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## The Reactivity of Dissolved Organic Matter for Disinfection By-Product Formation

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### Abstract

Dissolved organic matter (DOM) in 6 water samples collected from 4 surface waters were fractionated using some or all of 5 physicochemical separation processes (activated carbon and XAD-8 batch adsorption, alum coagulation, ultrafiltration (UF), and XAD-8 column fractionation). Activated carbon, XAD-8 batch adsorption and alum coagulation processes fractionated DOM by preferentially removing high-SUVA components from solution. The XAD-8 column method fractionated DOM into hydrophobic and hydrophilic components while UF separated DOM into different size fractions. Over 40 DOM fractions, characterized using carbon-normalized (specific) ultraviolet absorbance (SUVA), were obtained for each water. Trihalomethane (THM) and haloacetic acid (HAA<sub>9</sub>) formation after chlorination was quantified for each fraction. For each natural water, a strong correlation was observed between the SUVA values of DOM fractions and their THM and HAA<sub>9</sub> formations, *independent of the separation processes* used to obtain the fractions. Therefore, the correlation obtained for each water appears to represent its *natural disinfection by-product (DBP) reactivity profile*. However, SUVA is not a universal predictor of DOM reactivity because a unique DBP reactivity profile was obtained for each water tested. The distribution of SUVA within a source water and its relationship to reactivity were found to be more informative than the source water aggregate SUVA value. Individual DBP species also correlated well with the SUVA of DOM fractions in a single water. Formation of trichloroacetic acid (TCAA) was dominant over dichloroacetic acid (DCAA) for high-SUVA fractions, whereas the formation of TCAA and DCAA was comparable for low-SUVA fractions.

**Key words:** Natural organic matter (NOM), Chlorine, disinfection by-products (DBPs), Activated carbon, Coagulation, specific ultraviolet absorbance (SUVA), XAD-8, Fractionation.

### Introduction

One of the primary challenges faced by the drinking water treatment industry today is the formation of suspected carcinogenic disinfection by-products (DBPs), which occurs as a result of reactions between dissolved organic matter (i.e. DOM, the com-

ponents of natural organic matter passing through a 0.45- $\mu$ m filter) and oxidants/disinfectants such as chlorine. DOM is a heterogeneous mixture of various complex organic materials ranging from macromolecular humic substances to small molecular weight hydrophilic acids and various hydrocarbons (Thurman,

1985). Central to understanding how to control DBPs is a knowledge of the abundance and structure of DOM components and how they relate to reactivity.

Isolation of DOM from natural waters and subsequent fractionation into more homogeneous components facilitates characterization and reactivity studies. One commonly used method is resin adsorption chromatography (RAC), employing various synthetic resins (Leenheer, 1981; Malcolm, 1991). DOM fractions obtained from this method have been characterized using a range of proximate (e.g., elemental analysis) and spectroscopic techniques (e.g., pyrolysis GC/MS,  $^{13}\text{C}$ -NMR, and IR/FTIR). Characteristics of DOM determined using these techniques have been correlated with the formation of DBPs with varying degrees of success (Reckhow *et al.*, 1990; Bezbarua and Reckhow, 1997; Korshin *et al.*, 1997; Wu, 1998; Rostad *et al.*, 2000; Wu *et al.*, 2000). Although these techniques provide insight into the composition of DOM, they are only semi-quantitative, require large quantities of DOM for analysis, and are not practical for use by treatment plant personnel.

Another approach to probe the reactivity of DOM is the fractionation of a bulk source water using physicochemical separation processes commonly employed in drinking water treatment operations (e.g., coagulation/flocculation, granular activated carbon (GAC) adsorption, or membrane processes). The mixture of DOM components remaining in solution after treatment with a particular separation process is referred to as a *bulk water DOM fraction*. Physicochemically distinct DOM fractions can be obtained after treating a source water with different treatment processes or with a single treatment process using different operational conditions (e.g., coagulant dose). This approach has advantages over isolation and fractionation techniques, but also has inherent limitations. An important advantage is that the experimental protocol is simple. Another advantage in contrast with RAC is that the chemical integrity of the water sample is preserved, and changes in composition are minimal (e.g., DOM concentration never exceeds that of the source water, and DOM is not exposed to pH swings). Bulk water fractionation is done in the presence of original background inorganic matrix, which can provide practical information about the reactivity of a given source water. Bulk water fractionation does not require the recovery of adsorbed DOM, which is the

step that usually involves exposing DOM to large pH changes in the RAC method. This, however, poses a limitation - the fraction amenable to removal from solution is not isolated and studied directly. Furthermore, fractionation reduces the concentration of organic carbon remaining in solution, which limits characterization of DOM composition to measures that exhibit high sensitivity. One such parameter is specific ultraviolet absorbance ( $\text{SUVA}_\lambda = \text{UV}_\lambda / \text{DOC}$ , where  $\lambda$  is a specified wavelength).

UV absorbance of DOM solutions in the range 254-280 nm reflects the presence of unsaturated double bonds and  $\pi$ - $\pi$  electron interactions such as those found in aromatic compounds (Traina *et al.*, 1990). Therefore, by combining both DOC and UV absorbance into a single parameter, SUVA provides a measure of the aromatic content within DOM. SUVA can be determined quickly using a small volume of sample, does not require extensive sample pretreatment and requires readily available instrumentation that is straightforward to operate. These features have made SUVA an attractive way to characterize DOM, as reflected by its more frequent use over the past decade. Among all the different parameters available to characterize DOM, UV absorbance and SUVA have often correlated well with DBP formation (Edzwald *et al.*, 1985; Krasner *et al.*, 1989; Singer and Chang, 1989; Reckhow *et al.*, 1990; Najm *et al.*, 1994; Korshin *et al.*, 1997; Croue *et al.*, 2000).

The results from RAC and treatability or treatment plant studies, in general, indicated that THM and more recently HAA formation increase with UV or SUVA. The impact of different fractionation techniques (e.g., RAC vs. bulk water fractionation) on DBP correlations has not been investigated. Furthermore, the robustness of SUVA for prediction of DBP formation in a single batch of water has not been examined in detail. Finally, most of the DBP formation data were collected under *formation potential* rather than *uniform formation conditions* (UFC), which was developed in 1996 to represent average conditions in the US distribution systems (Summers *et al.*, 1996).

In our previous research, we examined uptake and fractionation of DOM in isolates and natural waters by GAC adsorption (Karanfil *et al.*, 2000; Kitis *et al.*, 2001a). Several wood- and coal-based GACs with significantly different pore size distributions and surface chemical properties were used. Several bulk water DOM fractions with a wide range of SUVA values were obtained for each surface wa-

ter examined, indicating that a relatively continuous *SUVA distribution* exists in natural waters. It was also found that the DBP reactivity of DOM fractions (i.e. THM and HAA<sub>9</sub> yields) closely correlates with SUVA; the reactivity for all the fractions obtained from a single water fell on a single correlation *independent of* the carbon type used to fractionate the DOM solution. Since strong correlations and unique patterns were observed for each natural water tested, it was hypothesized that *the SUVA distribution of a natural water represents an important characteristic of DOM components controlling the DBP formation. Each source water has an intrinsic “DBP reactivity profile” that is a function of its SUVA distribution, and that can be obtained by using physicochemical bulk water fractionation processes.* If this hypothesis is valid, then a single reactivity profile as a function of SUVA should be obtained independent of how the DOM fractions are obtained from a water sample.

The main objective of the work presented in this paper was to test this hypothesis by conducting 1) additional bulk water DOM fractionation experiments using batch-mode XAD-8 resin adsorption for the same water samples that were employed in our previous work (Kitis *et al.*, 2001a); and 2) new fractionation experiments using 2 new water samples where each water was fractionated using batch-mode activated carbon and XAD-8 adsorption, alum coagulation, ultrafiltration (UF) and RAC fractionation methods. 40–100 DOM fractions with different SUVA values were obtained from each water source. The fractions were chlorinated according

to UFC conditions, and correlations between DBP (both THM and HAA<sub>9</sub>) formation and SUVA were developed for each water separately. Therefore, it was possible to evaluate the validity of the DBP reactivity profile concept hypothesized above, the impact of different fractionation processes on the DBP correlations, and the robustness of SUVA to predict the DBP formation in a water sample.

Since different DOM fractions have been shown to exhibit different reactivities, the role of SUVA in DBP speciation was also evaluated. In addition, some of the bulk water fractionation techniques used in this study are well-suited for studying hydrophilic components of DOM. These components remain in solution after aggressive treatment conditions (e.g., high GAC, XAD-8 or alum doses). Although hydrophilic components generally do not absorb UV light in appreciable amounts, they have shown appreciable reactivity for DBP formation in some natural waters (Owen *et al.*, 1993; Korshin *et al.*, 1997).

## Materials and Methods

### Source waters

4 surface water sources, with a wide range of physicochemical properties, were used in this study (Table 1): the influents of Charleston (CH) (Edisto River) and Myrtle Beach (MB) (Inter-coastal Waterway) drinking water treatment plants in South Carolina, Tomhannock (TM) reservoir, the water supply for the city of Troy, and a stream draining a rural agricultural watershed in Rensselaer (RS) County in

**Table 1.** Selected compositional characteristics of the natural source waters<sup>a</sup>.

Parameter	Unit	CH	MB-A <sup>b</sup>	MB-B	TM-A <sup>b</sup>	TM-B	RS
DOC	(mg-C/l)	3.9	14.1	20.2	2.8	3.3	4.9
UV <sub>280</sub> <sup>c</sup> (absorptivity coefficient)	(cm <sup>-1</sup> )	0.124	0.421	0.707	0.053	0.048	0.114
SUVA <sub>280</sub> <sup>c</sup>	(l/mg-m)	3.20	3.01	3.51	1.89	1.45	2.34
Total Alkalinity	(mg CaCO <sub>3</sub> /l)	66	94	44	35	39	69
Total Hardness	(mg CaCO <sub>3</sub> /l)	27	40	26	76	54	77
pH	-	7.8	7.8	7.2	7.2	7.0	7.4
Bromide	(μg/l)	85	63	43	<25 <sup>d</sup>	<25	<25

<sup>a</sup>Values reported are the average of triplicate measurements.

<sup>b</sup>2 different batches are represented by A and B.

<sup>c</sup>A wavelength of 280 nm was selected for UV measurements to minimize the interference from sodium azide that was added (100 mg/l) to CH, MB-A, TM-A, and RS samples after collection to control biological activity. No sodium azide was added to MB-B and TM-B samples.

<sup>d</sup> Minimum reporting level was 25 μg/l.

New York. CH, MB-A, TM-A and RS samples were available from our previous work (Kitis *et al.*, 2001a). 2 new batches (represented as MB-B and TM-B) were collected from MB and TM waters for this study. For these new batches, a field-scale reverse osmosis (RO) system was used to isolate and concentrate DOM in order to facilitate subsequent fractionation experiments in the laboratory. Concentrated RO isolates were used as feed to the RAC and UF fractionation processes, whereas filtered (0.45- $\mu\text{m}$ ) raw water samples were used directly in coagulation and batch-mode GAC and XAD-8 adsorption experiments. In our previous work, mass balance calculations and subsequent reactivity experiments showed that over 95% of the DOM was recovered from each source with no impact on its original DBP reactivity during RO isolation (Kitis *et al.*, 2001b).

### DOM fractionation experiments

For bulk water fractionation of DOM, variable-dose bottle-point isotherms were conducted in completely-mixed batch reactors (CMBRs) using GAC and XAD-8 resin under oxic conditions. GAC or resin doses (generally 0.02-2.0 g GAC/l and 0.01-10 g XAD-8/l) were chosen to yield a nearly continuous fractionation (based on SUVA) while ensuring that changes in DOC and UV absorbance were sufficiently large for accurate quantification. CMBRs were kept well-mixed on a rotary tumbler for a period of 4 weeks (GAC) or 2 days (XAD-8 resin). All isotherms were conducted at room temperature ( $21 \pm 2$  °C). GAC isotherms were conducted without pH adjustment or buffer addition, while the solution pH was decreased to 2.5 in XAD-8 experiments to increase the uptake of DOM by the resin. After equilibration, the DOM solution remaining in each bottle (i.e. the DOM fraction) was separated from the adsorbent by filtration (0.7- $\mu\text{m}$ ) and analyzed for DOC concentration and pH. The pH of each fraction was then adjusted to the pH of the source water by buffering with phosphate (0.01 M). Buffering provided a constant pH for both subsequent UV absorbance measurements and chlorination experiments.

For fractionation with coagulation, jar tests were conducted using about 15 to 20 doses of alum ( $\text{Al}_2(\text{SO}_4)_3 \cdot 16\text{H}_2\text{O}$ ) (ranging from 0 to 0.5 g/l as alum). The jar test procedure included rapid mixing at 200 rpm for 1 min, flocculation at 35 rpm for 15 min, and quiescent settling for 1.5 h. Jar tests were performed at room temperature of  $21 \pm 2$  °C.

Solution pH was maintained between 5.5 and 6.0 by dosing with NaOH and/or HCl. After settling, DOM fractions were filtered with a 0.7- $\mu\text{m}$  filter prior to analysis for DOC concentration and pH. As with the adsorption experiments, the pH of the fractions was adjusted to the pH of the source water with 0.01 M phosphate buffer before UV absorbance measurements and chlorination experiments.

XAD-8 resin was employed in the RAC method to fractionate DOM into hydrophobic (HPO) and hydrophilic (HPL) fractions. The fraction adsorbed by the resin and subsequently back-eluted from the column using a pH 11 solution is designated HPO, while the fractions collected from the effluent of the column are designated HPL. Column eluant was sampled at different elution volumes to investigate the reactivities of different HPL fractions. After fractionation, both HPO and HPL fractions were stored as aqueous solutions with pH values adjusted to that of the source water (e.g., neutral range). The DOM fractions obtained from the batch- and column-mode XAD-8 resin adsorption are referred to as XAD-8 batch and XAD-8 column, respectively, throughout this paper.

Using a bench-scale hollow-fiber, cross-flow ultrafiltration system (A/G Technology Corporation, Needham, MA, USA), DOM in the MB-B sample was separated into 7 molecular weight (MW) fractions (<1, 1-3, 3-5, 5-10, 10-30, 30-100, and >100 kDa). Only the 3 smallest fractions and a >5 kDa fraction were generated for the TM-B sample because >5 kDa constituted only 11% of the total DOC. All DOM fractions obtained from all fractionation processes were stored as aqueous solutions in a refrigerator at 4 °C in the dark.

### Chlorination experiments

After calculating their SUVA, all the fractions and source waters were chlorinated according to the UFC protocol at  $\text{pH } 8 \pm 0.3$  (Summers *et al.*, 1996) with a minor change (i.e. phosphate instead of borate buffer was used). Each source water and its fractions were chlorinated at a constant  $\text{Cl}_2/\text{DOC}$  (mg as free chlorine/mg DOC) ratio, which provided a chlorine residual of  $1.0 \pm 0.4$  mg/l after 24-h contact time, ensuring that reactions were not chlorine limited. The  $\text{Cl}_2/\text{DOC}$  ratio, as determined by preliminary chlorination experiments, ranged from 2.5 to 5 for the surface waters tested in this study. These ratios are higher than the range (i.e. 1.2 to 1.8) reported for UFC conditions by Summers *et al.* (1996).

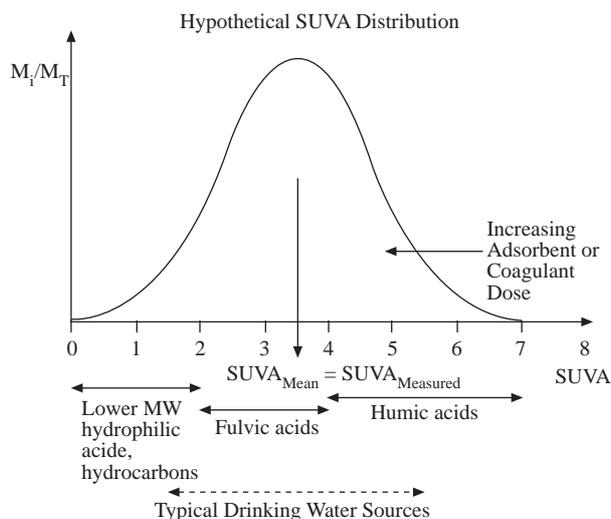
Experiments have shown that the higher ratios were partly due to chlorine demand created by sodium azide added to the CH, MB-A, TM-A and RS samples at the time of collection to promote biological stability. Therefore, sodium azide was not added to MB-B or TM-B samples. The DOM fractions of the MB-B and TM-B waters required  $\text{Cl}_2/\text{DOC}$  ratios of 2.5 and 4.5, respectively, for UFC experiments. The high ratio observed for the TM-B sample was attributed to an algal bloom at this source during the time of collection while the ratio for MB-B is likely a consequence of the hydrophobic nature of DOM in this source. The chlorinated samples were incubated at  $21 \pm 2$  °C, in the dark, for a 24-h reaction period. Residual free chlorine was measured using the Standard Method 4500-ClF (APHA, 1992) and was quenched with sodium sulfite prior to analysis for UV absorbance and DBPs. DBP formation was quantified in terms of THM, haloacetonitriles (HANs), haloketones (HKs), chloral hydrate (CHY), and chloropicrin (CP) according to USEPA method 551.1 (USEPA, 1996), and  $\text{HAA}_9$  according to Standard Method 6251 B (APHA, 1992) with some modifications, as described in detail elsewhere (Kitis, 2001). The measured DBP yields ranged between 1 and  $130 \mu\text{g}/\text{mg}$  DOC for THM and  $\text{HAA}_9$ , which are higher than the yields ( $20\text{-}50 \mu\text{g}/\text{mg}$  TOC) typically reported for UFC conditions (Summers *et al.*, 1996). The higher yields may be partly caused by the higher  $\text{Cl}_2/\text{DOC}$  ratios required to maintain a  $1 \pm 0.4 \text{ mg}/\text{l}$   $\text{Cl}_2$  residual after the 24-h contact time.

## Results and Discussions

### Fractionation patterns of DOM by selected physicochemical separation processes

In studies of DOM characterization, which utilize XAD resins to fractionate DOM, it has been shown that  $\text{SUVA}_{254}$  values for humic acid components are on the order of 4 to 6, while fulvic acids have  $\text{SUVA}_{254}$  on the order of 3, and hydrophilic acids have values of 2 or lower (Krasner *et al.*, 1996, Korshin *et al.*, 1997). Therefore, the available evidence suggests that a distribution in SUVA exists in natural waters. Figure 1 shows a hypothetical SUVA distribution for natural waters. The exact shape of such a distribution is difficult to determine and is likely to be water-specific. Recent data obtained from size exclusion chromatography studies using both UV and DOC detectors suggest that a Gaus-

sian type of SUVA distribution exists in some natural waters (Muller *et al.*, 2000).

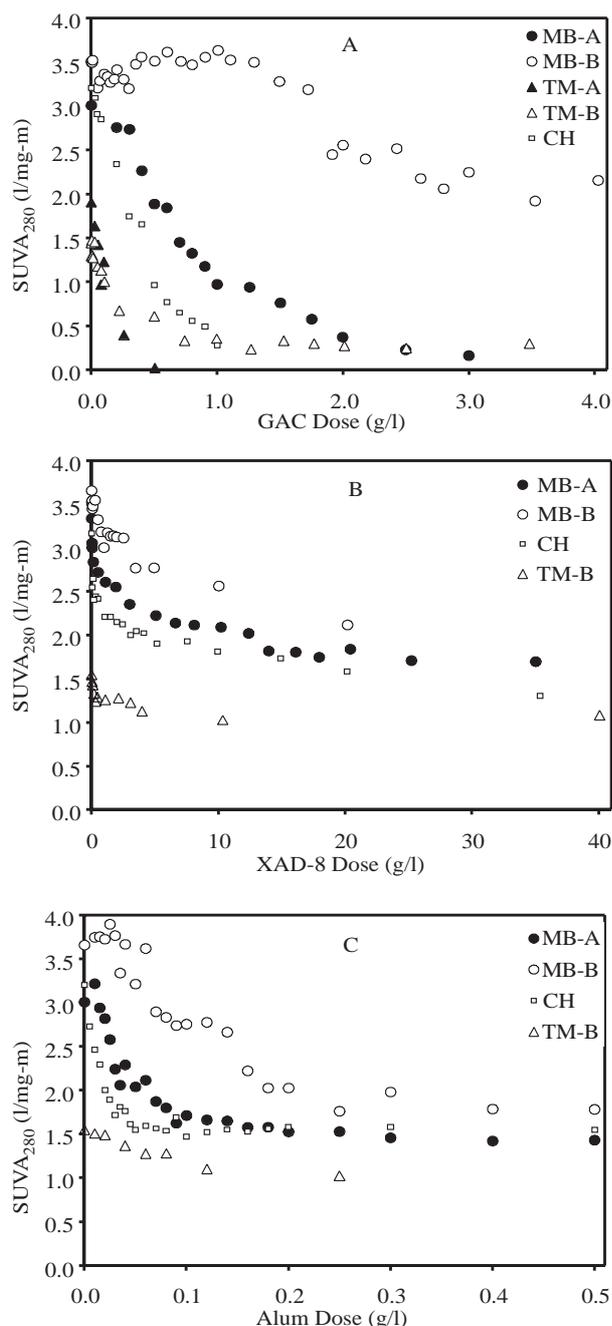


**Figure 1.** A hypothetical distribution of SUVA in natural waters.  $M_i/M_T$  is the mass fraction (on an organic carbon basis) of SUVA components in a particular water. The solid lines show typical components of DOM in a natural water. The dashed line depicts the range of  $\text{SUVA}_{254}$  typically reported for drinking water sources.

The results from our previous work and those in this study showed that SUVA remaining in solution decreased nonlinearly with increasing GAC dose, indicating that high-SUVA components of DOM were preferentially removed from solution by GAC adsorption (Figure 2A). These nonlinear trends provided additional indirect evidence that DOM is composed of components having different SUVA values, and that their distribution is relatively continuous.

XAD-8 batch adsorption exhibited trends similar to those observed during fractionation by GAC adsorption. Several DOM fractions having a wide range of SUVA values were obtained, and high-SUVA fractions were preferentially removed (Figure 2-B). However, SUVA was removed to a lesser extent as compared to GAC; none of the waters had fractions with  $\text{SUVA}_{280}$  less than 1.0 even at very large resin doses. A wider range of fractionation ( $\text{SUVA}_{\text{initial}} - \text{SUVA}_{\text{final}}$ ) was observed in waters having higher initial SUVA values, presumably reflecting a more aromatic character. This observation is consistent with the fact that XAD-8 resins are specified in the RAC method for the separation of humic and fulvic acids, which are known to be rich in aromatic

moieties (Thurman, 1985).



**Figure 2.** Fractionation of DOM based on SUVA by GAC (F400 as-received) adsorption (A), XAD-8 batch adsorption (B), and alum coagulation (C).

Similar to GAC and XAD-8 batch adsorption, alum coagulation also fractionated DOM by preferentially removing components having high SUVA

values (Figure 2C). Coagulation has been shown to preferentially remove hydrophobic, larger MW, and UV-absorbing fractions of DOM (Edzwald and Van Benschoten, 1990; Owen *et al.*, 1993; White *et al.*, 1997; Sinha, 1999). Therefore, as in XAD-8 batch adsorption, the degree of fractionation was larger in the high-SUVA waters. For the waters tested, high doses of alum resulted in SUVA<sub>280</sub> values ranging from 1.0 to 1.5. Coagulation was not as effective in removing low UV-absorbing fractions of DOM, probably those with smaller MW and more hydrophilic and acidic in character, an observation consistent with the literature (Owen *et al.*, 1993; White *et al.*, 1997). Overall, the DOM removal patterns observed with these 3 separation processes indicate that by increasing adsorbent or coagulant dose in small increments and preferentially removing high-SUVA fractions, it is possible to probe the SUVA distribution of a natural water from high to low values (Figure 1).

RAC (i.e. XAD-8 column) and UF processes are known to fractionate DOM through different mechanisms. The XAD-8 column method separates components of DOM with high affinity for the XAD-8 resin at low pH (i.e. 1-2) (HPO components subsequently back eluted with a basic solution) from those not adsorbed by the resin, which are eluted from the column (HPL fractions). UF fractionates DOM primarily based on size with no chemical addition and with minimal chemical interaction. DOM recoveries from RAC and UF fractionation processes ranged between 89.9 and 109.1% (as DOC), indicating minimal losses. The positive errors in the recovery were attributed to errors in the low-level DOC measurements and in the determination of the exact volumes of fractions. Detailed information about these fractionation techniques and their impact on DBP reactivity is discussed elsewhere in detail (Kitis *et al.*, 2002). Some important conclusions relevant to this work will be summarized in the following paragraphs.

A wide range of SUVA<sub>280</sub> values, from 2 to 6 and 0.5 to 2, was observed within the UF fractions of MB-B and TM-B waters, respectively. The SUVA value of a particular MW fraction from the MB-B water was always greater than that from the corresponding TM-B fraction. For MB-B water, SUVA increased with increasing MW. This suggests that larger MW fractions of DOM contain more unsaturated bonds (i.e. are more aromatic in character), which is consistent with the literature (Chin *et al.*, 1994). In contrast, no clear trend was apparent be-

tween SUVA and MW for the TM-B water. In fact, the largest MW fraction ( $>5$  kDa) had the lowest SUVA.

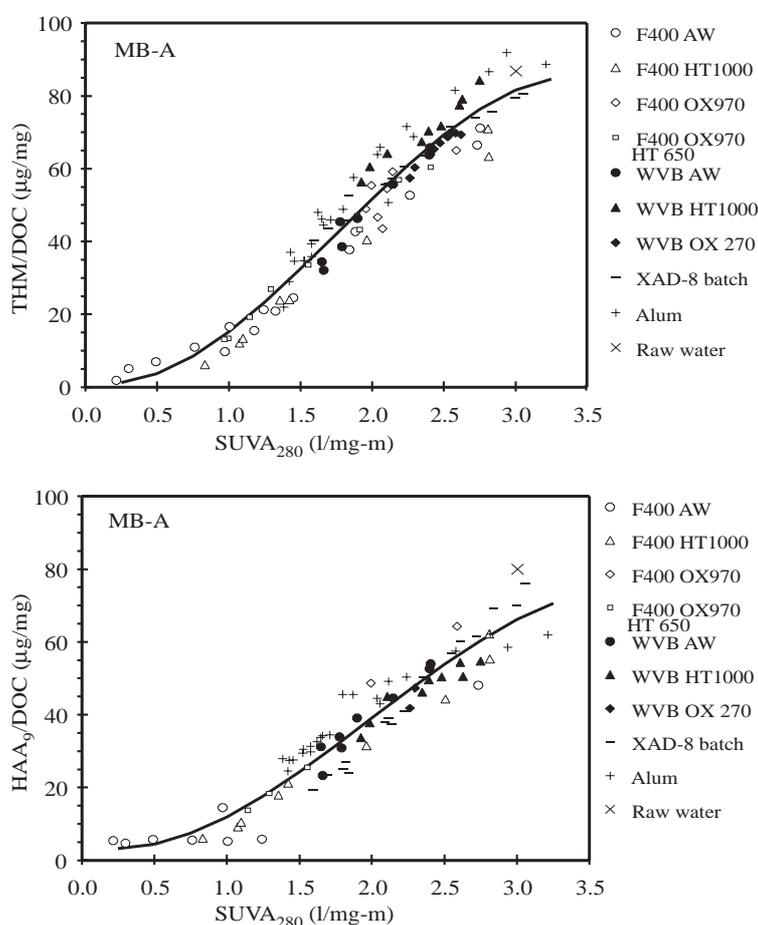
For both waters, the HPO RAC fraction had larger SUVA values than the HPL fractions and the source water. The  $SUVA_{280}$  values of HPO fractions were 4.2 and 2.2 for MB-B and TM-B water, respectively, while the average  $SUVA_{280}$  values of HPL fractions for the same waters were 2.2 and 1.0. These results suggest that the HPO fractions had larger aromatic content, consistent with that reported for humic acids and with reports in the literature (Reckhow *et al.*, 1990; Croue *et al.*, 2000).

A large number of DOM fractions (about 40-100 for each water) with a wide range of SUVA values were obtained from these 5 separation processes employing different separation mechanisms. In addition,

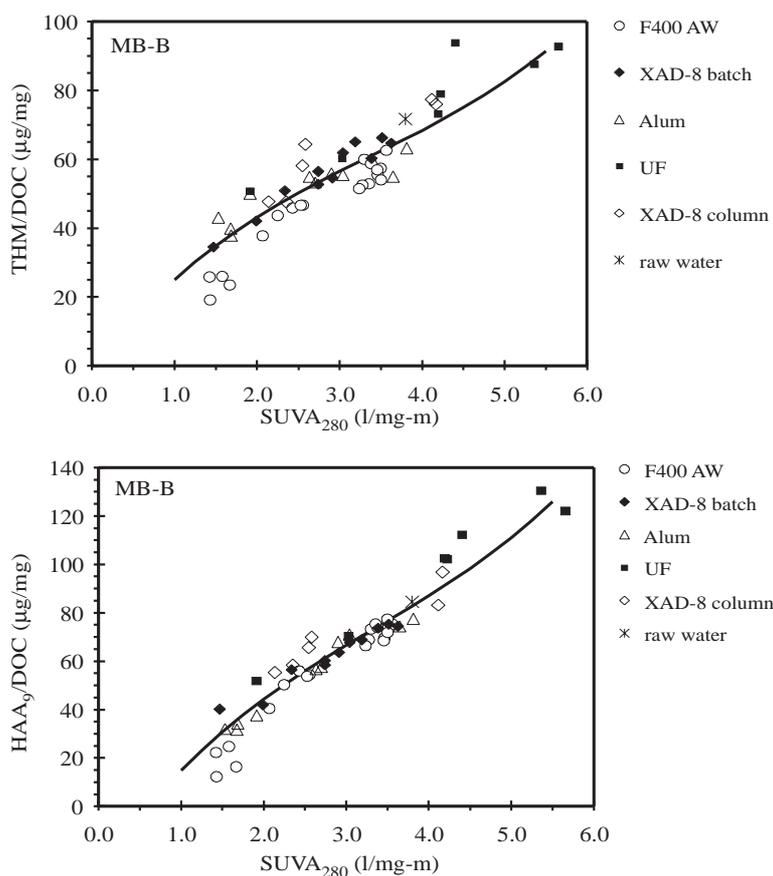
a wide spectrum of DOM mixtures for subsequent DBP reactivity experiments was provided by DOM fractions from 2 new batches of water (MB-B and TM-B), representing both recovered DOM and DOM components remaining in solution after treatment.

### DBP reactivity profiles

Following bulk water fractionation, all DOM fractions were chlorinated and DBP formation was measured. For all of the waters tested, THM and  $HAA_9$  were formed in similar amounts (on a mass basis), which were significantly higher than those of other DBPs (i.e. HANs, HKs, CHY, and CP), which were always less than  $4 \mu\text{g DBP}/\text{mg DOC}$ . Thus, only the THM and  $HAA_9$  results are discussed in this paper.



**Figure 3.** THM and  $HAA_9$  specific yields as a function of  $SUVA_{280}$  for all DOM fractions in MB-A water. F400 and WVB series are coal- and wood-based GACs, respectively. Abbreviations for carbons in the legend represent different degrees of surface modification as described in detail elsewhere (Karanfil *et al.*, 1999). The solid line represents the third order polynomial equation fit to the data with linear regression analysis.



**Figure 4.** THM and HAA<sub>9</sub> specific yields as a function of SUVA<sub>280</sub> for all DOM fractions in MB-B water. The solid line represents the third order polynomial equation fit to the data with linear regression analysis.

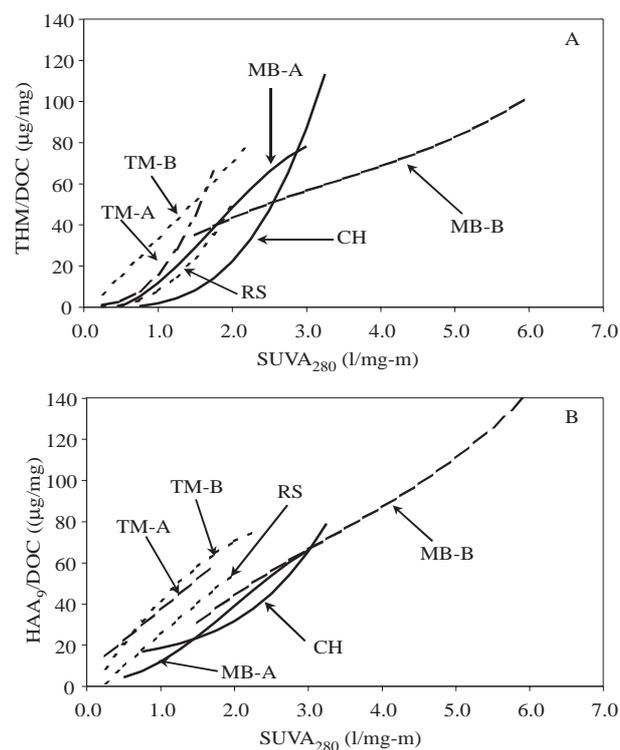
DBP formation was normalized by DOC to account for possible differences that could result from different DOC (i.e. precursor) concentrations. This ratio (i.e. THM/DOC or HAA<sub>9</sub>/DOC) is defined as the *specific yield*. For each water tested, DBP specific yields of all DOM fractions were plotted as a function of their SUVA values. By plotting DBP yields as a function of SUVA, it was possible to relate the reactivity to both UV absorbing and non-UV absorbing DOM components, since SUVA includes the DOC term that accounts for all organic matter components in a water sample. Independent of the fractionation technique employed, whether adsorption by GACs (with significantly different physicochemical characteristics in some experiments), adsorption by XAD-8 resin, coagulation by alum, UF or RAC fractionation, strong correlations between DBP specific yield and SUVA were obtained, as exemplified by the data for MB-A and MB-B waters shown in Figures 3 and 4, respectively. The specific

yields decreased drastically with decreasing SUVA. In general, it was found that there are 2 significantly different reactivity regions: in the low-SUVA region (i.e. usually smaller than 1.0 to 1.5), DOM fractions did not exhibit significant THM or HAA<sub>9</sub> formation, while in the high-SUVA region (SUVA > 1.0-1.5), THM and HAA<sub>9</sub> formation increased dramatically with increasing SUVA. The SUVA values corresponding to the inflection point in the reactivity profile varied from water to water and for some waters (e.g., MB-B, Figure 4) it was not possible to obtain fractions from the low SUVA region. Although not observed in this study, some recent RAC fractionation studies indicate that low SUVA components, enriched in proteins and aminosugars, can exhibit significant DBP formation (Croue *et al.*, 2001). However, it was also reported in the same study that SUVA is a good surrogate parameter, especially for natural waters with SUVA<sub>254</sub> higher than 2 (which is about 1.5 as SUVA<sub>280</sub>). These results indicate that

DOM has a heterogeneous reactivity, and that UV-absorbing DOM components are the major reactive sites responsible for DBP formation resulting from the reaction with chlorine.

Correlations between the specific DBP yields and SUVA were generated with linear regression analysis at the significance level of  $p < 0.001$  for each water tested (SAS Statistical package). First, second and third order polynomials were fit to all data collected for each water. Figure 5 shows the best regression fits to the data. The  $R^2$  values of the fits ranged between 0.81 and 0.97; third order polynomials produced the best fits for most data sets, especially for the reactivity profiles with 2 distinct reactivity regions (Figure 3), with the  $R^2$  values higher than 0.93. Although no physical meaning can be deduced from the curve fit parameters, these strong correlations support the hypothesis that the *SUVA distribution* of a natural water represents an important characteristic of DOM that correlates well with DBP formation. Because the DOM fractions obtained from GAC experiments did not undergo any significant changes in chemical composition, they are expected to represent the original reactivity of DOM in the source water. Because the reactivity of fractions obtained from XAD-8 batch adsorption and alum coagulation experiments follows the same trends as those from GAC experiments, we concluded that any changes in chemical composition had a negligible impact on reactivity. Therefore, the reactivity of fractions obtained from XAD-8 batch adsorption and alum coagulation also represents the original reactivity of DOM in the source water. Further evidence for this is the fact that the DBP reactivities of unfractionated source waters always fell on the reactivity profiles (Figures 3 and 4). In addition, the UF and RAC fractions represented the DBP reactivity of all DOM components in each water since it was possible to achieve over 90% DOM recoveries during these fractionation processes. Overall, the single correlation observed between specific DBP yields and SUVA values for a particular water *independent of the fractionation process employed to obtain the DOM fractions* appears to represent its *natural DBP formation reactivity profile*. Some recent data in the literature support this finding. Dickenson and Amy (2000) applied 3 treatment processes (activated carbon adsorption, ultrafiltration and ozonation/biotreatment) to clarified Seine River (SRW) water. These treatments produced 6 treated waters with different  $SUVA_{254}$  values. The treated waters and the original clar-

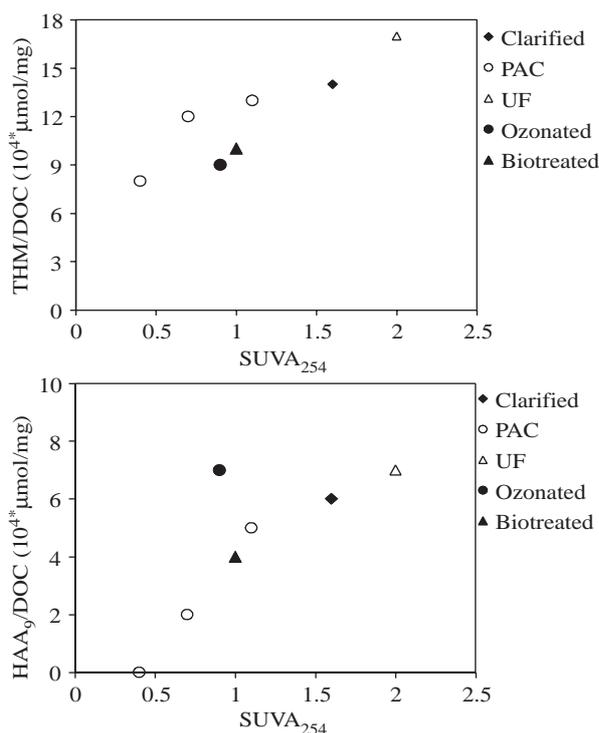
fied water were chlorinated according to UFC conditions. THM and HAA<sub>9</sub> formations were measured after a 24-h contact time. Although not plotted or discussed in their paper, we examined the correlations between THM and HAA<sub>9</sub> yields and  $SUVA_{254}$  of the treated samples. While the SUVA range was limited because SRW is a low SUVA water, and a relatively small number of fractions were examined in this study, good correlations were observed between both THM and HAA<sub>9</sub> yields and  $SUVA_{254}$  values of DOM fractions independent of the treatment processes employed, which is consistent with the reactivity profile concept proposed in this work (Figure 6).



**Figure 5.** DBP reactivity profiles of the tested waters (A:THM and B:HAA<sub>9</sub>). Each line represents the best fit to the whole data set with linear regression analysis.

Each source water tested in this study had a unique DBP reactivity profile (Figure 5). As a consequence, reactivity at a given value of SUVA varied widely. For example, at a  $SUVA_{280}$  of 1.5, the THMs and HAA<sub>9</sub> specific yields for all waters ranged from 12 to 52  $\mu\text{g}/\text{mg}$  DOC and from 21 to 60  $\mu\text{g}/\text{mg}$  DOC, respectively. Therefore, it is evident that although

the DBP reactivity profile, which is closely related to the SUVA distribution, reflects the heterogeneity of DOM components comprising a particular water, there are still significant differences between the reactivities of DOMs from different sources. Such differences are not captured by a single aggregate SUVA determination, but appear to have a noticeable impact on DBP formation. This finding is consistent with the differences observed among different correlations between DBP formation potentials and the SUVA of DOM isolates obtained from different sources that have been reported in the literature (Croue *et al.*, 2000).



**Figure 6.** THM and HAA<sub>9</sub> specific yields as a function of SUVA<sub>254</sub> for all DOM fractions in Seine River water as reported by Dickenson and Amy (2000).

There has been increasing recognition in recent years of the role played by hydrophilic DOM components in DBP formation. The DOM fractions remaining in solution after exposure to high doses of adsorbent or coagulant have low SUVA values and are hydrophilic in character, because adsorption and coagulation processes preferentially remove hydrophobic components. In addition, the SUVA values of hydrophilic DOM isolates from natural waters

are generally low (Croue *et al.*, 2000; Rostad *et al.*, 2000). Although reactivity profiles indicated that all the waters exhibited lower DBP specific yields at SUVA<sub>280</sub> values below about 1.5, THM and HAA<sub>9</sub> yields as high as 29 and 34 μg/mg DOC, respectively, were observed at a SUVA<sub>280</sub> of 1.0. Considering the more stringent DBP regulations expected in the future, the hydrophilic components of DOM may be problematic for water utilities treating waters with high concentrations of these components.

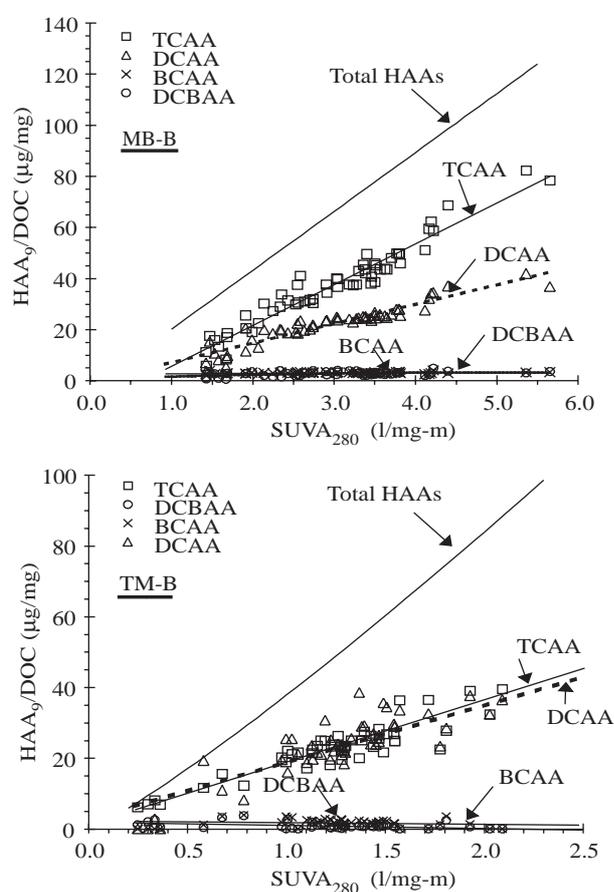
### Effect of SUVA on DBP speciation

Since individual DBP species may have different health effects, future regulations are expected to focus on individual species, in lieu of combined DBPs. Therefore, correlations between SUVA and the formation of individual DBP species were evaluated. Formation of chloroform correlated well with SUVA, and it was the dominant THM species observed in all the source waters and their fractions, primarily as a consequence of low bromide levels. Dichloro-(DCAA) and trichloro acetic acid (TCAA) were the dominant HAA species and both correlated well with SUVA. As with the brominated THMs, bromochloro-(BCAA) and dichlorobromo acetic acid (DCBAA) were formed in very small quantities. For most waters tested (except TM samples), TCAA formation was dominant at high SUVA values, while comparable degrees of TCAA and DCAA formation were observed at low SUVA values, causing the TCAA and DCAA profiles to cross in some cases (Figure 7). The crossover occurred at SUVA<sub>280</sub> values that ranged from 1.2 to 2.7 for all waters tested. It has been reported that the formation of trihalogenated HAAs exceeds that of dihalogenated species in high-humic (i.e. high SUVA) waters, whereas the opposite has been observed for low-humic waters (Hwang *et al.*, 2000). On the other hand, Croue *et al.* (2000) reported that there is a strong correlation between TCAA formation and SUVA, while the correlation for DCAA was poor. Overall, the findings of this study and those reported in the literature indicate that the precursors for TCAA and DCAA are different.

### Conclusions

For each natural water, a single correlation was observed between the SUVA values of DOM fractions and their THMs and HAA<sub>9</sub> formations, *independent of the separation process* used to obtain the frac-

tions. Therefore, the correlation obtained for each water appears to represent its *natural disinfection by-product (DBP) reactivity profile*. A unique reactivity profile as a function of SUVA was obtained for each water tested; therefore, site-specific reactivity profiles should be developed for each water source. The distribution of SUVA within a source water and its relationship to reactivity were found to be more informative than the source water aggregate SUVA value. Therefore, understanding how reactivity is correlated to SUVA may allow utilities to optimize the degree of treatment required to comply with the D/DBP regulations. Periodic development of reactivity profiles will allow utilities to assess and monitor the heterogeneity and reactivity of DOM in a source water with time.



**Figure 7.** HAA reactivity profiles for MB-B and TM-B samples. The lines represent the best fits to the experimental data using linear regression analysis.

DBP reactivity profiles indicated that DOM exhibited heterogeneous reactivity and SUVA is a good predictor of the DOM reactivity with chlorine in terms of THMs and HAA<sub>9</sub> yields and individual DBP species. Consistent with the reports in the literature, GAC and XAD-8 adsorption and alum coagulation preferentially removed high SUVA components from water and UV-absorbing moieties were the major reactive sites responsible for DBP formation. The results provided insight into the formation and speciation of HAAs from different DOM components. Formation of TCAA was dominant over DCAA for high-SUVA fractions, whereas the formations of TCAA and DCAA were comparable for low-SUVA fractions.

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### Nomenclature

BCAA	bromochloro acetic acid
CH	Charleston Edisto River
CHY	chloral hydrate
CMBRs	completely-mixed batch reactors
CP	chloropicrin
DCAA	dichloro acetic acid
DCBAA	dichlorobromo acetic acid
D/DBP	disinfectants/disinfection by-products
DOC	dissolved organic carbon
DOM	dissolved organic matter
GAC	granular activated carbon
HAA <sub>9</sub>	haloacetic acids
HANs	haloacetonitriles
HKs	haloketones
HPL	hydrophilic
HPO	hydrophobic

MB	Myrtle Beach Inter-Coastal Waterway	SUVA	specific ultraviolet absorbance
MW	molecular weight	TCAA	trichloro acetic acid
NOM	natural organic matter	THM	trihalomethanes
RAC	resin adsorption chromatography	TM	Tomhannock Reservoir
RO	reverse osmosis	TOC	total organic carbon
RS	Rensselaer County	UF	ultrafiltration
		UFC	uniform formation conditions

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