



# Environmental Assessment and Risk Analysis Element



## Research Project Summary

### Predicting the Occurrence of Disinfection By-Products in Drinking Water by Measuring the Components of Organic Carbon in Source Water Using a Novel Analytical Approach

#### Introduction

Among the regulated contaminants in drinking water is a class of volatile organic compounds called trihalomethanes. Trihalomethanes are disinfection by-products (DBPs); that is, they are formed when natural organic matter in raw water reacts with (or is oxidized by) chlorine during the disinfection step of routine water treatment. Some of the compounds regulated as DBPs are chloroform, bromoform, and dichlorobromomethane. Trihalomethanes can cause liver, kidney or central nervous system problems, and some are associated with an increased risk of certain types of cancer.

Natural waters, especially surface waters such as rivers and streams, contain microorganisms that may cause illness and even death. For this reason, it is necessary to disinfect raw waters to eliminate these microorganisms. While there are many types of disinfectants available today for water treatment, chlorine is the most used and has been for nearly 100 years. Because of the widespread use of chlorine, chlorinated by-products have been the focus of DBP research. However, natural organic matter can react with any oxidizing agent to produce DBPs.

Natural organic matter (NOM) is categorized into two groups, humic and non-humic substances. NOM is the largest organic constituent of both raw and finished drinking water with concentrations ranging from less than one (1) to about fourteen (14) parts-per-million. It is not known definitively which of these groups is responsible for the formation of DBPs. Humic substances constitute a major portion (about half) of the dissolved organic carbon from surface waters. They are complex mixtures of organic compounds with relatively unknown structures and chemical composition. Even the definition of humic substances is somewhat ambiguous and is frequently operationally defined according to the physical/chemical isolation procedure used to detect it. It would be useful to the drinking water industry to have a reliable way of predicting the formation of DBPs in order to minimize their occurrence in the water that reaches consumers' taps.

Currently, there are some methods that can be used to predict the formation of DBPs, including the total organic carbon (TOC) analysis and trihalomethane formation potential (THMFP). These are very time-consuming to perform and, in the end, do not provide specific information about DBP formation potential. The research described here provides information about an innovative, specific, and easy to use method to identify the reactive humic portion of natural organic matter and to thereby predict the formation of DBPs. The method involves the use of fluorescence spectroscopy. The technique has the potential to differentiate humic from non-humic and humic acid from fulvic acid originating from point sources or non-point source inputs.

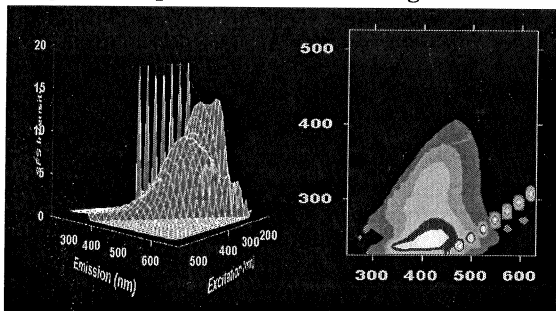
#### Methods

##### Fluorescence spectroscopy

All spectroscopic methods use some form of light energy. The light used to analyze the presence of NOM is in the Ultra-Violet (UV) range, the same range of light energy that causes sunburn of the skin. Like the skin, organic molecules absorb light of different energies. Normally, the easiest thing to measure is the amount of light absorbed by molecules in water, this is Ultra Violet spectroscopy (UV254). An alternative method that is more sensitive and less susceptible to interference is Fluorescence Spectroscopy. Fluorescence occurs when a molecule absorbs UV light and then emits light of a another energy. Fluorescence is a measure of the light that is emitted rather than the light absorbed. It is a more reliable, sensitive, and specific measurement of organic material in water.

When a water sample is subjected to light bombardment, organic material present will fluoresce. At this point, it is necessary to distinguish among the many organic materials in the sample causing the fluorescence. Since the amount and type of NOM in various NJ surface waters are unknown, conventional spectroscopy methods that use a single wavelength are inadequate to characterize the humic and non-humic substances present. Modern Fluorescence Instrumentation has the ability to analyze the entire range of wavelengths within three (3) minutes. All the material causes a scattering of peaks. In order to focus on the material of interest, it is useful to view the fluorescence data three-dimensionally. By handling the data in this way, a spectral fluorescence signature (SFS) is created. All of the information about how NOM absorbs and emits UV energy is contained in the SFS. An example of such an SFS is shown in Figure 1.

Figure 1: Spectral Fluorescent Signature



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. The signature is created by plotting the wavelength of light directed at the sample versus the emission of light (or fluorescence) versus the intensity of the fluorescence. The SFS is then used to identify the unique type of natural organic matter present in a particular sample. By separating out these different chemical types of NOM, the reactivity of that NOM type can be analyzed for DBP formation upon disinfection for that water source. Details about the method can be found in : Lippincott, R.L., Van D., and Marhaba T.F.; "Characterizing dissolved organic matter fractions using spectral fluorescent signatures and post processing by principal component analysis." Fresenius J Anal Chem, (1999) July 10, 1999.

### ***Separation of NOM into Groups Based on Chemical Characteristics and DBP Reactivity***

Water samples were passed through columns of different adsorbents to separate the NOM in the water into humic acid, fulvic acid and non-humic substances. NOM can be separated into "Water Liking" or Hydrophilic and "Water Hating" or Hydrophobic groups. Each group can contain organics that can act as an acid, base, or neutral compound. Each of these different constituents of NOM react differently when exposed to chlorine during the disinfection process at water treatment plants. In addition, each individual source water in the state will have different relative concentrations of each of these groups. A sample matrix containing humic acid and fulvic acid at various concentrations were analyzed. For details on the isolation and fractionation of the NOM, see Marhaba, Van & Lippincott, 1998.

**Table 1: Chemical Composition of Natural Organic Matter**

Hydrophobic	Hydrophilic
Acid: soil fulvic acids	Acid: organic compounds of the hydroxyl acid group
Neutral: a mix of hydrocarbon and carbonyl compounds such as sugars and humic substances	Neutral: organic compounds composed of polysaccharides
Base: humic substances containing amino acids, proteic materials, sugars and polysaccharides	Base: amphoteric proteinaceous material containing amino acids, amino sugars, peptides and proteins

To examine the reactive components of organic matter in relation to DBP formation, the humic acid and fulvic acid standard solutions were chlorinated with 100 ppm chlorine using calcium hypochlorite. After seven days, the samples were dechlorinated with ammonium chloride and analyzed for trihalomethane, haloacetonitrile and haloacetic acid formation by liquid-liquid extraction followed by gas chromatographic analysis. Fluorescence measurements were taken for humic acid and fulvic acid samples before and after chlorination to provide a visual means of determining which organic fractions react to form DBPs. Data from both analyses were used to determine the relationship between fluorescence and DBP formation. For additional information on the methods, see Kochar, 1999.

### ***Collection of Water Samples***

In the first phase of this project, river samples from the Passaic River Basin, the Raritan River, and the Millstone River were analyzed. In the second phase, water samples were collected from raw surface water as well as throughout the treatment system from the Raritan/Millstone and the Canal Road surface water treatment plants of Elizabethtown Water Company, located in central New Jersey.

All water samples were collected, preserved and transported in amber glass bottles by a member of the research team to ensure consistent quality control. Samples were kept cold (at 4°C) in coolers until delivery to the laboratory, where they were immediately stored in a refrigerator at this constant temperature until ready for processing and analysis. Samples were collected in 9-liter volumes and filtered through a 0.45 micron cellulose filter.

### ***Analysis of Data in Three-dimensional Plots***

In normal spectrophotometric analysis, a chemist would use one energy of light to obtain a response on a spectrometer. The responses are then calibrated against known concentrations of that compound. Using the SFS, the instrument collects thousands of responses across the entire range of energies so that no information about the NOM is lost. Sets of SFS signatures are then collected and the resulting raw data matrices are mathematically simplified using a statistical method called principal component analysis. By analyzing the organic matter present in the water samples by SFS, the analyst can mathematically predict a concentration value for all of the different chemical classes present in the water without chemically isolating each component. Once the concentration of each chemical component (fraction) of the organic matter is determined, the DBP formation can be precisely predicted. This type of approach allows the assessment of both source water potential for DBP formation and the determination of the effectiveness of each water treatment unit operation at removing DBP precursors.

## **Applied Research Using SFS**

Following the method development for the SFS technique, the research focused on applying the analysis to assess differences in disinfection processes used in New Jersey. The New Jersey drinking water purveyor selected for this part of the study was the Elizabethtown Water Company. Located on the confluence of the Raritan and Millstone Rivers in central New Jersey, the Elizabethtown Water Company has two sister water treatment facilities on each side of the river. These two plants draw their source water from a common intake structure. One plant is a newly constructed state-of-the-art Ozonation plant, while the facility on the other side of the river uses chlorination as its disinfection agent. This makes these two systems an ideal laboratory for studying the differences between different oxidants and plant configurations.

### ***Disinfection By-Product Formation after Ozonation versus Chlorination***

Several of the participating drinking water purveyors are considering or have changed to a stronger disinfecting agent called Ozone. Ozone has an advantage over chlorination in that it is more efficient in breaking apart larger NOM molecular structures into smaller ones. In addition, Ozone does not produce regulated chlorinated DBPs. Chemical changes in NOM result in the formation of organic by-products that contain more oxygenated chemical linkages than

are found in nature, making the materials more amenable to biodegradation. Typical compounds formed by Ozonation of NOM are oxalic acids, aldehydes, and ketones. Chlorination and Ozonation will have different effects on organic matter, depending upon the predominant fraction type.

### ***Coagulation to Remove Dissolved Organic Matter Fractions***

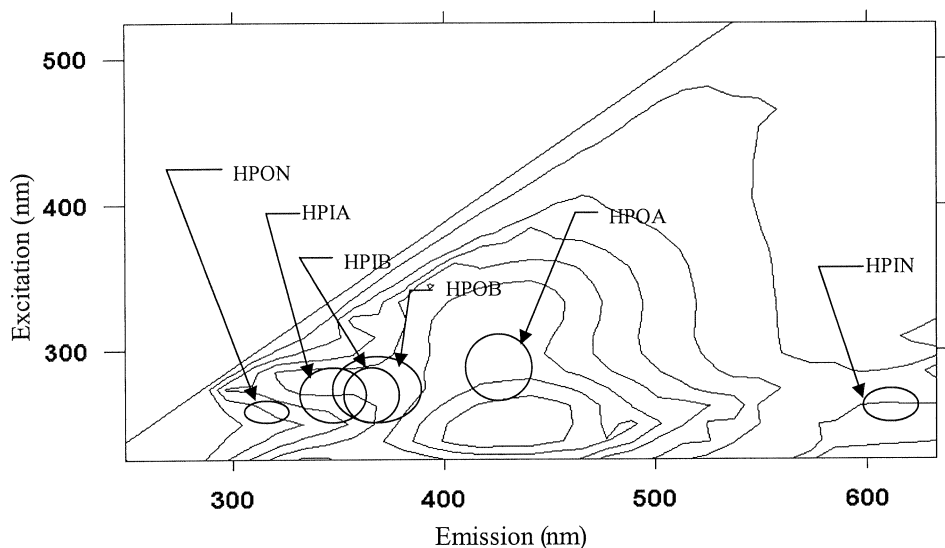
Various water treatment technologies target the removal of NOM without regard to the specific reactivity of the fractions. The ability of ozone to alter DBP precursors, while improving turbidity removal, has generated a great interest in the research of combining ozonation with other water treatment processes such as coagulation, chlorination, and granular activated carbon. Except for coagulation, these technologies are expensive. The concentration of the various fractions in the source waters is site-specific and, as the fractions are chemically dissimilar, it is possible that the optimal removal of each fraction occurs at different sets of coagulation conditions. In general, humic (hydrophobic) dissolved organic matter and higher-molecular weight dissolved organic matter are more efficiently removed than the other fractions using current treatment methods. The treatment challenge, from an economic perspective, is to develop coagulation conditions that remove sufficient DBP precursors to allow the use of free chlorine as a primary and residual disinfectant without exceeding the drinking water standards for DBPs. Coagulation was simulated by using jar-test apparatus. For a detailed description of the methods used, see Pipada, 1999.

## **Results**

### ***Fractionation of Natural Organic Matter into Six Groups***

Using the water samples from the river humic acid and river fulvic acid standards, a calibrated spectral fluorescent signatures database was created. Ten concentration levels were established for each fraction ranging from 0.5 ppm to 10 ppm. Each concentration was then subjected to a fluorescent spectrophotometric analysis. By developing the signatures for these standards, it was possible to visually identify the types of organics present in a natural water sample. Data from the generation of each spectral fluorescent signature were stored in a special database. Qualitatively, the two fractions (humic and fulvic) can be separated and characterized by their spectral fluorescent signatures. Each of these two fractions contain different acid, base, and neutral chemical characteristics which have unique emission signatures. Figure 2 shows the discrete chemical excitation and emission areas for each of the six NOM fractions.

**Figure 2: Discrete Chemical Fluorescent Zones of Natural Organic Matter Fractions**



For the method to be truly useful, the SFS needs to be able to mathematically predict these groups when they occur in mixtures, as in natural waters. Armed with the information on the mixtures, it was possible to develop a predictive model that accurately determined the concentration of the reactive NOM fractions for that specific raw water. Samples from the Passaic River Basin, Raritan River and Millstone River were analyzed. In all the samples that were analyzed, the hydrophilic acid fraction is most predominant (about 50%) of the dissolved organic matter in the water. This fraction also has the highest relative reactivity for the formation of DBPs.

### ***Removal of the Organic Matter Fractions after Ozonation, Chlorination, and Coagulation***

While aggregate dissolved organic carbon data shows moderate differences between the Ozonation plant and the conventional Chlorination plant, the differences are much more noticeable when the comparison is based on the actual, individual fractions. Because each organic fraction is comprised of different organic compounds which react differently in producing disinfection by-products, the aggregate dissolved organic carbon (measured using conventional methods) is limited in predicting the DBP formation potential and treatment effectiveness of the DBP precursors. The predominant fraction in a particular water sample would be anticipated to change due to season, climate and hydraulic variations of the surface water system. The examination of dissolved organic carbon alone reveals little information in addressing the issue of DBPs and precursors. Knowing the fraction provides insight into the effectiveness of

ozonation versus chlorination on removal of these precursors; the treatment unit operations were effective on some fractions but quite ineffective on others. Table 2 show the removal of NOM fractions at the two Elizabethtown water treatment facilities.

**Table 2: Overall removal of organic matter fractions using ozonation versus chlorination.**

Fraction	%Removal from OZONATION system	% Removal from CHLORINATION system
<b>Aggregate dissolved organic carbon</b>	<b>56</b>	<b>42</b>
Hydrophobic acid	97	48
Hydrophobic neutral	77	60
Hydrophobic base	60	30
Hydrophilic acid	45	5
Hydrophilic neutral	51	39
Hydrophilic base	40	75

Table 3 shows the results of the bench scale study for pH and alum dose versus the treatment plant removal efficiencies for each of the individual fractions. The hydrophobic acid and hydrophobic base fractions are more amendable to coagulation and have the highest reduction in total organic carbon using this method. The hydrophilic base and hydrophilic neutral fractions were less effectively removed by coagulation.

**Table 3. Overall removal of organic matter fractions using ozonation, chlorination and coagulation.**

Fraction	%Removal from ozonation system	% Removal from chlorination system	% Removal using coagulation (pH 6 and 40-60 mg/L alum dosage)
<b>Aggregate dissolved organic carbon</b>	<b>56</b>	<b>42</b>	
Hydrophobic acid	97	48	68.3
Hydrophobic neutral	77	60	51.6
Hydrophobic base	60	30	71.2
Hydrophilic acid	45	5	51.4
Hydrophilic neutral	51	39	44.3
Hydrophilic base	40	75	45.8

### **Disinfection By-Product Formation**

The six dissolved organic matter fractions showed the trihalomethane formation potential in the following order: Hydrophilic acid > hydrophobic acid > hydrophobic base > hydrophobic neutral > hydrophilic base > hydrophilic neutral.

Trihalomethanes were the predominant DBPs and haloacetonitriles produced were significantly lower for all the fractions as well as the mixtures. Although the hydrophilic base and neutral fractions had low trihalomethane formation potential, source waters containing predominantly hydrophilic substances may not necessarily meet the drinking water standards using alum coagulation alone, as these fractions are not well removed by this method. The typical mixtures used in the studies had an initial trihalomethane formation potential of 250 ppb. With enhanced coagulation (alum dosage 60 mg/L and lower pH values (pH of 6), the formation potential dropped to 87 ppb.

Because one of the objectives of this research was to use fluorescence signatures as a predictive tool for disinfection by-product formation, each sample had its SFS developed before and after chlorination.

### **Conclusions**

The SFS technique/model presented herein for the determination of DOM fractions in water is the first of its kind to target the six hydrophilic and hydrophobic fractions. The following conclusions are made based on DOM fractionation operations and data at the specified sampling locations and times described.

- Unique fluorescing properties for each of the six fractions were found.
- A multiple linear regression model that predicts the concentration of each fraction based on data (i.e., A, etc.) determined from fluorescence spectra was developed.
- The SFS technique coupled with the developed multiple linear regression model can be used for the rapid qualitatively and quantitatively determination of the six DOM fractions in water. The time consuming (several

work-days per sample) and highly involved isolation and fractionation technique can be substituted with the SFS technique, which requires minimal time (several minutes) and effort.

- The model, when applied to sample data from another watershed, generally showed a good fit indicating its application potential to other natural water sources.
- Due to its simplicity and the availability of on-line fluorescence spectrophotometers, the technique/model has the potential of being applied in water treatment, and source water assessment and characterization, for the spatial and temporal determination of problematic or DOM fractions of concern.

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If you would like to learn more about the technical specifics of this research, several technical briefs and journal articles are available from the project manager or in the DSRT director’s suite on the first floor of the 401 building on East State Street.

**Prepared By**  
**Robert L. Lippincott Ph.D.**  
**Eileen A. Murphy Ph.D.**

**January, 01**

**STATE OF NEW JERSEY**

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**Division of Science, Research & Technology**

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**Environmental Assessment & Risk Analysis Element**

*Dr. Eileen Murphy, Assistant Director*

Please send comments or requests to:  
Division of Science, Research and Technology,  
P.O.Box 409, Trenton, NJ 08625  
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