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Rapid delineation of humic and non-humic organic matter fractions in water

Taha F. Marhaba, PhD, PE *, Yong Pu

Department of Civil and Environmental Engineering, New Jersey Institute of Technology, University Heights, Newark, NJ 07102-1982, USA

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Abstract

Dissolved organic matter (DOM) in water is often characterized by aggregate parameters like dissolved organic carbon (DOC). DOM from conventional surface water treatment plant in Northern New Jersey was isolated and fractionated using resin adsorption chromatography into six different fractions, which were operationally categorized as hydrophobic acid, hydrophobic neutral, hydrophobic base, hydrophilic acid, hydrophilic neutral and hydrophilic base. The spectral fluorescent signatures (SFS) technique was developed for the quantitative identification of the six fractions by post-processing analysis that includes a statistical model. The SFS is the total sum of emission spectra of a sample at different excitation wavelengths, recorded as a matrix of fluorescent intensity in coordinates of excitation and emission wavelengths, in a definite spectral window. High sensitivity and rapid identification and quantification of DOM fractions are among the main features of the technique. Since hydrophobic and hydrophilic substances are considered more humic and non-humid in nature, respectively, the technique provided an opportunity to rapidly delineate source waters in terms of such categories.

Keywords: Fractionation; Dissolved organic matter (DOM); Rapid delineation; Fluorescence

1. Introduction

Dissolved organic matter (DOM) has been defined as having two main constituents — humic and non-humic substances. It consists of complex mixtures of organic

* Corresponding author. Tel.: +1-973-642-4599; fax: +1-973-596-5790.
E-mail address: Marhaba@ADM.NJIT.edu (T.F. Marhaba).

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compounds with relatively unknown structures and chemical composition. Humic substances have been known to make up a major portion of the DOM from surface waters, about 50–65% [1–3]. Aquatic humic substances are polar, straw-colored, organic acids that are derived from soil humus and terrestrial and aquatic plants as defined by Thurman and Malcolm [4] who also pioneered an isolation procedure by resin adsorption. Once isolated, humic substances can be subject to further fractionation. At pH level of 1, the precipitate is humic acid and the soluble fraction is fulvic acid. However, there are more to organic substances in DOM than just humic substances. To broaden the scope of DOM research, fractions of dissolved organic materials are usually defined operationally by the physical/chemical isolation procedure.

DOM was isolated from locations within three surface water treatment plants in New Jersey; one located on the Passaic River and the other two located on the Raritan and Millstone rivers. Internal sampling locations in the water treatment plants (effluents of unit processes) were selected where the expected variability of fractions' concentrations that were needed in the method development, herein. Resin adsorption methods were used to isolate six fractions: hydrophobic acid, hydrophobic neutral, hydrophobic base, hydrophilic acid, hydrophilic neutral, and hydrophilic base, defined as follows:

1. Hydrophilic base — amphoteric proteinaceous materials containing amino acids, amino sugars, peptides and proteins [5].
2. Hydrophilic acid — an organic compound of the hydroxyl acid group [5].
3. Hydrophilic neutral — an organic compound made up of polysaccharides [6].
4. Hydrophobic base — the portion of the humic substance retained by DAX-8 resin at normal pH (~ 7) which can be eluted by hydrochloric acid [5].
5. Hydrophobic acid — a soil fulvic [7].
6. Hydrophobic neutral — a mix of hydrocarbon and carbonyl compounds [5].

Humic and non-humic substances are considered hydrophobic and hydrophilic substances, respectively, based on the operational definition [5,8,9]. Humic and non-humic substances in DOM greatly vary from one source water to the next. This is due to complex nature of DOM which is a function of geography, geology, industrial and municipal discharges, natural landscape and water resources.

Dissolved organic carbon (DOC) is typically used as a parameter to measure organic content in water. But, DOC is an aggregate parameter and does not indicate the character of the organic matter in water. Hence, there is a need for a rapid technique that characterizes the chemical identity and reactivity of DOM. Orlov et al. [10] proved that fluorescent diagnosis of organic pollution in the water environment was a promising method especially for the identification of hydrocarbons in the open sea. The use of an on-line fluorescent technique as a diagnostic tool for water and wastewater control was investigated and discussed by Babichenko et al. [11]. The method does not require the labor-intensive and time-consuming pretreatment of the water sample. The fluorescence technique can be an alternative, which allows on-line processing and control at a reduced operating cost.

Analysis of natural water samples using excitation–emission matrix spectroscopy or spectral fluorescent signatures (SFS) shows this technique to have the potential in

characterizing the nature and source of DOM in natural waters [12]. The SFS is the total sum of emission spectra of a sample at different excitation wavelengths, recorded as a matrix of fluorescent intensity in coordinates of excitation and emission wavelengths, in a definite spectral window.

Fluorescence occurs when radiation is absorbed, and the excited species formed lose part of their excess energy by non-radiative means. Then, the remaining energy is emitted as radiation. This radiation is of a longer wavelength and lower energy than that which caused the excitation. More importantly, because this quantified amount of energy is dependent on the structure of the compound molecules, it is considered a signature, or SFS, which is particular to the nature of the compounds present. With modern day fluorescence spectrophotometers it is possible to scan the entire usable band in a short time period (e.g., 3 min) without sample pretreatment.

This paper presents the SFS coupled with post-processing method as a rapid technique that can be used for delineation or screening of DOM in water in terms of eight classified characteristics; humic, non-humic, three hydrophobic fractions and three hydrophilic fractions.

2. Methods

Several water treatment plants (from raw influent to finished effluent) in New Jersey were sampled for fractionation. The treatment plants were selected due to the wide range of fraction concentrations available, and differences in the treatment train. The treatment train of the Passaic Valley Water Commission (PVWC) WTP in Little Falls, NJ, was sampled April 26, 1998 and the DOM used for method development. The plant draws from the Passaic River and utilizes conventional treatment that includes coagulation/sedimentation, dual media filtration with intermediate and post chlorination. Other locations sampled for fractionation and use in method validation include the entire treatment trains (from influent to effluent) of the Raritan-Millstone (R/M) and the Canal Road (CR) surface water treatment plants (WTPs) in central New Jersey (Elizabethtown Water, Westfield, NJ). These systems were sampled on May 21, 1998. The plants draw water from the same two sources; the confluence of the Raritan and Millstone River and the Delaware and Raritan Canal, a different source water than the PVWC WTP. The R/M WTP utilizes conventional treatment with intermediate chlorination and post chloramination. The CR plant utilizes pre-ozonation, coagulation, sedimentation, intermediate ozonation, and granular activated carbon (GAC) multimedia filtration. Table 1 describes the WTPs, chemical feed, sampling locations and raw water quality in more detail.

Samples were directly collected, thermally secured and properly transported to ensure consistent quality control. Samples were refrigerated in the laboratory at 4°C throughout the 14-day holding time. Milli-Q water was used for all dilutions, solution preparation and final glassware washing.

2.1. Isolation and fractionation

A modified resin isolation and fractionation procedure to the one originated by Leenheer [5] was used in this research. The modified procedure was described by

Table 1
Description of Water Treatment Plants (WTP) (average daily data)

Unit process	PVWC WTP (04/16/1998)	R/M WTP (05/21/1998)	CR WTP (05/21/1998)
Plant flow (m^3/day)	210,000	380,000	90,000
Pre-ozone contact time (min) [dosage (mg/l)]	N/A	N/A	9.25 [0.25]
Pre-treatment chemicals [dosages (mg/l)]	Liquid alum [20–70], chlorine [4.7]	Liquid alum [27], sulfuric acid [20],	Liquid alum [23]
pH (coagulation chamber)	6	6	6
Sedimentation Type	Conventional	Tube settler	Conventional
Intermediate ozone contact time (min) [dosage (mg/l)]	N/A	N/A	30 [0.50]
Filter media	Anthracite sand	Anthracite sand garnet	Multi-media (GAC, sand, ilmenite) and dual-media (GAC, sand). GAC: EBCT = 10 min, 3 months in operation at time of sampling, replacement frequency ~ 6 months
Post-treatment chemicals (mg/l)	Sodium hypochlorite (1.0), sodium hydroxide (15.1)	Sodium hypochlorite (2.1), aqua ammonia (0.36), lime (12), zinc orthophosphate (0.44)	Sodium hypochlorite (1.7), aqua ammonia (0.37), sodium hydroxide (8.7), zinc orthophosphate (0.50)
Sampling locations for fractionation	Influent, sedimentation effluent, filter effluent and delivered	Influent, sedimentation effluent, filter effluent and delivered	Influent, pre-ozonation, effluent, sedimentation effluent, filter effluent and delivered
Influent DOC (mg/l)	4.60	4.00	4.00
Ozone–DOC ratio	N/A	N/A	0.06–0.13
Bromide (mg/l)	< 0.0046	0.03	0.03
Influent turbidity (NTU)	4.7	11	11
Influent pH	7.5	7.2	7.2
Alkalinity (mg/l as $CaCO_3$)	46	28	28
Hardness (mg/l as $CaCO_3$)	69	52	52

Marhaba et al. [12]. All samples were filtered through a 0.45-μm-cellulose filter to obtain the DOM. Amberlite resin DAX-8, a macroporous methylmethacrylate copolymer (Supelco, Bellefonte, PA), AG-MP-50, a strong acid, sulfonated, polystyrene macroporous resin (BioRad, Hercules, CA) and Duolite A7, a weak base, phenol-formaldehyde condensation macroporous resin (Supelco, Bellefonte, PA) were all purified by soxhlet extraction prior to being used in the process. As a result of the fractionation technique, six fractions of the DOM were isolated based on chemical characteristics. They were termed operationally as hydrophobic base, hydrophobic acid, hydrophobic neutral, hydrophilic base, hydrophilic acid and hydrophilic neutral. All fractions were preserved in the applicable eluting hydrochloric acid or sodium hydroxide and All fractions were preserved in the applicable eluting HCl or NaOH and refrigerated at 4°C. All elutions in this procedure were done in a forward direction or gravity flow (not backflush). This was done to facilitate the recovery procedure. Forward elution was conducted by Day et al. [8] and is the preferred flow configuration for the column. All chromatography columns were of borosilicate glass (Kontes, Vineland, NJ) with 20-μm polyethylene bed support disc.

The fractionation approach such as the one that is being used in this work is not valid without criticisms. Aiken and Leenheer [5] and Crum et al. [13] expressed concerns that since DOM materials must be exposed to extreme pH conditions during the process (i.e., less than 2 and greater than 10) that potential alteration in DOM structure and in natural chlorinated reactivities of the materials may be the consequences. General consensus is fractionation approach via resin adsorption is very tedious and time-consuming. Despite the drawbacks, Thurman [1] acknowledged that the approach has advanced our fundamental understanding of the nature and behavior of natural organic material in water. Although sample fractionation provided the opportunities to study the mechanism about which DOM interacts with chlorine, it is important to note that the collective behavior of the individual fractions may not be the same as the behavior of the unadulterated water sample in an actual water treatment plant.

2.2. Organic carbon analysis

DOC was used to measure the original non-fractionated and fractions' organic content. DOC was analyzed by an O.I. Analytical 700 system (O.I. College Station, TX) total organic carbon analyzer using the method of sodium persulfate oxidation (Standard Methods 5310-D) [14]. Original source samples were filtered through a 0.45-μm cellulose filter prior to analysis and fractionation to remove suspended particles. Five percent (5%) phosphoric acid was used to first acidify the sample which was then purged of total inorganic carbon (TIC) by nitrogen. Sodium persulfate was subsequently introduced as an oxidant in the process for the oxidation of the organic compounds at 100°C. As CO_2 is purged and trapped at the end of the oxidation process, an infrared photometric beam was used for the analysis of carbon mass. The analyzer was regularly calibrated with 1000-ppm potassium hydrogen phthalate (KHP) standard in either the TIC or TOC calibration mode, as recommended by the manufacturer. Each sample was prepared and diluted differently depending on whether the solvent was 0.1 N HCl, 1 N NaOH or 2 N NaOH. The analyzer was programmed accordingly with the proper

amount of acid, oxidant and reaction time as recommended by the manufacturer. At least three blanks were analyzed prior to the analysis of each sample to establish and verify the appropriate background for quality assurance and control. Duplicates were run randomly.

2.3. Fluorescence measurements

A fluorescence spectrophotometer (Hitachi, F-3010, Tokyo, Japan) equipped with 150 W ozone-free xenon lamp was used for fluorescence measurements. This instrument had single monochromators on both excitation and emission spectrometers. The blaze wavelength is 300 nm for excitation grating and 400 nm for the emission grating. Both grating have a blaze density of 900-groove mm^{-1}. The samples were recorded in a standard 1-cm quartz cuvette of 4-ml volume sample size. The photomultiplier has the capability of exciting samples and measuring emission from 220 to 730 nm. Samples in this research were excited from 225 to 525 nm wavelengths in the backward mode (i.e., starting with 525 nm) to minimize high-energy molecular damage, although tests have shown that either mode is acceptable. At each excitation (Ex) level, emission (Em) was recorded from Ex + 24 to 633 nm. An optimal stepwise increment of 12 nm was set for both excitation and emission measurements. SFS figures were then produced (excitation vs. emission vs. relative intensity). Spectral correction was performed to remove scatter (e.g., Raman and Raleigh) by a post-processing software code discussed later. Fig. 1 shows a typical SFS. The Ex and Em wavelengths window was selected on the basis of regions with most fluorescence. All samples were adjusted to a common neutral pH prior to analysis. Instrument calibration and standardization was performed according to the manufacturer's recommendations. Good spectroscopic practice was exercised to ensure that (a) the sample was free from weighing, volumetric and temperature errors, (b) the sample was completely dissolved and clear, (c) no bubbles have formed on the

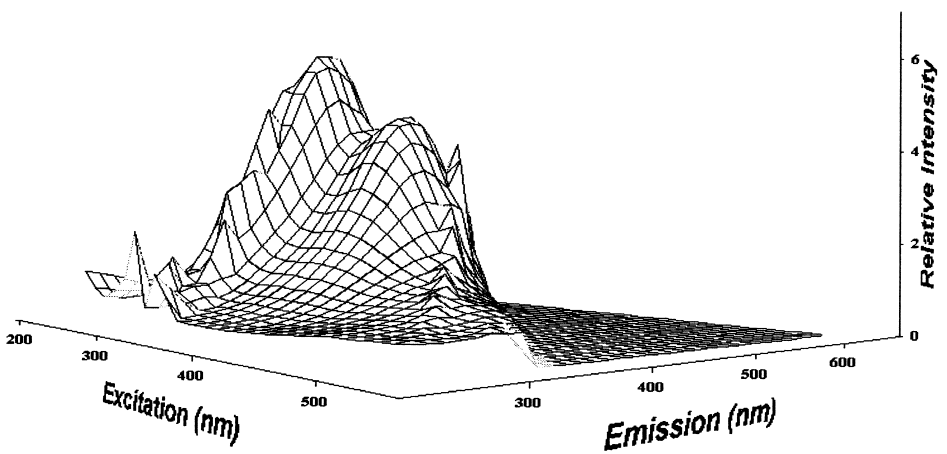

Fig. 1. Typical SFS of the raw water (CR WTP intake, sampled May 21, 1998).

cell windows, (d) adsorption on the cell walls was not occurring, (e) the cells were clean and oriented in the beam correctly, (f) the reference solution was subjected to exactly the same procedure as the sample, and (h) the slit width was corrected for the expected band width variance.

3. Results and discussion

3.1. DOM recovery and fraction mass

Twelve locations along the treatment trains of the CR, R/M, and PVWC WTPs were fractionated into the six fractions of hydrophobic (humic) and hydrophilic (non-humic) substances. Mass balance of the sum of fractions compared to the original unfractionated sample mass confirms the effectiveness of the fractionation procedure giving a $\pm 14\%$ tolerance of DOM recovery. Average efficiency of the process was 105% (standard deviation = 8.1). Day et al. [8] reported similar tolerance, which was due to loss of the hydrophilic acid fraction from the strong anionic nature of the AG-MP-1 resin. Variations from 8–12% were also reported by Croue et al. [9]. Surplus recovery in this study was probably due to the contribution of inorganics that were introduced in the process such as HCl and NaOH for acidity adjustment as well as elution. It should be noted that because NOM, and for that matter DOM, varied significantly on such parameters as temperature, seasons of the year and geographical locations of the watersheds, any such comparison should take those variations into account. Rotary vacuum evaporation of the fractions were not conducted because concentrated forms of the isolated fractions were not of interest to the study and certainly not at the expense of ''considerable'' losses of the volatile organic compounds [15]. Although the fractionation process is time-consuming, it provided the opportunity to isolate the components of the DOM. The fractionation procedure was repeated several times for different sampling points in the WTP prior to actually implementing the experimental strategy to statistically confirm the precision of the results.

3.2. SFS post-processing method development

All original (non-fractionated) samples and fractions were subject to fluorescent spectrophotometric scans (i.e., SFSs). An examination of the SFSs of individual fractions revealed major peaks and locations of such peaks that were unique for each fraction. These spectral regions were located between the Ex 225 and 261 nm emission spectra. The original non-fractionated samples SFSs were examined in such regions in order to link spectral characteristics to known fraction concentrations. Through trial and error, it was found that the rising slopes and areas under the spectra in these regions correlated to fraction concentrations. The following sections discuss the post-processing analysis of the SFSs.

3.3. Post-processing of SFS

Post-processing analysis of SFSs was performed and included (a) removal of spectral scatter (i.e., Raman and Raleigh), (b) measurement of fraction specific parameters (i.e., spectal slopes and areas), (c) development of statistical model, and (d) application of model.

Scatter removal was the first step in post-processing analysis of the raw SFS data files. Scatter was defined as a sharp increase (>12 relative intensity units) in the spectra and was removed through the use of a post-processing developed code (Matlab, MathWorks, Natick, MA). Scatter was removed by replacing the scatter relative intensity value with the previous value in the SFS database.

Upon filtering out the scatter, the required spectral parameters at Ex 225, 237, 249, and 261 nm emission spectra were determined by the post-processing developed code. These parameters were rising slope (Slope) or derivative spectra and spectral area (Area), as defined below. At each Ex emission spectrum, the starting intensity (i.e., at Em = Ex + 24 nm) and the maximum intensity (i.e., spectrum peak) is determined. The rising slope for each Ex emission spectrum is then calculated as:

$$\text{Slope} = \frac{[P - P_i]}{[\text{Em}_p - \text{Em}_i]} \quad (1)$$

P = Maximum relative intensity (relative intensity units); P_i = Relative intensity at Em_i (relative intensity units); Em_i = Starting emission wavelength of spectrum = Ex + 24 (nm); Em_p = Emission wavelength at maximum relative intensity (nm).

The area under each Ex emission spectrum (Area, in relative intensity units nm) determined by the post-processing code as the area from Em = Ex + 24 to 633 nm. The average Slope and Area of the four spectra is then calculated for use in statistical post-processing analysis.

3.4. Model development

A general linear regression model (GRL) was developed for predicting the concentration of each fraction over different treatment stages. The dependent variables were the concentrations of each fraction (mg/l). The independent variables selected for building the initial GRL model were Slope, Area, Treatment and Fraction. The interaction between Slope and Area (Slope × Area) was also included into the initial model as an independent variable since it was found to be more representative of a particular DOM fraction than either alone.

Among the five independent variables, Slope, Area and the product Slope × Area were quantitative variables, while the Treatment and Fraction variables were qualitative. The Treatment variable had four sub-classes: influent, sedimentation effluent, filtration effluent and plant effluent. Likewise, there were six sub-classes associated with the Fraction qualitative variable: hydrophobic acid (HPOA), hydrophobic base (HPOB), hydrophobic neutral (HPON), Hydrophilic acid (HPIA), hydrophilic base (HPIB), and hydrophilic neutral (HPIN). There were three sub-classes adopted in the initial model to

describe the Treatment variable. These sub-classes were taken as influent (Inf.), sedimentation effluent (Sedi.), and filtration effluent (Filt.). For example, to calculate the concentration of influent, the value of Inf. was set to 1 and the values of Sedi. and Filt. sub-classes were set to 0. To calculate the concentration of filtration effluent, the value of Filt. was set 1 and the values of the other two sub-classes were set to 0. If the values of all of the selected sub-classes were set to 0, the model calculated the concentration of plant effluent. The same principle was applicable to the qualitative variable of Fraction of which five of its sub-classes were used to develop the GRL model. The data of quantitative variables and the sub-classes of qualitative variables for PVWC WTP were used to build the GRL model and is provided in the Table 2.

The initial GRL model was written as:

$$C = \beta_0 + \beta_1 \times \underline{\text{Area}} + \beta_2 \times \underline{\text{Slope}} + \beta_3 \times \underline{\text{Slope}} \times \underline{\text{Area}} + \beta_4 \times \underline{\text{HPOA}} + \beta_5 \times \underline{\text{HPOB}} + \beta_6 \times \underline{\text{HPON}} + \beta_7 \times \underline{\text{HPIA}} + \beta_8 \times \underline{\text{HPIB}} + \beta_9 \times \underline{\text{Inf.}} + \beta_{10} \times \underline{\text{Sedi.}} + \beta_{11} \times \underline{\text{Filt.}} \quad (2)$$

Where: C = predicted fraction concentration (mg/l); Area = area of emission spectrum where the fraction major peak exists (intensity nm); Slope = rising slope of the corre-

Table 2
Data of PVWC WTP used for model development

Slope (intensity/nm)	Area (intensity nm)	Inf.	Sedi.	Filt.	HPOA	HPOB	HPON	HPIA	HPIB	C (mg/l)
0.048	962.04	1	0	0	1	0	0	0	0	0.54
0.048	962.04	1	0	0	0	1	0	0	0	0.33
0.048	962.04	1	0	0	0	0	1	0	0	0.45
0.048	962.04	1	0	0	0	0	0	1	0	1.11
0.048	962.04	1	0	0	0	0	0	0	1	0.15
0.048	962.04	1	0	0	0	0	0	0	0	0.20
0.172	518.52	0	1	0	1	0	0	0	0	0.34
0.172	518.52	0	1	0	0	1	0	0	0	0.29
0.172	518.52	0	1	0	0	0	1	0	0	0.51
0.172	518.52	0	1	0	0	0	0	1	0	0.25
0.172	518.52	0	1	0	0	0	0	0	1	1.38
0.172	518.52	0	1	0	0	0	0	0	0	0.25
0.010	578.28	0	0	1	1	0	0	0	0	0.32
0.010	578.28	0	0	1	0	1	0	0	0	0.20
0.010	578.28	0	0	1	0	0	1	0	0	0.37
0.010	578.28	0	0	1	0	0	0	1	0	0.92
0.010	578.28	0	0	1	0	0	0	0	1	0.28
0.010	578.28	0	0	1	0	0	0	0	0	0.21
0.038	227.28	0	0	0	1	0	0	0	0	0.24
0.038	227.28	0	0	0	0	1	0	0	0	0.21
0.038	227.28	0	0	0	0	0	1	0	0	0.34
0.038	227.28	0	0	0	0	0	0	1	0	0.81
0.038	227.28	0	0	0	0	0	0	0	1	0.23
0.038	227.28	0	0	0	0	0	0	0	0	0.20

sponding fraction spectral major peak (intensity/nm); HPOA = 1 for HPOA fraction concentration, otherwise 0; HPOB = 1 for HPOB fraction concentration, otherwise 0; HPON = 1 for HPON fraction concentration, otherwise 0; HPIA = 1 for HPIA fraction concentration, otherwise 0; HPIB = 1 for HPIB fraction concentration, otherwise 0; Inf. = 1 for influent concentration, other wise 0; Sedi. = 1 for sedimentation effluent concentration, other wise 0; Filt. = 1 for filtration effluent concentration, otherwise 0; β = regression coefficients.

3.5. Model refinement

Data of the treatment train of the PVWC WTP were used to refine the initial model using a statistical software (*MINITAB 12*, Minitab, State College, PA). The regression results are listed in Table 3. The regression analysis indicated that Sedi, Inf., and Filt. highly correlated with other independent variables. Their impacts on predicting the concentrations of each fraction could be represented through those highly correlated variables and thus were removed from the model. The revised model was

$$C = -0.0074 + 0.0003548 \times \text{Area.} + 3.317 \times \text{Slope} - 0.00445 \times \text{Slope} \times \text{Area} + 0.10875 \times \text{HPOA} + 0.0040 \times \text{HPOB} + 0.16475 \times \text{HPON} + 0.80225 \times \text{HPIA} - 0.0225 \times \text{HPIB} \quad (3)$$

The test result of *F*-ratio was 22.85. With 95% confidence, 8 and 15 degrees of freedom, $F(8, 15; 0.05) = 2.64$. Since the *F*-ratio was higher than *F*-critical, it was concluded that the refined model was appropriate to predict concentrations of fractions. The small *P*-value for this test (0.001) further confirmed this conclusion. The R^2 was 92.4% (adjusted was 88.4%), indicating good correlation between the dependent variable, *C*, and the independent variables.

Table 3
Model coefficients and analysis of variance

Coefficient	Value
Constant	−0.0074
Slope	3.317
Area	0.0003548
Slope × Area	−0.00445
HPOA	0.10875
HPOB	0.00400
HPON	0.16475
HPIA	0.80225
HPIB	−0.02550
F-critical (8,15; 0.05)	2.64
F-ratio	22.85
P-value	0.001
R^2	92.4%

3.6. Model verification

The revised model was applied to predict the concentrations of fractions at the PVWC, CR and R/M WTPs. Model application results and corresponding actual concentration are provided in Tables 4 and 5. Table 5 also provides the statistical analysis for predicted and actual concentrations for CR and R/M WTPs. The paired *t*-test had a value of 1.15. Given $\alpha = 0.05$ and $N - 1 = 41$, the t_c was 2.02, higher than the paired *t*-test value. Therefore, statistically there was no significant difference between the predicted concentrations and the actual concentrations for CR and R/M WTPs. Generally, there is good prediction to the actual concentration except for humic substances at Sedimentation and Effluent of CR WTP. One reason may be the different water source of CR from PVWC.

3.7. SFS post-processing method application

Determining the concentrations of DOM fractions using SFS post-processing analysis has potentially many advantages over using the typical DOC aggregate parameter. Some of those advantages are as follows:

- Rapid (minutes instead of days using resin isolation/fractionation methods) determination of six DOM fractions with minimal sample pretreatment. The sum of the six DOM fractions is also a prediction of the DOC.
- Rapid on-line determination of DOM fractions in a water treatment plant. For example, water utilities could apply the method to determine problematic fractions and

Table 4
Prediction of PVWC (mg/l)

Fractionation		PVWC			
		Inf.	Sedi.	Filt.	Eff.
HPOA	p	0.40	0.46	0.31	0.27
	a	0.54	0.34	0.32	0.24
HPOB	p	0.29	0.35	0.21	0.16
	a	0.33	0.29	0.20	0.21
HPON	p	0.45	0.51	0.37	0.33
	a	0.45	0.51	0.37	0.34
Humic	p	1.14	1.32	0.89	0.76
	a	1.32	1.14	0.89	0.79
HPIA	p	1.09	1.15	1.01	0.96
	a	1.11	1.38	0.92	0.81
HPIB	p	0.26	0.32	0.18	0.14
	a	0.15	0.25	0.28	0.23
HPIN	p	0.29	0.35	0.21	0.16
	a	0.20	0.40	0.21	0.20
Non-humic	p	1.64	1.82	1.40	1.26
	a	1.46	2.03	1.41	1.24

Note: p = predicted, using model. a = actual, determined by fractionation.

Table 5
Verification and prediction for CR and RM (mg/l)

Fractionation		CR				RM		
		Inf.	Sedi.	Filt.	Eff.	Sedi.	Filt.	Eff.
HPOA	p	0.42	0.71	0.32	0.35	0.66	0.26	0.29
	a	0.46	0.21	0.12	0.11	0.34	0.50	0.19
HPOB	p	0.32	0.60	0.22	0.25	0.56	0.16	0.18
	a	0.23	0.01	0.01	0.01	0.18	0.20	0.12
HPON	p	0.48	0.77	0.38	0.41	0.72	0.33	0.34
	a	0.69	0.33	0.30	0.28	0.65	0.12	0.49
Humic	p	1.22	2.08	0.92	1.01	1.94	0.75	0.81
	a	1.38	0.55	0.43	0.4	1.17	0.82	0.8
HPIA	p	1.12	1.40	1.02	1.05	1.36	0.95	0.98
	a	1.83	1.35	1.12	0.90	1.67	1.40	1.11
HPIB	p	0.29	0.58	0.19	0.22	0.53	0.13	0.15
	a	0.15	0.12	0.11	0.08	0.21	0.14	0.15
HPIN	p	0.32	0.60	0.21	0.24	0.55	0.15	0.20
	a	0.79	0.61	0.53	0.47	0.30	0.15	0.18
Non-humic	p	1.73	2.58	1.42	1.51	2.44	1.23	1.33
	a	2.77	2.08	1.76	1.45	2.18	1.69	1.44
Paired *t*-ratio					1.15			
t-critical (0.025, 41)					2.02			

Note: p = predicted, using model. a = actual, determined by fractionation.

optimize on their removal through treatment. For example, in a recent study by Marhaba et al. [12] it was reported that hydrophilic acid was the most problematic fraction towards the formation of trihalomethanes (THMs) and haloacetic acids (HAAs). Hence, the SFS post-processing method may be used as a method to predict hydrophilic acids and optimize on its reduction in water treatment.

· Enables economic spatial and temporal investigation of watershed. Humic and non-humic substances are considered hydrophobic and hydrophilic substances, respectively, based on the operational definition [5,8,9]. One example would be to characterize humic (i.e., hydrophobic substances) and non-humic substances (i.e., hydrophilic substances) in the watershed in order to ''pin-point'' potential point and non-point sources. Another example would be to target the source of problematic fractions to disinfection by-products (DBPs), such as hydrophilic acid, in the watershed.

4. Summary and conclusion

NOM resin isolation and fractionation into six hydrophobic and hydrophilic substances was performed on sampling locations within three water treatment plants in New Jersey. SFS were performed on the original non-fractionated samples and fractionated

samples. Post-processing analysis was performed on the SFSs and included spectral scatter removal. Unique spectral regions within the original non-fractionated samples were found and were linked to fraction concentrations using such parameters as spectral slopes and areas. Additional post-processing analysis was performed on the unique regions of the SFSs to include a general regression model. The model predicts the six fraction concentrations from a single SFS of a water sample with reasonable accuracy. The whole process takes minutes vs. days for resin isolation/fractionation procedures. The sum of the predicted hydrophilics and hydrophobics substances is also a prediction of the non-humic and humic content of the water sample. Hence, rapid delineation or screening of waters may be performed rapidly and cost effectively, and with reasonable precision and accuracy using this technique for source water or watershed management studies.

The SFS post-processing method requires minimal sample pretreatment and takes minutes to perform instead of days for isolation and fractionation methods. The method is in its preliminary stages of development and is the first analytical chemometric technique to rapidly predict DOM fractions in water. Refinement of the technique/model will be needed for its application to other water sources. However, the many advantages of this application warrant further verification.

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Notation

D/DBP	Disinfectant/Disinfection By-Product
DBP	Disinfection By-Product
DOC	Dissolved Organic Carbon
DOM	Dissolved Organic Matter
ESWTR	Enhanced Surface Water Treatment Rule
FP	Formation Potential
HAAs	Haloacetic Acids
ICR	Information Collection Rule
LLE	Liquid–liquid-extraction
MCL	Maximum Contaminant Level
MDL	Minimum Detection Limit
MRDL	Maximum Residual Disinfectant Level
NOM	Natural Organic Matter
PV	Passaic Valley Water Commission

THMs	Trihalomethanes
TIC	Total Inorganic Carbon
TOC	Total Organic Carbon
WTP	Water Treatment Plant

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