

See discussions, stats, and author profiles for this publication at: <https://www.researchgate.net/publication/9030097>

Weishaar JL, Aiken GR, Bergamaschi BA, Fram MS, Fujii R, Mopper K.. Evaluation of specific ultraviolet absorbance as an indicator of the chemical composition and reactivity of diss...

ARTICLE *in* ENVIRONMENTAL SCIENCE AND TECHNOLOGY · NOVEMBER 2003

Impact Factor: 5.33 · DOI: 10.1021/es030360x · Source: PubMed

CITATIONS

1,064

READS

1,482

6 AUTHORS, INCLUDING:



Brian A Bergamaschi

United States Geological Survey

113 PUBLICATIONS 2,619 CITATIONS

SEE PROFILE



Miranda S. Fram

United States Geological Survey

50 PUBLICATIONS 1,805 CITATIONS

SEE PROFILE



Roger Fujii

United States Geological Survey

34 PUBLICATIONS 1,534 CITATIONS

SEE PROFILE



Kenneth Mopper

Old Dominion University

146 PUBLICATIONS 9,441 CITATIONS

SEE PROFILE

Evaluation of Specific Ultraviolet Absorbance as an Indicator of the Chemical Composition and Reactivity of Dissolved Organic Carbon

JAMES L. WEISHAAR,[†]
 GEORGE R. AIKEN,^{*,†}
 BRIAN A. BERGAMASCHI,[‡]
 MIRANDA S. FRAM,[‡] ROGER FUJII,[‡] AND
 KENNETH MOPPER[§]

U.S. Geological Survey, 3215 Marine Street,
 Boulder, Colorado 80303, and U.S. Geological Survey,
 6000 J Street, Placer Hall, Sacramento, California 95819

Specific UV absorbance (SUVA) is defined as the UV absorbance of a water sample at a given wavelength normalized for dissolved organic carbon (DOC) concentration. Our data indicate that SUVA, determined at 254 nm, is strongly correlated with percent aromaticity as determined by ¹³C NMR for 13 organic matter isolates obtained from a variety of aquatic environments. SUVA, therefore, is shown to be a useful parameter for estimating the dissolved aromatic carbon content in aquatic systems. Experiments involving the reactivity of DOC with chlorine and tetra-methylammonium hydroxide (TMAH), however, show a wide range of reactivity for samples with similar SUVA values. These results indicate that, while SUVA measurements are good predictors of general chemical characteristics of DOC, they do not provide information about reactivity of DOC derived from different types of source materials. Sample pH, nitrate, and iron were found to influence SUVA measurements.

Introduction

Environmental scientists are increasingly emphasizing the geochemical and ecological roles of organic matter in aquatic ecosystems. Organic matter in aqueous systems often controls geochemical processes by acting as a proton donor or acceptor and as a pH buffer, by affecting the transport and degradation of pollutants, and by participating in mineral dissolution and precipitation reactions. Organic matter may also control the depth of the photic zone in surface waters, influence the availability of nutrients, and serve as a carbon substrate for microbially mediated reactions. In addition, these reactive substances are potential precursors for the formation of disinfection byproducts (DBPs) resulting from water treatment practices. Dissolved organic carbon (DOC) comprises the vast majority of the organic matter in most water samples.

Predicting the chemical reactivity of DOC in a given sample, however, is hampered by its intrinsic chemical complexity. Recently, studies have demonstrated that aro-

matic carbon content and the absorbance of UV light, general characteristics of the pool of molecules that comprise DOC, are important indicators of DOC reactivity in a number of environmental processes (1–8). For instance, strong correlations have been observed between the pyrene binding coefficient, *K*_{DOC}, and the molar absorptivities ($\lambda = 280$ nm) and aromatic carbon contents of aquatic humic substances from a variety of environments (1). Similarly, the reactivity of DOC and aquatic humic substances with oxidants, such as chlorine (2, 3) and ozone (4), is strongly dependent on the aromaticity of the organic matter. Aromaticity has also been shown to be an important indicator of DOC reactivity for interactions with coagulants (5) and inorganic species, including mercury (6–8). There is significant interest on the part of environmental chemists, geochemists, and ecologists, therefore, in improved characterization methods that will lead to better definition of the roles played by DOC in environmental and geochemical processes.

Variations in the amount and nature of organic matter, especially with respect to changes in the aromatic carbon content, have also become significant factors for designing strategies for water treatment. Aquatic humic substances within the DOC are generally thought to be the primary precursors for trihalomethanes (THM) and many other DBPs (2). Aquatic humic substances comprise the aromatic fraction of DOC and are amenable to removal from water by coagulation (5). The recently promulgated U.S. Environmental Protection Agency (USEPA) Disinfectants and Disinfection Byproducts Final Rule mandates the use of enhanced coagulation or enhanced softening during water treatment to remove total organic carbon (the sum of DOC and POC, particulate organic carbon) from water for the purpose of reducing the formation of DBPs (9). The amount of removal required depends on the chemical characteristics of the raw water, including the specific UV absorbance, SUVA₂₅₄. SUVA₂₅₄ is defined as the UV absorbance at 254 nanometers measured in inverse meters (m⁻¹) divided by the DOC concentration measured in milligrams per liter (mg L⁻¹). SUVA₂₅₄ is an "average" absorptivity for all the molecules that comprise the DOC in a water sample and has been used as a surrogate measurement for DOC aromaticity (10). Water agencies are exempt from the requirements to use enhanced coagulation or enhanced softening if SUVA₂₅₄ for either the raw water or treated water is less than 2.0 L mg⁻¹ m⁻¹ because experiments have shown that coagulation and softening are generally not effective methods for removing DOC with such low SUVA₂₅₄ values. The assumptions behind this use of SUVA are that SUVA₂₅₄ is a good indicator of the humic fraction of the DOC, and coagulation is effective at removing the humic fraction. DBP precursors associated with the humic fraction are consequently removed. Measurements of UV absorbance have, therefore, taken on new significance for the drinking water industry and the USEPA, as these measurements will be a basis for compliance with USEPA regulations.

At this time, the most direct measurement of aromaticity of natural organic matter is provided by ¹³C NMR spectroscopy; however, this method requires expensive, sophisticated instrumentation and significant sample preparation. Clearly, a simpler method for estimating aromaticity of DOC in a given sample is desirable. The earlier studies that addressed the use of SUVA₂₅₄ as a surrogate for aromaticity were based on analyses of sediment and soil humic acids and a limited number of aquatic fulvic acids (1, 10, 11). Unfortunately, the earlier work led investigators to conflicting conclusions with regard to the application of SUVA₂₅₄ to estimate aromaticity of aquatic humic substances. In this paper we present the

* Corresponding author phone: (303)541-3036; fax: (303)447-2505; e-mail: graiken@usgs.gov.

[†] U.S. Geological Survey, Boulder, CO.

[‡] U.S. Geological Survey, Sacramento, CA.

[§] Current Address: Old Dominion University, Chemistry Department, Norfolk, VA 23529.

TABLE 1. SUVA₂₅₄ Values and Percent (%) Character of Humic Substance Samples by ¹³C NMR

sample	Al-I ^b (%)	Al-II ^c (%)	Al-III ^d (%)	Ar ^e (%)	C-I ^f (%)	C-II ^g (%)	SUVA ₂₅₄ (L mg ⁻¹ m ⁻¹)
Suwannee River FA	29.3	12.0	7.0	24.8	21.1	5.9	3.2
IHSS Suwannee River FA	27.0	15.0	5.0	28.0	19.0	6.0	3.6
Ogeechee River FA	39.4	7.5	3.1	26.6	20.2	3.3	3.8
Ogeechee River HA	24.7	10.4	7.3	40.8	15.1	1.6	5.3
Coal Creek FA	34.7	8.1	1.6	28.0	23.1	4.5	3.9
Coal Creek HA	22.2	7.6	5.3	36.0	20.2	3.4	5.1
Hillsborough Canal HPOA	44.4	5.0	1.2	27.5	21.7	0.1	3.5
U3 Everglades HPOA	40.7	7.5	0.4	23.6	23.6	4.1	3.5
Williams Fork FA	32.5	12.6	4.9	24.4	19.4	6.2	3.0
Upper Shingobee HPOA	44.7	10.7	2.7	21.7	20.2	0.2	2.9
Pony Lake FA ^a	42.0	16.6	6.6	16.5	16.7	2.2	1.7
Lake Fryxell HPOA	46.4	14.5	4.4	15.2	19.6	0.0	1.8
Pacific Ocean FA	56.9	13.4	1.2	7.3	19.5	1.6	0.6

^a Data from refs 34 and 35. ^b Al-I (0–62 ppm) = aliphatic carbons. ^c Al-II (62–90 ppm) = heteroaliphatic carbons (carbohydrates, alcohols, etc.). ^d Al-III (90–110 ppm) = anomeric carbons. ^e Ar (110–160 ppm) = aromatic carbons. ^f C-I (160–190 ppm) = carboxyl carbons. ^g C-II (190–220 ppm) = ketonoic carbons.

results of a study designed to assess the efficacy of SUVA₂₅₄ as an indicator of aromaticity and chemical reactivity for aquatic organic matter samples from a wide range of source waters. In addition, we discuss potential interferences for the determination of SUVA₂₅₄ on samples of surface and groundwater.

Experimental Section

Whole water samples were collected as part of the U.S. Geological Survey National Stream Quality Accounting Network (NASQAN) sampling program between April and June 1999. Thirty-four samples were collected from sampling sites located in 16 states. The samples are representative of a wide range of riverine environments. All samples were filtered in the field through AquaPrep 600 filter capsules with Supor filter media (0.45 μ m, Pall Gellman) and shipped on ice to Boulder, CO for further analysis. All chemicals utilized were reagent grade or higher quality.

UV-visible absorbance measurements were performed on a Hewlett-Packard photodiode array spectrophotometer (model 8453) between 200 and 800 nm with distilled water as the blank. A quartz cell with 1.0 cm path length was used. Samples were allowed to warm to room temperature before measurement. Duplicates and measurement of the distilled water were made every 10–12 samples to ensure instrument stability. DOC measurements were performed on an OI Analytical Model 700 TOC analyzer. SUVA₂₅₄ values were determined by dividing the UV absorbance measured at λ = 254 nm by the DOC concentration and are reported in the units of liter per milligram carbon per meter. Iron content was measured as milligrams per liter total iron utilizing a Hach DR/2000 direct reading spectrophotometer and Hach FerroVer AccuVac ampules. The effects of sample pH on UV absorbance were assessed by adjusting sample pH of whole waters samples with concentrated H₃PO₄.

Well-characterized organic matter isolates were obtained from various locations in the United States and Antarctica representing aquatic environments with different types of organic source materials. Samples were isolated on Amberlite XAD-8 resin according to methods described by Aiken et al. (12). Sample identities and chemical characteristics are given in Table 1. Quantitative ¹³C NMR spectra were measured on solutions of approximately 100 mg/mL of the sodium salt of each isolate dissolved in H₂O–D₂O (1:1), adjusted to pH 7, in 10 mm tubes on a Varian spectrometer (Model 300) at 75.429 MHz using inverse gated-decoupling with an 8-s delay (13). The ¹³C NMR spectra were electronically integrated (14). The region from 110 to 160 ppm was assigned as the aromatic region of the spectrum (15). SUVA₂₅₄ data were determined

as described above on solutions containing approximately 5 mg C/L in distilled water. The effects of nitrate and ferric iron on UV absorbance were determined by the addition of NaNO₃ and FeCl₃·6H₂O to solutions of isolates. Nitrate effects were studied over a concentration range of 0–100 mg NO₃⁻/L, whereas the concentration range for Fe³⁺ was 0–3.5 mg Fe/L.

Trihalomethane (THM) formation was determined for the isolates utilizing THM formation potential (THMFP) conditions by chlorinating 2–3 mg C/L solutions of the isolates in distilled, organic-free water (16). The solutions were chlorinated at 3 times the DOC concentration utilizing a sodium hypochlorite dosing solution buffered to pH 8.3. Samples were incubated at 25 °C for 1 and 7 days. THM concentrations were measured by purge-and-trap GC/ECD utilizing a Tekmar-Dorman AquaPrep 50 autosampler, a Tekmar-Dorman LSC 2000 purge-and-trap concentrator, and a Hewlett-Packard 6890 GC with ECD detector. THM formation of the NASQAN filtered whole water samples was determined utilizing uniform formation conditions (UFC) (17). UFC conditions are more representative of drinking water treatment conditions, with residual chlorine concentrations of 1.0 \pm 0.4 mg free chlorine per liter after 24 h incubation time at 20 °C and at a pH of 8.0. THM concentrations were measured on the same instrumentation listed above. Specific total THM formation (STTHM_{24h}) values are calculated by dividing the THM concentration by the DOC concentration of the sample before chlorination. The term formation potential in specific total THM formation potential (STTHMFP_{7d}) and THM formation potential (THMFP) is used to signify an incubation time of 7 days.

Organic matter isolate samples were analyzed by tetramethylammonium hydroxide (TMAH) thermochemolysis followed by GC/MS (18). Approximately 0.5 mg of dried sample material was utilized for the analysis. After the sample was reacted with the TMAH at 250 °C for 30 min a 2–4 μ L aliquot of the solution was injected cool, on-column onto a Supelco, fused silica deactivated guard column (2.5m \times 0.53 mm) press-connected to a J&W DB5-MS capillary column (30m \times 0.25 mm, i.d., 1 μ m film thickness), which was installed in a Hewlett-Packard model 5890 GC. The GC oven was temperature programmed with an initial hold at 60 °C for 5 min before a 4 °C/min increase to 240 °C followed by a 20 °C/min increase to 280 °C and a final hold of 18 min (70 min total run time). Eluting compounds were detected by a Hewlett-Packard model 5972A mass selective detector (MSD) in the electron ionization (EI) and/or methane-chemical ionization (methane-CI) mode and identified by their mass spectra with the aid of the Wiley MS Library.

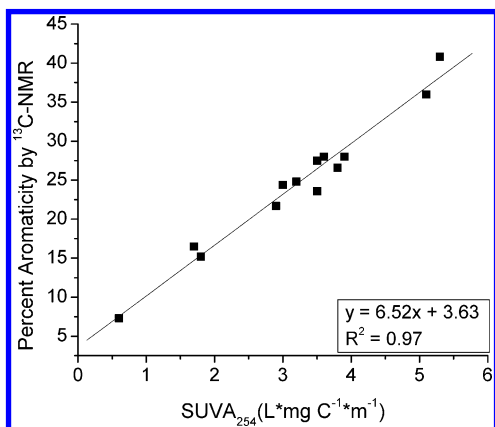


FIGURE 1. SUVA₂₅₄ versus percent aromaticity determined by ¹³C NMR.

Results and Discussion

UV Absorbance of Dissolved Organic Carbon. The UV spectra ($\lambda = 200\text{--}380\text{ nm}$) for water samples and the hydrophobic acid (HPOA) fractions of DOC are featureless with absorptivity increasing toward shorter wavelengths, similar to those noted for humic substances from many environments (19). In general, UV spectroscopy has little value for studying functionality in DOC and, unlike IR and NMR spectroscopy, cannot be used for the direct determination of functional groups in these materials (19). However, UV spectroscopy can provide some structural information about the organic matter in a water sample. Spectra obtained for a complex mixture of molecules, such as DOC, are generally considered to represent the average of individual compounds that comprise the mixture (20).

The absorbance of UV light by a molecule depends on the electronic structure of the molecule. The UV spectrum, therefore, indicates the presence of specific bonding arrangements in the molecule. In the case of absorption in the near UV ($\lambda = 200\text{--}380\text{ nm}$), conjugated systems, such as those in aromatic molecules, generally have the greatest absorptivities (21), while other electronic structures do not absorb in this portion of the UV region. An advantage of the structural selectivity of UV absorption is that characteristic features or bonding arrangements may be recognized in molecules of varying complexity (21), or, in the case of DOC, in mixtures of varying complexity. When measured in the near UV, many of the bonds present in a complex molecule, or complex mixtures of molecules, are transparent to UV radiation, and increased structural complexity does not necessarily result in increased spectral complexity. It is possible, therefore, to determine the presence of general structural characteristics in a sample, although, it should be noted that individual aromatic molecules absorb UV light to varying degrees, i.e., they have different absorptivities. ¹³C NMR spectroscopy is based on different principles, and the aromatic region of the NMR spectrum (110–160 ppm) is actually a measure of sp² hybridized carbon atoms bound to other carbon atoms and includes both aromatic and unsaturated carbon atoms, such as those contained in olefins.

Since present limitations in instrument sensitivity make NMR measurements on whole water samples impractical, chemical relationships need to be extrapolated from concentrated material isolated from whole water samples. Data presented in Figure 1 compare SUVA₂₅₄ values for 13 organic matter isolates versus percent aromaticity determined by quantitative, liquid state ¹³C NMR. A strong correlation ($R^2 = 0.97$) exists between the SUVA₂₅₄ and NMR data. The isolates chosen for this study were obtained from diverse environments (marine to dark water rivers), are representative of aquatic humic substances evolved from a variety of source

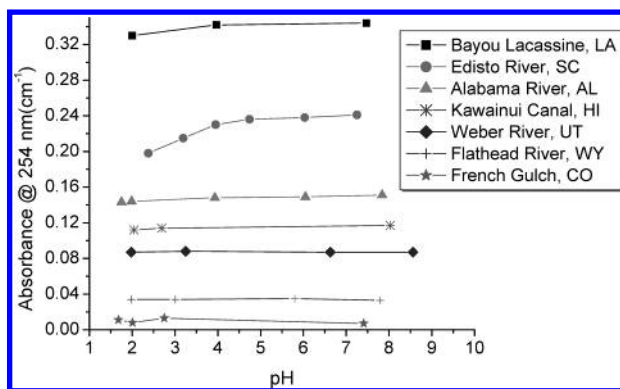


FIGURE 2. UV absorbance determined at $\lambda = 254\text{ nm}$ versus pH for several filtered whole water samples.

materials (22), and possess different chemical properties. In particular, the samples cover the range of reported values for aromatic carbon content for similar materials isolated from surface waters. The strong correlation between SUVA₂₅₄ and NMR data for the DOC isolates provides strong support for the use of SUVA₂₅₄ as an indicator of aromaticity of aquatic humic substances, in particular, and, by extension, DOC, as a whole. Our results are in general agreement with those reported by Traina et al. (10) and Chin et al. (23). The nonzero intercept for the linear regression between SUVA₂₅₄ and percent aromaticity may reflect the abundance of isolated, unconjugated olefin moieties, which contain sp² hybridized carbon atoms, but absorb shorter wavelengths of UV light.

These data suggest the strong correlation between SUVA and aromatic carbon content is of significant utility in assessing the nature or general chemical composition of DOC because it provides an integrated estimate of aromatic content across functional classes, provided the influence of confounding variables is small. The measurement itself is nondestructive and requires small sample volumes. It can easily be incorporated as a characterization tool in studies of the chemical transformation of DOC. In combination with chromatographic fractionation, SUVA can provide a measure of the aromaticity of various fractions of the DOC, including aquatic humic substances, which comprise the hydrophobic acid fraction of DOC obtained using XAD-8 resin (12). These measurements can be made on relatively small sample volumes (1 L compared to 10–100s of liters) with significantly less sample processing compared to procedures designed to provide sufficient amounts of isolated organic matter for ¹³C NMR analyses.

Effect of pH on UV Absorbance Measurements. The effect of sample pH on the absorption of UV light for a number of whole water samples is demonstrated in Figure 2. In general, relatively minor differences in UV absorption were observed for most samples between pH 2.0 and 8.6, consistent with the small effect expected from the protonation of carboxyl groups with decreasing pH. According to Silverstein et al. (21), sodium salts of carboxylic acids show absorption at wavelengths and intensities that are comparable to the samples. The Edisto River filtered whole water sample showed a large decrease in UV absorbance at low pH. The Edisto River is a “dark-water” stream in South Carolina that contained 0.4 mg L⁻¹ iron. The change in UV absorption for this sample is potentially due to pH effects on organic matter interacting with iron and, possibly, aggregation of organic matter at low pH. In our experiments with the Edisto sample, no losses of DOC were noted at lower pH values. DOC losses at lower pH values are possible, however, for samples containing relatively large concentrations of humic substances, such as “dark-water” samples, due to the effects of pH on the solubility of humic acid.

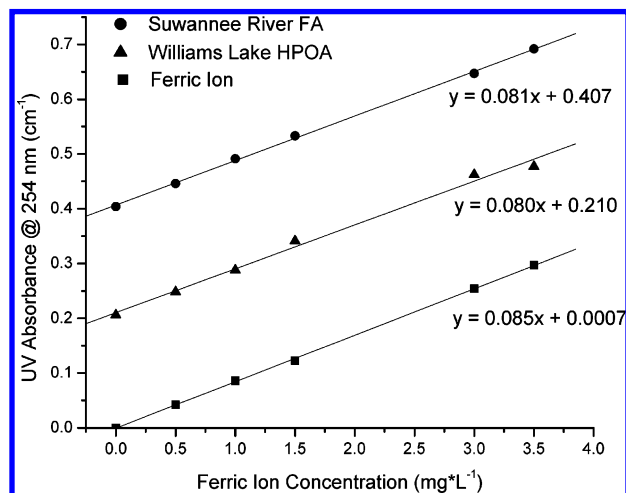


FIGURE 3. The effect of increasing ferric ion (Fe^{3+}) concentration on the UV absorbance of solutions ($[\text{DOC}] = 9.5 \text{ mg C/L}$) of Suwannee River FA and Williams Lake HPOA determined at $\lambda = 254 \text{ nm}$.

The effect of pH on the DOC samples presented in this study is less than observed for soil humic substances (24). The small dependency of UV absorbance on pH in the range of 2–8.6 means that, within this pH range, it is unnecessary to adjust the pH to a constant value to compare results between samples. According to Hem (25) most ground and surface waters in the United States have pH values ranging from 6.0 to 8.5. Values greater than 9.0 and less than 6.0 are unusual, although possible. In addition, the results presented in Figure 2 suggest that, in many cases, UV absorbance measurements made on samples preserved by acidification to pH 2 will yield the same results as measurements made on unpreserved samples. It should be noted, however, that the preservation of DOC samples involving acidification (26) often could result in $\text{pH} < 2$, and it should not be assumed that acidified samples are generally appropriate for UV absorbance determinations. Standard methods for measurement of UV absorbance suggest that samples should not be acidified to pH values below 4 (26).

Potential Interferences. Particles and inorganic species that absorb light in the near UV, such as iron and nitrate, can interfere with the UV absorbance of DOC. Particles interfere with UV absorbance measurements by both scattering and absorbing light. Measurements should, therefore, be made on filtered samples. Samples that precipitate after filtration must be refiltered.

Iron can be present in ground and surface waters as either ferrous (Fe^{2+}) or ferric (Fe^{3+}) iron. Generally, concentrations are less than 0.50 mg/L in aerated water, although concentrations in groundwater can be greater (27). Both Fe^{2+} and Fe^{3+} absorb UV light across the wavelengths of interest. Absorbance versus concentration curves (Figure 3) for Fe^{3+} at $\lambda = 254 \text{ nm}$ indicate that a concentration of 0.02 mg/L will produce an absorbance of 0.002 cm^{-1} at $\lambda = 254 \text{ nm}$, which is the standard deviation for the absorbance measurements of the whole water samples. Similar results are obtained at $\lambda = 280 \text{ nm}$, another wavelength commonly used in the determination of UV absorbance. The effects of increasing Fe^{3+} concentration on the UV absorbance of solutions containing two different organic matter isolates (Williams Lake HPOA, $\text{SUVA}_{254} = 2.2 \text{ L mg}^{-1} \text{ m}^{-1}$ and Suwannee River FA, $\text{SUVA}_{254} = 3.2 \text{ L mg}^{-1} \text{ m}^{-1}$) are shown in Figure 3. In these experiments, solutions containing 9.5 mg C/L of the respective isolate were amended with Fe^{3+} . In all cases, the absorbances were additive, and the slope of the absorbance versus concentration curve for the spiked sample was similar to the slope of the curve for iron alone, indicating that, in these cases, Beer's Law is upheld. Fe^{3+} concentrations in the

range commonly found in water samples, $0\text{--}0.5 \text{ mg L}^{-1}$, add only $0\text{--}0.04 \text{ cm}^{-1}$ to the UV absorbance at 254 nm of water samples. For many waters, therefore, the UV absorbance resulting from Fe is negligible; however, in the case of groundwaters and some surface waters, Fe content should be taken into consideration.

NO_3^- can also interfere with UV absorbance measurements and is commonly present in uncontaminated surface waters at concentrations less than 1.0 mg/L (27) although concentrations of 5 mg/L are not uncommon (28). Concentrations can also be significantly greater in groundwater. The spectrum for NO_3^- (not shown) indicates an absorption maximum at 210 nm with a shoulder at $\lambda = 222 \text{ nm}$. At higher concentrations ($> 40 \text{ mg/L}$) the tail of the NO_3^- peak is measurable at $\lambda = 254 \text{ nm}$ and also at $\lambda = 280 \text{ nm}$, although to a lesser degree. Since NO_3^- is detectable at these longer wavelengths at concentrations approximately eight times those expected in surface waters, interferences from NO_3^- are generally limited to groundwaters or samples which have been amended with NO_3^- , possibly by the addition of nitric acid or other NO_3^- -containing compounds. Additions of NO_3^- to organic matter isolates resulted in significant increases in adsorption at NO_3^- concentrations greater than 40 mg/L , although the effect of NO_3^- is significantly less than observed for iron. For example, an absorbance at 254 nm of 0.01 requires $> 100 \text{ mg/L NO}_3^-$ but only 1 mg/L Fe^{3+} in solution. The absorbances of DOC and NO_3^- were found to be additive, as expected, indicating no interactions between the nitrate and organic matter.

SUVA as an Indicator of Reactivity. Aromaticity is a general characteristic of the pool of molecules that comprise DOC. Neither UV nor NMR spectroscopic analyses of DOC provide specific information about the individual molecules contained in the samples. This limitation is demonstrated by the results of tetramethylammonium hydroxide (TMAH) thermochemolysis analyses of isolated organic matter from the Florida Everglades (U3 HPOA, Hillsborough Canal HPOA) and Ogeechee River FA (Table 2). In the TMAH reaction, acidic oxygen sites within organic matter, specifically lignin dimers containing a $\beta\text{-O-4}$ bond, are methylated (29). The method has been primarily used to determine the presence of lignin-derived compounds in a sample. The four isolates yielded different results despite having similar SUVA_{254} values as well as percent aromatic carbon contents determined by ^{13}C NMR (Table 1). No identifiable reaction products were found for the Everglades FA sample in the TMAH analysis, and less than 10 were found for the Hillsborough Canal HPOA sample, whereas over 30 identifiable reaction products were identified for the Ogeechee and Suwannee River samples. Table 2 shows a partial list of the identified compounds and their relative mole percent carbon recoveries. Included in this list are the lignin tracer reaction products benzoic acid, 3,4-dimethoxy-, methyl ester and benzoic acid, 3,4,5-trimethoxy-, methyl ester. The dimethoxy compound is the reaction product of TMAH and vanillic acid, a known terrestrially derived lignin tracer contained in the cell walls of vascular plants, while the trimethoxy compound is the reaction product of syringic acid, which is a less general lignin tracer produced mainly by angiosperms (30, 31). These lignin tracers only appear in the Ogeechee and Suwannee River sample. The Everglades samples are derived from saw-grass peats and cattails and have less lignin than the higher plants that are a major source of organic matter in the Ogeechee and Suwannee Rivers. Clearly, the compositional differences between these samples are not reflected in the SUVA_{254} data.

Of particular significance for drinking water providers is the usefulness of SUVA as an indicator of reactivity in the formation of DBPs. Croue et al. (32) presented data indicating a reasonable correlation between SUVA_{254} for isolated fractions of organic matter from a variety of locations and

TABLE 2. TMAH Thermochemolysis Reaction Products and Corresponding Relative Mole Percent Carbon Composition for Organic Matter Isolates Having Similar SUVA Values

compound name	Ogeechee River FA SUVA = 3.8 (%)	Suwannee River FA SUVA = 3.2 (%)	Hillsborough Canal HPOA SUVA = 3.5 (%)	U3 Everglades HPOA SUVA = 3.5 (%)
butanedioic acid, dimethyl ester	0.703	0.934	0.225	
butanedioic acid, methyl-, dimethyl ester	0.452	0.364	0.127	
benzoic acid, methyl ester			0.004	
phenol, 2-methoxy	0.219			
benzene, 1,2-dimethoxy	0.187			
phenol, 2-nitro-	0.086			
furan, 2-(methoxymethyl)-	0.069			
hexanedioic acid, dimethyl ester	0.073			
benzene, 1,2,3-trimethoxy-	0.217			
benzoic acid, methoxy, methyl ester			0.004	
benzoic acid, 4-methoxy-,methyl ester	0.360	0.226		
isonicotinic acid-D1-.alpha.-D2	0.109			
benzene, 1,3,5-trimethoxy-	0.367	0.409		
1H-pyrrole-2-carboxylic acid, 5-ethyl	0.249			
benzaldehyde, 3-phenoxy	0.247			
phenol, 2-(ethylthio)-	0.209			
2,4,6-trimethoxytoluene	0.435	0.459		
1,4-benzenedicarboxylic acid, dimethyl ester	0.273	0.166		
ethanone, 1-(3,4-dimethoxyphenyl)-	0.333			
benzoic acid, 3,5-dimethoxy-, methyl ester	0.372	0.336		
benzoic acid, 3,4-dimethoxy-, methyl ester [vanillic acid]	1.754	1.174		
benzeneacetic acid, 3,4-dimethoxy, methyl ester	0.300			
benzoic acid, 3,4,5-trimethoxy-, methyl ester [syringic acid]	0.475	0.468		
2-propen-1-one, 1-(2-hydroxyphenyl)-3-(4-toluene)	0.451			
1,2,4-benzenetricarboxylic acid, trimethyl ester	0.162			
1,2-benzenedicarboxylic acid, dibutyl ester	4.991	4.717		
eicosane [internal standard]	2.676	2.565	2.603	2.593
1,3,5-triazine-2,4-diamine, 6-chloro- <i>N</i> -ethyl		0.194		
1-phenanthrenecarboxylic acid, 1,2,3,		2.077		
1,2-benzenedicarboxylic acid, 3-nitro		0.602	0.931	

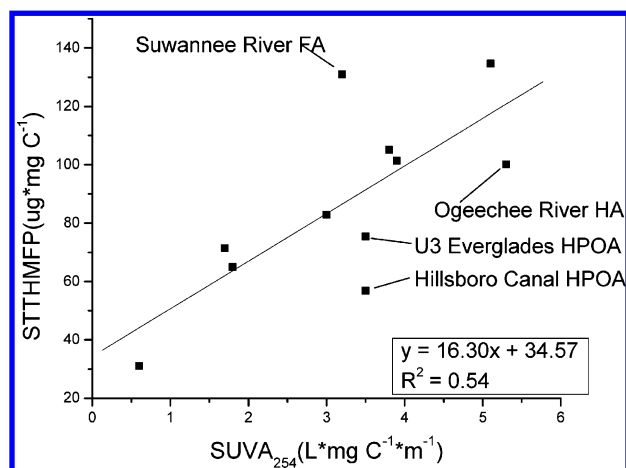


FIGURE 4. STTHMFP_{7d} versus SUVA₂₅₄ for the isolate organic matter samples.

STTHMFP_{72h} and total organic halogen formation potential (TOXFP), especially for samples isolated from the same locations. Other research has indicated that the correlation between SUVA₂₅₄ and STTHMFP_{7d} is weak for whole water samples when data are compared from diverse systems (16). We noted significant scatter for SUVA₂₅₄ and STTHMFP_{7d} data for 11 of the 13 isolates (Figure 4). Comparing samples with similar SUVA₂₅₄ values, the Everglades samples have STTHMFP_{7d} values one-third to one-half lower than the Ogeechee River FA sample. These results suggest compositional differences between the samples that are not reflected in the SUVA₂₅₄ value and are consistent with the results of the thermochemolysis analyses.

The overall applicability of SUVA₂₅₄ as an indicator for THMFP of whole waters was assessed for 34 filtered samples

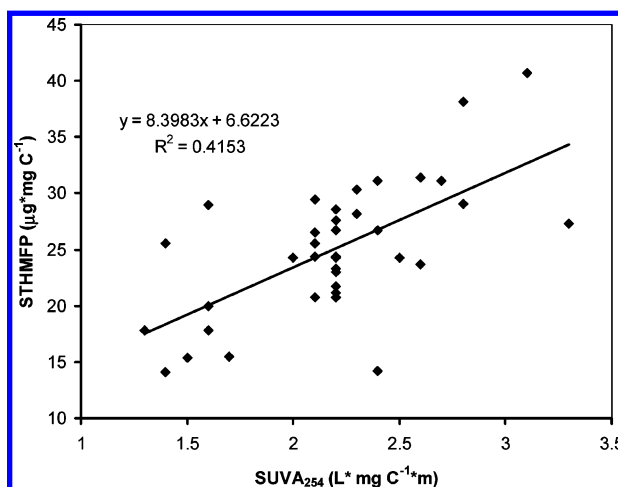


FIGURE 5. STTHM_{24h} versus SUVA₂₅₄ for filtered whole waters.

obtained from major river systems throughout the conterminous United States, including the Mississippi River, Rio Grande, Colorado River, and major tributaries of these rivers. Figure 5 shows a weak significant correlation between SUVA₂₅₄ and STTHM_{24h} for this group of samples ($R^2 = 0.41$). These results agree with those reported by Fram et al. (16) obtained using a different set of surface waters (92 sites). Both studies suggest that nonaromatic compounds present in whole water samples contribute to the generation of THMs and that SUVA₂₅₄ is a weak universal indicator of reactivity for the formation of THMs for whole water samples. The correlations for the individual river systems analyzed separately were found to be better than for the set of all samples, but these correlations were also generally weak. Clearly, SUVA₂₅₄ appears to be a better indicator of the reactivity of the

compounds that comprise aquatic humic substances (Figure 4) than for the DOC present in whole water samples. However, despite the stronger correlation for the isolates, there is significant scatter in the data.

The poorer correlation observed for the whole water samples suggests the presence of THM precursor material in the DOC that is not UV absorbent and is not extractable with the XAD-8 resin. The usefulness of SUVA as an indicator of DOC reactivity with disinfectants is complicated, in part, by the heterogeneity of the DOC. A large number of organic compound groups that comprise DOC react with chlorine to produce chloroform as a product. These include aromatic compounds (e.g. phenols), β -ketones, pyrroles (e.g. chlorophyll), and proteins (33). Some of these materials either do not absorb in the UV at $\lambda = 254$ nm or have small absorptivities and do not contribute significantly to SUVA₂₅₄. In addition, not all aromatic molecules react with chlorine to produce chloroform. Thus, some compounds that contribute to the overall UV absorbance may be inert with respect to THM formation, and some THM precursor compounds may not contribute to the overall UV absorbance.

The results from experiments involving the reactivity of DOC with specific chemical reactants, such as TMAH and NaOCl, indicate variable reactivities for samples with similar SUVA₂₅₄ values. These results illustrate a seemingly obvious but often overlooked feature of DOC samples, namely that the chemical compositions of samples having similar average properties, such as those determined by spectroscopic techniques (e.g. UV/Vis, C¹³-NMR, fluorescence), elemental analysis, or molecular weight analyses, may be very different. Of practical significance, the weak correlation observed between SUVA₂₅₄ and the formation of THMs for whole water samples suggests that SUVA is a weak indicator of DOC reactivity with chlorine when considering diverse samples. Stronger correlations have been noted for processes involving less specific reactions, such as interactions with coagulants (5), the inhibition of calcite precipitation (7), and the dissolution of cinnabar (8). In recent years, there has been an increase in the publication of papers describing the use of spectroscopic methods, such as UV absorbance and fluorescence (3, 36–38), to provide information about the composition and reactivity of DOC. These methods are of interest to chemists, ecologists, and environmental engineers, in addition to the drinking water community. In general, the results presented in this paper suggest that caution is warranted in estimating the composition and reactivity of DOC derived from a wide range of environments and source materials when using these methods.

Acknowledgments

This work was supported by the U.S. Environmental Protection Agency through Interagency Agreement DW14937972-01-0, the office of Naval Research through grant N0014-93-1-1130 and the National Science Foundation through grant OCE0096426. We thank Rick Hooper, Valerie Kelly, and U.S. Geological Survey field personnel for assistance with field sampling from sites associated with the USGS NASQAN program. The use of brand names in this report is for identification purposes only and does not imply endorsement by the U.S. Geological Survey.

Literature Cited

- Chin, Y.-P.; Aiken, G.; Danielson, K. *Environ. Sci. Technol.* **1997**, *31*, 1630–1635.
- Reckhow, D. A.; Singer, P. C.; Malcolm, R. *Environ. Sci. Technol.* **1990**, *24*, 1655–1664.
- Li, C.-W.; Benjamin, M. M.; Korshin, G. V. *Environ. Sci. Technol.* **2000**, *34*, 2570–2575.
- Westerhoff, P.; Aiken, G.; Amy, G.; DeBroux, J. *Water Res.* **2003**, *33*, 2265–2276.
- Randtke, S. J. Disinfection By-Product Precursor Removal by Coagulation and Precipitative Softening. In *Formation and Control of Disinfection By-Products in Drinking Water*; Singer, P. C., Ed.; American Water Works Association: Denver, CO, 1999; Chapter 12, pp 237–258.
- McKnight, D. M.; Bencala, K. E.; Zellweger, G. W.; Aiken, G. R.; Feder, G. L.; Thorn, K. A. *Environ. Sci. Technol.* **1992**, *26* 1388–1396.
- Hoch, A. R.; Reddy, M. M.; Aiken, G. R. *Geochim. Cosmochim. Acta* **2000**, *64*, 61–72.
- Waples, J. S. Master of Science, University of Colorado, 2001.
- U.S. Environmental Protection Agency. Federal Register 63(69390). 1998.
- Traina, S. J.; Novak, J.; Smeck, N. E. *J. Environ. Qual.* **1990**, *19*, 151–153.
- Novak, J. M.; Mills, G. L.; Bertsch, P. M. *J. Environ. Qual.* **2003**, *21*, 144–147.
- Aiken, G.; McKnight, D.; Thorn, K.; Thurman, E. *Org. Geochem.* **1992**, *18*, 567–573.
- Aiken, G.; McKnight, D.; Harnish, R.; Wershaw, R. *Biogeochem.* **1996**, *34*, 157–188.
- Wilson, M. A. *J. Soil Sci.* **1981**, *32*, 167–186.
- Wershaw, R. Applications of Nuclear Magnetic Resonance Spectroscopy for Determining Functionality in Humic Substances. In *Humic Substances in Soil, Sediment and Water: Geochemistry, Isolation, and Characterization*; Aiken, G., McKnight, D., Wershaw, R., MacCarthy, P., Eds.; John Wiley and Sons Ltd.: 1985; pp 561–582.
- Fram, M. S.; Fujii, R.; Weishaar, J. L.; Bergamaschi, B. A.; Aiken, G. *How DOC Composition May Explain the Poor Correlation Between Specific Trihalomethane Formation Potential and Specific UV Absorbance*; Water-Resources Investigations Report 99-4018B; Charleston, SC, 1999; pp 423–430.
- Summers, R. S.; Hooper, S. M.; Shukairy, H. M.; Solarik, G.; Owen, D. J. *Am. Water Works Assoc.* **1996**, 80–93.
- Hatcher, P.; Nanny, M.; Minard, R.; Dible, S.; Carson, D. *Org. Geochem.* **1995**, *23*, 881–888.
- MacCarthy, P.; Rice, J. A. Spectroscopic Methods (Other than NMR) for Determining Functionality in Humic Substances. In *Humic Substances in Soil, Sediment, and Water: Geochemistry, Isolation and Characterization*; Aiken, G., McKnight, D., Wershaw, R., Eds.; John Wiley & Sons: New York, 1985; Chapter 21, pp 527–559.
- Miller, W. L. Recent Advances in the Photochemistry of Natural Dissolved Organic Matter. In *Aquatic and Surface Photochemistry*; Helz, G. R., Zepp, R. G., Crosby, D. G., Eds.; Lewis Publishers: Ann Arbor, 1994; Chapter 7, pp 111–127.
- Silverstein, R. M.; Bassler, G. C.; Morrill, T. C. *Spectrometric Identification of Organic Compounds*, 3rd ed.; John Wiley & Sons: New York, 1974.
- McKnight, D. M.; Aiken, G. R. Sources and Age of Aquatic Humus, in *Aquatic Humic Substances*; Hessen, D. O., Tranvik, L. J., Eds.; Springer: New York, 1998; Vol. 133, pp 9–39.
- Chin, Y.-P.; Aiken, G.; O'Loughlin, E. *Environ. Sci. Technol.* **1994**, *28*, 1853–1858.
- Bloom, P. R.; Leenheer, J. Vibrational, Electronic, and High-energy Spectroscopic Methods for Characterizing Humic Substances. In *Humic Substances II: In Search of Structure*; Hayes, M. H. B., Malcolm, R., Swift, R. S., Eds.; John Wiley & Sons: New York, 1989; Chapter 14, pp 409–446.
- Hem, J. D. *Study and Interpretation of the Chemical Characteristics of Natural Water*; United States Government Printing Office: Washington DC, 1978.
- American Public Health Association, American Water Works Association, and Water Pollution Control Federation. *Standard Methods for the Examination of Water and Wastewater*, 19th ed.; Washington, DC, 1995.
- van der Leeden, F.; Troise, F. L.; Todd, D. K. *The Water Encyclopedia*, 2nd ed.; Lewis Publishers, Inc.: Chelsea, MI, 1990.
- Goolsby, D. A.; Battaglin, W. A. *Nitrogen in the Mississippi Basin - Estimating Sources and Predicting Flux to the Gulf of Mexico*; 135-00; United States Geological Survey: 2000.
- Filley, T. R.; Minard, R. D.; Hatcher, P. G. *Org. Geochem.* **1999**, *30*, 607–621.
- Hedges, J. I.; Mann, D. C. *Geochim. Cosmochim. Acta* **1979**, *43*, 1803–1807.
- Hedges, J.; Ertel, J. R. *Anal. Chem.* **1982**, *54*, 174–178.
- Croue, J. P.; DeBroux, J. F.; Amy, G. L.; Aiken, G.; Leenheer, J. In *Formation and Control of Disinfection By-Products in Drinking Water*; Singer, P. C., Ed.; American Water Works Association: Denver, 1999; pp 65–93.

- (33) Larson, R. A.; Weber, E. J. *Reaction Mechanisms in Environmental Organic Chemistry*; Lewis Publishers: Ann Arbor, MI, 1994.
- (34) McKnight, D.; Aiken, G.; Smith, R. *Limnol. Oceanogr.* **1991**, *36*, 998–1006.
- (35) McKnight, D.; Andrews, E.; Spaulding, S.; Aiken, G. *Limnol. Oceanogr.* **1994**, *39*, 1972–1979.
- (36) Korshin, G. V.; Kumke, M. U.; Li C.; Frimmel, F. H. *Environ. Sci. Technol.* **1999**, *33*, 1207–1212.
- (37) Langhals, H. In *Refractory Organic Substances in the Environment*; Frimmel, F. H., Abbt-Braun, G., Heumann, K. G., Hock, B., Ludemann, H. D., Spiteller, M., Eds.; Wiley-VCH: Weinheim, Federal Republic of Germany, 2002; pp 200–214.
- (38) McKnight, D. M.; Boyer, E. W.; Westerhoff, P. K.; Doran, P. T.; Kulbe, T.; Anderson, D. T. *Limnol. Oceanogr.* **2001**, *46*, 38–48.

Received for review February 7, 2003. Revised manuscript received June 27, 2003. Accepted July 1, 2003.

ES030360X