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Fluorescence spectroscopy for the characterization of total organic carbon and disinfection by-product formation

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ABSTRACT

FLUORESCENCE SPECTROSCOPY FOR THE CHARACTERIZATION OF TOTAL ORGANIC CARBON AND DISINFECTION BY-PRODUCT FORMATION

by
Matthew Brendan Washington

One of the concerns facing the drinking water industry is the formation of disinfection by-products (DBPs) during the disinfection stage of treatment. Organic DBPs form during the oxidation of the natural organic matter (NOM) found in natural waters by the application of a disinfectant, such as chlorine.

NOM is composed of two aggregate materials, humic and non-humic substances. It is unknown which portions of NOM react with the oxidant to form DBPs. Methods used to predict the formation of DBPs include total organic carbon (TOC) analysis and Trihalomethane Formation Potential (THMFP), which are time consuming and do not give specific information. This research explored the use of fluorescence spectroscopy to identify the humic portion of NOM and to predict the formation of DBPs.

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by
Matthew Brendan Washington

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APPROVAL PAGE

FLUORESCENCE SPECTROSCOPY FOR THE CHARACTERIZATION OF TOTAL ORGANIC CARBON AND DISINFECTION BY-PRODUCT FORMATION

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To all the overworked and underpaid graduate students.

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CHAPTER 1

INTRODUCTION

1.1 Objective

The objective of this thesis is to explore the use of fluorescence spectroscopy as a surrogate measurement for total organic carbon (TOC) analysis, and as a predictive tool for disinfection by-product (DBP) formation due to the presence of humic substances in drinking water sources. The research conducted to meet these objectives was part of an ongoing study intended to correlate components of TOC to water treatment plant operations and DBPs. Funding for the project was provided by the New Jersey Department of Environmental Protection.

Monthly samples are collected in conjunction with three water treatment plants (WTPs) and six sewage treatment plants (STPs) in Central New Jersey. Monthly samples analyzed in this research are for September and October of 1997. The participating WTPs are the Elizabethtown Water Company (EWC) Raritan-Millstone and Canal Road treatment plants, the North Jersey District Water Supply Company (NJDWSC) Wanaque treatment plant, and the Passaic Valley Water Commission (PVWC) Little Falls treatment plant. The participating STPs are Parsippany-Troy Hills, Rockaway Valley, Two Bridges, Wayne, Pompton Lakes, and Wanaque. The monthly samples are analyzed for total organic carbon and fluorescence. This data is analyzed by linear regression to determine the relationship between fluorescence and TOC.

In an attempt to examine the reactive components of TOC in relation to DBP formation, a sample matrix of humic and fulvic acid standard solutions was prepared at varying concentrations and chlorinated for seven days. After seven days, the samples were dechlorinated with ammonium chloride and analyzed for trihalomethane (THM) and haloacetonitrile (HAN) formation by liquid-liquid extraction gas chromatography. Fluorescence measurements were taken for humic and fulvic acid samples of identical concentrations before and after chlorination to provide a visual means of determining what organic fractions react to form DBPs. Data for both analyses are analyzed to determine the relationship between fluorescence and DBP formation.

1.2 Project History

As stated above, the work done for the completion of this thesis has been a part of a larger investigation currently being conducted at NJIT. This research project, "Determination of Organic Substances by Spectral Fluorescent Signatures", is ongoing and is funded by the NJDEP. The research proposal was accepted in May 1997, and work began during the summer of 1997. The results discussed here are from preliminary exploratory experiments completed during the summer and fall of 1997. These are intended to provide a basis for the further research called for in the proposal.

CHAPTER 2

BACKGROUND

2.1 Drinking Water Concerns

Natural organic matter (NOM) is a term used to describe the organic material typically present in natural waters. The NOM in these waters can significantly affect many aspects of water treatment, particularly in the application of disinfectants. NOM reacts with many of the disinfectants used to treat drinking water, such as chlorine, chloramine, and ozone, to form a variety of disinfection by-products (DBPs) [17]. Many of these DBPs have adverse health effects in humans (i.e. carcinogenic or mutagenic effects). The primary DBPs of concern include the trihalomethanes (THMs), haloacetic acids (HAAs), and haloacetonitriles (HANs) [17].

NOM is typically divided into two categories, the humic fraction and the non-humic fraction. The humic fraction consists of humic and fulvic acids (hydrophobic acids), while the non-humic fraction consists of hydrophilic acids and biochemicals (amino acids, proteins, and carbohydrates) [9]. Traditionally, most research has concerned the role of humic substances in the formation of DBPs, but recently additional attention has been given to the role non-humic substances play as well [9].

2.2 The Nature of Humic Substances

The humic substances are a complex group of organic materials whose structure is not well defined. The division of humic substances into humic and fulvic acids is based on solubility in dilute acid and dilute base. Fulvic acids are soluble in both dilute acid and dilute base. Humic acids are soluble in dilute base but are precipitated by dilute

acid. A third category, humin, is insoluble in both dilute acid and dilute base [16]. Some authorities group humin with humic acid, stating that the humins have the same characteristics as humic acids but are insoluble in dilute base because they are associated with clay minerals in natural waters. It is believed that the fulvic acids are the predominant group of humic substances in natural water [1], [8], [9], [10], [16].

Although the chemical structure of the humic substances is not precisely known, the nature of the major functional groups is fairly well defined. Some of these functional groups are shown in Figure 1.

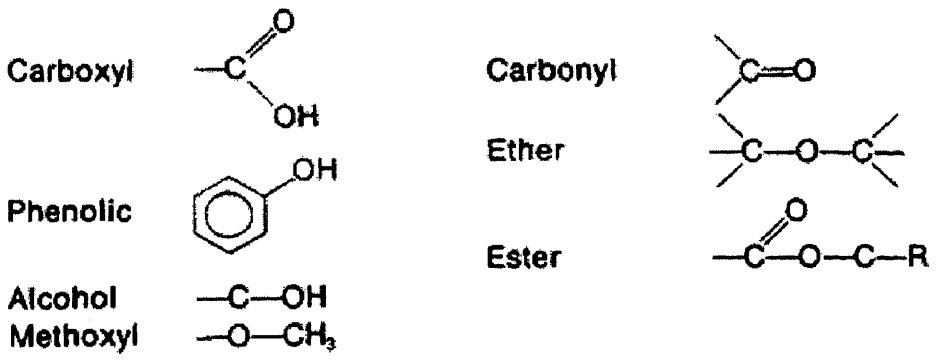


Figure 1 Functional Groups Found in Humic and Fulvic Acids
Source: [16]

The exact composition of a humic or fulvic acid has yet to be defined. A given humic substance might have all the functional groups represented in its structure, or it may have only a few groups within its structure. The distribution of the functional groups in a sample may not be the same from one sample to the next.

Table 1 Functional Group Distribution (Percent of Oxygen Present)

Functional Group	Humic Acids	Fulvic Acids
Carboxyl	14 – 45	58 – 65
Phenol	10 – 38	9 – 19
Alcohol	13 – 15	11 – 16
Carbonyl	4 – 23	4 – 11
Methoxyl	1 – 5	1 – 2

Source: [16]

The functional group distribution, in terms of percent of oxygen in the indicated functional group, is shown in Table 1.

2.3 Disinfection By-Products

Water intended for human consumption will invariably contain some microorganisms or viruses. For this reason, it is necessary to treat water with a disinfectant, which in many cases will be chlorine. Chlorine has been the disinfectant of choice for nearly 100 years and is used by the majority of water treatment systems. Due to the widespread use of chlorine, chlorinated by-products are usually considered to be more of a concern than the by-products that result from the use of other oxidants, such as ozone or chloramine. Chlorinated DBPs form when free chlorine is added to water and forms hypochlorous acid (HOCl) [17]. Chlorine will act as an oxidant and react with the natural organic matter (NOM) present.

The generalized equation describing the formation of the halogenated DBPs is:

$$HOCl + Br^- + NOM \rightarrow \text{THMs and Other Halogenated DBPs}$$

The majority of the halogenated DBPs that result from the addition of chlorine to drinking water are THMs, HAAs, HANs, cyanogen halides, halopicrins, haloketones, haloaldehydes, and halophenols. In the absence of bromide ion (Br^-), only the chlorinated by-products are formed. In the presence of bromide, free chlorine (HOCl) rapidly oxidizes bromide to hypobromous acid (HOBr), which then reacts, along with the remaining HOCl, with NOM to produce the mixed chloro-bromo DBPs [15], [16].

It has been found that THMs and HAAs are the most common DBPs found in water treatment processes. The U.S. Environmental Protection Agency (USEPA) has set a maximum contaminant level (MCL) of 100 μg/L for total THMs (TTHMs) and has proposed a new MCL of 80 μg /L [18]. In addition to these standards, a proposed MCL for HAA5 has been set at 60 μg /L [18]. Lower MCLs on TTHMs and HAA5 are also anticipated. Hence, a determination of the organic substances responsible for forming the DBPs is important for the minimization of DBP formation in water treatment systems. TTHMs is defined as the sum of four individual THMs: chloroform, bromoform, dibromochloromethane, and bromodichloromethane. HAA5 is defined as the sum of five HAAs: monochloroacetic acid (MCAA), dichloroacetic acid (DBAA), trichloroacetic acid (TCAA), monobromoacetic acid (MBAA), and dibromoacetic acid (DBAA).

2.4 Fluorescence Spectroscopy

One potentially useful tool in the analysis of humic substances is fluorescence spectroscopy. In the simplest of terms, fluorescence occurs when a material absorbs and then emits light. At the ground state, the molecule absorbs light and transits to the excited state. The molecule loses a portion of the exciting energy as vibrational energy, transits to a lower vibration level with no radiation emitted, and then returns to the ground state while emitting a kind of optical energy. This is called "fluorescence".

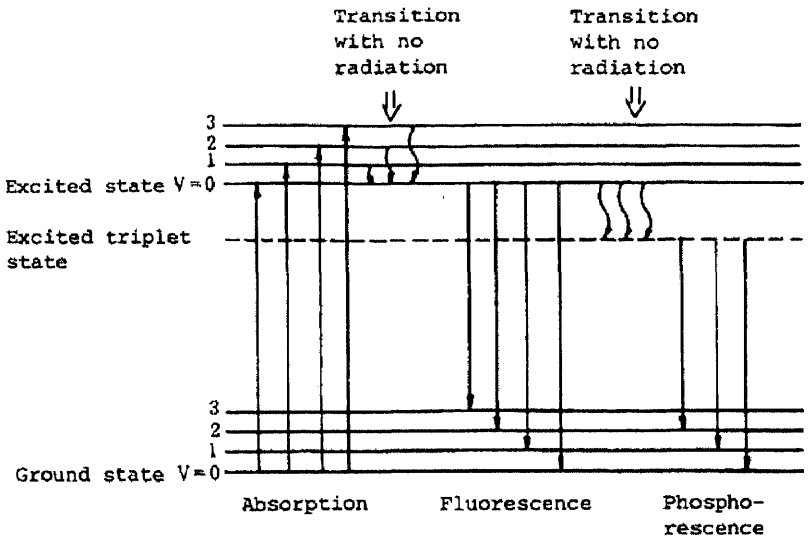


Figure 2 Optical States of an Excited Molecule
Source: [4]

Figure 2 provides an illustration of fluorescence, as well as the other optical states an excited molecule might reach. The molecule that transits without emitting radiation to the triplet state also emits optical energy when it is returned to the ground state. This optical energy is called "phosphorescence" [4].

The method typically used to investigate the organic properties of water is UV absorbance (often at wavelengths near 254 nm). Fluorescence is, in essence, the reverse of absorption, as it measures the light that is absorbed and then released [13]. Conventional fluorescence spectra are obtained by using one of two spectroscopic modes. The emission spectrum is recorded by measuring the relative intensity of radiation emitted as a function of wavelength for a fixed excitation wavelength. Or, the excitation spectrum is recorded by measuring the emission intensity at a fixed wavelength while varying the excitation wavelength [13]. Since a portion of the light absorbed by a substance is lost by vibrational relaxation, light that is emitted must be at a longer wavelength than the excitation light, according to Stoke's law [4].

Optical emission different from fluorescence may be observed during the analysis. This will often be one of three types of scattering effects: (1) Rayleigh scattering, (2) Raman scattering, and (3) Second-order Ray scattering. Rayleigh scattering will appear where the excitation wavelength is equal to the emission wavelength [13]. Raman scattering will appear where the emission wavelength is slightly longer than the excitation wavelength. Second-order Ray scattering will occur where the emission wavelength is equal to twice the excitation wavelength. Scattering peaks are not caused by any organic materials that might be present in the solution [4]. Instead, scattering peaks are due to interaction between the lights being used to analyze the sample and the solvent that the sample has been prepared in.

Table 2 Locations of Raman Peaks for Typical Solvents

	Emission Wavelengths		
Excitation Wavelength	Water	Ethanol	Chloroform
248	271	267	___
313	350	344	346
365	416	405	410
405	469	459	461
436	511	500	502

Source: [4]

Table 2 lists the location of Raman peaks for some typical solvents. Peaks due to scatter can be differentiated from a peak due to fluorescence by the fact that emission wavelength of a fluorescence peak remains constant for varying excitations, while a scattering peak will have a different emission wavelength for every excitation wavelength.

2.5 Spectral Fluorescence Signatures

Due to the presence of scattering peaks, it can become difficult to determine whether or not a peak is caused by an analyte of interest. One option for eliminating this problem is to view fluorescence data three-dimensionally. Techniques for utilizing fluorescence data in this manner are referred to as Total Luminescence Spectroscopy or Spectral Fluorescence Signatures (SFS) [3], [8]. The SFS can be viewed as a matrix of excitation and emission wavelengths. In a three-dimensional plot of

fluorescence data, a narrow line cutting diagonally through the plot represents scatter peaks, while fluorescence peaks are represented by broad contours.

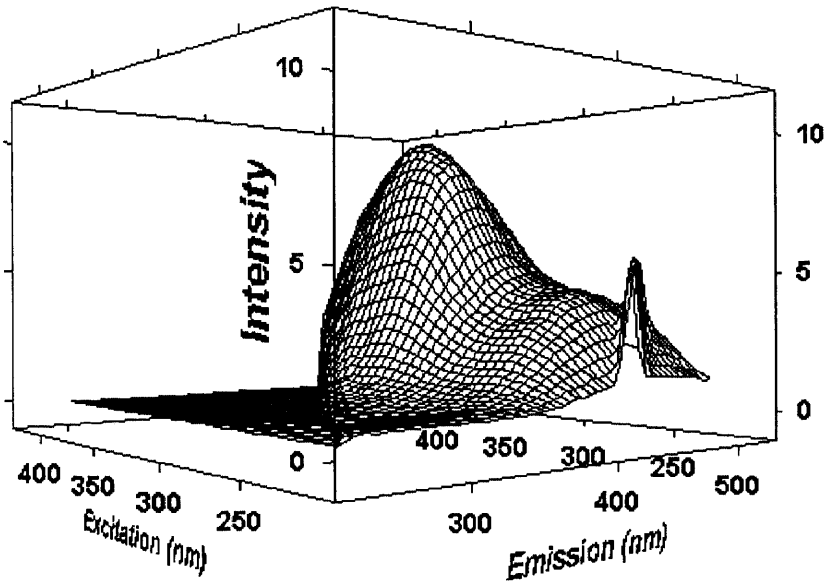


Figure 3 Spectral Fluorescence Signature

Figure 3 is an example of what the signature for a sample might show. For this work, three-dimensional plots will be used to locate areas which will be representative of humic and non-humic substances in water. Three data points will be chosen: one to represent a humic acid, one to represent a fulvic acid, and one to represent a non-humic substance. The intensity value at that point will be used to develop relationships between fluorescence and other properties of humic and non-humic substances.

Fluorescence is an intrinsic property of humic material. Specifically, some of the aromatic compounds incorporated in humic substances are fluorescent (i.e. the

fluorophores) [8], [9]. Correlations have been developed between fluorescence and dissolved organic carbon (DOC), and fluorescence has been found to be a function of NOM source, pH, and molecular weight [8], [9]. The ultimate goal of this project is to develop correlations between fluorescence and TOC for sample locations in the watersheds served by the WTPs and STPs participating in this project, and to use these correlations to predict, and ultimately eliminate, the formation of DBPs.

CHAPTER 3

METHODOLOGY

3.1 Experimental Objectives

The investigation that will be conducted to meet the objectives discussed in Chapter 1 consists of several phases. The first step involves developing an automated data collection system to enhance the development of the Spectral Fluorescence Signature (SFS) so that data is collected in a consistent manner for all samples of interest. The next step will be to develop a set of signatures that act as standards for further investigations. These standards will include deionized water and standard humic and fulvic acids. The next phase of the investigation is to collect TOC and fluorescence data for the watershed samples in order to discover any correlations that exist between the two analytical tools. The final phase will involve preparing chlorinated humic and fulvic acid solutions, and measuring the by-products that form as well as collecting pre-chlorination and post-chlorination fluorescence data.

3.2 Materials

All the chemicals used in this investigation were of the highest quality available. The humic and fulvic acid standards were purchased from the International Humic Substances Society (IHSS), and were used in the condition in which they were received. Standards used for the calibration of instruments were purchased from Ultra Scientific Corp., Aldrich Chemical Corp., Supelco Corp., or Sigma Corp. Pure forms of the DBPs were purchased from Aldrich, and all other chemicals were reagent grade or better from Fisher Scientific.

3.3 Fluorescence Data Collection

The development of a SFS requires the collection of a large number of data points for each sample; each plotted in three dimensions. This data collection would be excessively time consuming and render the scope of work attempted impossible. To solve this problem, a two-step solution was utilized as described below.

The data required to build the SFS was collected using the Hitachi F-3010 Fluorescence Spectrophotometer. To automate the collection of data, a computer program was written using Microsoft QuickBASIC© to control data collection over an RS-232 interface with the instrument. The program has the ability to send commands to the instrument for altering the wavelengths, conducting the measurement, and receiving the results in a series of tab-delimited text files. The source code for this program can be seen in Appendix A. Once the data has been collected, it is imported into the Galactic© GRAMS32 spectroscopy software for viewing in three dimensions.

3.4 Fluorescence Standards

To allow comparisons to be made between samples from a variety of sources, a set of standards were developed and their signatures used as a baseline for the remaining analysis. Fluorescence readings were taken under the following conditions: (1) excitation wavelengths are varied between 225 nm and 525 nm, (2) emission wavelengths are varied between 249 nm and 633 nm, and (3) the change in wavelength between readings is 12 nm. Blank samples consisting of deionized and organic free water were used to identify scattering peaks and serve as a baseline reading. Humic and fulvic acid solutions at

varying concentrations were prepared and their signatures were used to serve as a basis for identifying organic substances in the samples received from the drinking water and sewage treatment plants. The standards were prepared in the laboratory and stored at 4 degrees Centigrade. No preservatives were added nor were any pH adjustments used to prepare the standards. The sample were placed in the instrument using a four-sided quartz polished fluorescence cuvette, with a stopper in place to ensure that the samples will not evaporate or volatilize while fluorescence data is being collected.

3.5 Total Organic Carbon Analysis

Analysis of TOC was performed by the persulfate oxidation method, as described in *Standard Methods for the Examination of Water and Wastewater 5310 B.* No preservatives were added to the samples nor was the pH be adjusted prior to the analysis. All samples were stored at 4 degrees Centigrade.

The TOC analysis was performed using an OI Analytical TOC Analyzer capable of measuring both organic and inorganic carbon. The instrument is equipped with an autosampler to ensure an identical injection for all samples. The calibration parameters were stored in the instrument's memory, and data was logged using the attached printer. Data from the printout were logged in a spreadsheet for analysis.

3.6 Disinfection By-Product Formation Potential

The ultimate goal of this investigation is to predict the formation of disinfection by-products using the SFS of a sample. To investigate this possibility, a sample matrix of humic and fulvic acid samples was prepared. The SFS of each sample was developed using the same procedure as the standards. The samples were buffered to a pH of 7 and chlorinated to a concentration of 20 ppm as Cl_2 using calcium hypochlorite. These chlorinated samples were incubated for 7 days at 25 degrees Centigrade. After the incubation period, the samples will be dechlorinated with ammonium chloride and analyzed for THMs and HANs using liquid-liquid extraction gas chromatography (GC), as described in EPA Method 551.1. In addition to this analysis, a post-chlorination SFS was developed for comparison with the pre-chlorination SFS.

The liquid-liquid extraction GC analysis was performed using a Varian 3400 Gas Chromatograph equipped with two electron capture detectors (ECDs) and an autosampler to ensure that the injection procedure is identical for all samples. The primary column was a DB-1 Column and the confirmation column was a DB-1301 Column, both manufactured by J&W Scientific©. Data was collected using a computer equipped with PC Minichrom software. The Minichrom© software was used to store the calibration and analytical parameters required for this method.

3.7 Quality Assurance and Quality Control

To ensure that the results of this investigation are valid and to identify the source of any errors, several quality assurance and quality control (QA/QC) measures were utilized. In addition to the fluorescence QA/QC, the TOC analysis and the THM/HAN analysis both require additional QA/QC protocols.

For all analyses, reagent blanks were tested to ensure there are no impurities or interferences that will alter the results in some unexpected way. Duplicate analyses were run for approximately 10 percent of all samples to ensure that the analysis is repeatable and to determine if any errors went undetected in the experiment. The calibration of all instruments was checked on a regular basis by running samples of known concentrations to determine if recalibration was required.

The THM/HAN analysis required two additional QA/QC measures. Decafluorobiphenyl was added to each sample prior to the liquid-liquid extraction for use as a surrogate standard. In addition to this standard, 4-Bromofluorobenzene (4-BFB) was added to each sample after the extraction for use as an internal standard. The surrogate standard was used to determine the accuracy of the extraction procedure by comparing its known concentration with the concentration determined by the Gas Chromatograph. The internal standard was added in identical amounts to the extract for each sample. The response recorded from the ECD for the internal standard was used to quantify the amount of other materials present in the sample.

CHAPTER 4

RESULTS AND DISCUSSION

4.1 Scope of Experiments

The results of the experiments discussed in Chapter 3 are presented here in three sections. The first of these is a discussion of the development of SFSs for the humic and fulvic acid standards. The second section is a discussion of the relationship between fluorescence and TOC for the samples collected from the watersheds and treatment plants. Finally, a discussion of the relationship between fluorescence and DBP formation in humic and fulvic acids is presented.

4.2 Humic and Fulvic Acid Standards

The first step in this investigation was to investigate the fluorescent properties of humic and fulvic acid standards, as they make up a significant fraction of the organic materials in water. By developing the SFSs for these standards, it will be possible to visually identify the types of organics present in a water sample. As was discussed in Chapter 2, there is a significant difference in the molecular structure of humic and fulvic acids. Due to this fact, it can be expected that there will be differences between the SFS for a humic acid standard and a fulvic acid standard.

The first standard to be analyzed was a deionized water blank. This was done to determine a fluorescence baseline and to locate areas where scattering peaks might appear. There are two areas in the water SFS where scattering is seen to be a concern. This SFS contains both Raman and Second-order Ray scattering. The Raman scatter appears where the emission wavelength is approximately 30 nm longer than the

emission wavelength, and the Second-order Ray scatter appears where the emission wavelength is equal to twice the excitation wavelength. The SFS for the deionized water blank can be seen in Figure 4.

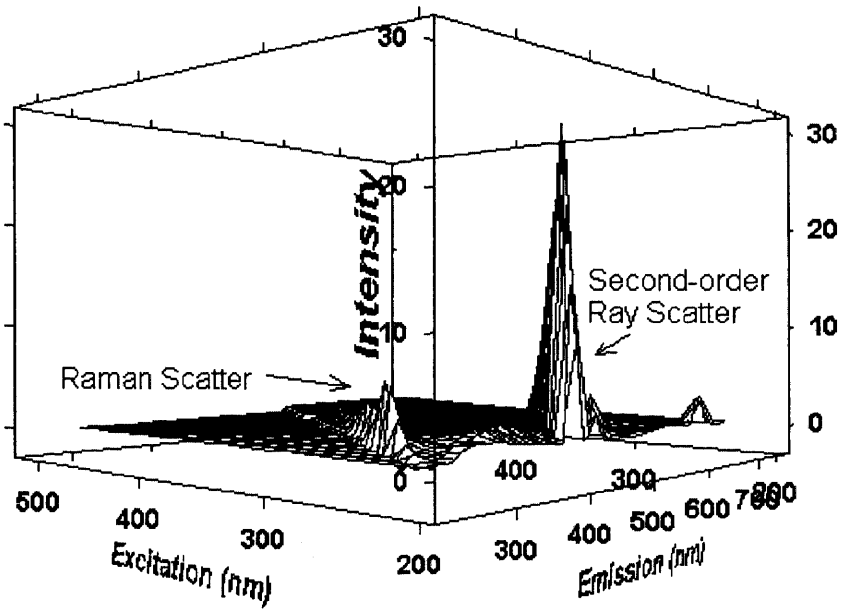


Figure 4 SFS of a Deionized Water Blank

The signatures for the humic and fulvic acid standards were surprisingly similar. Both types of humic material have two peaks in their signature centered about an emission wavelength of 450 nm. The first peak is highest at about an excitation wavelength of 250 nm, and the second is highest at about an excitation wavelength of 350 nm. The only noticeable differences between the different materials were the heights of the different peaks, and the intensity of the scattering. In every case, Raman scattering can be neglected. The location of the fluorescence peaks of interest is far enough away from the location of the Raman scatter that it will not interfere the

fluorescence measurement. The Second-order Ray scattering peaks will need to be accounted for, as the line of peaks caused by this scatter will appear within the fluorescence peak. The Second-order Ray peaks will not interfere with the measurement of individual fluorescence values, but they may cause problems if the peak area of a fluorescence peak was to be calculated. An example of this is shown in Figure 5, and again in Appendix B.

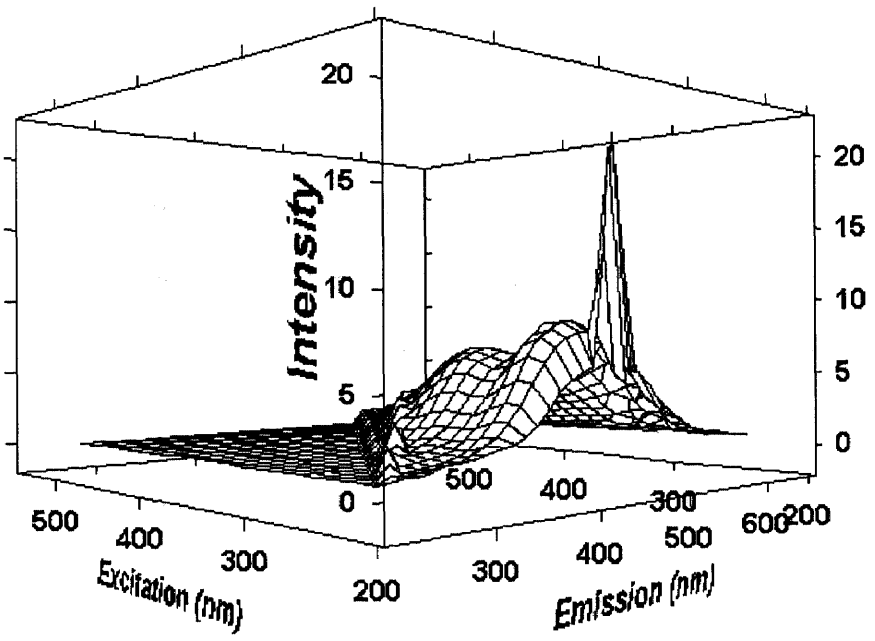


Figure 5 River Humic Acid Standard (16 ppm) SFS

Based on observations made in the examination of several SFSs for various samples, it can be concluded that the magnitude of the Second-order Ray peaks may be a function of the sample pH. In the higher concentration humic standards (>100 ppm), the pH will be lowered and these scattering peaks become almost unnoticeable.

An illustration of this can be seen in Figure 3. Figure 3 shows a solution of 130 ppm of humic acid, and the Second-order Ray peaks cannot be seen.

While the locations of peaks were the same in the fulvic acids and in the humic acids, the peak intensity varied according to the source from which the standard was derived. If only one fluorescence point is considered for each standard, the intensity of this point can be plotted versus the concentration of the standard solution. This will allow a relationship to be quantified between the two parameters. The results of this type of analysis are presented in Table 3. For each of the six types of standard humic material, two excitation-emission wavelength pairs were analyzed. The first of these pairs is located at excitation 250 nm and emission 450 nm. The second wavelength pair is located at excitation 350 nm and emission 450 nm. For each pair, the concentration of the humic material was plotted with the fluorescence intensity measured at that pair. Four different concentrations of each type of standard humic material were used, ranging in concentration from 1 to 20 ppm. These plots can be seen in Appendix C.

In each plot, a straight line was then drawn through the points, and the equation for the line was calculated. These relationships are presented in Table 3, along with the R^2 value for the relationship. The R^2 value is a measure of the statistical validity of a relationship. A value of 1.00 is considered a perfect fit, and lower values indicate weaker relationships. For each of these relations, fluorescence intensity is represented as F, and humic concentration is represented as C.

Table 3 Relationship Between Fluorescence and Concentration of Humic Material

Material	Wavelength Pair (nm) (Excitation, Emission)	Relationship (F=Fluorescence Intensity, C=Concentration)	Number of Samples, n	R^2
Peat Fulvic	250, 450	F = 6.5270 + 0.79552 C	4	0.732
Peat Fulvic	350, 450	F = 2.2033 + 0.66369 C	4	0.941
Peat Humic	250, 450	F = 3.7345 + 0.17696 C	4	0.916
Peat Humic	350, 450	F = 2.1696 + 8.1057e-2 C	4	0.813
River Fulvic	250, 450	F = 8.7636 + 0.50467 C	4	0.942
River Fulvic	350, 450	F = 3.1716 + 0.58040 C	4	0.984
River Humic	250, 450	F = 3.2082 + 0.38974 C	5	0.855
River Humic	350, 450	F = 1.4144 + 0.29212 C	5	0.972
Soil Fulvic	250, 450	F = 11.606 + 1.1162 C	4	0.943
Soil Fulvic	350, 450	F = 4.2310 + 0.92898 C	4	0.983
Soil Humic	250, 450	F = 0.57007 + 0.30299 C	4	0.985
Soil Humic	350, 450	F = 0.35338 + 0.13950 C	4	0.982

It is interesting to note that in nearly every case the humic standards have a stronger relationship with the (350, 450) wavelength pair than with the (250, 450) pair. The SFS for a humic substance will have a larger peak located at the (250, 450) wavelength pair, so it would seem that there would be a stronger correlation to between concentration and the fluorescence intensity at this point. It would appear

that this is not the case. With both materials showing strong statistical relationships using the (350, 450) wavelength pair, it can be concluded that fluorescence values measured at this point in the SFS will prove to be more useful than any other fluorescence value for quantitative analysis of humic substances.

4.3 TOC Analysis

It has been known for some time that there is a strong correlation between UV absorbance and total organic carbon [9]. It is also known that this relationship will vary with the location of the samples being analyzed, and will exhibit seasonal variations as well [9]. As was noted in Chapter 2, fluorescence has been described as the inverse of UV absorbance. It should then be expected that the relationship between TOC and fluorescence will also change with location and with the time of year the samples were collected.

For the purposes of this experiment, each sample that was analyzed for TOC also had its SFS developed. From the signature, three fluorescence intensity values were tabulated. These points included the two peaks mention in Section 4.2 (the 250, 450 and 350, 450 wavelength pairs), as well as the peak at excitation wavelength 240 nm and emission wavelength 360 nm. This point was chosen due to the presence of a peak centered about this point in some of the watershed samples. This peak was assumed to be a non-humic organic. This was of interest because non-humic organics are also thought to be precursors to DBP formation, and may also contain some carbon, which would result in an increased value for TOC [9].

For this experiment, samples collected in September and October of 1997 (termed Fall 97) were analyzed for both TOC and fluorescence. The results of these analyses were tabulated by location and by month of collection. The locations used to classify the samples were the PVWC treatment plant, NJDWSC treatment plant, EWC Raritan-Millstone treatment plant, EWC Canal Road treatment plant, Passaic River watershed, and Raritan-Millstone River watershed. Samples collected at the sewage treatment plant outfalls were included in the Passaic River watershed. The relationships derived from this analysis are presented in Table 4 set of samples.

These relationships were developed by plotting the fluorescence intensity from one of the two wavelength pairs noted in Section 4.2 along with the TOC values measured for the sample. A straight line was passed through the points in the plot, and the equation for this line was calculated. These plots can be found in Appendix D. Only relationships with R^2 values greater than 0.50 are presented here. Fluorescence is represented in Table 4 as F, and TOC is represented as C. No relationship was found to exist between TOC and the fluorescence measured at the (240, 360) wavelength pair.

Table 4 Relationship Between TOC and Fluorescence

Season	Location	Wavelength Pair (nm) (Excitation, Emission)	Relationship (F=Fluorescence Intensity, C= TOC)	Number of Samples, n	R^2
Fall 97	All samples	350, 450	F = - 0.91079 + 4.1036 C	91	0.737
Fall 97	All Samples	250, 450	F = 0.82313 + 5.9112 C	91	0.671
Oct 97	Canal Road	250, 450	F = - 0.69040 + 5.2917 C	8	0.778
Oct 97	Canal Road	350. 450	F = - 0.19626 + 2.3905 C	8	0.781
Oct 97	NJDWSC	250, 450	F = 1.6695 + 3.2722 C	6	0.980
Oct 97	NJDWSC	350, 450	F = 0.77620 + 1.4431 C	6	0.926
Oct 97	Passaic River	250, 450	F = 2.7306 + 5.1263 C	17	0.711
Oct 97	Passaic River	350, 450	F = 0.32751 + 3.2699 C	17	0.856
Oct 97	PVWC	250, 450	F = - 4.3373 + 8.1494 C	10	0.865
Oct 97	PVWC	350, 450	F = - 3.1401 + 4.6304 C	10	0.825
Oct 97	Raritan River	250, 450	F = 2.3374 + 3.9139 C	10	0.783
Oct 97	Raritan River	350, 450	F = 0.32294 + 2.6662 C	10	0.957

As was the case in developing equations for the relationships between concentration of humic material and fluorescence, the relationships between fluorescence and TOC are statistically stronger using the (350, 450) wavelength pair.

In every case where a relation was found for a location using both wavelength pairs, the R^2 value was higher for the (350, 450) wavelength pair. It was not possible to derive a relationship between fluorescence and TOC for all the sites examined. In these cases, the September 97 samples in particular, not enough fluorescence data was collected at a particular site to sufficiently plot a line. In others, the R^2 value was below 0.5 of which the results are not presented here.

4.4 DBP Formation Potential

Two attempts were made to derive a relationship between fluorescence and the formation of disinfection by-products. The first attempt was made using a sample matrix which contained solutions of each type of humic and fulvic acid. Due to a problem with the water used to prepare the sample matrix, no consistent results were obtained from this first attempt. All the samples in the matrix were found to have chloroform concentrations that were outside the measurement range of the gas chromatograph used for this experiment.

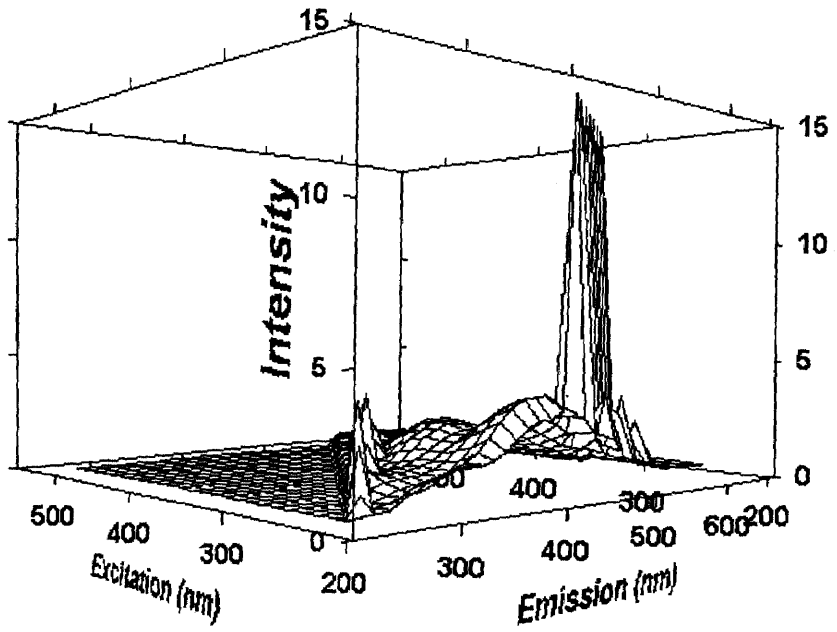
Much better results were obtained from the second attempt. The second sample matrix was prepared using a better quality water than the first, and only contained samples of river-derived fulvic acid. Samples were prepared in triplicate at five different concentrations ranging from 1 to 20 ppm. Since one of the goals of this research is to use fluorescence as a predictive tool for DBP formation, each sample had its SFS developed prior to chlorination. The same three fluorescence points used in the TOC analysis were tabulated along with the total trihalomethanes (TTHMs) and total haloacetonitriles (THANs) for each sample. The results for each concentration

were averaged to account for variability caused by the volatility of the analytes. It was then possible to plot fluorescence versus TTHMs and THANs for this river fulvic acid. These plots can be found in Appendix E. For each plot, a straight line was drawn through the points and the equation for the line was calculated. The relationships derived from these plots are summarized below in Table 5.

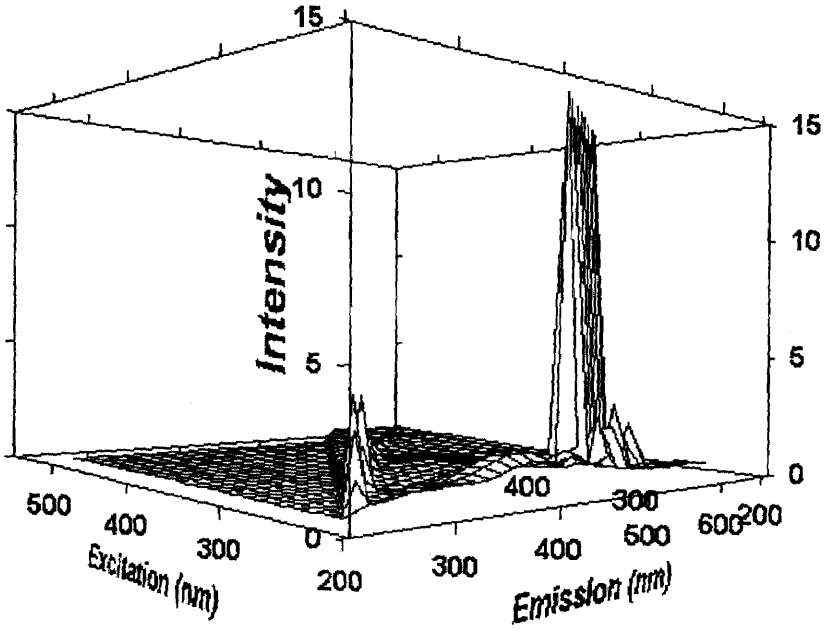
Table 5 Relationship Between DBP Formation and Fluorescence

DBP	Wavelength Pair (nm) (Excitation, Emission)	Relationship (F=Fluorescence, C=DBPFP)	Number of Samples, n	R^2
TTHM	250, 450	F = - 2.0718 + 0.15897 C	5	0.987
TTHM	350, 450	F = - 2.0544 + 0.11008 C	5	0.999
THAN	250, 450	F = - 2.5932 + 3.9993 C	5	0.979
THAN	350, 450	F = - 2.3992 + 2.7637 C	5	0.987

As was the case in both the TOC and the humic standard studies discussed in this chapter, there is a stronger relationship when fluorescence is measured at the 350, 450 wavelength pair. From these results, it can be concluded that there is a strong correlation between fluorescence and the formation of disinfection by-products. The DBP results presented here are for a single fulvic acid, so it should be interesting to see if similar correlations exist for other types of humic substances.



a. Pre-Chlorination SFS



b. Post-chlorination SFS

Figure 6 Pre- and Post-chlorination SFS for a Fulvic Acid Solution (2 ppm)

A post-chlorination SFS was developed for each sample in this experiment. It is interesting to note some of the differences that exist between the pre- and post-chlorination signatures. An example of this is presented in Figure 6.

The chlorine dosage of 20 ppm was chosen as it was thought that this would be sufficient to oxidize enough of the organic matter present in the sample to form the maximum DBPs. After chlorination, the peak located at the (350, 450) wavelength pair is greatly diminished, but the peak located at the (250, 450) pair remains. This may begin to explain the stronger relationships between fluorescence at the (350, 450) pair and the other parameters of interest in this research. It may be that the functional groups within a humic substance will fluoresce with greater intensity at the (250, 450) wavelength pair, but the fractions of a humic substance that register as total organic carbon and react to form by-products will fluoresce at the (350, 450 pair). Additional pre- and post-chlorination figures can be viewed in Appendix F.

CHAPTER 5

CONCLUSIONS

5.1 Overview

This objective of this research was to investigate the ways in which fluorescence spectroscopy might be used in the characterization of total organic carbon and as a predictive tool in the formation of disinfection by-products. This was accomplished by examining a series of humic and fulvic acid standards and then applying the results to a series of watershed and treatment plant samples collected in September and October of 1997. These examinations allowed preliminary quantitative relationships to be developed between fluorescence and TOC, and between fluorescence and DBPFP. This preliminary investigation has been intended to serve as a basis for future research in this area.

5.2 Humic and Fulvic Acid Standards

The following conclusions can be drawn from the examination of the humic and fulvic acid standards:

1. Humic and fulvic acids will have similar spectral fluorescence signatures. These signatures will have two peaks at an emission wavelength of 450 nm. The first peak will be located at an excitation wavelength of 250 nm, and the second will be located at an excitation wavelength of 350 nm.
2. There is a strong correlation between the concentration of a humic substance in solution and fluorescence. The correlation will be stronger if fluorescence is measured at the (350, 450) wavelength pair than if measured at the (250, 450) wavelength pair.

5.3 Total Organic Carbon

The following conclusions can be drawn from the TOC analysis of the Passaic River and Raritan-Millstone watershed and treatment plant samples collected in September and October of 1997:

1. There is a strong correlation between fluorescence and total organic carbon. The correlation will be stronger if the (350, 450) wavelength pair is used to take the fluorescence measurement than if the (250, 450) pair is used.
2. The correlation between fluorescence and TOC is strongest for sample matrices composed of samples from one location. This relationship varies from site to site, and must be derived separately for each location.
3. A statistically valid correlation can be drawn between fluorescence and TOC by considering the Passaic River and Raritan-Millstone watersheds as one sample matrix. While the relationship is not as strong as the one drawn from smaller, more localized sample matrices, it does have an R^2 value above 0.70.
4. More sampling and analysis would be needed to support the above statistical relationships with a higher confidence level.

5.4 Disinfection By-Product Formation

The following conclusions can be drawn from the results of the DBP Formation Potential test conducted using a standard river fulvic acid:

1. There is a strong correlation between fluorescence and the formation of trihalomethanes. The correlation is better if the (350, 450) wavelength pair is used to

measure fluorescence, but the relationship will still be strong if the (250, 450) wavelength pair is used.

2. There is a strong correlation between fluorescence and the formation of haloacetonitriles. The correlation is better if the (350, 450) wavelength pair is used to measure fluorescence, but the relationship will still be strong if the (250, 450) wavelength pair is used.
3. Prior to chlorination, the fulvic acid samples showed two peaks in their SFS. The first of these is located at the (250, 450) wavelength pair, and the other is located at the (350, 450) wavelength pair. After chlorination, the peak at excitation 350 was greatly diminished, while the peak at excitation 250 was mostly unchanged. This may be caused by the structure of the fulvic acid itself.

CHAPTER 6

RECOMMENDATIONS FOR FUTURE RESEARCH

6.1 Scope of Current Work

The preliminary research presented here is part of an ongoing investigation into the nature of humic substances in drinking water and their potential for forming harmful by-products. This preliminary work should be considered as a basis for future research. The observations and conclusions reached in the analysis of data need to be confirmed either through additional tests, or by applying the methods used to reach these conclusions to additional materials to determine if the relationships found between fluorescence and traditional testing parameters will hold true for additional substances.

6.2 Fluorescence Standards for Non-Humic Organic Substances

The work presented here was primarily focused on the study of humic precursors to the formation of DBPs in water treatment. The development of a SFS for a particular humic or fulvic acid and using this as a standard will allow one to begin to identify the presence of humic substances in water at least on a qualitative basis, and eventually a quantitative basis. However, humic substances are not the only type of organic substance present in water. As can be seen in the results of the watershed SFS investigation conducted, a peak appeared in some samples that can be identified as neither a humic acid nor a fulvic acid. It must be caused by the presence of some other organic substance. These peaks may be caused by non-humic organic substances. Further investigations are required to determine these organic substances within the SFS.

6.3 DBP Formation for Additional Humic Substances

The work presented here deals only with the Suwanee River fulvic acid in the investigation of disinfection by-product formation. While fulvic acids make up the majority of humic substances found in natural waters, it would be beneficial to carry out experiments similar to the ones conducted here for humic acids and fulvic acids derived from other sources. Initially, the peat and soil fulvic acids and the peat, soil, and Suwanee River humic acids that were used in the development of the SFS standards should be tested for DBP formation. It should be expected that there would be a statistically significant relationship between fluorescence and DBP formation in the additional humic substances similar to the one found for the Suwanee River fulvic acid, and running such additional experiments will also help confirm the results of the work done here.

6.4 Verification of TOC-Fluorescence Correlation

The relationships between fluorescence and TOC that were developed in the course of this work should be considered to be preliminary results. These should be verified by collecting and analyzing additional samples. This additional data can be used to test the relationships that have already been found, as well as updating these relationships by including them in the data sets used in developing them for better confidence. Additional samples must be analyzed in a method similar to the one used here for in order to help characterize the ways in which organic matter varies from one season to the next.

6.5 DBP Formation for Varying Chlorine Dosage

The investigation conducted as part of this project considered only a single chlorine dosage of 20 ppm when looking at the formation of DBPs. The goal in using this dosage was to determine a maximum value of by-product that might form from disinfection by completely oxidizing the humic substances in water. While this type of experiment provides interesting observations on the nature of humic material in water, it may not be particularly useful to the parties most interested in this type of information, namely drinking water treatment plants.

The dosage used for this work, 20 ppm, is much higher than would typically be seen in water treatment, and as a result the amount of THMs and HANs that form will be much higher than would be expected in the treatment plant effluent. An interesting study would be to investigate the DBPs that form due to humic materials for a series of increasing chlorine dosages. By preparing several identical sample matrices of fulvic acid solutions and chlorinating each matrix with a higher chlorine dose, a series of relationships may be generated by plotting fulvic acid concentration or fluorescence vs. DBP formation. If a treatment plant operator possessed a set of curve such as this, he would only need to take a fluorescence reading on a sample of plant influent and find his chlorine dosage on the chart. He would then be able get a reasonable estimate on the amount of DBPs that might be expected to form in his treatment process.

APPENDIX A

DATA COLLECTION PROGRAM SOURCE CODE

A.1 Program Overview

This section presents the source code for the computer program written to collect data from the Hitachi F-3010 Fluorescence Spectrophotometer. The program is designed to be executed within Microsoft QuickBASIC, or it can be compiled to create an executable file, which can be run separately. Lines beginning with REM are remarks that are ignored while the program executes. They are provided to explain to the reader and any future users exactly how fluorescence data has been collected and stored during the course of this research.

A.2 Source Code

```
CLS
REM The RS-232 interface is opened between the computer and instrument.
FileName$ = "COM2:4800,O,7,1"
OPEN FileName$ FOR RANDOM AS #1
REM String variables are declared. These will be used to name the collected data files.
dir1$ = "c:\sfs_data"
extension$ = ".prn"
extension2$ = ".txt"
slash$ = "\"
REM The instrument is set to receive remote commands.
PRINT #1, "REMOTE 1"
```

```
INPUT #1, a$

IF a$ <> "@" THEN PRINT "Cannot connect" ELSE PRINT "Connected"

PRINT #1, "PRINTMODE 1"

INPUT #1, a$

IF a$ = "@" THEN PRINT "Data will be sent to external computer" ELSE PRINT "error": STOP

PRINT #1, "STATUS 1"

INPUT #1, a$

IF a$ = "@" THEN PRINT "F3010 Set to STATUS 1" ELSE PRINT "error": STOP

REM The user inputs the wavelength ranges to collect fluorescence data.

INPUT "excitation, min.="; exmin

INPUT "excitation, max.="; exmax

INPUT "emission, max.="; emmax

INPUT "step value="; delta

REM The user provides a name for the sample.

REM This name will be used to create a directory to store files related to this sample.

INPUT "file to list excitation spectra; do not use a file extension:"; sample$

newdir$ = dir1$ + slash$ + sample$

REM The directory for the sample is created.

MKDIR newdir$

CHDIR newdir$

REM A list of the excitation wavelengths is created.

REM This list is used by GRAMS to create the three dimensional SFS.

list$ = sample$ + extension2$

newlist$ = newdir$ + slash$ + list$
```

```
REM The program begins writing a list of excitation wavelengths.
OPEN newlist$ FOR OUTPUT AS #3
REM Data is collected beginning with the minimum excitation wavelength.
WHILE exmin <= exmax
PRINT #1, "EXGOTO"; exmin
INPUT #1, a$
INPUT #1, S$
IF S$ = "STATUS 01" THEN PRINT "SUCCESS-EX" ELSE STOP
REM A file is created to hold emission wavelengths and intensity values.
REM One file will be created for each excitation wavelength used.
file$ = STR$(exmin)
filetowrite$ = "ex" + file$
MID$(filetowrite$, 3, 1) = "_"
filetowriteb$ = filetowrite$ + extension$
newfile$ = newdir$ + slash$ + filetowriteb$
PRINT filetowrite$
PRINT filetowriteb$
PRINT newfile$
REM The program adds to the list of excitation wavelengths.
PRINT #3, filetowrite$
REM The program begins writing emission wavelength and intensity data.
OPEN newfile$ FOR OUTPUT AS #2
emmin = exmin + (delta * 2)
REM The program begins a loop to vary the emission wavelength.
```

```
REM This will allow intensity data to be collected for each wavelength of interest.
WHILE emmin <= emmax
PRINT "Setting Em"
PRINT #1, "EMGOTO"; emmin
INPUT #1, a$
INPUT #1, S$
IF S$ = "STATUS 01" THEN PRINT "SUCCESS-EM" ELSE STOP
REM A 1.5 second delay is used to prevent the RS-232 interface from freezing.
t1 = TIMER
tready = t1 + 1.5
WHILE t1 < tready
t1 = TIMER
WEND
PRINT #1, "DATA"
INPUT #1, a$
INPUT #1, D$
MID$(D$, 1, 4) = "    "
D2$ = LTRIM$(D$)
PRINT #2, D2$
REM A second delay is used to prevent the program from freezing.
t2 = TIMER
tready = t2 + 1
WHILE t2 < tready
t2 = TIMER
```

```
WEND

emmin = emmin + delta

PRINT "New Em= "; emmin

WEND

REM The emission loop is exited and the next excitation wavelength is set.

exmin = exmin + delta

REM The data file for the previous excitation wavelength is closed.

CLOSE #2

REM The excitation loop is exited.

WEND

REM The program relinquishes control of the instrument.

PRINT #1, "LOCAL"

INPUT #1, a$

IF a$ = "@" THEN PRINT "Closing connection" ELSE PRINT "error": STOP

REM The list of excitation wavelengths is closed.

CLOSE #3

REM The RS-232 interface is closed.

CLOSE #1

REM The program terminates execution.

END
```

APPENDIX B

HUMIC STANDARD SFS

The following figures are intended to illustrate the similarities between the signatures for the humic and fulvic acid standards. Each signature displays two peaks located in the same areas, with the only difference being a difference in the magnitude of the peaks. In each case, the peaks in a fulvic acid signature will be higher than the peaks for a humic acid signature. These figures do not include every standard humic substance analyzed. Instead, one standard of similar concentration for each type of humic substance is presented below, with the exception of the River Humic Acid standard, which was presented in Chapter 4.

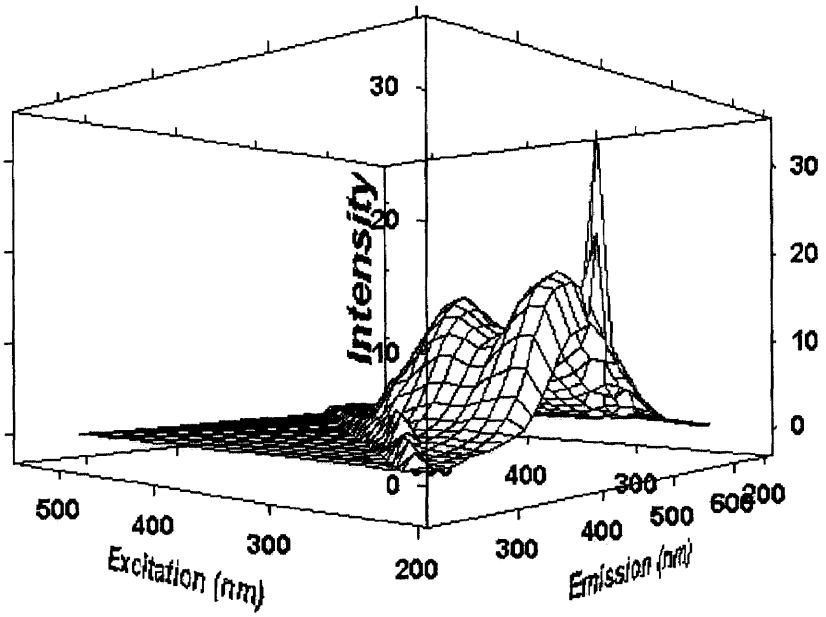


Figure B.1 River Fulvic Acid Standard (15 ppm) SFS

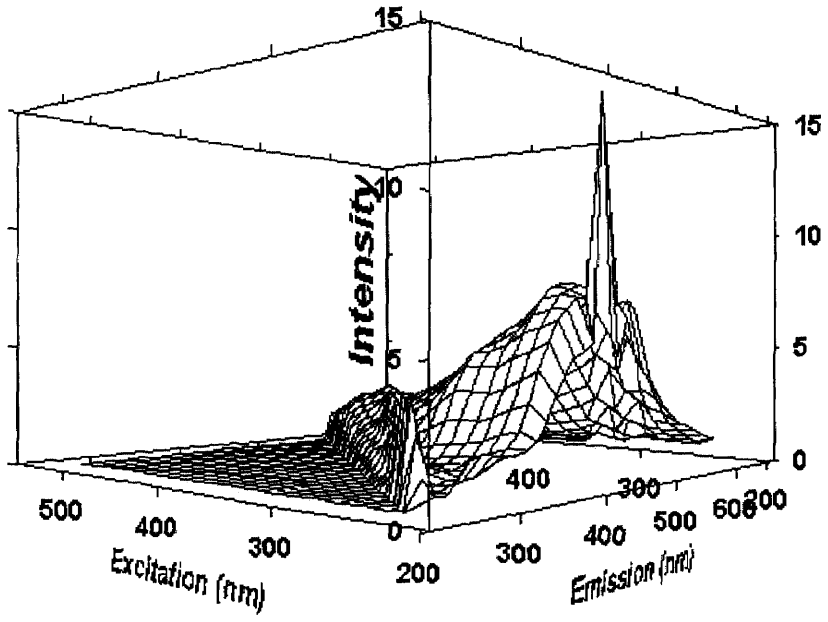


Figure B.2 Peat Humic Acid Standard (20 ppm) SFS

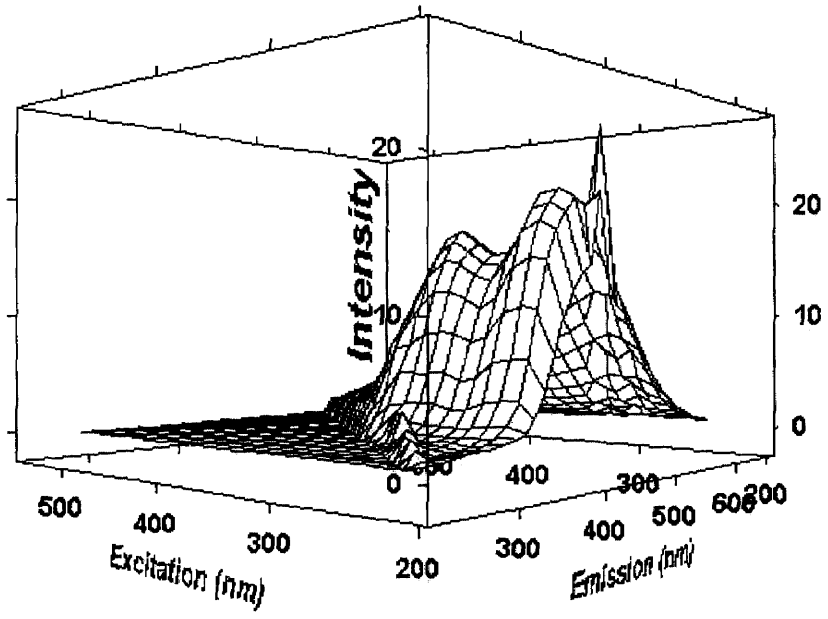


Figure B.3 Peat Fulvic Acid Standard (20 ppm) SFS

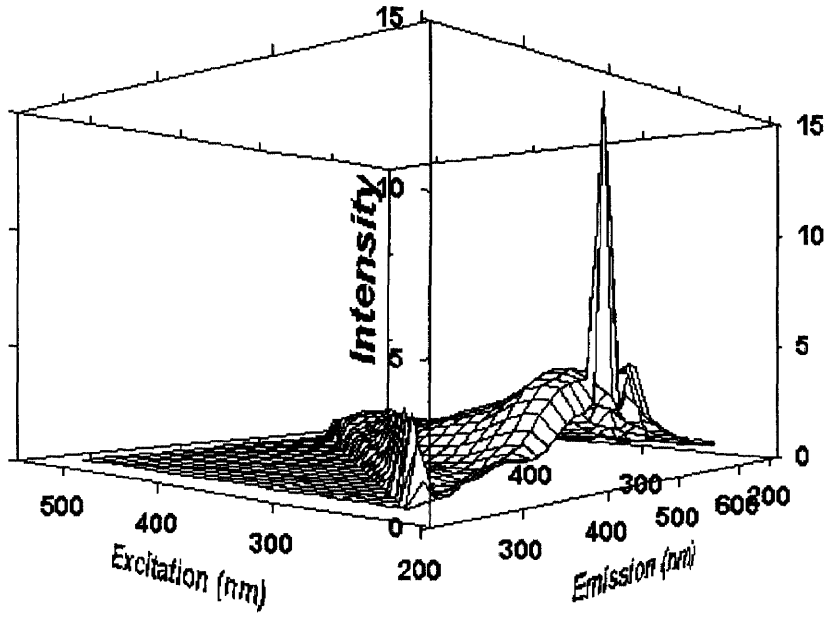


Figure B.4 Soil Humic Acid Standard (16 ppm) SFS

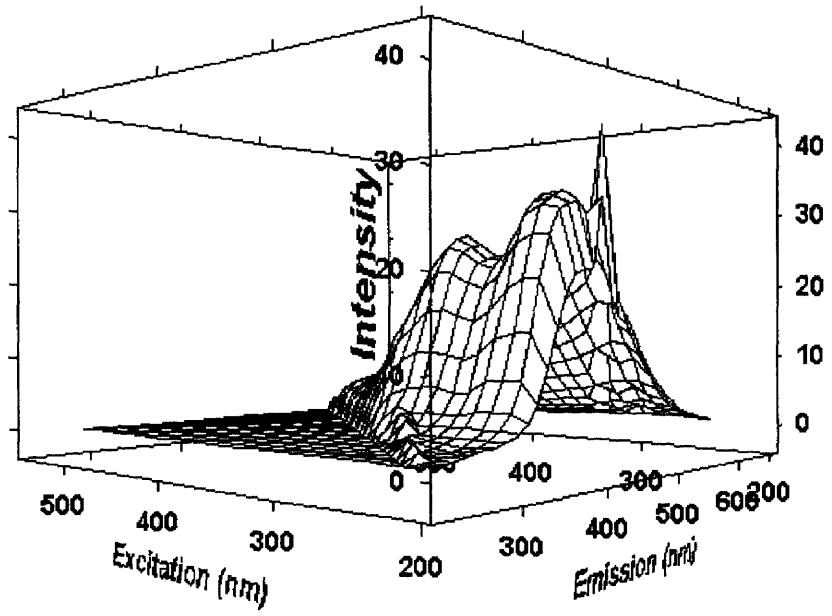


Figure B.5 Soil Fulvic Acid Standard (19 ppm) SFS

APPENDIX C

HUMIC CONC. VS. FLUORESCENCE GRAPHS

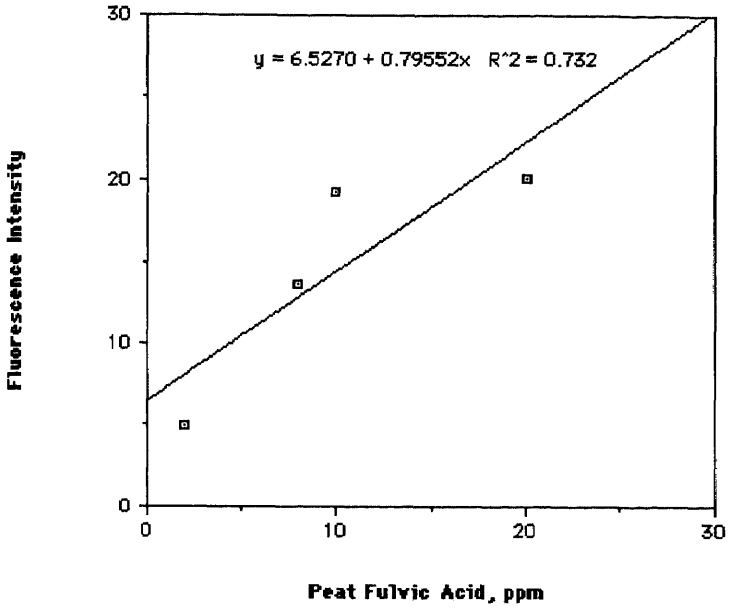


Figure C.1 Fluorescence vs. Peat Fulvic Acid Concentration, Measured at Excitation Wavelength 250 nm

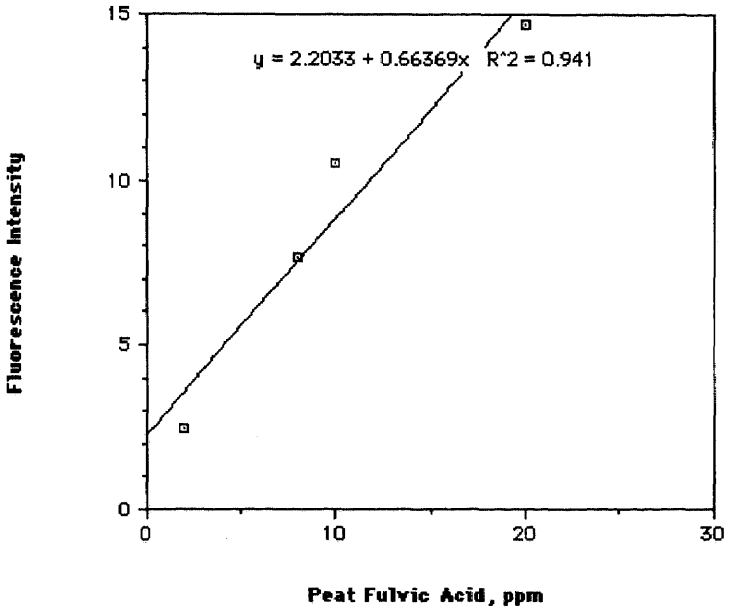


Figure C.2 Fluorescence vs. Peat Fulvic Acid Concentration, Measured at Excitation Wavelength 350 nm

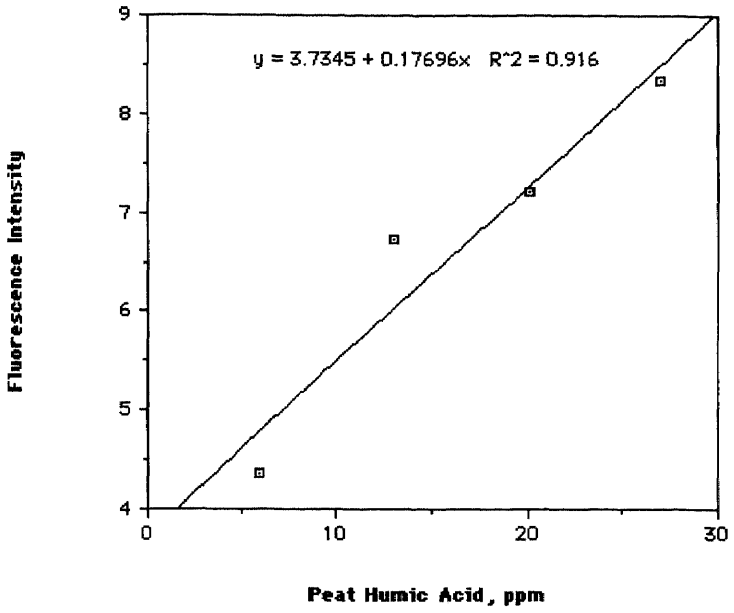


Figure C.3 Fluorescence vs. Peat Humic Acid Concentration, Measured at Excitation Wavelength 250 nm

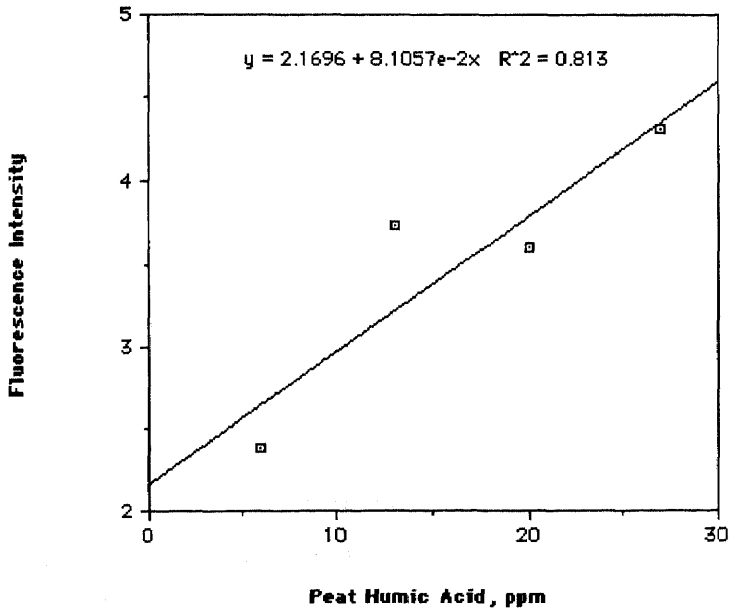


Figure C.4 Fluorescence vs. Peat Humic Acid Concentration, Measured at Excitation Wavelength 350 nm

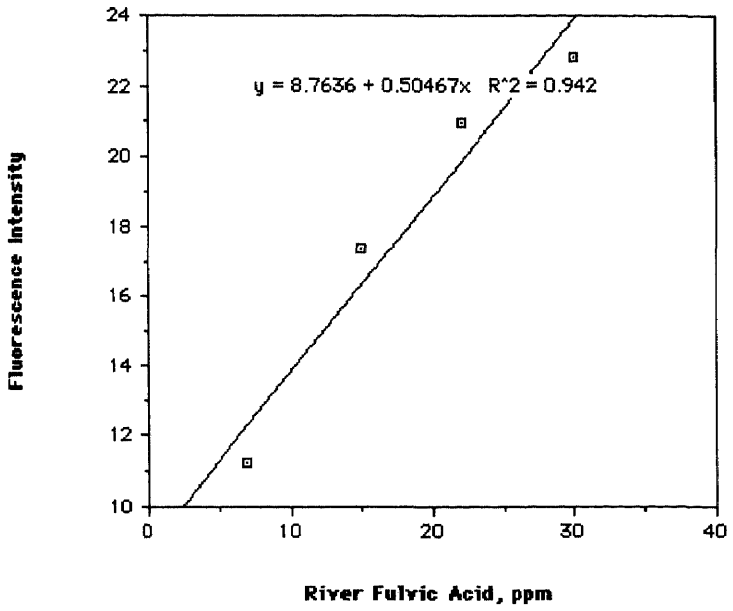


Figure C.5 Fluorescence vs. River Fulvic Acid Concentration, Measured at Excitation Wavelength 250 nm

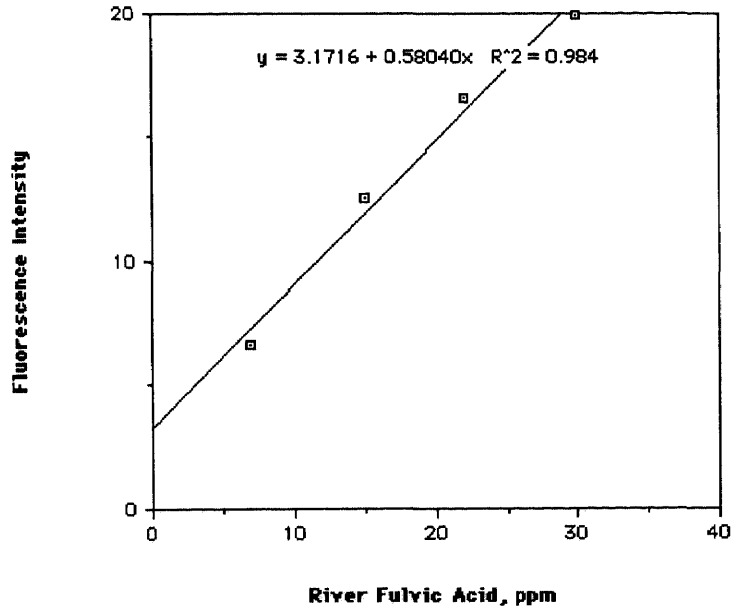


Figure C.6 Fluorescence vs. River Fulvic Acid Concentration, Measured at Excitation Wavelength 350 nm

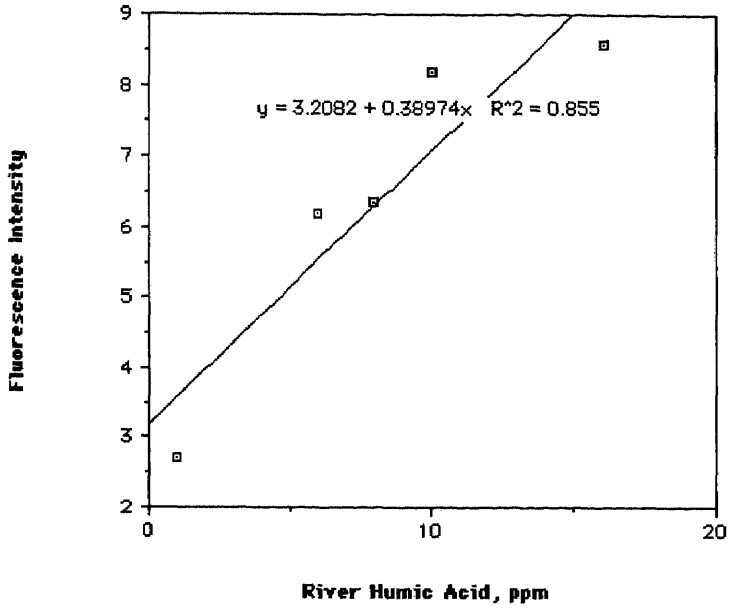


Figure C.7 Fluorescence vs. River Humic Acid Concentration, Measured at Excitation Wavelength 250 nm

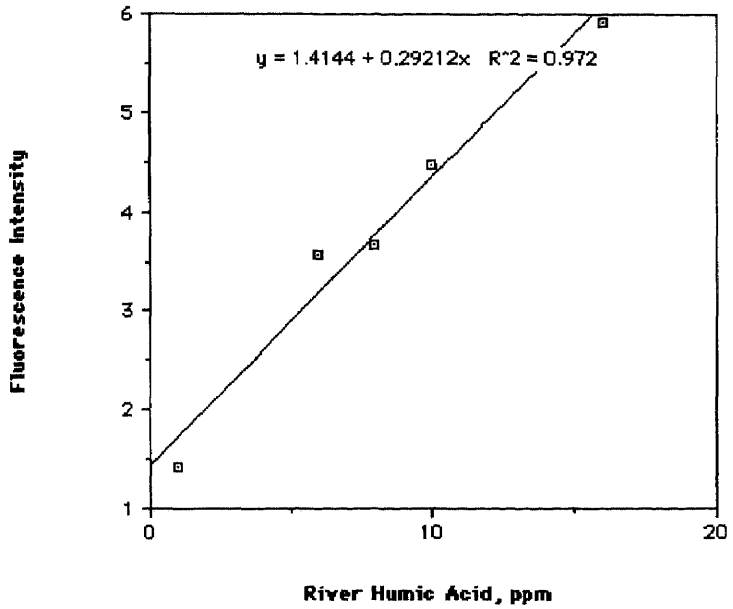


Figure C.8 Fluorescence vs. River Humic Acid Concentration, Measured at Excitation Wavelength 350 nm

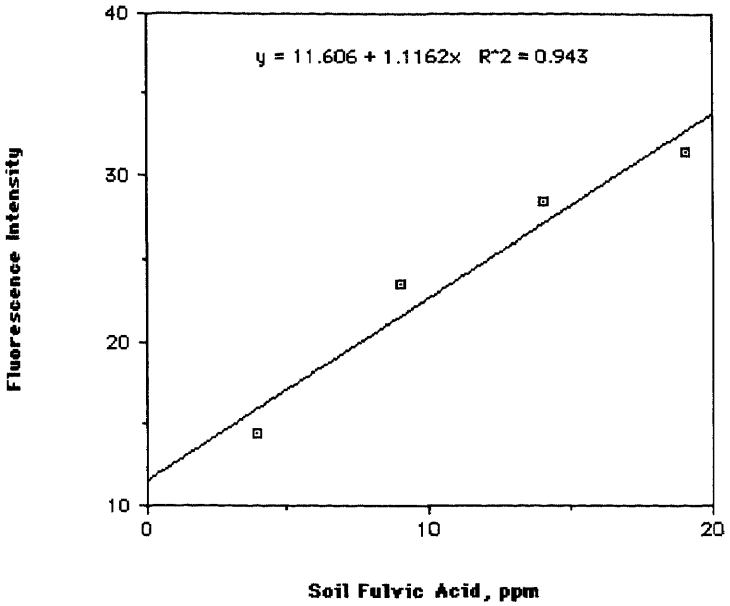


Figure C.9 Fluorescence vs. Soil Fulvic Acid Concentration, Measured at Excitation Wavelength 250 nm

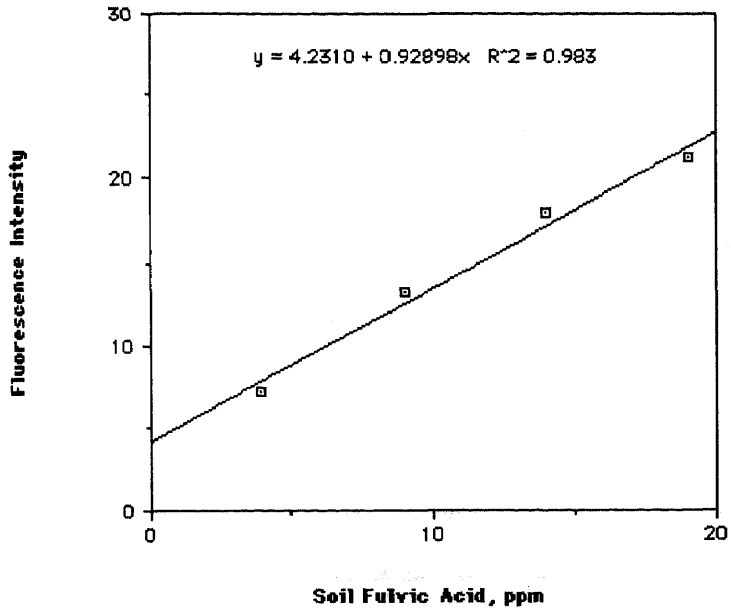


Figure C.10 Fluorescence vs. Soil Fulvic Acid Concentration, Measured at Excitation Wavelength 350 nm

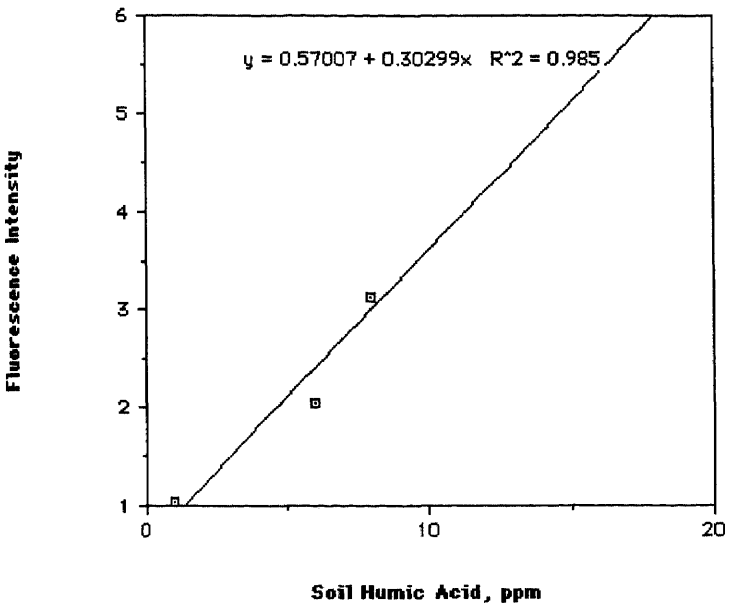


Figure C.11 Fluorescence vs. Soil Humic Acid Concentration, Measured at Excitation Wavelength 250 nm

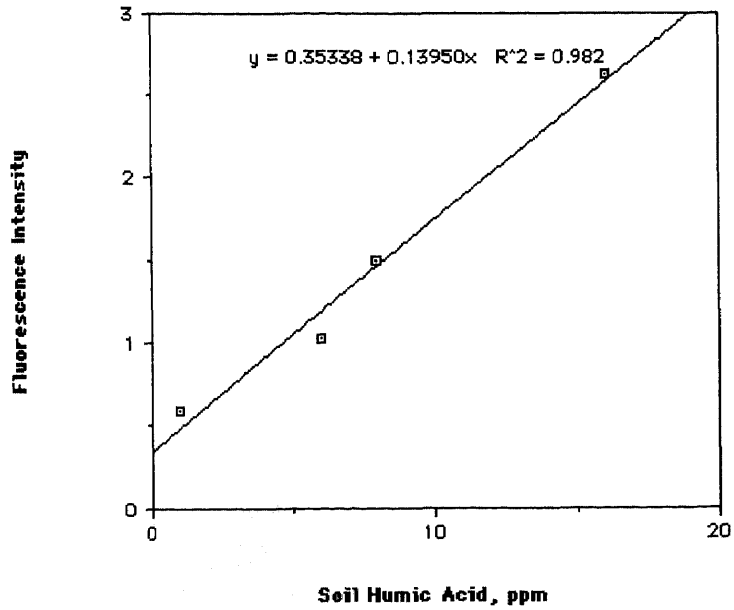


Figure C.12 Fluorescence vs. Soil Humic Acid Concentration, Measured at Excitation Wavelength 350 nm

APPENDIX D

TOC VS. FLUORESCENCE GRAPHS

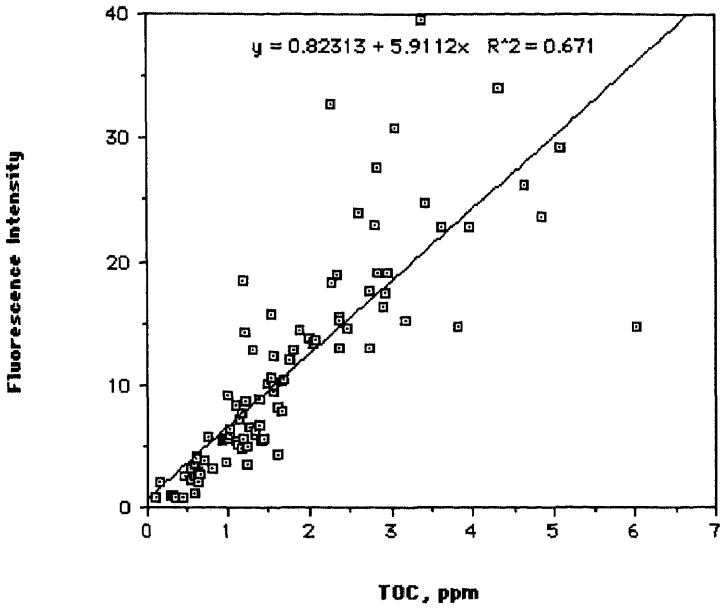


Figure D.1 Fluorescence vs. TOC (All samples), Measured at Excitation 250 nm

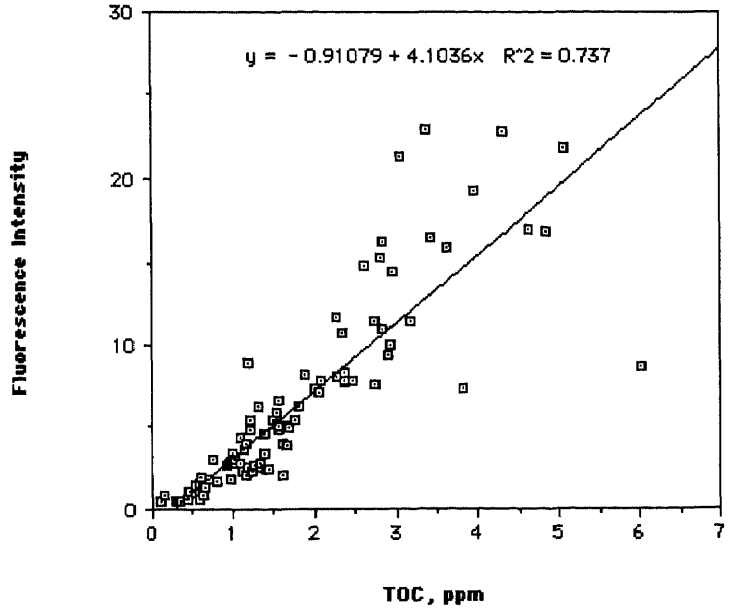


Figure D.2 Fluorescence vs. TOC (All samples), Measured at Excitation 350 nm

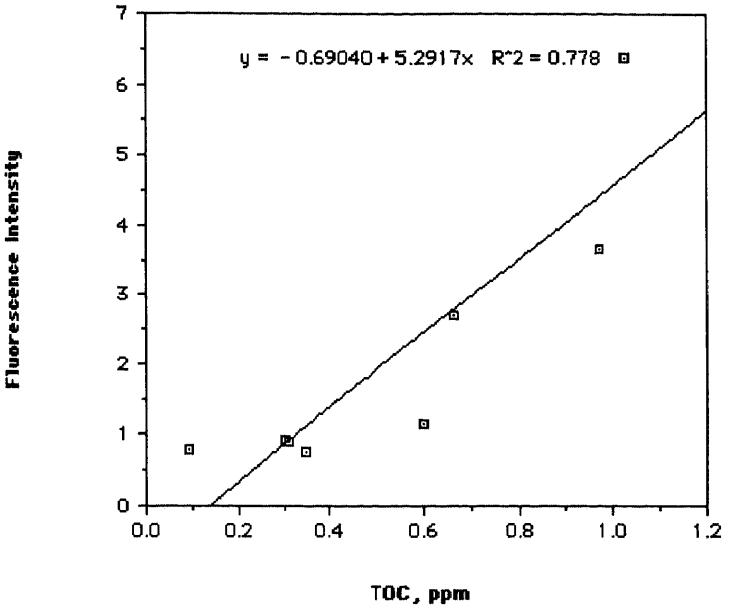


Figure D.3 Fluorescence vs. TOC (October 1997 Canal Road WTP), Fluorescence Measured at Excitation 250 nm

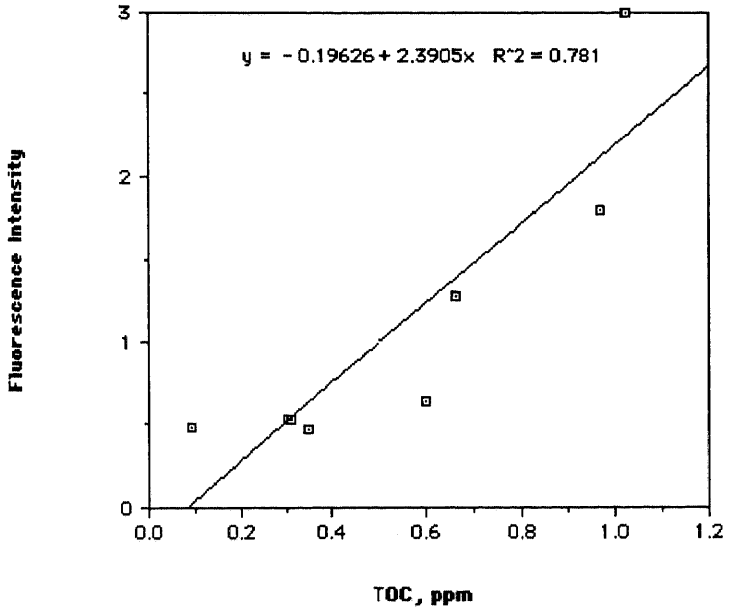


Figure D.4 Fluorescence vs. TOC (October 1997 Canal Road WTP), Fluorescence Measured at Excitation 350 nm

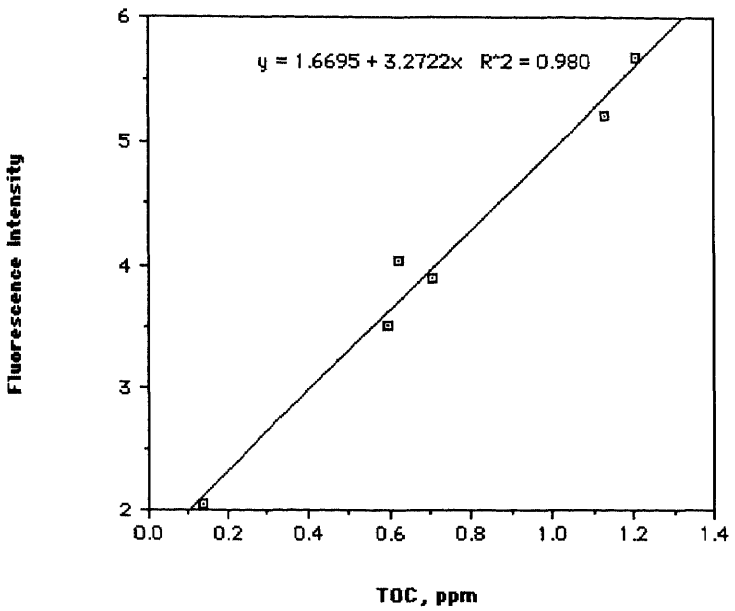


Figure D.5 Fluorescence vs. TOC (October 1997 NJDWSC WTP), Fluorescence Measured at Excitation 250 nm

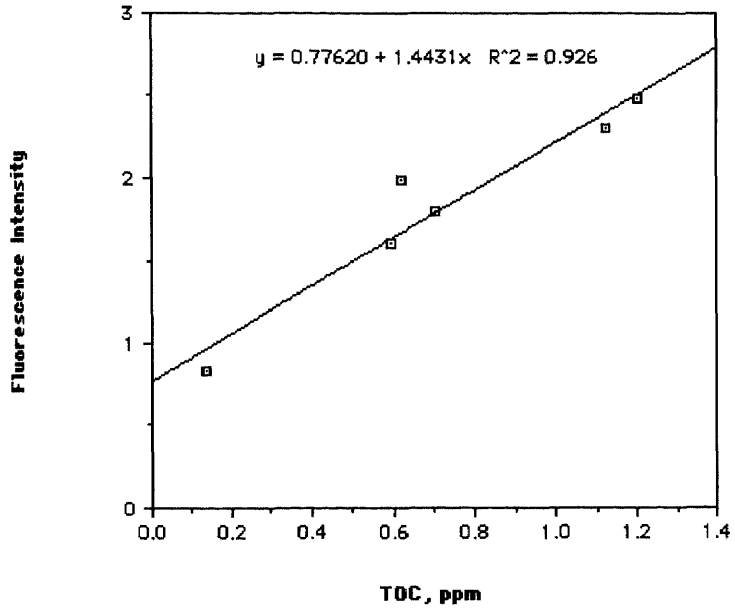


Figure D.6 Fluorescence vs. TOC (October 1997 NJDWSC WTP), Fluorescence Measured at Excitation 350 nm

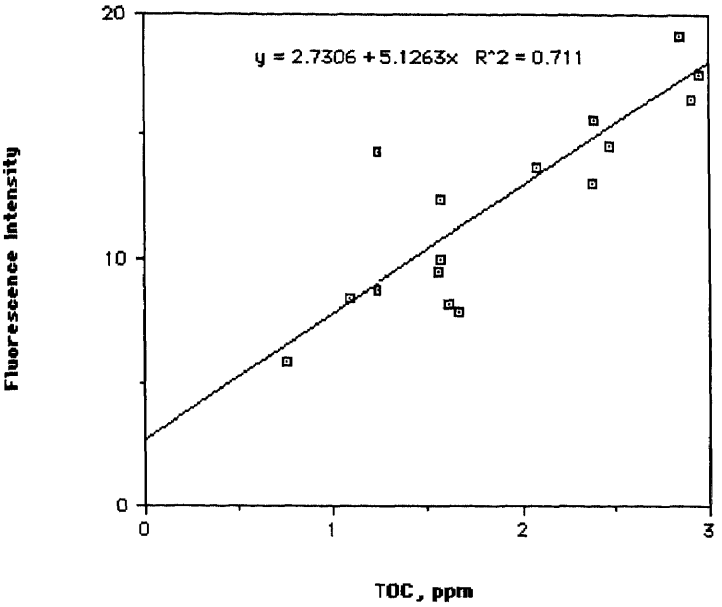


Figure D.7 Fluorescence vs. TOC (October 1997 Passaic River Watershed), Fluorescence Measured at Excitation 250 nm

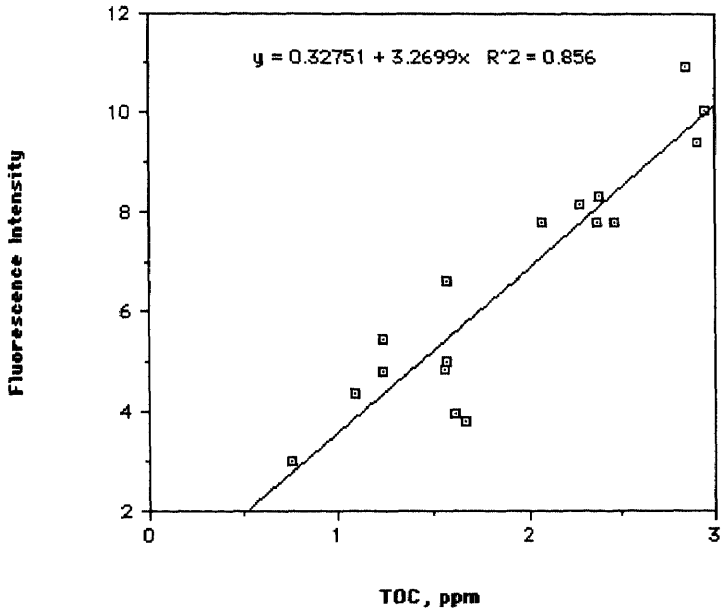


Figure D.8 Fluorescence vs. TOC (October 1997 Passaic River Watershed), Fluorescence Measured at Excitation 350 nm

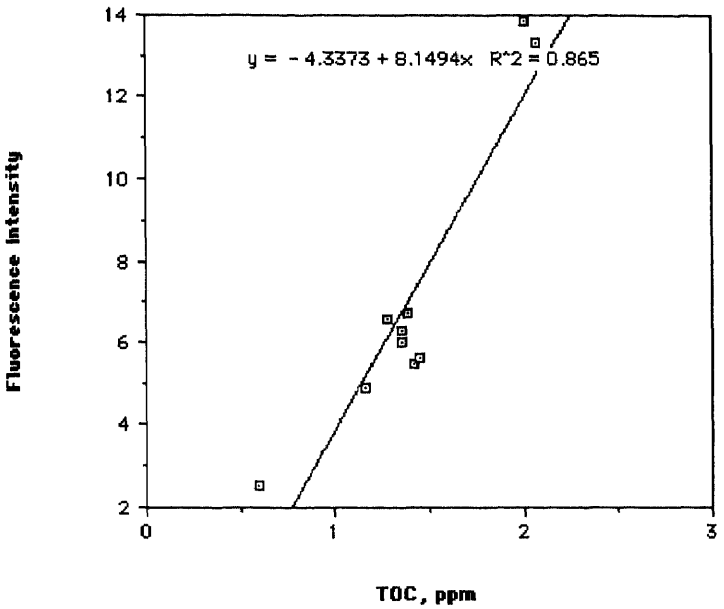


Figure D.9 Fluorescence vs. TOC (October 1997 PVWC WTP), Fluorescence Measured at Excitation 250 nm

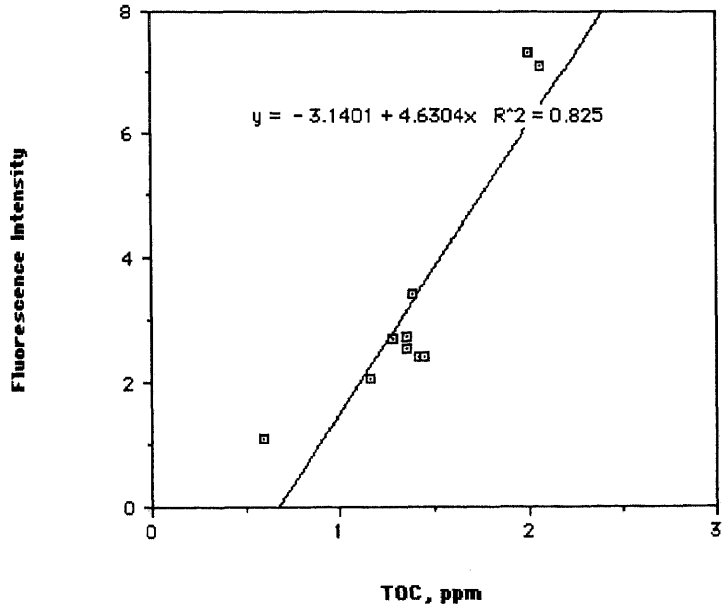


Figure D.10 Fluorescence vs. TOC (October 1997 PVWC WTP), Fluorescence Measured at Excitation 350 nm

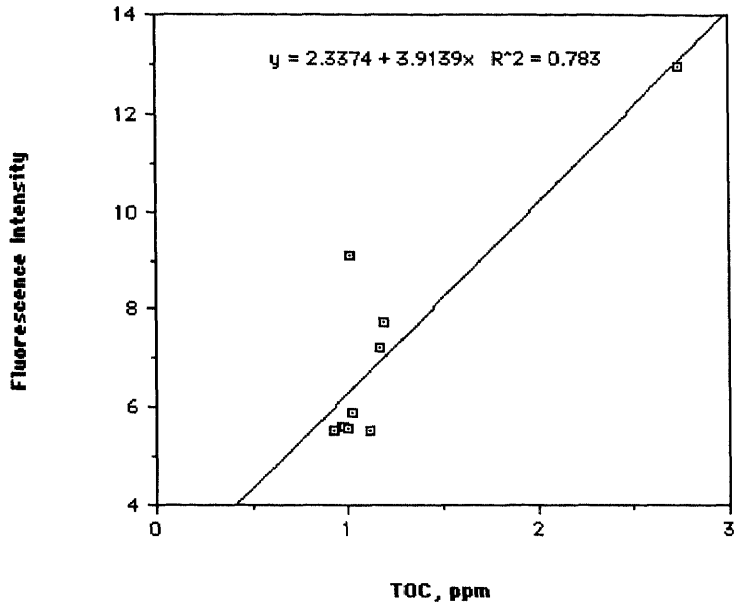


Figure D.11 Fluorescence vs. TOC (October 1997 Raritan River Watershed), Fluorescence Measured at Excitation 250 nm

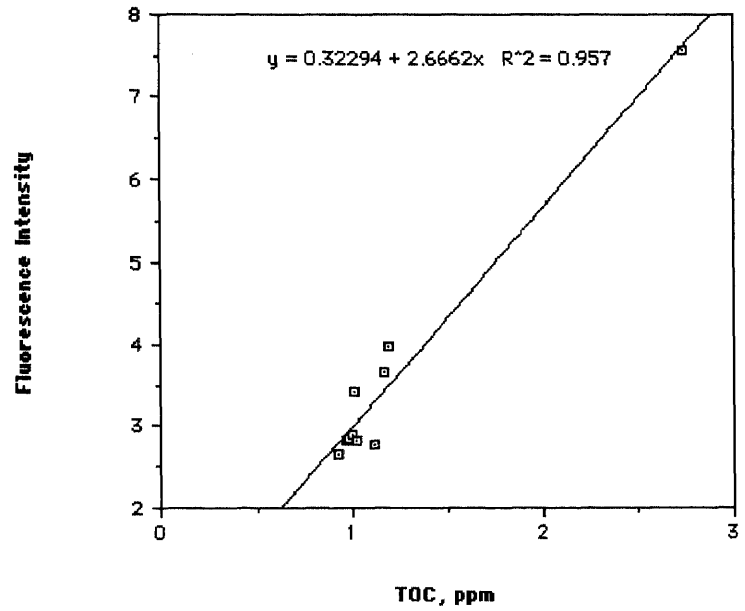


Figure D.12 Fluorescence vs. TOC (October 1997 Raritan River Watershed), Fluorescence Measured at Excitation 350 nm

APPENDIX E

DBPFP VS. FLUORESCENCE GRAPHS

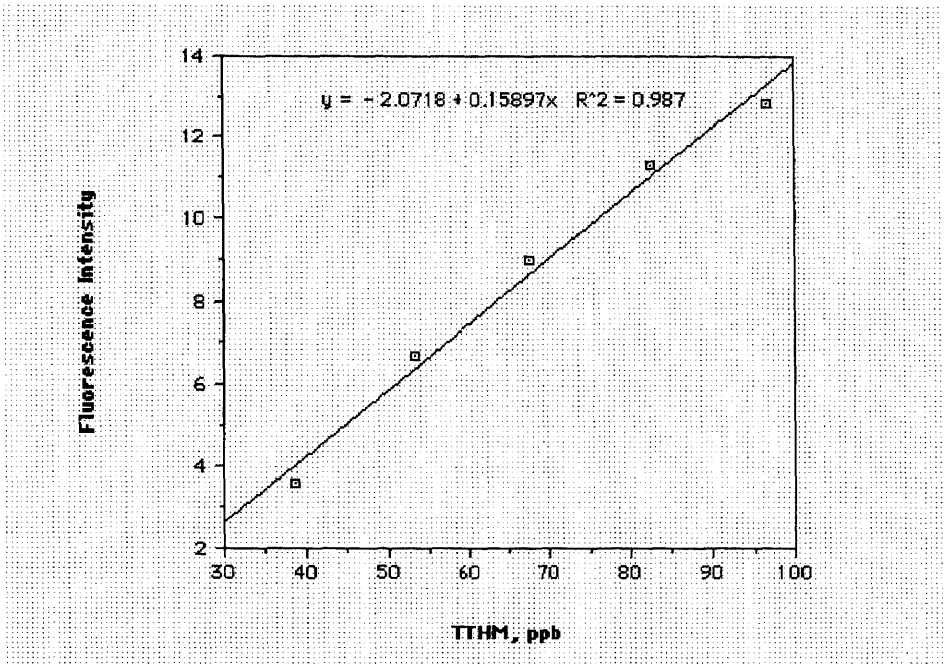


Figure E.1 Fluorescence vs. THMFP, Fluorescence Measured at Excitation Wavelength 250 nm

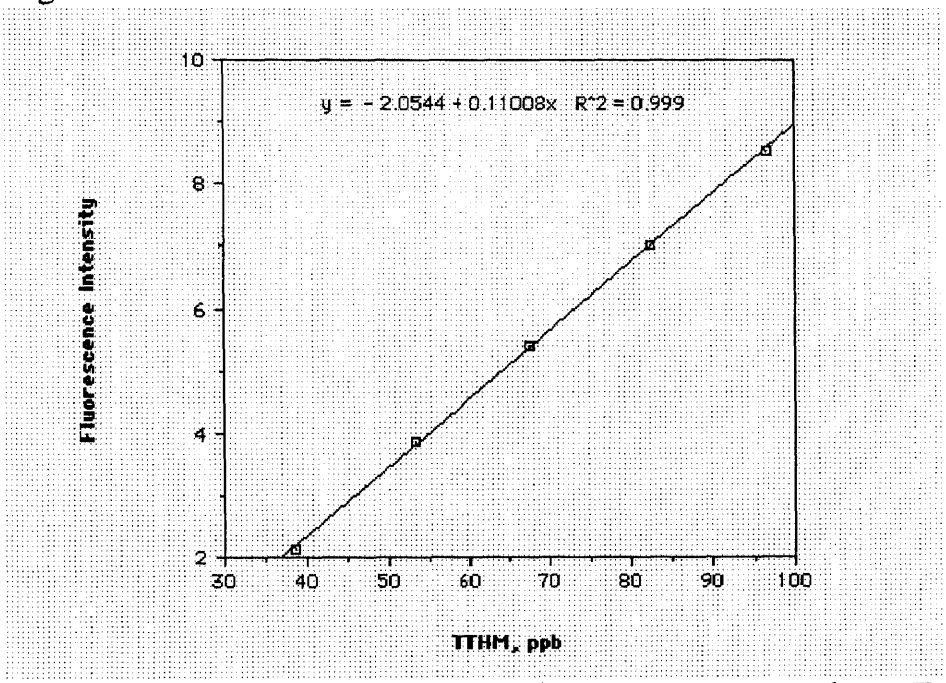


Figure E.2 Fluorescence vs. THMFP, Fluorescence Measured at Excitation Wavelength 350 nm

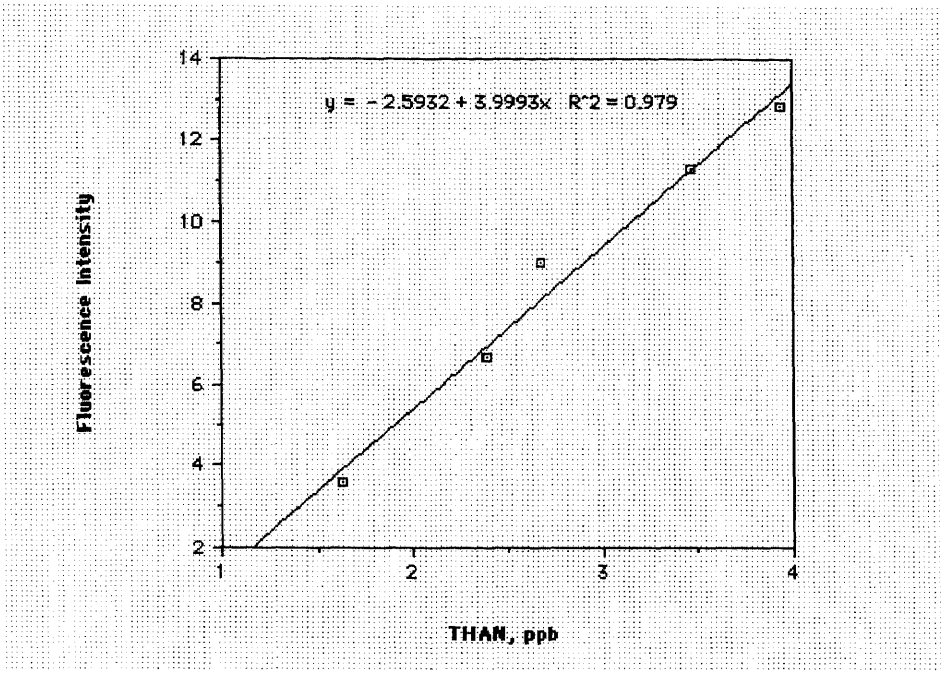


Figure E.3 Fluorescence vs. HANFP, Fluorescence Measured at Excitation Wavelength 250 nm

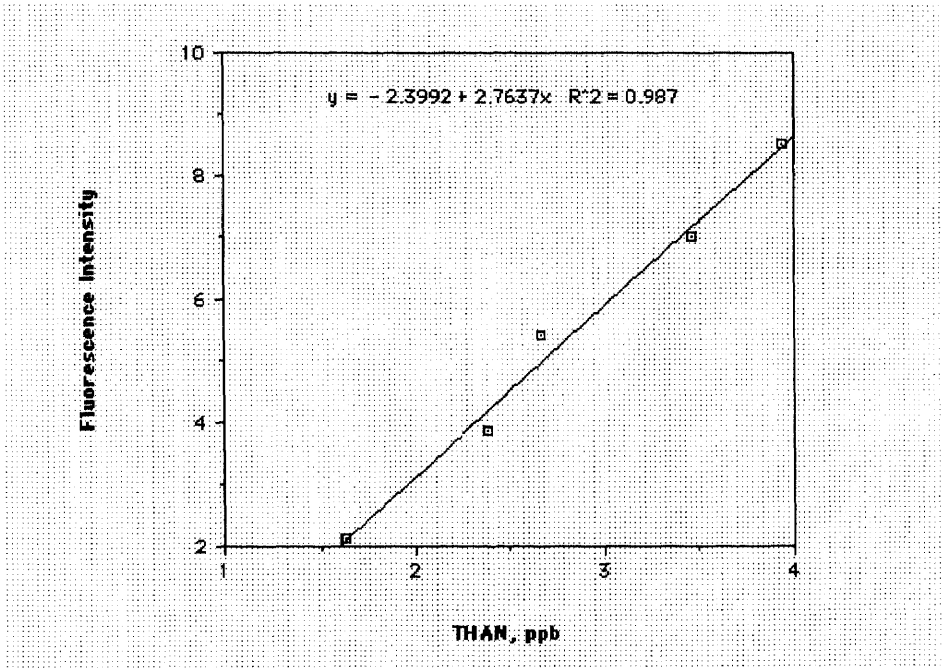


Figure E.4 Fluorescence vs. HANFP, Fluorescence Measured at Excitation Wavelength 350 nm

APPENDIX F

PRE- AND POST-CHLORINATION SFS

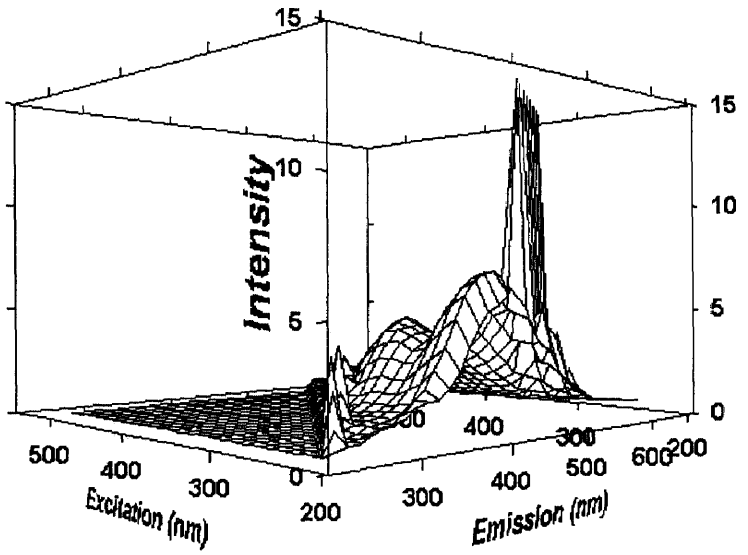


Figure F.1 Fulvic Acid (4 ppm), Pre-Chlorination SFS

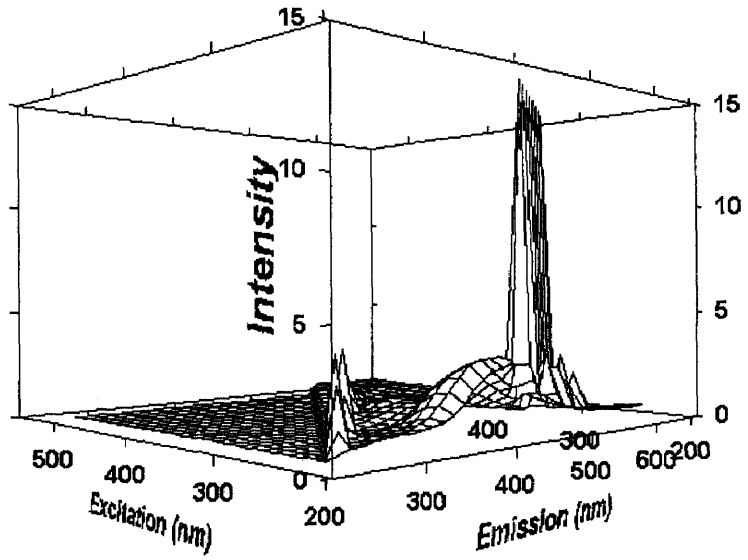


Figure F.2 Fulvic Acid (4 ppm), Post-Chlorination SFS

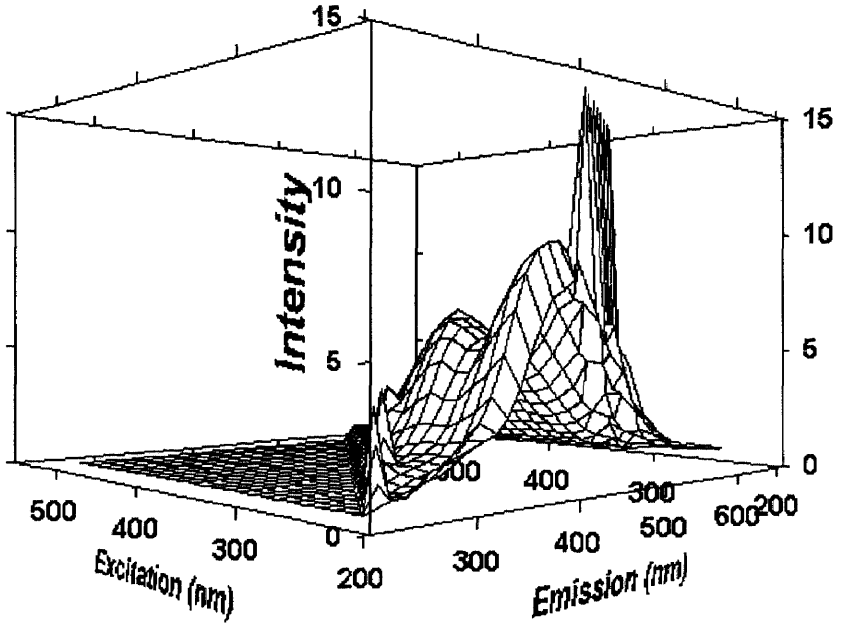


Figure F.3 Fulvic Acid (6ppm), Pre-Chlorination SFS

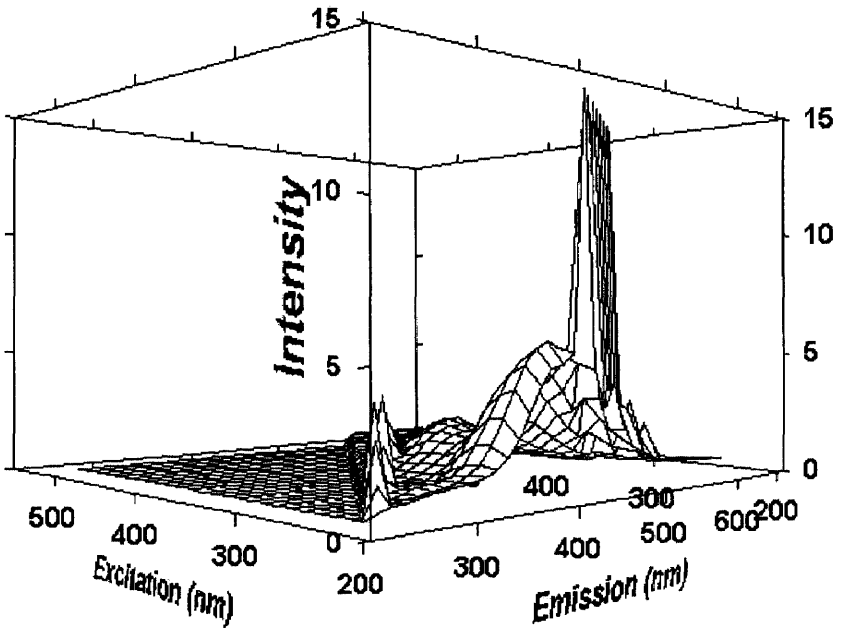


Figure F.4 Fulvic Acid (6 ppm), Post Chlorination SFS

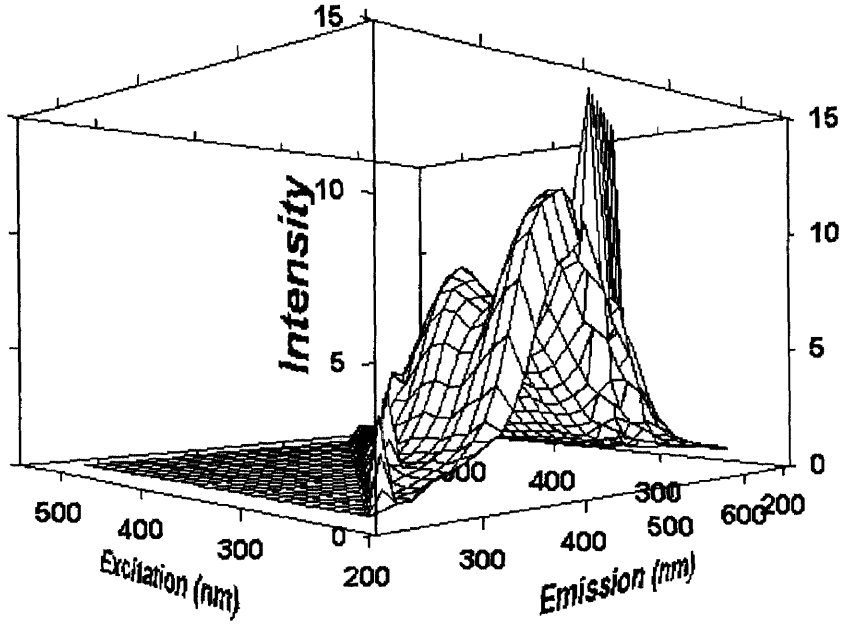


Figure F.5 Fulvic Acid (8 ppm), Pre-Chlorination SFS

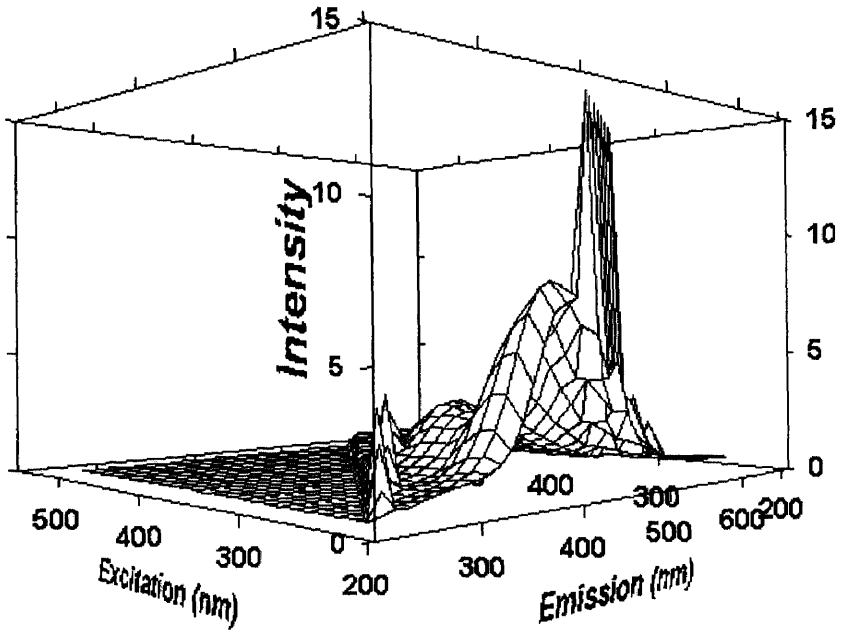


Figure F.6 Fulvic Acid (8 ppm), Post-Chlorination SFS

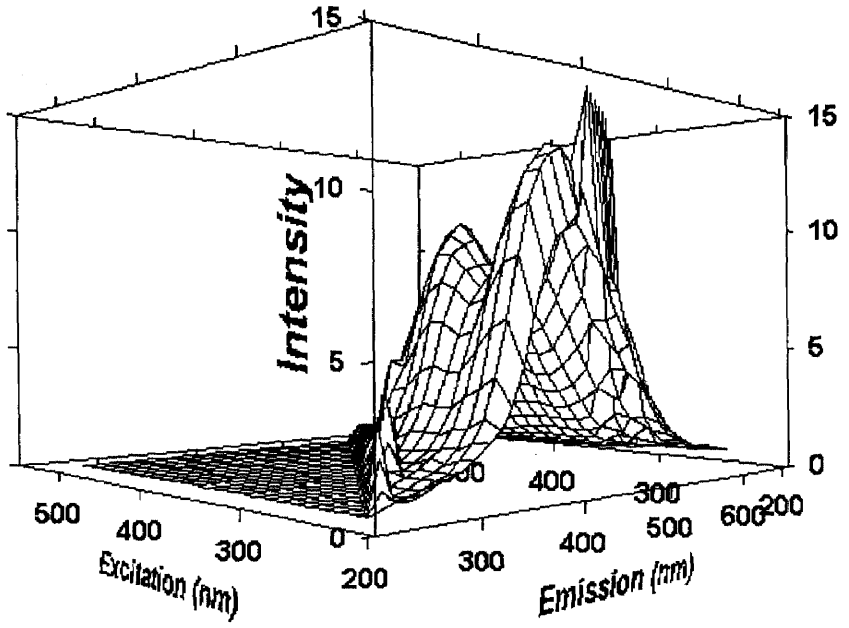


Figure F.7 Fulvic Acid (10 ppm), Pre-Chlorination SFS

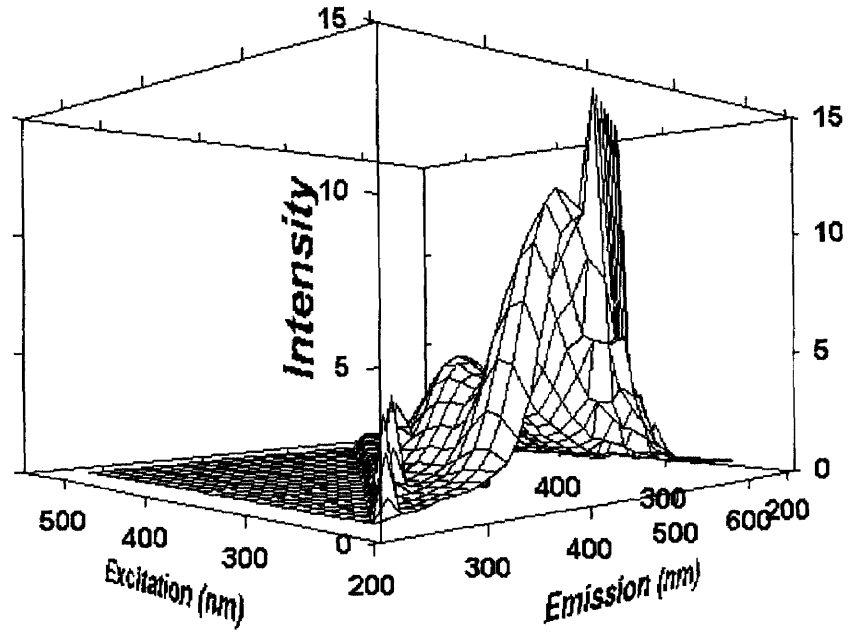


Figure F.8 Fulvic Acid (10 ppm), Post-Chlorination SFS

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