waters. DOC derived from all of the Twitchell drainage and soil waters contained more aromatic carbon than the main stem river waters (Figure 3) as expected, given the abundance of peat soils on Twitchell Island. Although the highest STHMFP values were found in some Twitchell samples, many of the Twitchell samples have STHMFP values between 6 and 12 mmol/mol, indistinguishable from the main stem river samples (Figure 3), indicating that some of the aromatic carbon derived from the peat soils must be non-reactive.

Conclusions

1. Specific UV absorbance and specific THMFP do not correlate on a regional scale within the Delta and tributaries, suggesting that SUVA may not be useful for the prediction of THMFP in Delta-derived drinking waters.
2. Specific THM formation potential is not correlated with aromaticity of DOC isolates from the full range of natural waters in the Delta region, 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.

References Cited

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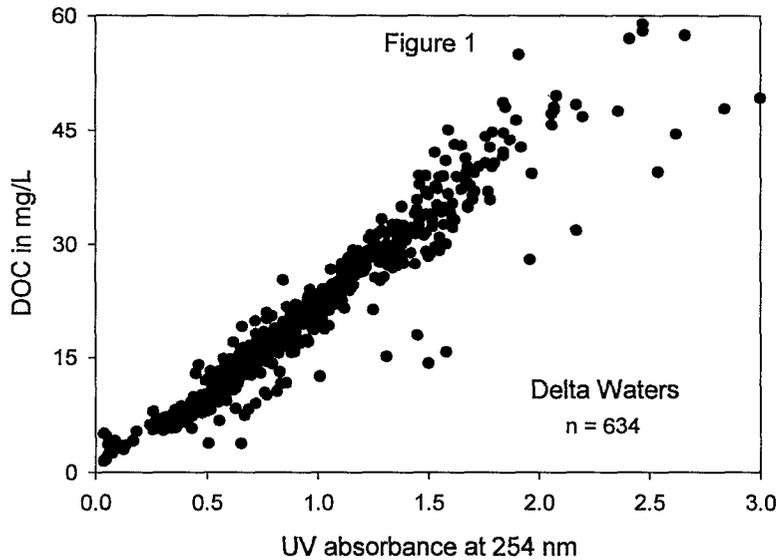


Figure 1. UV absorbance at 254 nm versus DOC content in mg/L for whole water samples from the Sacramento-San Joaquin Delta. UV absorbance measured in 1 cm path length cell.

Figure 2. UV absorbance at 254 nm versus molar trihalomethane formation potential (THMFP) in $\mu\text{Mol/L}$ for whole water samples from the Sacramento-San Joaquin Delta.

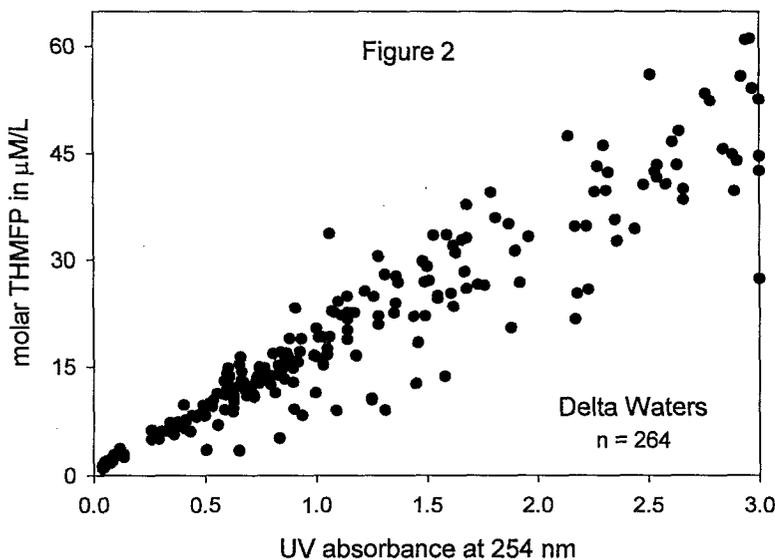




Figure 3. Specific trihalomethane formation potential (STHMFP) in units of mmol THM per mol C (‰) versus specific UV absorbance at 254 nm (SUVA) in units of absorbance per mol C for whole water samples from the Sacramento-San Joaquin Delta.

Figure 4. Specific trihalomethane formation potential (STHMFP) in units of mmol THM per mol C (‰) versus percent aromatic carbon as measured by ^{13}C -CPMAS-NMR for XAD-8 and XAD-4 isolates from Delta waters.

