Title
The Effects of Dissolved Organic Matter on Pollutant Removal and Formation in Aquatic Environment: From Stormwater to Drinking Water

Author
Hsu, Meng-Horng

Publication Date
2012

UNIVERSITY OF CALIFORNIA

Los Angeles

The Effects of Dissolved Organic Matter on Pollutant Removal and Formation in Aquatic Environment: From Stormwater to Drinking Water

A dissertation submitted in partial satisfaction of the requirements for the degree Doctor of Environmental Science and Engineering

by

Meng-Horng Hsu

2012

ABSTRACT OF THE DISSERTATION

The Effects of Dissolved Organic Matter on Pollutant Removal and Formation in Aquatic Environment: From Stormwater to Drinking Water

by

Meng-Horng Hsu
Doctor of Environmental Science and Engineering
University of California, Los Angeles, 2012
Professor Irwin Suffet

Hydrophobic organic pollutants (HOPs), such as polyaromatic hydrocarbons primarily from automobile exhausts and dissolved organic matter (DOM) are ubiquitous in the aquatic environment. The association between DOM and HOPs as a bound interaction of DOM-HOPs minimizes the bioavailability of free HOPs and their potential health effects. In addition, DOM is also the precursor of disinfection by-products involving the disinfection treatment processes.

It is very important to understand the relationship between free and bound HOPs, disinfection by-products, and DOM in drinking water treatment, stormwater runoff and dry weather flow of aquatic environment. This thesis will explore the binding phenomenon between HOPs and DOM in raw and treated water from water treatment plants, after powdered activated carbon treatment, and in stormwater runoff and dry weather flow.

This thesis also introduced the analytical methodologies for characterizing DOM and the hazardous potential of HOPs and thus understanding their relationship. DOM characteristics were measured for: 1) total concentration of organic carbon by dissolved organic carbon (DOC), 2) aromaticity by UV absorbance and specific UV absorbance (SUVA), and 3) size distribution by ultrafiltration (UF), 4) polarity by polarity rapid assessment method (PRAM), 5) UV and fluorescent chemical components by UV spectrometer and fluorescence excitation-emission matrix (EEM) and fluorescence regional integration (FRI). Hazardous potential of HOPs was measured by fluorescence quenching determined partition coefficient K_{DOM}.

Studies have been completed and showed that monitoring both the free and bound forms of HOPs as well as disinfection by-products (such as, trihalomethanes) and their relationship to DOM during drinking water treatment processes is necessary to better understand drinking water quality and give more effective suggestions to optimize treatment processes. In addition, this work showed the relationship between DOM and HOPs in equilibrium with DOM-HOPs needs definition on a seasonal basis to understand the bioavailability of HOPs in dry weather flow and stormwater runoff events. The determination of free and total HOPs has not been considered in the California “State Implementation Plan” for water quality-based effluent limits of HOPs. A method using a standard probe- perylene has been developed to be able to evaluate these situations on a site specific basis since DOM is site specific.

Key findings of this study were: 1) DOM characteristics are different from site to site and affect pollutants removal and formation. 2) Bulk SUVA shows a positive correlation with Log K_{DOM} ($R^2=74\%$). Thus, DOM with more aromatic structure can result in higher binding between HOPs and DOM. 3) DOM with higher concentration, aromaticity, and molecular weight can have more ability to form THMs. 4) Under the conditions studied, PAC (20 mg/L) is an effective method to control both THMs and the hazard potential of HOPs. 5) DOM in urban runoff with higher molecular weight and aromaticity can associate with more HOPs. As a result, the distribution of HOPs affected by DOM in urban runoff needs definition on a seasonal basis and runoff types.

The dissertation of Meng-Horng Hsu is approved.

Jennifer A. Jay

Keith D. Stolzenbach

Michael K. Stenstrom

Irwin H. Suffet, Committee Chair

University of California, Los Angeles

2012

TABLE OF CONTENTS

C. Chapter 3:

D. Chapter 4:

E. Chapter 5:

Bioavailability of Hydrophobic Organic Pollutants (HOPs) in Urban Runoff

F. Chapter 6:

ACKNOWLEDGEMENTS

I wish to acknowledge all the people without whose I might never have reached to this point in my career. First, I thank complete support of my wife, Chien-Hui Yu, my daughter, Doreen Hsu, and my parents. Thank you for your encouragement and 100% mental support all the time. I would like to thank my awesome committee, the best scientists and educators. Over the years, I have come to realize how much I have learned from my advisor, Dr. Mel Suffet. Dr. Suffet has been an example and inspiration of both his deep knowledge and passion for science. He is not only my advisor, but also a friend with full support. Dr. Michael Stenstrom has instructed me a lot in wastewater and stormwater issues to lead me into another important water fields. I thank Dr. Keith Stolzenbach and Dr. Jenny Jay for their long time support and concerns about my academic success. I thank Dr. Ben Schwegler gave me such a valuable opportunity allowing me to gain practical experience and directed me to finish my dissertation. He is a great role model of an entrepreneurial scientist and engineer.

Second, I wish to acknowledge those individuals who have helped me greatly during my doctoral work. Dr. David Kimbrough, Dr. Christopher Gabelich, and Dr. Dian Tanwidjaja assisted me to get samples from drinking water treatment plants. Frank dela Vara, Janina Jarvis, and Carlos Campos instructed me stormwater management program and helped me to get samples from the fields. Christina Cheng, Jennifer Tsoi, Carmen Seetho, David Quiros, Vincent Duong, Arthur Roh, Hazel Cheung, Jonathan Lee, and other fellow Bruins for all your help and support in the laboratory.

VITA

2002	Project Assistant MWH Global Taipei, Taiwan
2003	B.S. Environmental Engineering National Cheng Kung University Tainan, Taiwan
2005	M.S. Environmental Engineering National Cheng Kung University Tainan, Taiwan
2003-2005	Research and Teaching Assistant National Cheng Kung University Tainan, Taiwan
2006-2007	Executive Officer Military Police, Republic of China (Taiwan) Army Taipei, Taiwan
2007-2008	Project Manager Environmental Quality Protection Foundation Taipei, Taiwan
2008-2011	Graduate Student Researcher University of California, Los Angeles Los Angeles, California

2011-2012	Research and Development Associate Walt Disney Imagineering Los Angeles, California

A. Chapter 1: Thesis Introduction

A.1 Introduction and Background

Dissolved Organic Matter (DOM)

Dissolved organic matter (DOM) is a heterogeneous mixture of hundreds of aromatic and aliphatic organic compounds containing nitrogen, oxygen, and sulfur functional groups from decomposing natural organic matter by microorganisms in natural waters (1-3). DOM components include humic acids, fulvic acids, humin, amino acids, proteins, sugars, and polysaccharides (2-4). DOM transformation is a very important issue in water treatment processes because DOM is one of the main components to cause disinfection by-product formation (3-7) and membrane fouling (8-10) that can negatively affect drinking water quality.

DOM also has the ability to associate with hydrophobic organic pollutants (HOPs), such as polycyclic aromatic hydrocarbons (PAHs), chlorinated pesticides, and polychlorinated biphenyls in natural waters and during drinking water, reclaimed water, and wastewater treatment processes (11-13). The interaction between HOPs and DOM affects the bioavailability of pollutants and their resulting toxicity. Therefore, the interaction of HOPs and DOM during water treatment processes can affect the toxicity of hydrophobic organic contaminants, such as PAHs. Simultaneously as this occurs, DOM can form disinfection by-product such as trihalomethanes which are potentially carcinogenic. What fraction of DOM affects the bioavailability of HOPs and what fraction of DOM affects the formation of disinfection by-products is not understood.

Hydrophobic Organic Pollutants (HOPs)

HOPs are defined as those compounds with a log octanol-water partition coefficient over five. PAHs are a group of representative HOPs that include over 100 different chemicals. PAHs are primarily generated from incomplete fossil fuel burning, oil spills, and other industrial processes (14). The U.S. Environmental Protection Agency (US EPA) has listed 16 PAHs as priority pollutants in the aquatic environment due to toxicity and potential carcinogenicity (15). Of these PAHs, the U.S. EPA has set drinking water standards of 200 ng/L for benzo(a)pyrene (US EPA) (16). The European Union Directive 98/83/EC sets the maximum total concentration of four PAHs (benzo(b)fluoranthene, benzo(k)fluoranthene, benzo(ghi)perylene, and indeno(1,2,3-cd)pyrene) at 100 ng/L in drinking water, and at 10 ng/L for benzo(a)pyrene (17).

Several researchers began to find that HOPs can bind with DOM during the 1970 to 1980s (18-21). This phenomenon significantly affects the fate and transport of HOPs in the aquatic environment. In 1982, Carter and Suffet were the first to show quantitative data for binding behavior between DOM and one of the HOPs, namely DDT. In addition, Carter and Suffet proposed the idea for understanding the free and bound portions in the aquatic environment according to the partition coefficient, K_{DOM} (11). Equation 1 describes the binding behavior between DOM and HOPs via K_{DOM}.

$$\text{PAH (soluble, free)} + \text{DOM} \overset{K_{DOM}}{\Longleftrightarrow} \text{PAH} - \text{DOM (bound)} \quad (1)$$

Figure 1 showed an example that illustrates that some parts of the PAHs present were dissolved in the water solution and some parts of PAHs were bound to the black materials which represents DOM in the water. When free PAHs bind with DOM to form the DOM-PAHs bound together, they are not bioavailable and thus not toxic. Thus, free PAHs are the bioavailable hazardous form. The partition coefficient between DOM and HOPs, K_{DOM}, describes the relative amount of free HOPs (See Equation 1).

The natural organic matter that forms DOM in a natural water is uniquely defined by the source of organic matter and its microbial breakdown. Therefore, each natural waters will have unique DOM mixture of organic molecules of different sizes and polarities and thus also a unique interaction with HOPs that can be measured as the K_{DOM}. Thus, there will be different toxicity level of HOPs in each raw, treated and finished drinking waters. Since it is not possible to predict K_{DOM}, it is necessary to have a simple, quick, accurate, reliable, and consistent experimental methods to obtain the K_{DOM} information from the water of interest.

DOM interacts with HOPs through hydrophobic binding and forms humic-solute mixtures in the aqueous phase. This interaction can change due to DOM oxidation (e.g. chlorination or ozonation), DOM coagulation, and DOM sorption (e.g., activated carbon adsorption or sorption to suspended solids). The binding increases the overall solubility of HOPs in water by facilitating their sorption to DOM, and therefore, potentially enhancing their transport (11-13). However, sorption to DOM can potentially also serve as an environmentally friendly decontamination agent (22-24). Moreover, interaction with DOM can decrease the toxicity and bioavailability of HOPs, such as PAHs (25-27). Furthermore, the relationship between specific characteristics of DOM and trihalomethane formation potential and interaction of DOM with HOPs need to be disentangled.

Analytical Methods for Measuring the Potential Formation of Free HOPs in Aquatic Environment

Due to the limitation of experimental techniques at ng/L levels and the variability of DOM at different locations, the interaction between HOPs and DOM are not well defined in aquatic environment. This is especially needed for the freely dissolved form of HOPs, which are hazardous and bioavailable. Thus, it is necessary to monitor and measure free HOPs from the source waters, through the drinking water treatment process and in the drinking water supply.

Several researchers studied detection methods for free and bound portion of HOPs in surface waters and sediment pore water. The most popular methods used for these kind of experiments are solid phase microextraction (SPME) combined with GC/MS (28-34) and fluorescence quenching (25-27). Both SPME and fluorescence quenching methods have the advantage of analysis without changing the original water quality conditions. As a result, these methods do not change the equilibrium of the partition between DOM and HOPs.

In addition, fluorescence quenching is also a sensitive and precise method. SPME is a quick extraction method without any solvent which is environmental friendly. On the other hand, each of these two methods also has their own disadvantages. For the fluorescence quenching method, several assumptions need to be evaluated. For SPME, during the extraction process, DOM might attach on the SPME fiber for long extraction time and affect the final equilibrium results. Due to these problems, it is important to understand the relationship between these two analytical methods. Doll et al. (1999) (35) and Mackenzie et al. (2002) (36) used phenanthrene and pyrene, respectively, to compare these two methods and found that K_{DOM} derived by fluorescence quenching was larger than the SPME method.

Holbrook et al. (2005) (37) also applied the fluorescence techniques including fluorescence excitation-emission matrix (EEM), fluorescence regional integration and fluorescence quenching to understand the impacts of reclaimed wastewater on the surface water. Their results found that wastewater treatment facilities, including advanced treatment facilities from reclaimed wastewater to supplemental drinking water sources, can affect the components of organic matter in the receiving water body and thus change the behavior between organic matter and other HOPs.

Different components and characteristics (e.g. size, polarity, chemical components, etc.) of DOM affect the ability of PAHs to bind with DOM. Therefore, different water sources, treatment processes, and samples taken at different times can have different K_{DOM} values. Considering the complexity to measure K_{DOM} and the importance to get this information at waters of interest, a consistent method is needed to measure K_{DOM} (38). Perylene, a less hazardous PAH was chosen as a probe to determine K_{DOM} in different waters.

A.2 Statement of Objectives of the Thesis

Since understanding the relationship between free and bound HOPs, disinfection by-products, and DOM in raw water, drinking water and treatment processes, stormwater runoff and dry weather flow of aquatic environment is necessary and very important, this research project has the following objectives to complete.

The first objective of this research project is to develop methodology to monitor the potential formation of free HOPs during water treatment and also a monitoring program to understand the relationship between HOPs and the characteristics of DOM.

The second objective of research project is to understand the relationship between different characteristics of DOM and disinfection by-products in terms of total trihalomethanes (THMs) in raw and treated water during drinking water treatment processes.

The third objective of this research project is to explore the behaviors between DOM characteristics, binding behavior between DOM and HOPs, and the formation of disinfection by-products at different sources of raw water before and after powdered activated carbon (PAC) treatment. In short, DOM can decrease HOPs toxicity by binding with HOPs. On the other hand, DOM is the precursor of disinfection by-products generating e.g. trihalomethanes. Therefore, this paper is to begin to understand the changes of DOM characteristics and its effect on the association HOPs with DOM and trihalomethane formation potential before and after water treatment. This should enable better optimization of water treatment processes by decreasing trihalomethanes and simultaneously keeping water safer to drink by keeping a lower hazard potential of HOPs.

The forth objective of this research project is to understand how dissolved HOPs distribute in urban runoff including stormwater runoff and dry weather flow affected by different DOM characteristics. The behavior of fate and transport of HOPs during different seasons will also be studied. HOPs existing in stormwater and dry weather flow can impair the water quality of receiving water bodies going to drinking water sources significantly.

This research thesis is to understand the effect of DOM on pollutant removal and formation in aquatic environment. The thesis develops methodologies and a monitoring program to measure the potential hazard of HOPs and different DOM characteristics. Knowing the relationships between the potential hazard of HOPs, disinfection by-products, and DOM characteristics; and how HOPs distribute in stormwater runoff and dry weather flow affected by DOM in different seasons can help to optimize water quality management.

A.3 Figures

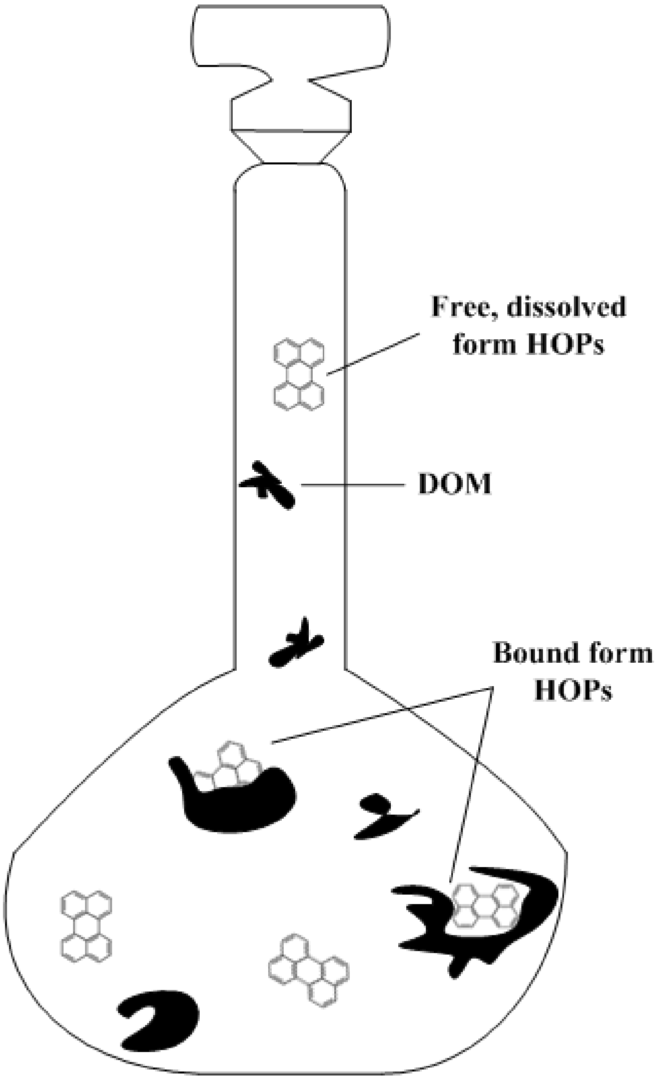

Figure 1. The illustration of binding behavior between DOM and HOPs (11, 36)

A.4 Reference

1. Chen, W.; Westerhoff, P.; Leenheer, J. A.; Booksh, K., Fluorescence excitation - Emission matrix regional integration to quantify spectra for dissolved organic matter. *Environ. Sci. Technol.* **2003,** *37*, (24), 5701-5710.

2. Stevenson, F. J., *Humus Chemistry, Genesis Composition, Reaction.* 2nd ed.; John Wiley & Sons: New York, 1994.

3. Thurman, E. M., *Organic Geochemistry of Natural Waters.* Dr. W. Junk Publishers.: Dordrecht, The Netherlands: Martinus Nijhoff, Netherlands, 1985.

4. Krasner, S. W.; Croue, J. P.; Buffle, J.; Perdue, E. M., Three approaches for characterizing NOM. *J. Am. Water Work Assoc.* **1996,** *88*, (6), 66-79.

5. Amy, G. L.; Thompson, J. M.; Tan, L.; Davis, M. K.; Krasner, S. W., EVALUATION OF THM PRECURSOR CONTRIBUTIONS FROM AGRICULTURAL DRAINS. *J. Am. Water Work Assoc.* **1990,** *82*, (1), 57-64.

6. Singer, P. C., Humic substances as precursors for potentially harmful disinfection by-products. *Water Sci. Technol.* **1999,** *40*, (9), 25-30.

7. Zhang, X. G.; Minear, R. A., Characterization of high molecular weight disinfection byproducts resulting from chlorination of aquatic humic substances. *Environ. Sci. Technol.* **2002,** *36*, (19), 4033-4038.

8. Amy, G.; Cho, J., Interactions between natural organic matter (NOM) and membranes: Rejection and fouling. *Water Sci. Technol.* **1999,** *40*, (9), 131-139.

9. Lee, N. H.; Amy, G.; Croue, J. P.; Buisson, H., Identification and understanding of fouling in low-pressure membrane (MF/UF) filtration by natural organic matter (NOM). *Water Res.* **2004,** *38*, (20), 4511-4523.

10. Taniguchi, M.; Kilduff, J. E.; Belfort, G., Modes of natural organic matter fouling during ultrafiltration. *Environ. Sci. Technol.* **2003,** *37*, (8), 1676-1683.

11. Carter, C. W.; Suffet, I. H., BINDING OF DDT TO DISSOLVED HUMIC MATERIALS. *Environ. Sci. Technol.* **1982,** *16*, (11), 735-740.

12. Chiou, C. T.; Malcolm, R. L.; Brinton, T. I.; Kile, D. E., WATER SOLUBILITY ENHANCEMENT OF SOME ORGANIC POLLUTANTS AND PESTICIDES BY DISSOLVED HUMIC AND FULVIC-ACIDS. *Environ. Sci. Technol.* **1986,** *20*, (5), 502-508.

13. Ravacha, C.; Rebhun, M., BINDING OF ORGANIC SOLUTES TO DISSOLVED HUMIC SUBSTANCES AND ITS EFFECTS ON ADSORPTION AND TRANSPORT IN THE AQUATIC ENVIRONMENT. *Water Res.* **1992,** *26*, (12), 1645-1654.

14. Woodhead, R. J.; Law, R. J.; Matthiessen, P., Polycyclic aromatic hydrocarbons in surface sediments around England and Wales, and their possible biological significance. *Mar. Pollut. Bull.* **1999,** *38*, (9), 773-790.

15. Santos, F. J.; Galceran, M. T., The application of gas chromatography to environmental analysis. *Trac-Trends Anal. Chem.* **2002,** *21*, (9-10), 672-685.

16. *USEPA* Website; http://water.epa.gov/drink/contaminants/basicinformation/benzo-a-pyrene.cfm.

17. European Comission, Council Directive 98/83/EC; *Off. J. Eur. Commun.* 1998, L330, 32.

18. Boehm, P. D.; Quinn, J. G., SOLUBILIZATION OF HYDROCARBONS BY DISSOLVED ORGANIC-MATTER IN SEA-WATER. *Geochim. Cosmochim. Acta* **1973,** *37*, (11), 2459-2477.

19. Hassett, J. P.; Anderson, M. A., ASSOCIATION OF HYDROPHOBIC ORGANIC-COMPOUNDS WITH DISSOLVED ORGANIC-MATTER IN AQUATIC SYSTEMS. *Environ. Sci. Technol.* **1979,** *13*, (12), 1526-1529.

20. Poirrier, M. A.; Laseter, J. L.; Bordelon, B. R., ADSORPTION AND CONCENTRATION OF DISSOLVED C-14 DDT BY COLORING COLLOIDS IN SURFACE WATERS. *Environ. Sci. Technol.* **1972,** *6*, (12), 1033-&.

21. Wershaw, R. L.; Burcar, P. J.; Goldberg, M. C., INTERACTION OF PESTICIDES WITH NATURAL ORGANIC MATERIAL. *Environ. Sci. Technol.* **1969,** *3*, (3), 271-&.

22. Molson, J. W.; Frind, E. O.; Van Stempvoort, D. R.; Lesage, S., Humic acid enhanced remediation of an emplaced diesel source in groundwater. 2. Numerical model development and application. *J. Contam. Hydrol.* **2002,** *54*, (3-4), 277-305.

23. Rebhun, M.; DeSmedt, F.; Rwetabula, J., Dissolved humic substances for remediation of sites contaminated by organic pollutants. Binding-desorption model predictions. *Water Res.* **1996,** *30*, (9), 2027-2038.

24. Van Stempvoort, D. R.; Lesage, S.; Novakowski, K. S.; Millar, K.; Brown, S.; Lawrence, J. R., Humic acid enhanced remediation of an emplaced diesel source in groundwater. 1. Laboratory-based pilot scale test. *J. Contam. Hydrol.* **2002,** *54*, (3-4), 249-276.

25. Backhus, D. A.; Gschwend, P. M., FLUORESCENT POLYCYCLIC AROMATIC-HYDROCARBONS AS PROBES FOR STUDYING THE IMPACT OF COLLOIDS ON

POLLUTANT TRANSPORT IN GROUNDWATER. *Environ. Sci. Technol.* **1990,** *24*, (8), 1214-1223.

26. Backhus, D. A.; Golini, C.; Castellanos, E., Evaluation of fluorescence quenching for assessing the importance of interactions between nonpolar organic pollutants and dissolved organic matter. *Environ. Sci. Technol.* **2003,** *37*, (20), 4717-4723.

27. Schlautman, M. A.; Morgan, J. J., EFFECTS OF AQUEOUS CHEMISTRY ON THE BINDING OF POLYCYCLIC AROMATIC-HYDROCARBONS BY DISSOLVED HUMIC MATERIALS. *Environ. Sci. Technol.* **1993,** *27*, (5), 961-969.

28. Bondarenko, S.; Gan, J., Simultaneous Measurement of Free and Total Concentrations of Hydrophobic Compounds. *Environ. Sci. Technol.* **2009,** *43*, (10), 3772-3777.

29. Georgi, A.; Reichl, A.; Trommler, U.; Kopinke, F.-D., Influence of sorption to dissolved humic substances on transformation reactions of hydrophobic organic compounds in water. I. Chlorination of PAHs. *Environ. Sci. Technol.* **2007,** *41*, (20), 7003-7009.

30. Hawthorne, S. B.; Grabanski, C. B.; Miller, D. J.; Kreitinger, J. P., Solid-phase microextraction measurement of parent and alkyl polycyclic aromatic hydrocarbons in milliliter sediment pore water samples and determination of K-DOC values. *Environ. Sci. Technol.* **2005,** *39*, (8), 2795-2803.

31. Porschmann, J.; Kopinke, F. D.; Pawliszyn, J., Solid-phase microextraction for determining the binding state of organic pollutants in contaminated water rich in humic organic matter. *Journal of Chromatography A* **1998,** *816*, (2), 159-167.

32. Ramos, E. U.; Meijer, S. N.; Vaes, W. H. J.; Verhaar, H. J. M.; Hermens, J. L. M., Using solid-phase microextraction to determine partition coefficients to humic acids and bioavailable concentrations of hydrophobic chemicals. *Environ. Sci. Technol.* **1998,** *32*, (21), 3430-3435.

33. Van der Wal, L.; Jager, T.; Fleuren, R.; Barendregt, A.; Sinnige, T. L.; Van Gestel, C. A. M.; Hermens, J. L. M., Solid-phase microextraction to predict bioavailability and accumulation of organic micropollutants in terrestrial organisms after exposure to a field-contaminated soil. *Environ. Sci. Technol.* **2004,** *38*, (18), 4842-4848.

34. Xu, Y.; Spurlock, F.; Wang, Z.; Gan, J., Comparison of five methods for measuring sediment toxicity of hydrophobic cantaminants. *Environ. Sci. Technol.* **2007,** *41*, (24), 8394-8399.

35. Doll, T. E.; Frimmel, F. H.; Kumke, M. U.; Ohlenbusch, G., Interaction between natural organic matter (NOM) and polycyclic aromatic compounds (PAC) - comparison of fluorescence quenching and solid phase micro extraction (SPME). *Fresenius J. Anal. Chem.* **1999,** *364*, (4), 313-319.

36. MacKenzie, K.; Georgi, A.; Kumke, M.; Kopinke, F. D., Sorption of pyrene to dissolved humic substances and related model polymers. 2. Solid-phase microextraction (SPME) and fluorescence quenching technique (FQT) as analytical methods. *Environ. Sci. Technol.* **2002,** *36*, (20), 4403-4409.

37. Holbrook, R. D.; Breidenich, J.; DeRose, P. C., Impact of reclaimed water on select organic matter properties of a receiving stream-fluorescence and perylene sorption behavior. *Environ. Sci. Technol.* **2005,** *39*, (17), 6453-6460.

38. Burkhard, L. P., Estimating dissolved organic carbon partition coefficients for nonionic organic chemicals. *Environ. Sci. Technol.* **2000,** *34*, (22), 4663-4668.

B. Chapter 2:

Research Paper 1

Understanding the Interaction of Hydrophobic Organic Pollutants (HOPs) and Dissolved Organic Matter (DOM) in Raw and Treated Drinking Water

B.1 Abstract

Hydrophobic organic pollutants (HOPs) and dissolved organic matter (DOM) are ubiquitous in the aquatic environment. The dissolved aqueous form of non-polar organic chemicals such as polyaromatic hydrocarbons (PAHs) are hazardous and have defined drinking water Maximum Contaminant Levels. However, DOM interacts with HOPs to form DOM complexes that are less toxic as the DOM-PAHs are less bioavailable. The effect of this interaction is not considered in environmental or drinking water standards. The objective of this paper is to evaluate DOM as a protection for HOPs in environmental and drinking waters. Perylene was developed as a low toxicity probe for HOPs. Partition coefficient between DOM and perylene (K_{DOM} = [bound perylene] / [DOM][free perylene]) was used to characterize the interaction. DOM characteristics including size, polarity, chemical functionality, and partition coefficient, changed at different sources of water and stages of water treatment processes. The K_{DOM} had higher correlation with SUVA (R^2 =0.74). Bulk UV_{254}, fulvic acid fluorescence, DOM size fractions for 10 – 5 kDa in TOC, UV_{254} > 5 kDa had correlation coefficients of 0.44 to 0.58 with K_{DOM}. The results

demonstrated DOM with higher aromaticity and molecular weight bind more HOPs and thus can reduce the hazard from free hydrophobic contaminants.

B.2 Introduction

Dissolved organic matter (DOM) measured as dissolved organic carbon (DOC) in natural waters is a heterogeneous combination of aromatic and aliphatic organic compounds coming from biological decomposition of natural organic matter (1-3). The molecular weight of DOM is about 500 kDa to > 10,000 kDa (3). The DOM contains functional groups of C, S and N. Fluorescence analysis notes 5 DOM fractions represented by aromatic proteinaceous compounds I and II, microbial by-products, fulvic acids, and humic acids (1, 3). Fulvic and humic acids are defined by the XAD Resin isolation method as sub-fractions of DOM (4). The transformation of DOM is critically important in environmental water because its control of toxicity and transport of metals and hydrophobic organic compounds (HOPs) (5-7). DOM is also important in water treatment processes because of this control of toxicity and it is one of the main components to cause disinfection by-products (DBPs) formation (3, 8-11) and membrane fouling (12-14).

DOM can be associated with HOPs, such as polycyclic aromatic hydrocarbons (PAHs) and polychlorinated biphenyls (PCBs) in natural waters and during drinking water treatment processes (5-7). The interaction between HOPs and DOM as a DOM---HOP association lowers the bioavailability of pollutants and their resulting toxicity. Thus, interaction of DOM in the environment by photolysis, biolysis etc. or during treatment processes, such as, coagulation and adsorption on activated carbon could increase or decrease the interaction of DOM and HOPs, and thus effect their hazard (15-20).

HOPs are defined as those compounds with a log octanol-water partition coefficient over five. PAHs are a group of hydrophobic compounds that include over 100 different chemicals. PAHs are primarily generated from incomplete fossil fuel burning, oil spills, and other industrial processes (21). The U.S. Environmental Protection Agency (U.S. EPA) has listed 16 PAHs as priority pollutants in the aquatic environment due to toxicity and potential carcinogenicity (22). U.S. EPA lists one of the PAHs- benzo(a)pyrene at 200 ng/L as maximum contaminant levels (MCLs) in drinking water (23). Also, European Union Directive 98/83/EC sets the maximum total concentration of four PAHs (benzo(b)fluoranthene, benzo(k)fluoranthene, benzo(ghi)perylene, and indeno(1,2,3-cd)pyrene) at 100 ng/L in drinking water and for benzo(a)pyrene at 10 ng/L (24).

DOM interacts with organic pollutants through hydrophobic binding and forms humic-solute mixtures in the aqueous phase. Since the equilibrium binding phenomenon between PAH and DOM is a linear relationship, the equation described by Carter and Suffet (1982) (5) is applicable.

$$C_s = K_{DOM} C_{free} \quad (1)$$

Cs is the DOM-bound PAH. C_{free} is the free specific PAH concentration and K_{DOM} is the equilibrium binding coefficient normalized to the DOM. It has been shown that DOM in different natural waters has different K_{DOM} values for same PAH. Thus, the K_{DOM} is site specific (1, 5, 25-27). No standard PAH has been use to define a scale of reactivity of different DOM types.

The primary objective of this paper is to develop a PAH probe to measure the potential amount of DOM associated PAHs and the amount of free PAHs in natural and drinking waters. This also could be used to define a standard method scale of reactivity of different DOMs. The secondary objective is to enable an understanding of the interaction between HOPs and DOM in different environments. Understanding the changes in DOM characteristics at different sources of water and stages of water treatment can offer valuable information to assess and manage the environmental risk from PAHs caused by oil spills, industrial discharges or even highways runoff. The third objective is to determine if there are any relationships between K_{DOM} and different parameters of DOM measurements to reduce the hazard from free hydrophobic contaminants in environmental waters and drinking waters.

B.3 Experimental

Perylene (Aldrich, red label, >99% purity) was tested as an HOP probe because it is easy to fluorescence and less hazardous in a laboratory setting than other PAHs. The following general characteristics of DOM were measured by 1) ultrafiltration (UF) for size distribution (28), 2) polarity by the polar rapid assessment method (PRAM) (29), 3) fluorescence excitation-emission matrix (EEM) and fluorescence regional integration (FRI) for chemical components (30, 31), 4)

UV absorbance at 254 nm and 5) specific UV_{254} absorbance (SUVA) for molecular structure such as aromaticity. More details were described in supporting information.

Determination of K_{DOM}

This study used 1) fluorescence quenching (FQ) and 2) solid-phase microextraction (SPME) combined with gas chromatography-mass spectrometry (GC/MS) to determine the free and associated fraction of PAH with DOM in aquatic system. SPME measures free PAH concentration and causes a negligible depletion of solute from the samples to make sure that the sorption process has a negligible effect on the equilibrium between DOM and hydrophobic chemicals. The main advantages of SPME include fast extraction process and minimal manipulation of the samples (32). The FQ method determines the DOM/water partition coefficient (K_{DOM}) accurately and without needing to separate DOM from the water samples. These methods thus complement each other and allow for determination of free and DOM associated PAH concentrations at “real world” ug/L to ng/L concentrations.

Solid Phase Microextraction (SPME)

A 1 cm long SPME fibers coated with ploydimethylsiloxane (PDMS) with 100 μm were purchase from Supelco Corp. (Bellefonte, PA). New fibers were conditioned in the GC injector at 250 °C for 0.5 h. 40 ml water samples were loaded into 40 ml amber bottles with PTFE/silicone septum to prevent photodegradation of PAH. All samples were run at room temperature (20 °C). The SPME fiber was immersed into the sample solution 1 cm from the surface and the solution was stirred with a PTFE-coated magnetic bar (10mm × 6mm o.d.) at 1000 rpm. The extraction time was 60 min to ensure negligibly small fraction (<0.01%) of perylene was removed by the PDMS coated fiber to maintain the equilibrium between the dissolved perylene and DOM (33). The analyte was then desorbed from the SPME fiber by injection into the GC splitless inlet at 275 °C for 4 minutes during which the column temperature was kept at 200 °C.

GC/MS System

The chromatographic analysis was performed using a Varian 450 GC coupled to a Varian 220 mass selective spectrometer equipped with an inert ion source and a split-splitless injection port. Helium (99.9999% purity) was maintained at a constant pressure of 85 psi and used as the carrier gas at a flow rate of 1.5 mL/min. A Rxi-1MS (RESTEK Corp., Bellefonte, PA 16823) capillary column (100% dimethyl polysiloxane) (60 m × 0.25 mm i.d., 0.5 µm film thickness) was used. After the sample was desorbed from the SPME in the GC splitless inlet at 275 °C for 4 minutes, the injector was switched to the split mode. Afterward the fiber was withdrawn, and the column temperature increased to 275 °C at a rate of 20 °C /min and held for 27.5 min. The ionization was carried out in the electron impact (EI) mode (70 eV). The electron multiplier voltage was set automatically. Perylene was quantified in the selected ion monitoring mode.

Fluorescence Quenching to Measure $K_{DOM\,(P)}$

The sorption coefficient of DOM ($K_{DOM\ (P)}$) was determined by fluorescence quenching (FQ) method (25). The percentage of bound PAH can be determined by equation 2 (34):

$$\%bound = \frac{K_{DOM}[DOM]}{1 + K_{DOM}[DOM]} \times 100 \qquad (2)$$

For $K_{DOM\ (P)}$ determination experiments, perylene was diluted in methanol to 4 mg/L perylene stock solution and stored in an amber bottle at 4 °C. Stock solution was diluted to 0.3 µg/L perylene and added to DOM diluted samples to a final concentration of three-fourths of the reported solubility 0.4 µg/L in water (35). Methanol volumetric concentration was below 0.1% in the final sample with DOM and was not expected to interfere with the sorption behavior of perylene to DOM and the sorption of SPME (18). The relationship between C_{total} to C_{free} can be derived from Equation 1. Equation 1 can also be expressed as:

$$\frac{C_{bound}}{[DOM]} = \frac{C_{total} - C_{free}}{[DOM]} = K_{DOM} C_{free} \qquad (3)$$

where C_{total} and C_{bound} are the total and bound PAH concentrations (w/v). Rearranging equation 3 provides

$$\frac{C_{total}}{C_{free}} = 1 + K_{DOM}[DOM] \qquad (4)$$

Therefore, K_{DOM} can be obtained by plotting C_{total}/C_{free} against the concentration of DOM with a y-axis intercept set to 1.

Sample Preparation for K_{DOM} Studies

The reference DOM studied was from the Suwannee River in Florida purchased from International Humic Substances Society (IHSS). The DOM stock solution was made to be 40 mg C/L as dissolved organic carbon (DOC) and then diluted in series to be tested. Na_2HPO_4 and KH_2PO_4 (Fisher Scientific) were used as phosphate buffer to adjust Suwannee River DOM (SRDOM) to be pH 7.6 and conductivity 668 us/cm to be more like natural water conditions. Forest Fire Water Sample (FFWS) was prepared by leaching dry ash of leaves and branches from Santa Barbara (collected at N +34° 27' 18.05", W -119° 43' 41.03"). Water samples of treatment processes were from Soldier Canyon Filtration Plant (SCFP), Colorado (only influent water), Metropolitan Water District of Southern California, La Verne, CA (influent and effluent), Castaic Lake Water Agency (CLWA) in Santa Clarita, CA and the Long Beach Water Department (LBWP), Long Beach, CA. All the water utilities use coagulation. The CLWA is the only utility using ozonation before coagulation. The samples represent the water after each unit operation. The water quality parameters for this study are listed in supporting information.

All samples were filtered through 0.7 μm glass fiber membranes (Whatman Corp., Sanford, ME) prior to any analysis procedure to remove filterable organic matter and microorganisms which may consume DOM. All membranes were baked for 24 hours at 100 °C and rinsed before use to reduce leaching of organics from the membranes during filtration.

B.4 Results and Discussion

The primary objective of this paper is to develop a PAH probe to measure the potential amount of DOM associated PAHs and the amount of free PAHs in natural and treated waters. This also could be used to define a scale of reactivity of different DOM by a standard method.

The first step of this study was to see if fluorescence quenching could be used as a general method able to measure the potential amount of DOM associated PAHs in any natural and drinking waters. Perylene was tested as a PAH probe. The relationship between the K_{DOM} measured by FQ and the free PAH concentration measured by SPME was studied. Derivation of a robust relationship between SPME and FQ would allow the use of the simpler fluorescence quenching method as a general method for characterizing DOM.

Comparison of Measurement Methods of Log K_{DOM} by FQ and SPME

The ability of PAHs to bind with DOM will be different for different waters because of different components and characteristics (e.g. size, polarity, chemical components, etc.) of DOM. As a result, different water sources, different treatment process waters, and even different samples of different sampling time may have different partition coefficients (1). Figure 1 is the relationship of K_{DOM} values derived by FQ and SPME combined with GC/MS methods for seven different water samples with perylene as the PAH probe. For the measurements of FQ, the Stern-Volmer plots displayed strong correlations (R^2 are from 0.69 to 0.97) and y-intercepts were statistically indistinguishable from 1 indicating that DOM samples demonstrated complete perylene quenching (Table S3) (20). The result of Figure 1 shows that at higher or lower K_{DOM} range, the K_{DOM} values obtained by SPME method had larger error. However, the K_{DOM} values were not significant difference between FQ and SPME methods within K_{DOM} values from 4 to 6 at 95% confidence level. The reason might be due to the fluorescence lifetime of perylene is only 5.5 nanoseconds (ns), therefore, using perylene could possibly prevent other quenchers (e.g. O_2) to inflate K_{DOM} values (20). This study was able to use perylene (fluorescence life time = 5.5 ns) as a PAH probe to get a relationship $K_{FQ} \fallingdotseq K_{SPME}$. Other studies using phenanthrene (fluorescence life time = 60 ns) to get $K_{FQ} \fallingdotseq 2 \times K_{SPME}$ and using pyrene (fluorescence life time = 200 ns) to get $K_{FQ} \fallingdotseq 2 \times K_{SPME}$ (26, 27). In this study, the water samples were analyzed by FQ method to get K_{DOM} values. Considering FQ is much more easily completed and provides acceptable K_{DOM} values, perylene was accepted as a PAH probe to compare different DOM.

Using Perylene as a Hydrophobic Organic Pollutants (HOPs) Indicator

The K_{DOM} values shown in Tables 1 and 2 were determined by FQ method with perylene as a probe. These tables show the higher the K_{DOM} values of water samples represent the PAHs in the water that are potentially less hazardous because more PAHs are bound to DOM. The physical meaning of K_{DOM} is the binding "ability" of a specific DOM. K_{DOM} is unitless as presented in equation (1). % bound equation (equation 2) is derived by equation (1) as shown below.

$$C_{s(w/w)} = K_{DOM} C_{free(w/v)} \quad (1)$$

$$\frac{C_{bound}}{[DOM]} = \frac{C_{total} - C_{free}}{[DOM]} = K_{DOM} C_{free} \quad (1.5)$$

$$\%bound = \frac{K_{DOM}[DOM]}{1 + K_{DOM}[DOM]} \times 100 \quad (2)$$

When using the equation (2) calculating the % bound of PAH, it has considered the total amount of DOM in the water. Therefore, higher total [DOM] (more DOM in terms of TOC) and higher K_{DOM} (higher binding ability) will result in higher % bound fraction and less % free hazardous fraction of PAH. However, the binding ability K_{DOM} affected by different DOM characteristics dominates the % bound and % free distribution. Figure 2 shows the plots of the % bound according to equation 2 versus the DOC concentration of DOM for a variety of values of Log K_{DOM} values from 4.0 to 6.5 from Carter and Suffet (1982) (5). The probe perylene can be used to predict the free concentration of a related cancer causing PAH, such as benzo(a)pyrene by using perylene as an indicator by transferring the % free portions of perylene into % free portions of BaP according to the proportion of the hydrophobicity using relative Log K_{ow}.

The drinking water standard of BaP in the United States is set at 200 ng/L and Log K_{ow} is 6.0 (36). Therefore, BaP is less hydrophobic than perylene with a Log K_{ow} of 6.5. Consequently, if the result of free perylene (test probe) is determined to be over 200 ng/L, then BaP would be over the drinking water standard. In addition, this study used the real K_{DOM} data of perylene and BaP from Hawthorne et al. (2005) (37) and compared the real % bound values from the study and the % bound values by model prediction of Figure 2. The result shows strong correlation between real % bound values and model % bound values (% $\text{bound}_{\text{Real}} \fallingdotseq$ % $\text{bound}_{\text{Model}}$, $R^2 = 0.79$). The reason might be due to perylene and BaP that have the same molecular weight, similar structures and chemical characteristics. As a result, this study used much less toxic perylene as a probe to understand the interactions between BaP and DOM.

Table 1 reveals that the K_{DOM} values of SRDOM and ASRDOM were higher than FFWS and SCFP even though SRDOM and FFWS had the same DOM concentration. This is due to different DOM components coming from different microbial degradation of the NOM presented. The hazardous potentials of % free perylene were different and thus BaP were different. In Table 1 and 2, the free perylene and BaP concentrations were derived by % free portions and obtained by assuming 200 ng/L as reference concentration for the chemicals of pollution. Table 1 also shows that FFWS and SCFP had a higher hazardous potential (higher free perylene and BaP concentration) for water supply. However, the reference DOM, SRDOM and ASRDOM, had more ability to associate with perylene and BaP and had higher K_{DOM} values.

Table 2 presents different free fractions of perylene and BaP after different unit operations at CLWA and LBWD and in and out of the MWD Plant. It is obviously that following the treatment processes at the three water treatment plants, the hazardous fractions of perylene and BaP increased as a result of decreasing of K_{DOM} values. Therefore, water treatments eliminated much of the DOM that can bind to PAHs and increased the potential dangers of PAHs that existed or could be added to the treated waters. Furthermore, the raw water at LBWD had higher K_{DOM} than CLWA and MWD. This may indicate that groundwater (LBWD raw water) had greater amount of DOM than lake water (CLWA raw water). Besides, DOM in groundwater might have characteristics that make it more likely to bind to PAHs than the DOM in lake water.

In order to understand the possible BaP distribution in human stomachs, this study also used hydrochloric acid (HCl) to acidify the treated water of CLWA to pH 2.5 to simulate the environment of the human stomach. Human stomach is a very complicated systems. At this case, we only considered pH factor as a beginning. The acidified treated water of CLWA had 78% free perylene present (156 ng/L) and 83% free BaP was calculated (166 ng/L). Thus, the stomach has a less hazardous dose than the treated water of CLWA. However, it was still 83% of the limit. BaP might be less hazardous in human stomachs because the lower pH environment would make DOM in a more coiled conformation and this would increase the sites to bind with BaP (5). A similar phenomenon was observed in samples of SRDOM and ASRDOM where lowering the pH increased the K_{DOM} value.

Understanding the Interaction between HOPs and DOM in Different Natural Waters

The Relationship between K_{DOM} and Different Parameters of DOC

An objective was to determine if there are any relationships between K_{DOM} and different parameters of DOC to reduce the hazard from free HOPs in environmental waters and drinking waters. Another objective is to enable an understanding of the interaction between HOPs and DOM in different environments. No relationship between a K_{DOM} and the nature of the specific DOM characteristics has ever been developed. Understanding the changes in DOM characteristics at different sources of water and stages of water treatment can offer valuable information to assess and manage the environmental risk of HOPs.

Size Characterization by Ultrafiltration

Figure 3 is the molecular size fractions of DOM for four source waters- SRDOM, ASRDOM, FFWS and SCFP. The UF results indicate that different source waters have different size fraction distributions. The DOM for SRDOM and ASRDOM was mainly composed of 10 - 5 kDa fraction. The sum of > 10 kDa and 10 - 5 kDa fraction percentages were up to 80% for both SRDOM and ASRDOM, indicating that the DOM of Suwannee River was dominated by higher molecular weight size fractions. Moreover, > 10 kDa fraction of SRDOM (pH=5.2) was about 10% higher than ASRDOM (pH=7.6) because higher hydrogen ion concentration will make the molecular size of the humic materials increase (5). Similarly, the > 10 kDa fraction of FFWS was over 40%. In contrast, the size fractions of SCFP were with the majority 10 - 1 kDa and the least > 10kDa.

Figure 4 is the UF analysis of CLWA and LBWD process waters. For CLWA process waters, the main fraction of DOM in raw was 10 - 5 kDa. After ozonation process, the 10 - 5 kDa fraction decreased and the lower molecular weight fractions- 5 - 1 kDa, < 1 kDa, increased. Other researches have also shown ozone to decrease the MW of DOM (38, 39). Ozonation transformed DOM components from higher molecular weight fractions into lower molecular weight fractions to reduce the electrostatic barriers of particles to coagulate. Therefore, after coagulation, the size fractions of > 10 kDa and 10 - 5 kDa increased to approximate 80%. Ozonation process has been known to facilitate the coagulation process by destabilizing and aggregating the particles in the water (40). CLWA treatment processes mainly removed 10 - 5 kDa fraction of DOM and increased 5 - 1 kDa fraction.

For LBWD process waters , raw water DOM was dominated by > 10 kDa fraction; and 5 - 1 kDa and < 1 kDa fractions were less than 20%. The DOM components after coagulation were composed of 20% - 30% for each different size fractions. The result indicates that most > 10 kDa DOM fraction decreased to smaller fractions by coagulation in LBWD.

For MWD water comparing raw and treated water, the raw water DOM was dominated by > 10 kDa fraction (42%). In addition, MWD treatment processes mainly removed 10 - 5 kDa fraction (from 23% to 0%) of DOM and increased 5 - 1 kDa fraction which was similar to CLWA processes result. > 10 kDa and < 1 kDa fractions stayed similarly throughout the processes. Figure 4 also shows that different water sources and water treatment processes would have different DOM size fraction distributions.

PRAM Analysis

Figure 5 is the PRAM analysis of four source waters. It is obviously that for all samples, the retention coefficients (RCs) for that measures negatively charge material (NH_2 cartridges) were significantly higher than C18 cartridge that measures hydrophobic compounds and the Diol cartridges that measures hydrophilic compounds. The charge RCs for all samples were from approximate 60% to 80% indicating that DOM components in either DOM standard (SRDOM and ASRDOM) or natural source waters going into the water treatment plants had significant negative charge characteristics. Under ambient conditions, DOM was dominated by negative charge as a result of deprotonation of phenolic and carboxylic functional groups (2). The NH_2 RCs of ASRDOM (pH=7.6) and SRDOM (pH=5.2) were 78% and 61%, respectively. The negative charge DOM portions of ASRDOM increase was due to more deprotonation of acid groups at higher pH. The C18 RC of FFWS was about 10% and higher than the DOM standard, SRDOM and ASRDOM. The higher C18 RC of FFWS indicated more hydrophobic components and might be due to the effect of fire on organic matter. Hydrophobic substances can be generated by the heating of decomposing plant organisms and mineral soil (41). Therefore, the DOM of FFWS would be more hydrophobic because FFWS was made by leaching of ashes and burnt materials of forest fire.

Figure 6 is the PRAM analysis of CLWA and LBWD process waters. For both CLWA and LBWD process waters, the RCs of negatively charge molecules decreased following the treatment processes indicating some removal of DOM through the process because of DOM's negative charge characteristic. For both CLWA and LBWD treatment processes, overall NH_2 RCs decreased about 30% which was similar to the result of Rosario-Ortiz et al. (2009) (32%) (42). Similar results were also obtained in MWD samples (supporting information). The RC_s of NH_2 for MWD decreased from 60% for raw water to 45% for treated water. In CLWA process samples, Figure 6 shows that ozonation significantly decreased both RC_s of C18 and Diol, respectively. The ozonation process might decrease the non-polar fractions by adding oxygen atoms and thus transform DOM to be more polar fractions. Then ozone continued to break down polar fractions to become smaller molecules. After coagulation, the non-polar and polar fractions of DOM increase might be due to the charge neutralization of coagulation process from negative charge fractions. The results also match the phenomenon observed in UF analysis of CLWA samples (ozonation decreased DOM size and coagulation increased DOM size).

For LBWD samples, the raw water sample which was from groundwater had the highest NH_2 RC of 96% among all samples in this study. Moreover, after coagulation NH_2 RC decrease was as the reduction of negatively charge in CLWA, showing the charge neutralization mechanism of coagulation. The non-polar components of DOM remained approximate 10% throughout the treatment process. However, the polar components increased after the treatment process.

FRI Analysis

This research used a fluorescence spectrophotometer to identify the characteristics of the DOM composition of all water samples. Figure 7 shows FRI results of each treatment process of CLWA and LBWD. In different treatment process waters, fulvic acids and humic acids were the main components of DOM and percentages range were from 40% to 47% and 21% to 27% for CLWA; 48% to 53% and 18% to 22% for LBWD, respectively. High fulvic and humic acids inputs indicate of terrestrially derive source organic matter. The FRI results of MWD raw and treated water also showed the same conclusion. Also, coagulation decreased fulvic acids in CLWA and fulvic and humic acids in LBWD indicating coagulation process as the critical processes to control DOM composition. The reason might be that fulvic and humic acids have higher molecular weight and more negative charges, thus coagulation can be more efficient to remove fulvic and humic acids.

The Correlations between K_{DOM} and DOM Characteristics and the Implication

This research also examined the correlations between Log K_{DOM} values and DOM characteristics by linear regression and R-squared values to understand which factors affect perylene partition behavior. The results were shown in Table S4 and Figure S7. By comparing all factors in this study, Log K_{DOM} demonstrated strong and positive correlation with bulk SUVA ($R^2 = 0.74$), and other moderate relationship ($R^2 > 0.50$) with bulk UV_{254} ($R^2 = 0.50$), fluorescence distribution of fulvic acids ($R^2 = 0.58$), UV_{254} for > 10 kDa fraction ($R^2 = 0.54$) and UV_{254} for > 10 kDa fraction

(R^2= 0.52). Log K_{DOM} demonstrated negative strong relationship with < 1 kDa (R^2 = 0.87). Since UV_{254} and SUVA were both relevant measures of aromaticity of DOM, binding phenomenon appears to happen on the aromatic structures and double bonds of DOM, however, the aromatic structure of DOM < 1 kDa fraction might not be favorable to binding behavior.

Chin et al. (1987), and Tanaka et al. (1997) also found DOM with higher molecular weight and aromatic content can result in higher binding ability between pyrene and DOM (43, 44). The DOM concentration for testing of these studies is from 0 to 40 mg C/L and pyrene working concentration is ug/L level. DOM with higher molecular weight and aromaticity enhances the solubility of pyrene, and thus affect the fate and transport of pyrene in the aquatic environments.

In addition to size and aromaticity, K_{DOM} was also correlated with fluorescence distribution of fulvic acids (R^2 =0.58). Fulvic acids might be the main components to bind with perylene. Thus, fulvic and humic acids were already available from separation of natural water body, it is possible that they can be used to reduce the immediate pollution (free part) of HOPs in water in the future. For oil spills or industrial leaking, HOPs might be sudden pollution events and cause toxicity to aquatic organisms and pollute surface water, drinking water or groundwater. Fulvic and humic acids might be able to serve as a potential remediation method for HOPs in aquatic environment. Rebhun et al. (1996) also proposed to use dissolved humic substance (DHS) to remediate contaminated site according to the hydrophobic binding of organic contaminants and DHS (17).

B.5 Figures

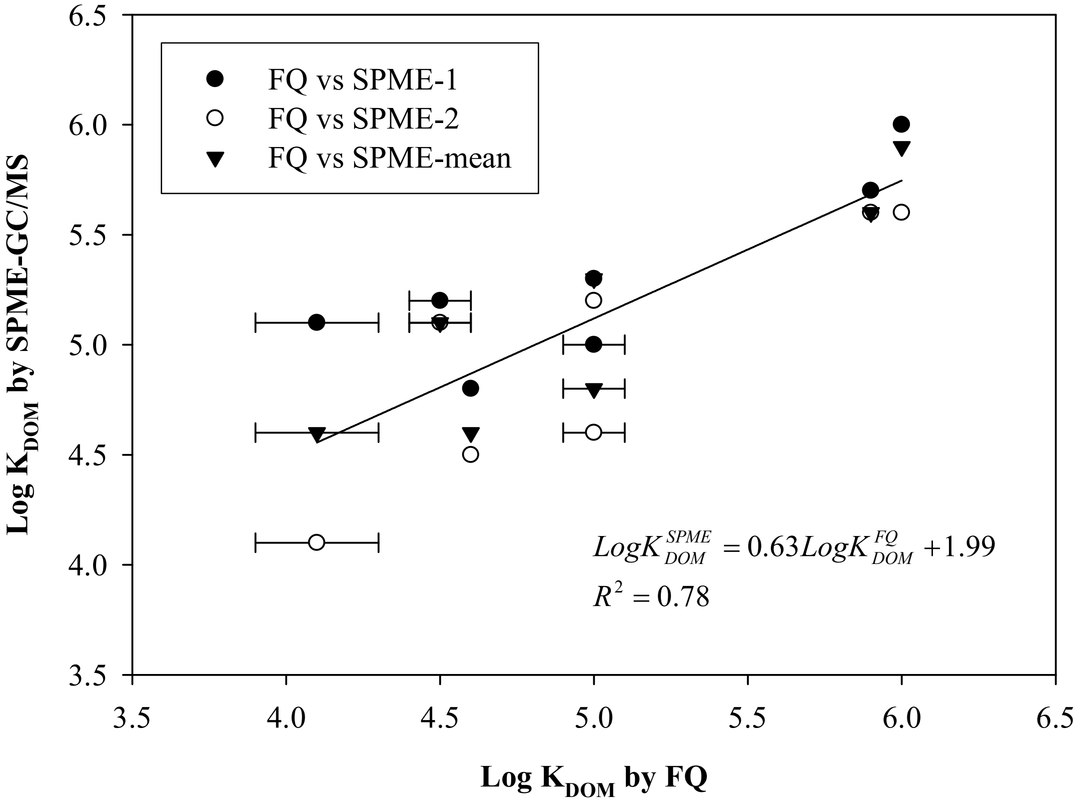

Figure 1. The comparison results of $K_{DOM\,(P)}$ derived by SPME-GC/MS and FQ for 7 different water samples (Perylene was used as the PAHs probe).

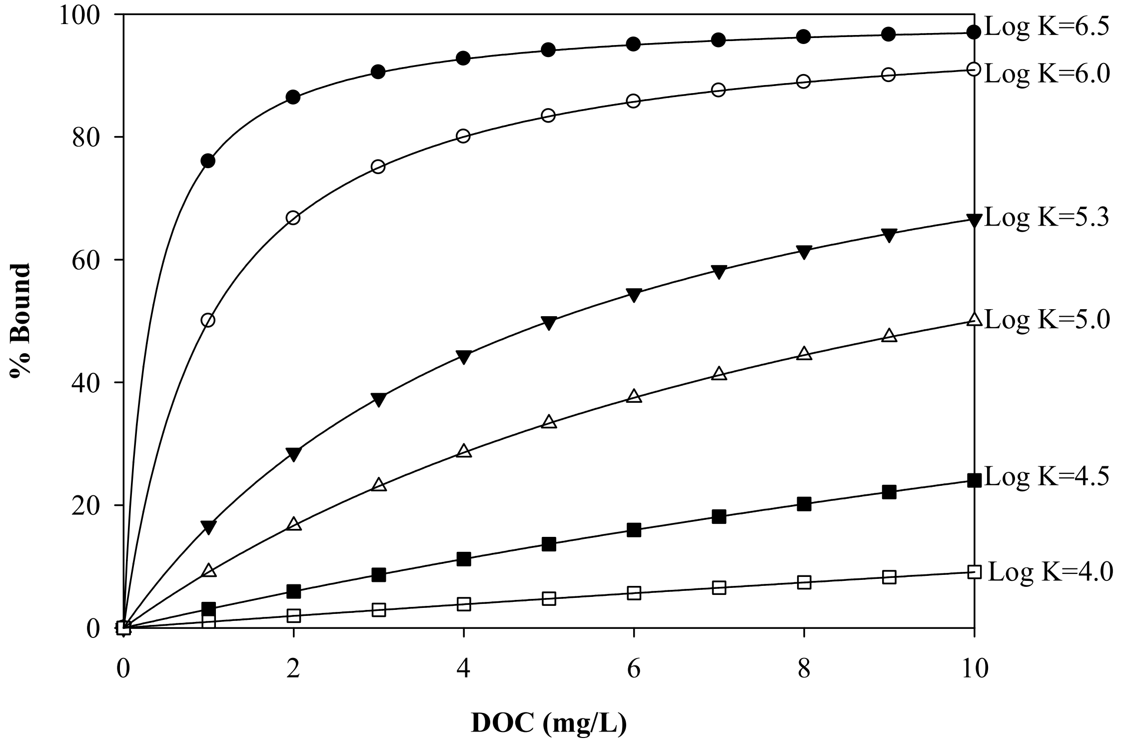

Figure 2. Data fitting results of eq 2 for a variety of values of log K (log K from 4.0 to 6.5)

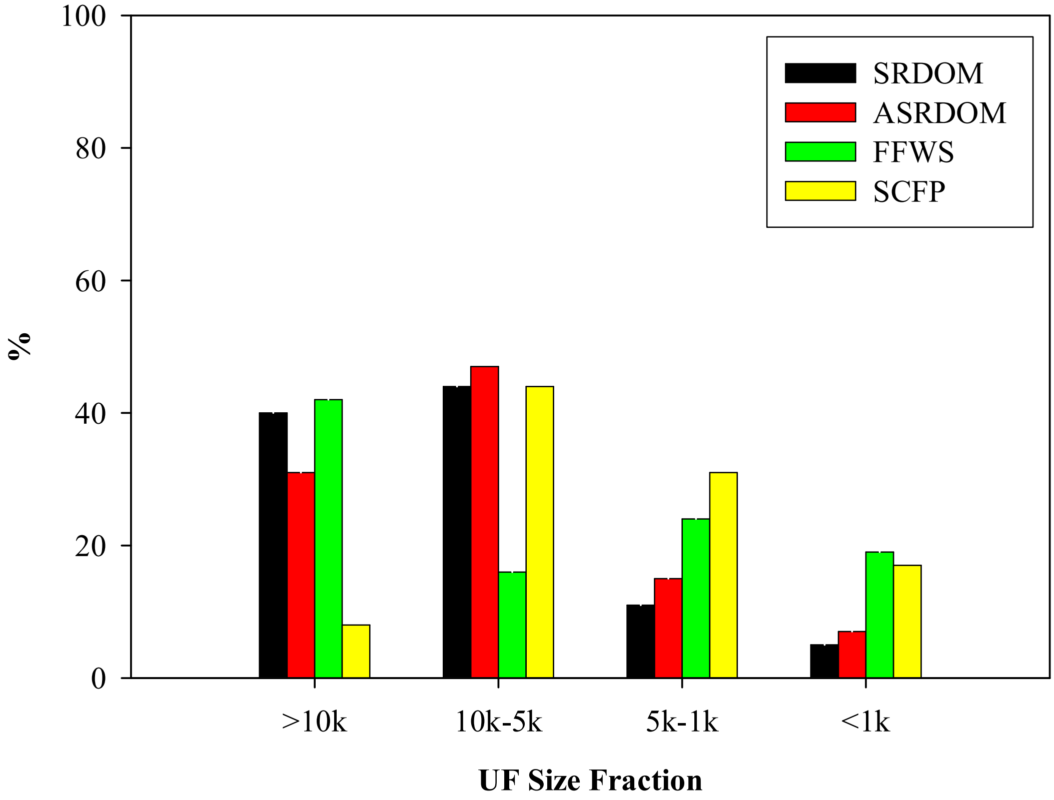

Figure 3. Ultrafiltration analysis of four source waters. [a] Suwannee River DOM (SRDOM); [b] adjusted Suwannee River DOM (ASRDOM); [c] Forest Fire Water Sample (FFWS); [d] Soldier Canyon Filtration Plant (SCFP).

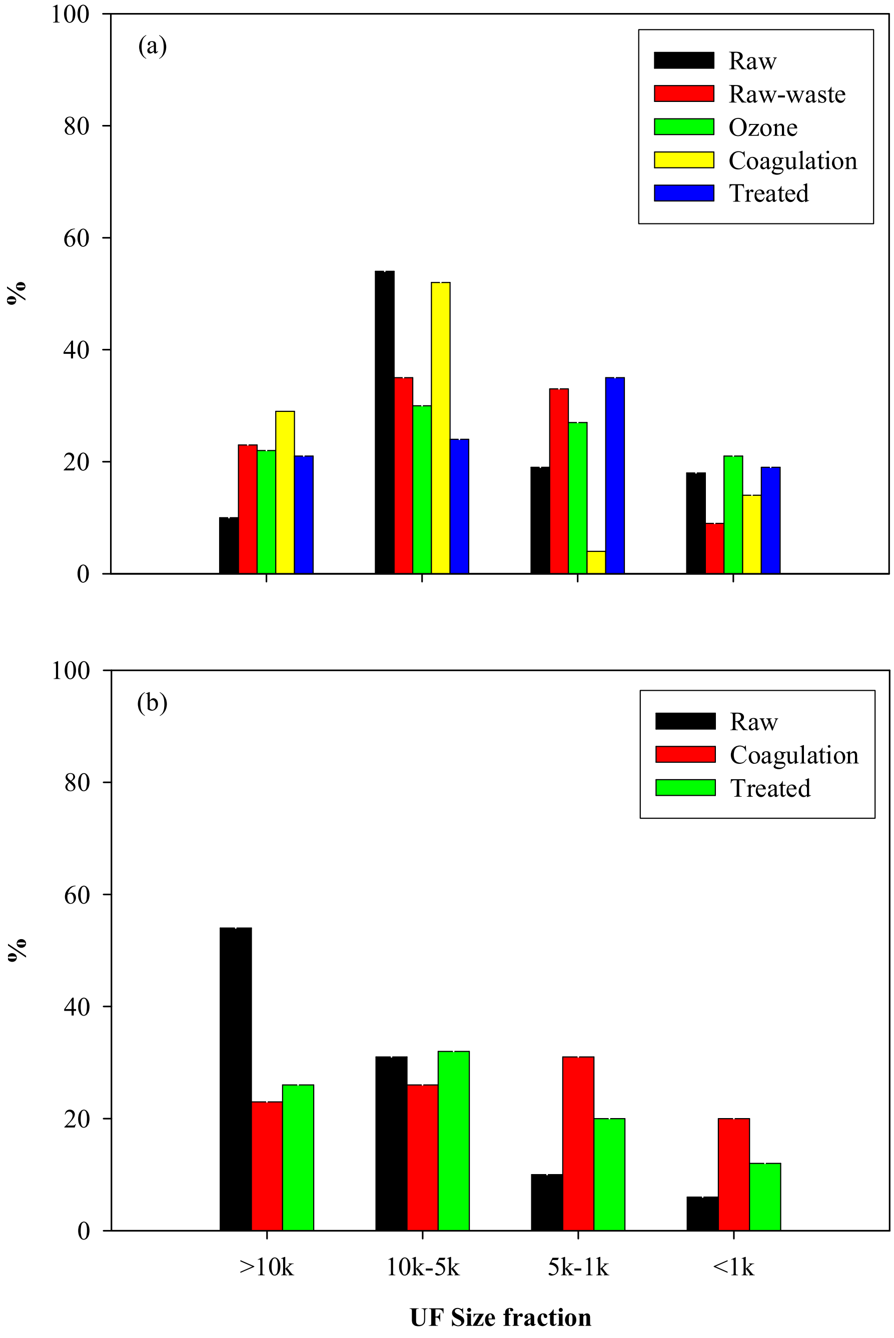

Figure 4. Ultrafiltration analysis of process waters of (a) Castaic Lake Water Agency (CLWA), (b) Long Beach Water Department (LBWD).

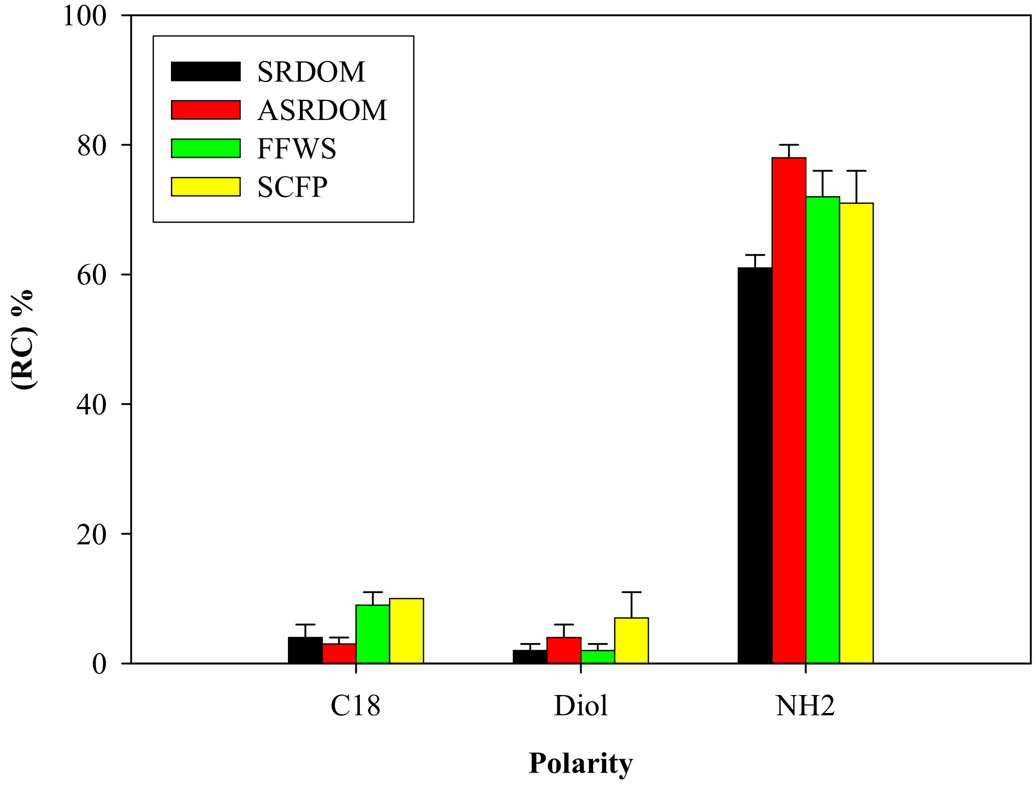

Figure 5. Polarity analysis of four source waters. [a] Suwannee River DOM (SRDOM); [b] adjusted Suwannee River DOM (ASRDOM); [c] Forest Fire Water Sample (FFWS); [d] Soldier Canyon Filtration Plant (SCFP).

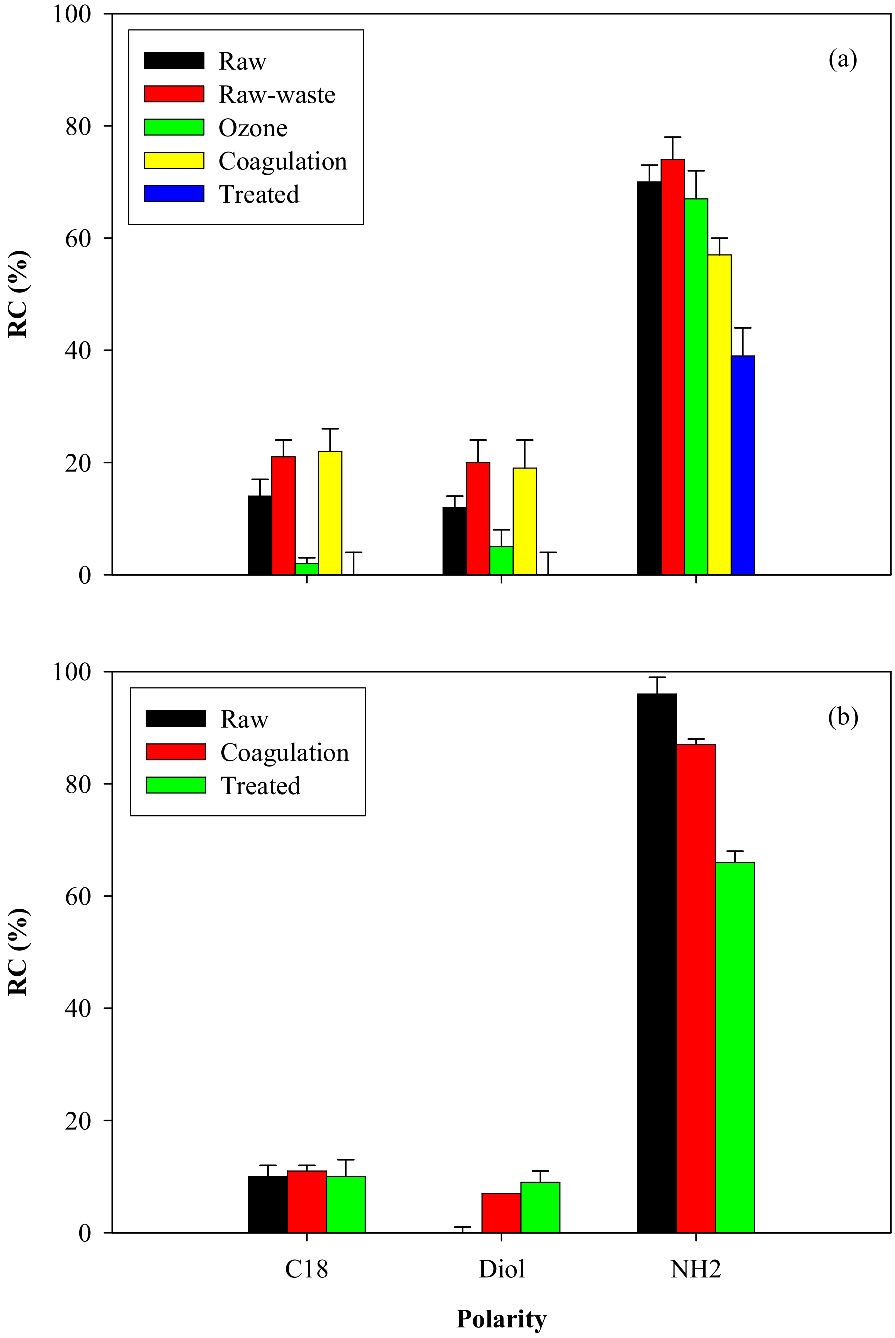

Figure 6. Polarity analysis of process waters of (a) Castaic Lake Water Agency (CLWA), (b) Long Beach Water Department (LBWD).

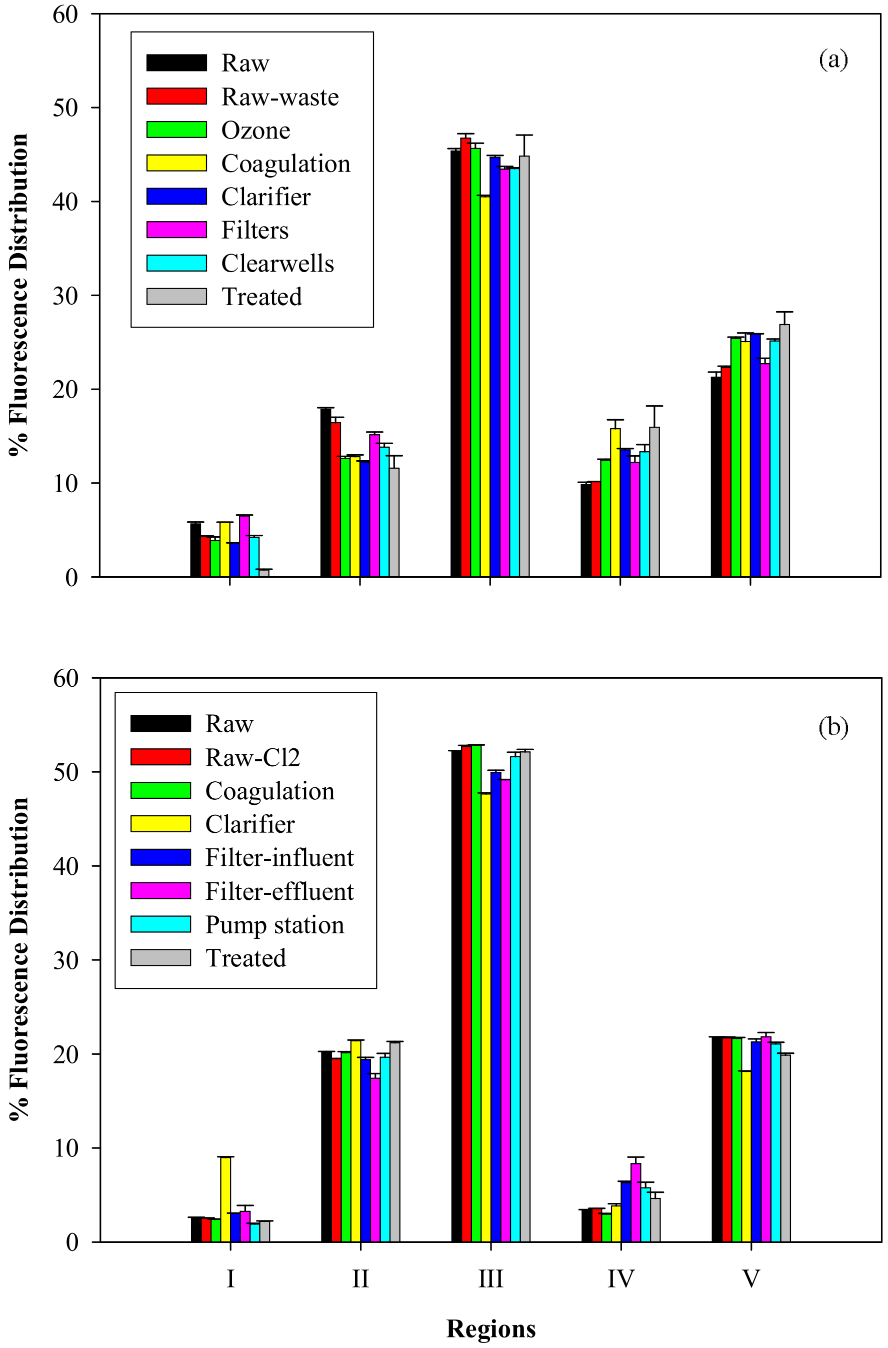

Figure 7. Fluorescence regional integration results of each treatment process of (a) Castaic Lake Water Agency (CLWA) and (b) Long Beach Water Department (LBWD).

B.6 Tables

Table 1. Free fraction of perylene determined by fluorescence and calculated fraction of benzo(a)pyrene (BaP) for different surface waters

Water Sample	**DOC (mgC L^{-1})**	**Log K_{DOM}**	**Free Perylene (ng L^{-1})**	**Free BaP (ng L^{-1})**
SRDOM[a] (pH=5.2)	10	6.0	18	30
ASRDOM[b] (pH=7.6)	10	5.9	22	34
FFWS[c]	10	4.6	142	146
SCFP[d]	3.2	5.0	156	162

[a] Suwannee River DOM. [b] adjusted Suwannee River DOM. [c] Forest Fire Water Sample. [d] Soldier Canyon Filtration Plant.

Table 2. Free fraction of Perylene determined by fluorescence and calculated fraction of benzo(a)pyrene (BaP) after different unit operations

Water Sample	DOC (mgC L^{-1})	Log K_{DOM}	Free BaP (ng L^{-1})	Free BaP (%)
CLWA[a]				
Raw	2.2	5.0	172	86
Ozone	2.1	4.8	182	91
Coagulation	1.9	4.6	190	95
Treated	2.3	4.1	196	98
LBWD[b]				
Raw	2.6	5.8	104	52
Coagulation	1.6	4.9	182	91
Treated	2.0	4.6	188	94
MWD[c]				
Raw	2.6	5.0	166	83
Treated	2.3	4.6	186	93

[a] Castaic Lake Water Agency. [b] Long Beach Water Department. [c] Metropolitan Water District of Southern California.

B.7 Supporting Information

Experimental

Experiments to identify K_{DOM} by SPME-GC/MS and FQ methods are outlined in Figure S1. The experimental monitoring program was shown in Figure S2. The water quality parameters studied are listed in Table S1.

DOC METHODS

Ultrafiltration

DOM was size fractionated by ultrafiltration (UF) was completed by the method of Revchuk and Suffet (2009) (28) through Millipore YM (regenerated cellulose, negatively charged) 1,000 (1k), 10,000 (10k) molecular weight cut off (MWCO), and PB (polyethersulfone, negatively charged) 5,000 (5k) MWCO membranes (Millipore Corp., Billerica, MA). To reduce leaching of DOC, membranes were soaked three times (30 min each time) in deionized (DI) water (Milli-Q Plus water system, Millipore Corp., Bedford, MA) and then in 5% NaCl solution over night. UF was performed in Millipore solvent-resistant stirred cells (XFUF 076 01). The final step was to rinse the membranes with 100 ml DI water right before filtration. 200 ml of bulk solution was added to the cell and 100 ml was filtered under 55 psi nitrogen gas. Each membrane was discarded after one use. Fractions were analyzed for DOC by a Shimadzu TOC 5050, Total

Organic Carbon Analyzer and UV_{254} by a Shimadzu UV-1700, Pharmaspec UV-Vis spectrophotometer (Shimadzu Corp. Columbia, MD). All samples were completed in duplicate.

Polarity Rapid Assessment Method

DOM polarity was identified by the polar rapid assessment method (PRAM) under ambient water quality conditions without any pretreatment (29). Analysis takes into account the effect of pH and ionic strength on the structure of DOM under ambient conditions. Solid phase extraction (SPE) cartridges were cleaned by passing Milli-Q water to remove UV absorbing impurities. Parallel SPE cartridges with different sorbent polarities were used to adsorb DOM. The SPE cartridges include C18 (non-polar, hydrophobic), Diol (polar, hydrophilic), and NH2 (weak anion exchanger, negative charge). Ambient sample flow through each SPE cartridge was maintained at 1.2 mL/min for 8 min using a syringe pump (KD Scientific, Model 100, Holliston, MA). Effluent was collected from 4 to 8 minutes after initial breakthrough, and the absorbance at 254 nm was measured (UV 1700 Pharma Spec, Shimadzu) to get retention coefficient (RC). The RC is defined as $1-(C_{max}/C_o)$ in percentage, where C_{max} is the maximum absorbance of the samples after breakthrough and C_o is the absorbance of the original sample. PRAM experiments were performed in triplicate. The effluent was also analyzed by fluorescence spectroscopy to record the excitation emission matrix (EEM).

Fluorescence Spectroscopy

Fluorescence spectroscopy, a highly sensitive and rapid method for the identification of DOM characteristics, was used to obtain the excitation-emission matrix (EEM) (30). The five regions represent aromatic proteinaceous compounds I and II, fulvic acids, microbial by-products, and humics (1). EEM spectroscopy was measured by fluorescence spectrophotometer (Varian, R3896). Using parameters were modified from Holbrook, et al. (2005) (31). Excitation wavelengths spanned from 220 to 470 nm in 5 nm increments, and the emission wavelengths spanned from 280 to 580 nm in 4 nm increments using an integration time of 0.1s and a bandwidth of 10 nm.

The fluorescence intensities of spectra were normalized by Raman peak, which was measured daily at pair excitation-emission wavelengths of 350 and 397 nm in deionized water (DI water) (Milli-Q water) and described as intensity unit (IU). All data were obtained by Matlab (version 7.4.0.287, R2007a, Natick, MA) to exclude the water-scattering peaks from Raleigh and Raman scattering (45).

Adjusted EEMs were quantified by the fluorescence regional integration (FRI) method to quantify and analyze fluorescence EEM spectra based on the integration of the total surface and subsequent divisions of the surface into five regions (1). Table S2 lists the regions and their associated excitation and emission regions.

Results and Discussion

Correlation of Size and Polarity

In order to begin to understand the correlation between size and polarity characteristic, this study also examined the filtrated samples by PRAM analysis for CLWA process samples. Figure S3 shows the RCs of C18, Diol and NH_2 cartridges of the filtrates of ultrafiltration 10 kDa, 5 kDa and 1 k Da membranes, For RCs of C18 and Diol cartridges, there was no consistent and significant trend. However, for NH_2 cartridge, the RCs decreased from UF size < 10 kDa to < 1 kDa in each process water in CLWA. The result indicates that the negative charge DOM components might have higher molecular weight.

FRI Analysis of DOM Size Characterization

In Figure S4, the FRI result of SRDOM shows fulvic acids and humic acids were the main components which were about 60% and 30%, respectively. Other components of SRDOM were 11% aromatic protein like BOD_5, 2% aromatic protein like tyrosine, and 1% microbial by-products.

The FRI technique was also used to quantify the chemical composition by size fractions in this study. Figure S4 presents the FRI results of samples of the SRDOM, ASRDOM, FFWS, and SCFP at different size fractions. For all four source water samples, fulvic acids were the main components of DOM. After ultrafiltration, the significant increase in regions I and II (aromatic proteins) were revealed. For the 1 kDa UF filtrate, there was 3% and 10% more fluorescence distribution in regions I and II (proteinaceous material) than there was for SRDOM bulk. For the 5 kDa UF filtrate, there was 5 % and 8 % more fluorescence distribution in regions I and II than there was for SRDOM bulk. Similarly, the FRI results of FFWS and SCFP at different size fractions which had similar trend of distributions of SRDOM. This result indicates that the proteinaceous materials had lower molecular weight. Furthermore, 10 kDa UF filtrate contained more fulvic acids (region III) and humic acids (region V) than 1 kDa and 5 kDa filtrates, suggesting that the humic and fulvic acids were higher molecular weight. Rosario-Ortiz et al. also indicated humic and fulvic acids have correlation with higher molecular weight (29). Compared to SRDOM and ASRDOM, the FFWS presented higher distributions in aromatic protein regions. The reason might be FFWS was composed of more complex aromatic structures of lignin from wood (46).

Figure S5 is the FRI results of UF fractions for the raw and treated water samples of CLWA and LBWD to represent the changes in DOM compositions resulting from the treatment processes. Fulvic acids were dominated for all samples across all size fractions from 35% to 50%. For CLWA, most fulvic acids were not removed by the processes. On the contrary, about 4% of bulk DOM in the aromatic proteins I category and about 10% of the < 5 KDa and < 1 kDa fractions DOM in the aromatic proteins II category were removed. The result illustrates that CLWA treatment processes mainly removed larger and smaller proteinaceous substances of DOM. For LBWD, there was no significant variation in the percentages of aromatic proteins II, fulvic acids, microbial by-products and humic acids for all size fractions. Nevertheless, the percentages of < 1 kDa fraction of DOM in the aromatic proteins I category doubled the amount after treatment.

The result found here supports the aromatic proteins I category result of CLWA. The trend of portions of fulvic acids and humic acids decreased and proteinaceous materials increased after ultrafiltration (< 10 kDa - < 1 kDa) was also identical to Figure 9.

FRI Analysis of DOM Polarity Characterization

The FRI results of SRDOM, FFWS, and SCFP after PRAM analysis are illustrated in Figure S6. In the fulvic and humic acids regions, a decrease in the percentage of fluorescence distribution in the PRAM effluent samples corresponded to the materials that were retained on the SPE sorbents. NH_2 had the lowest percentage of fluorescence distribution of fulvic and humic acids, and thus it can retain relatively more fulvic and humic acids than C18 and Diol. It also indicates that fulvic and humic acids had more negative charge than other components. On the contrary, in the regions of aromatic proteins I and II, the fluorescence distribution percentages were higher in the PRAM effluent than the bulk. This might be due to releasing of these materials after fractions removal, especially after sorption of fulvic and humic acids. Rosario-Ortiz et al. also found similar results that after removal of the non-polar fraction of the DOM by adsorption onto C18, two peaks representing aromatic proteins and microbial by-products appeared in the EEM spectra (47).

Discussion

The K_{DOM} values obtained in this study have no significant difference between FQ and SPME methods within Log K_{DOM} values from 4 to 6 at 95% confidence level. As a result, FQ and SPME methods can complement each other by using a PAH probe- perylene. The FQ method is a relative easy method to determine $K_{DOM\,(P)}$ values in contrast to other methods including SPME. Therefore, water treatment agency can get a quick understanding of HOPs distribution by FQ method testing $K_{DOM\,(P)}$ values. This information can better secure natural waters and drinking water quality, but also can help to optimize water treatment processes and maintain it quality.

Natural source water and the influent water of water treatment plants had higher Log K_{DOM} values contrast to other treated process water. As a result, if there was a pollution event caused by HOPs, these waters had more ability to bind with HOPs and made HOPs less bioavailable, and thus decreased hazard potential. In contrast, if toxic HOPs were added by terrorist attack into the water after treatment, it would be more hazardous for treated water, since the water treatment processes altered DOM characteristics to be less able to bind with HOPs.

Conclusions

This study developed a PAH probe to measure the potential amount of DOM associated PAHs and the amount of free PAHs in natural and drinking waters. The perylene probe defines a standard method scale of reactivity of different DOMs.

The interaction between HOPs and DOM in different environments showed the partition coefficient between DOM and perylene (K_{DOM}) had higher correlation with SUVA (R^2 =0.74), and moderate correlation with UV_{254} (R^2 =0.50), fluorescence distribution of fulvic acids (R^2 =0.58), UV_{254} for > 10 kDa fraction (R^2 =0.54), and UV_{254} for > 10 kDa fraction (R^2=0.52). The results indicate DOM in natural water and drinking water treatment process with higher molecular weight and higher content of aromaticity can bind more HOPs.

DOM was mainly composed of fulvic and humic acids with negative charges and higher molecular weight. Weishaar et al. (2003) also indicated that aquatic humic substances comprise the aromatic fractions of DOC, and SUVA is a good indicator of the humic fractions of the DOC (48).

Characterization of DOM and using perylene as a PAH probe can help to understand the behaviors between HOPs and DOM. It is also very important that water treatment plant operators know the possible distribution of HOPs by the monitoring program developed in this study. Then if there is a HOPs pollution event happened in the water treatment plant, the operator can response more quickly and effectively. Furthermore, by removing the specific characteristics of DOM generating DBPs and keeping the specific characteristics of DOM binding with HOPs, would have a better drinking water quality.

Figures

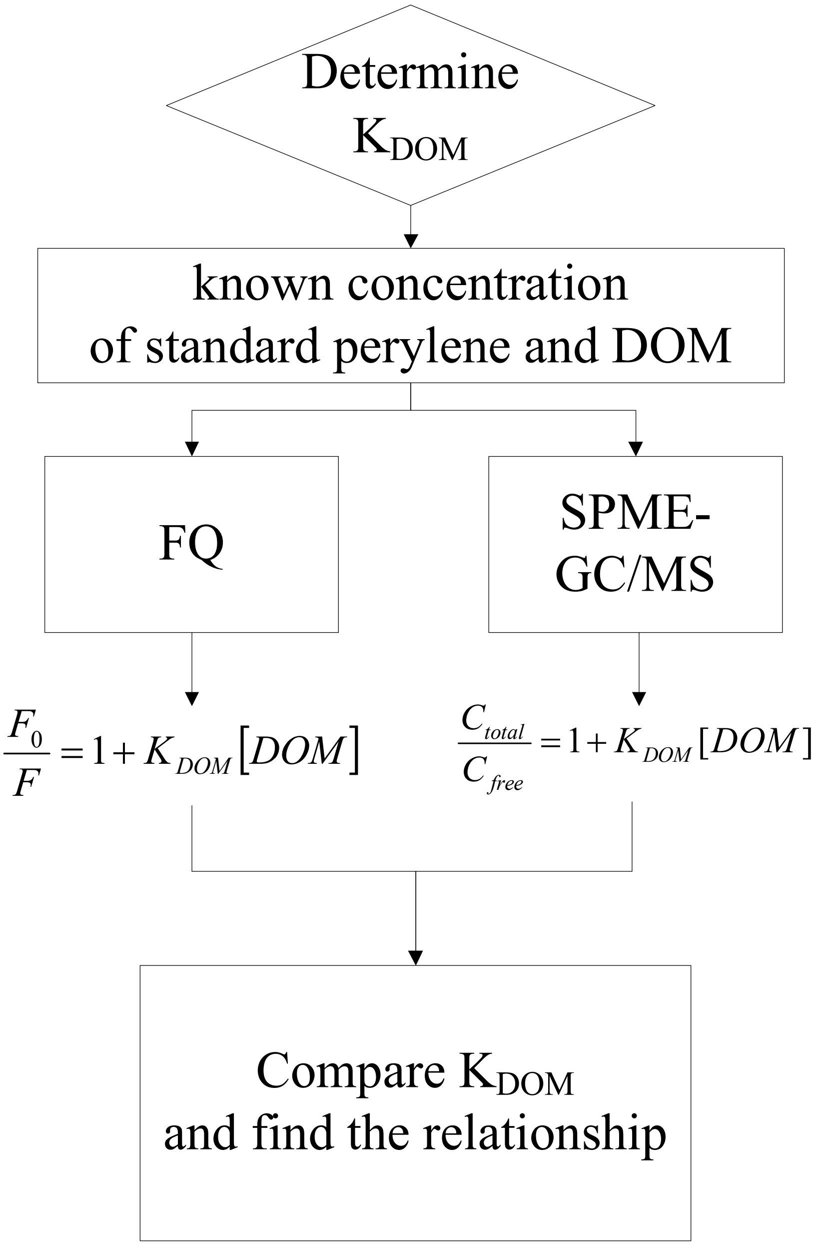

Figure S1. K_{DOM} measurement by SPME-GC/MS and fluorescence quenching (FQ) methods.

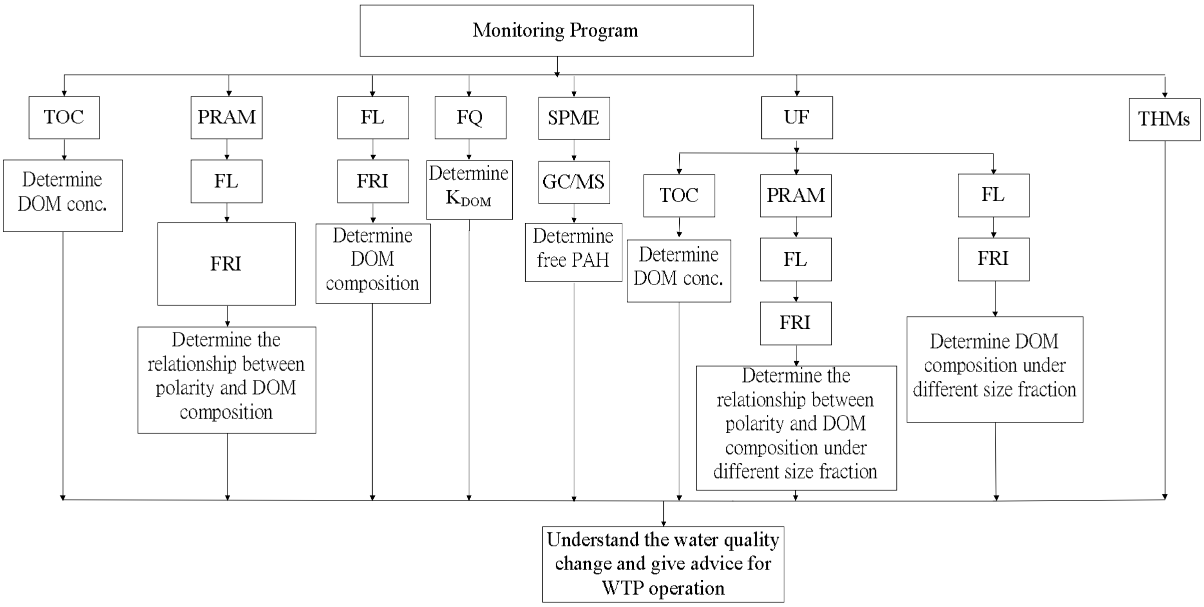

Figure S2. Flow Chart is a sample monitoring scheme to try to understand the conditions of PAH and DOM and their relationship. (TOC: TOC analysis to determine DOM in terms of mg C/L, PRAM: polarity rapid assessment method, FL: fluorescence excitation emission matrix, FRI: fluorescence regional integration, FQ: fluorescence quenching, UF: ultrafiltration, SPME: solid phase microextration, THMs: trihalomethanes, WTP: water treatment plant.)

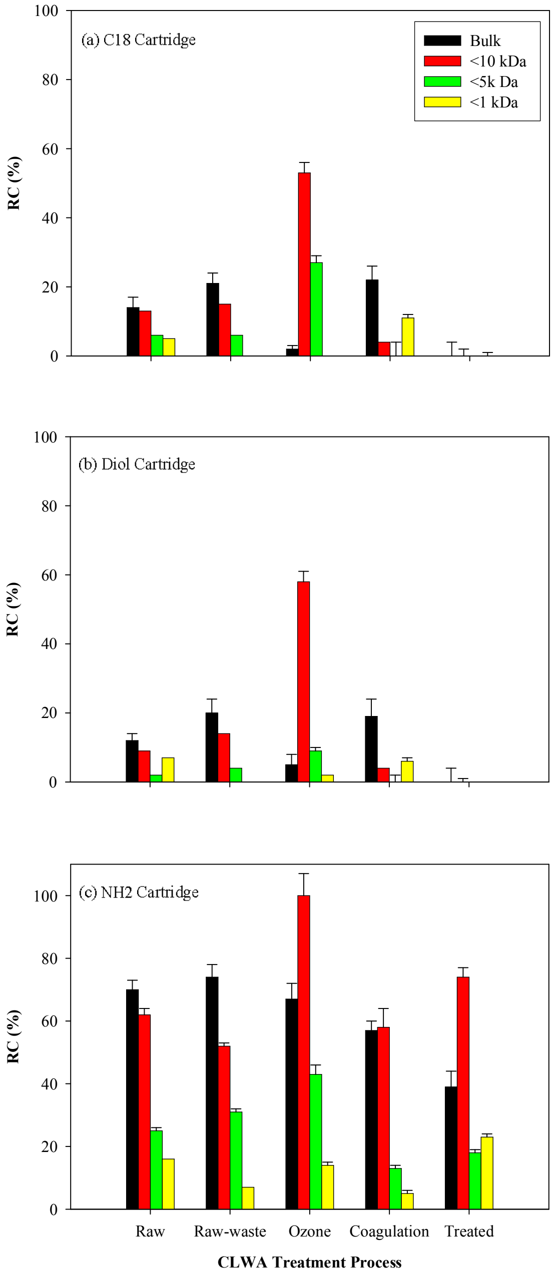

Figure S3. The correlation of size and polarity of CLWA process samples- (a) C18 ,(b) Diol, (c) NH_2 cartridges.

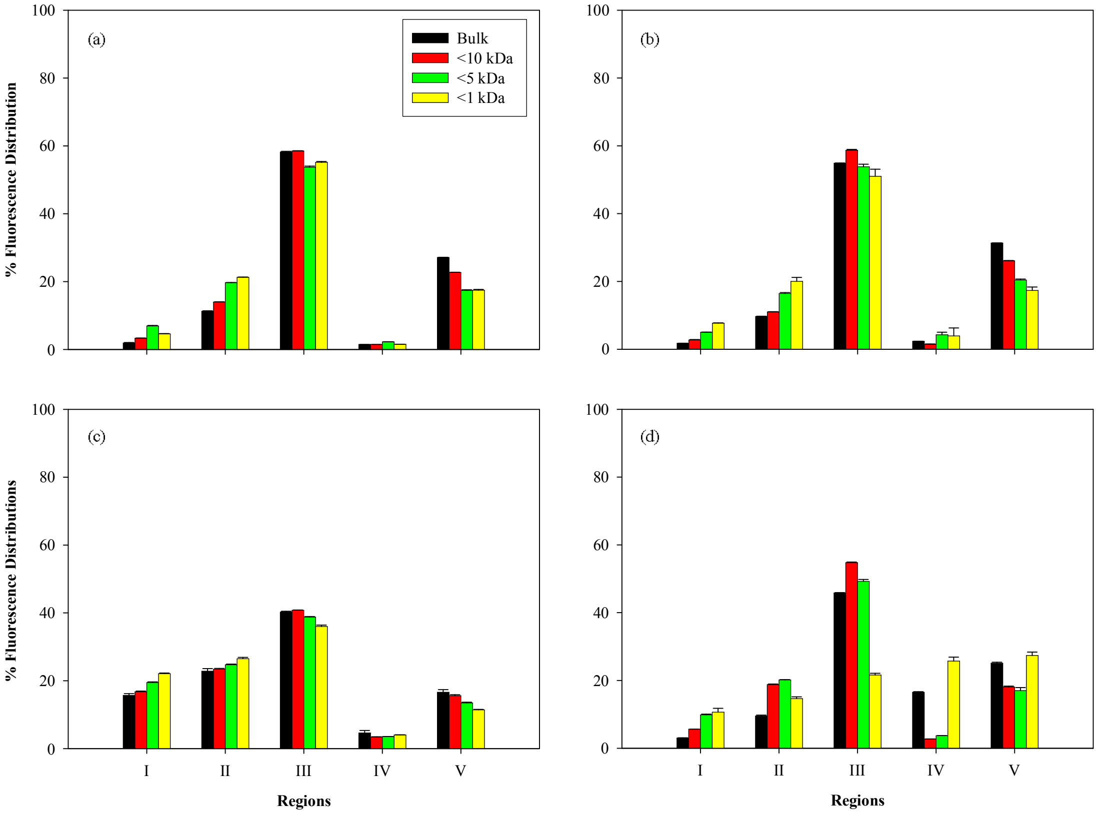

Figure S4. FRI results of the bulk and UF filtrate samples of (a) SRDOM, (b) ASRDOM, (c) FFWS, and (d) SCFP.

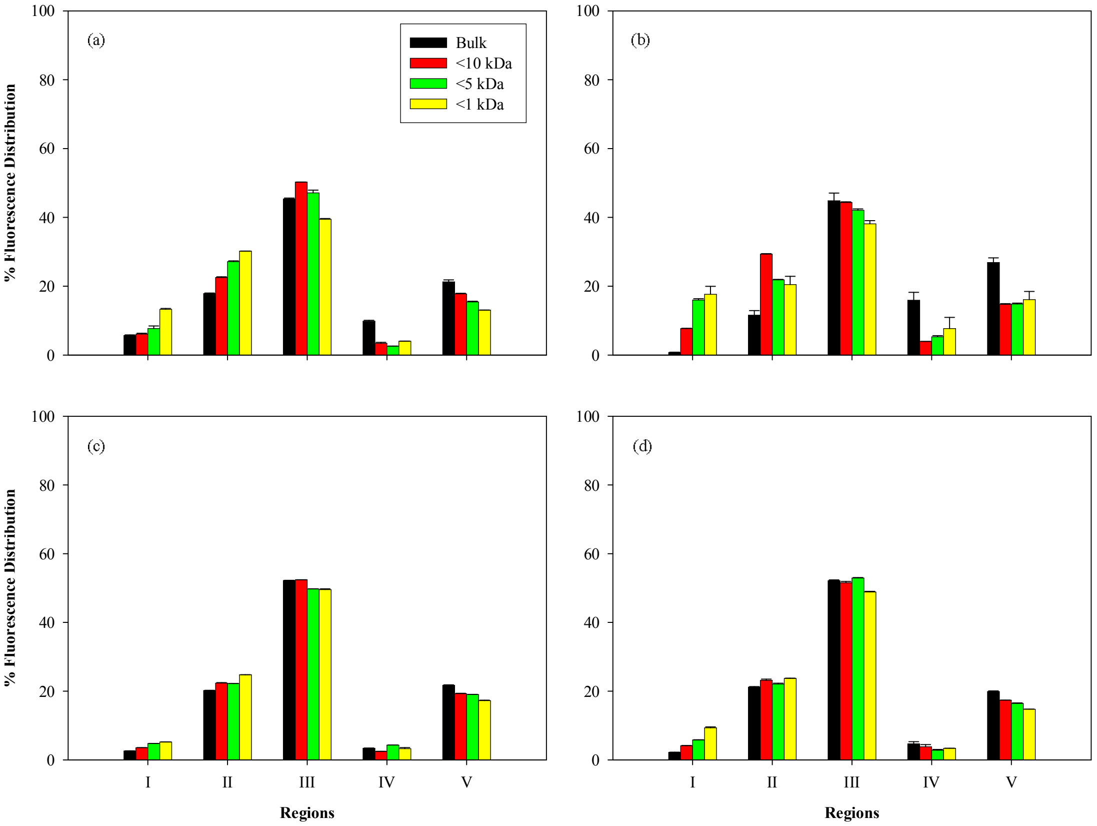

Figure S5. FRI results of the bulk and UF filtrate samples of (a) Raw water of CLWA, (b) Treated water of CLWA, (c) Raw water of LBWD, and (d) Treated water of LBWD.

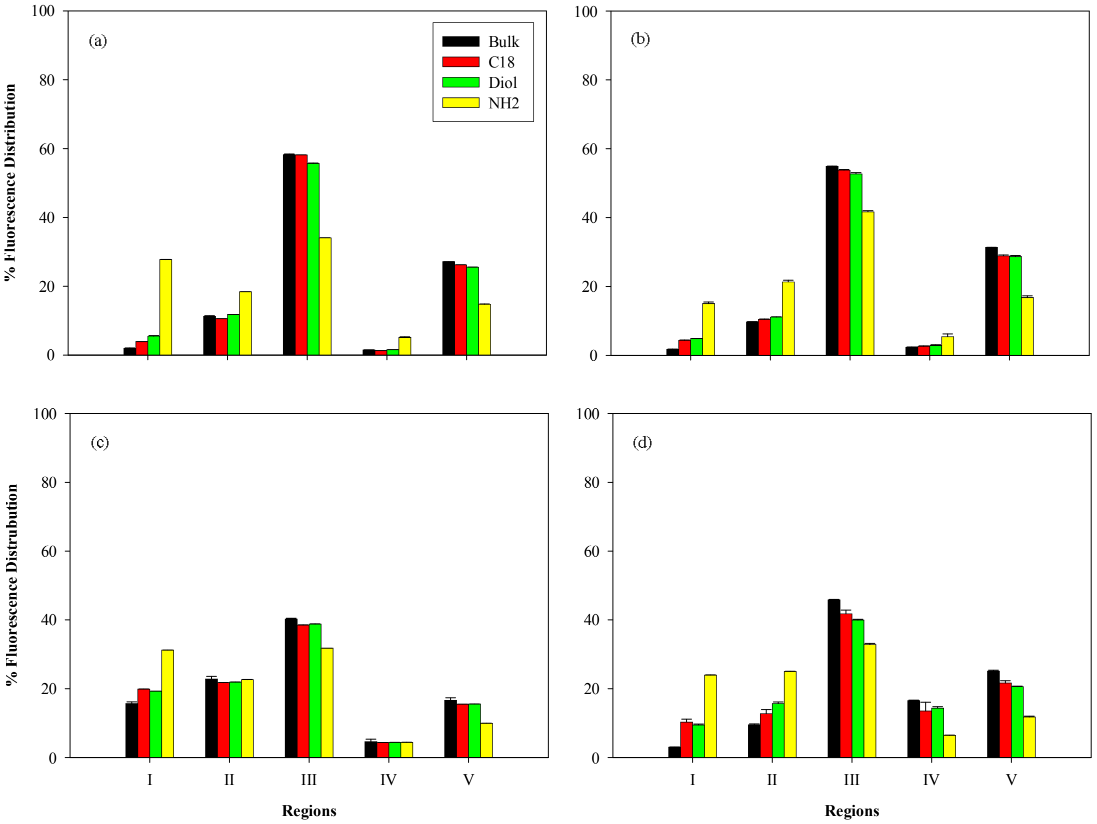

Figure S6. FRI results of the bulk and PRAM effluent samples of (a) the Suwannee River, (b) ASRDOM, (c) Forest Fire Water Sample, and (d) SCFP.

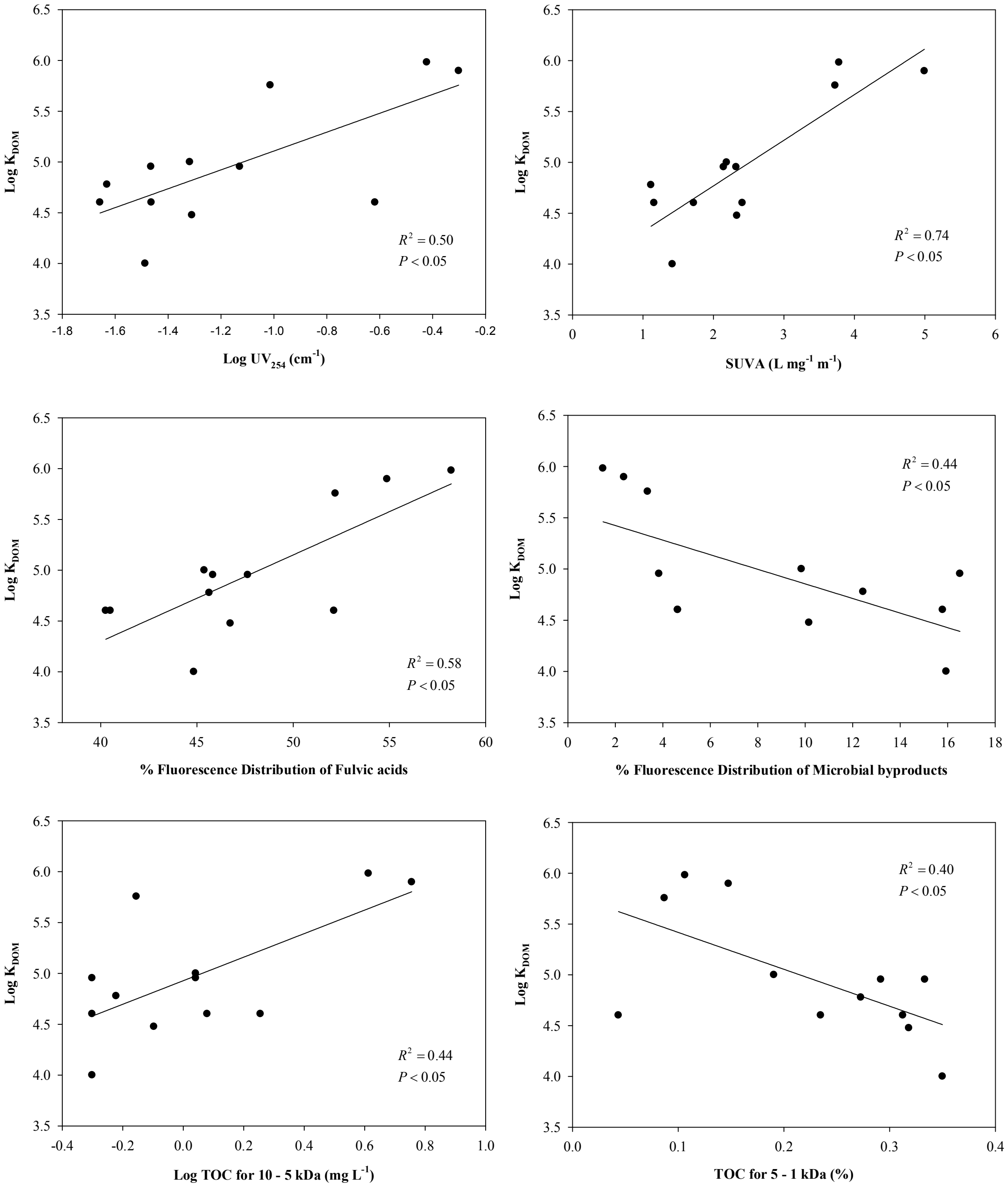

Figure S7-1. Correlations between Log K_{DOM} and DOM characteristics

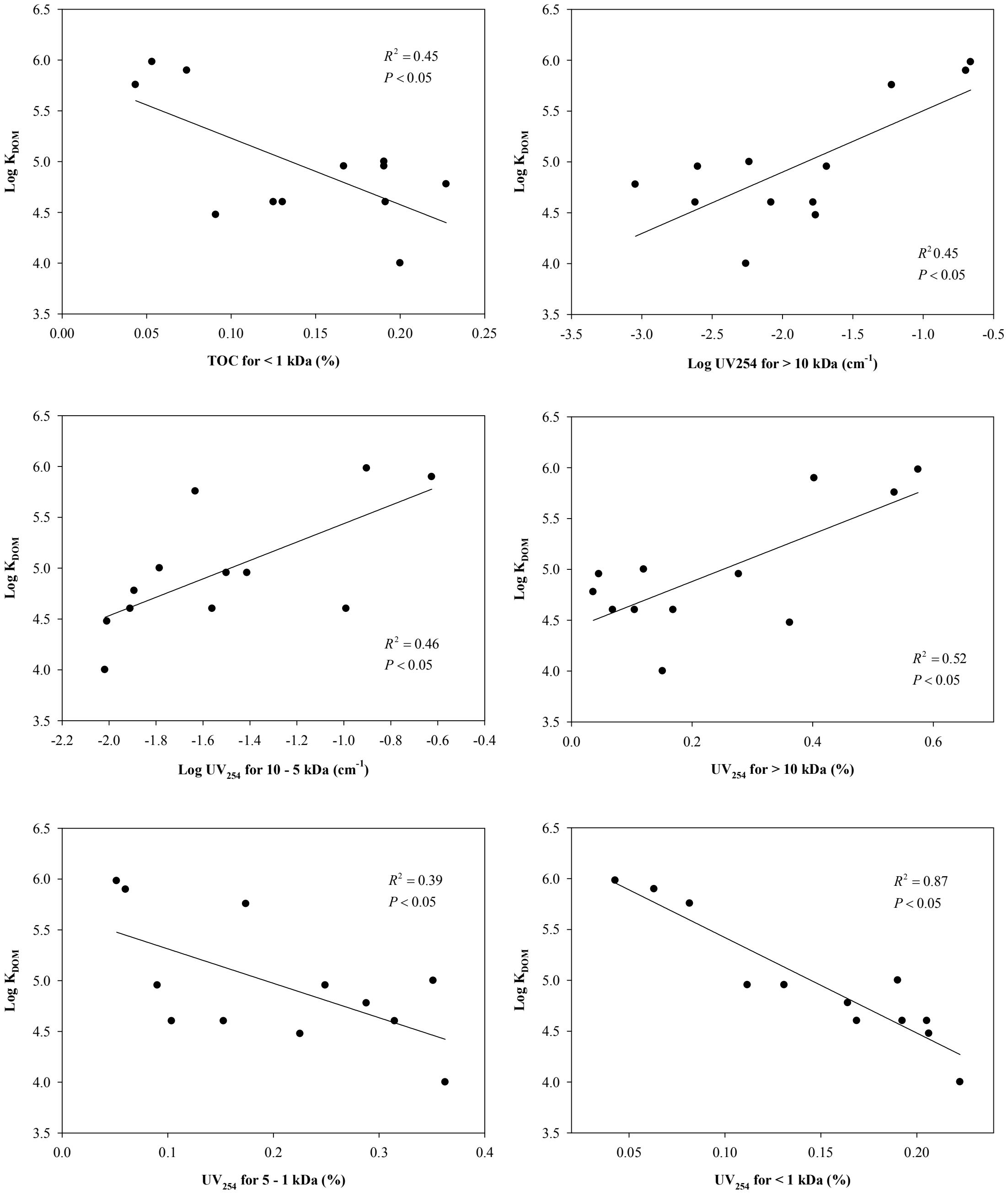

Figure S7-2. Correlations between Log K_{DOM} and DOM characteristics

Tables

Table S1. Water quality parameters for samples

samples	TOC (mg L^{-1})	UV_{254} (cm^{-1})	SUVA (L mg^{-1} m^{-1})	pH	Conductivity (us cm^{-1})
SRDOM[a]	10.0	0.3782	3.8	5.2	49
ASRDOM[b]	10.0	0.4994	5.0	7.6	425
FFWS[c]	10.0	0.2410	2.4	7.2	668
SCFP[d]	3.2	0.0743	2.3	7.5	114
CLWA[e]					
Raw	2.2	0.0481	2.2	8.0	300
Raw-waste	2.1	0.0490	2.3	8.2	290
Ozone	2.1	0.0234	1.1	7.9	290
Coagulation	1.9	0.0220	1.1	8.0	284
Treated	2.3	0.0326	1.4	8.1	271
LBWD[f]					
Raw	2.6	0.1226	3.8	8.5	378
Coagulation	1.6	0.0343	2.1	8.0	385
Treated	2.0	0.0344	1.7	8.2	418
MWD[g]					
Raw	2.6	0.0481	2.6	8.5	861
Treated	2.3	0.0342	2.3	8.3	873

[a] Suwannee River DOM. [b] adjusted Suwannee River DOM. [c] Forest Fire Water Sample. [d] Soldier Canyon Filtration Plant. [e] Castaic Lake Water Agency. [f] Long Beach Water Department. [g] Metropolitan Water District of Southern California.

Table S2. Characterization of DOM and location of FRI regions (1).

Region	Characterization of DOM	Excitation Range (nm)	Emission Range (nm)
I	Aromatic proteins I	220-250	280-332
II	Aromatic proteins II	220-250	332-380
III	Fulvic acids	220-250	380-580
IV	Microbial by-products	250-470	280-380
V	Humic acids	250-470	380-580

Table S3. Summary of K_{DOM} obtained by FQ and SPME-GC/MS methods.

Methods	**FQ**[a]						**SPME-GC/MS**		
Samples	DOM (mg L^{-1})	DOM range (mg L^{-1})	K_{DOM} (L mg^{-1})	Log K_{DOM}	y-intercept[g]	R^2	K_{DOM} (L mg^{-1})	Log K_{DOM}	R^2
SRDOM[b]	10.0	2-14.0	0.96 ± 0.00	6.0 ± 0.0	1.06 ± 0.03	0.94	0.92 ± 0.71	5.9 ± 0.4	0.88
ASRDOM[c]	10.0	1.7-10.0	0.79 ± 0.03	5.9 ± 0.0	0.66 ± 0.02	0.97	0.44 ± 0.06	5.6 ± 0.1	0.99
FFWS[d]	10.0	2-14.0	0.04 ± 0.00	4.6 ± 0.0	0.98 ± 0.02	0.94	0.04 ± 0.01	4.6 ± 0.2	0.79
SCFP[e]	3.2	1.6-9.4	0.09 ± 0.01	5.0 ± 0.1	0.99 ± 0.00	0.89	0.07 ± 0.02	4.8 ± 0.2	0.93
CLWA[f]-Raw	2.2	1.1-6.2	0.10 ± 0.01	5.0 ± 0.0	1.05 ± 0.09	0.83	0.18 ± 0.04	5.3 ± 0.1	0.92
CLWA-Raw-waste	2.1	1.1-6.1	0.03 ± 0.01	4.5 ± 0.1	1.02 ± 0.03	0.69	0.13 ± 0.02	5.1 ± 0.1	0.76
CLWA-Treated	2.3	1.2-7.5	0.01 ± 0.01	4.1± 0.2	0.98± 0.00	0.81	0.07± 0.08	4.6± 0.7	0.88

[a] fluorescence quenching. [b] Suwannee River DOM. [c] adjusted Suwannee River DOM. [d] Forest Fire Water Sample. [e] Soldier Canyon Filtration Plant. [f] Castaic Lake Water Agency. [g] Range signifies 95% confidence limit.

Table S4. Correlations between Log K_{DOM} and DOM characteristics.

Parameters	**unit**	**Relationship**	**R^2**
UV_{254}	cm^{-1}	+	**0.50**
SUVA*	$L\ mg^{-1}\ m^{-1}$	+	**0.74**
Fulvic Acids	%	+	**0.58**
Microbial by-products	%	-	**0.44**
TOC for 10-5 kDa	$mg\ L^{-1}$	+	**0.44**
TOC for 5-1 kDa	%	-	**0.40**
TOC for < 1 kDa	%	-	**0.45**
UV_{254} for > 10 kDa	cm^{-1}	+	**0.54**
UV_{254} for 10-5 kDa	cm^{-1}	+	**0.46**
UV_{254} for > 10 kDa	%	+	**0.52**
UV_{254} for 5-1 kDa	%	-	**0.39**
UV_{254} for < 1 kDa*	%	-	**0.87**

*** Indicates a significant correlation**

B.8 References

1. Chen, W.; Westerhoff, P.; Leenheer, J. A.; Booksh, K., Fluorescence excitation - Emission matrix regional integration to quantify spectra for dissolved organic matter. *Environ. Sci. Technol.* **2003**, *37*, (24), 5701-5710.

2. Stevenson, F. J., *Humus Chemistry, Genesis Composition, Reaction.* 2nd ed.; John Wiley & Sons: New York, **1994**.

3. Thurman, E. M., *Organic Geochemistry of Natural Waters.* Dr. W. Junk Publishers.: Dordrecht, The Netherlands: Martinus Nijhoff, Netherlands, **1985**.

4. Cronan, C. S.; Aiken, G. R., CHEMISTRY AND TRANSPORT OF SOLUBLE HUMIC SUBSTANCES IN FORESTED WATERSHEDS OF THE ADIRONDACK PARK, NEW-YORK. *Geochim. Cosmochim. Acta* **1985**, *49*, (8), 1697-1705.

5. Carter, C. W.; Suffet, I. H., BINDING OF DDT TO DISSOLVED HUMIC MATERIALS. *Environ. Sci. Technol.* **1982**, *16*, (11), 735-740.

6. Chiou, C. T.; Malcolm, R. L.; Brinton, T. I.; Kile, D. E., WATER SOLUBILITY ENHANCEMENT OF SOME ORGANIC POLLUTANTS AND PESTICIDES BY DISSOLVED HUMIC AND FULVIC-ACIDS. *Environ. Sci. Technol.* **1986**, *20*, (5), 502-508.

7. Ravacha, C.; Rebhun, M., BINDING OF ORGANIC SOLUTES TO DISSOLVED HUMIC SUBSTANCES AND ITS EFFECTS ON ADSORPTION AND TRANSPORT IN THE AQUATIC ENVIRONMENT. *Water Res.* **1992**, *26*, (12), 1645-1654.

8. Krasner, S. W.; Croue, J. P.; Buffle, J.; Perdue, E. M., Three approaches for characterizing NOM. *J. Am. Water Work Assoc.* **1996**, *88*, (6), 66-79.

9. Amy, G. L.; Thompson, J. M.; Tan, L.; Davis, M. K.; Krasner, S. W., EVALUATION OF THM PRECURSOR CONTRIBUTIONS FROM AGRICULTURAL DRAINS. *J. Am. Water Work Assoc.* **1990**, *82*, (1), 57-64.

10. Zhang, X. G.; Minear, R. A., Characterization of high molecular weight disinfection byproducts resulting from chlorination of aquatic humic substances. *Environ. Sci. Technol.* **2002**, *36*, (19), 4033-4038.

11. Singer, P. C., Humic substances as precursors for potentially harmful disinfection by-products. *Water Sci. Technol.* **1999**, *40*, (9), 25-30.

12. Lee, N. H.; Amy, G.; Croue, J. P.; Buisson, H., Identification and understanding of fouling in low-pressure membrane (MF/UF) filtration by natural organic matter (NOM). *Water Res.* **2004**, *38*, (20), 4511-4523.

13. Taniguchi, M.; Kilduff, J. E.; Belfort, G., Modes of natural organic matter fouling during ultrafiltration. *Environ. Sci. Technol.* **2003**, *37*, (8), 1676-1683.

14. Amy, G.; Cho, J., Interactions between natural organic matter (NOM) and membranes: Rejection and fouling. *Water Sci. Technol.* **1999**, *40*, (9), 131-139.

15. Van Stempvoort, D. R.; Lesage, S.; Novakowski, K. S.; Millar, K.; Brown, S.; Lawrence, J. R., Humic acid enhanced remediation of an emplaced diesel source in groundwater. 1. Laboratory-based pilot scale test. *J. Contam. Hydrol.* **2002**, *54*, (3-4), 249-276.

16. Molson, J. W.; Frind, E. O.; Van Stempvoort, D. R.; Lesage, S., Humic acid enhanced remediation of an emplaced diesel source in groundwater. 2. Numerical model development and application. *J. Contam. Hydrol.* **2002**, *54*, (3-4), 277-305.

17. Rebhun, M.; DeSmedt, F.; Rwetabula, J., Dissolved humic substances for remediation of sites contaminated by organic pollutants. Binding-desorption model predictions. *Water Res.* **1996**, *30*, (9), 2027-2038.

18. Backhus, D. A.; Gschwend, P. M., FLUORESCENT POLYCYCLIC AROMATIC-HYDROCARBONS AS PROBES FOR STUDYING THE IMPACT OF COLLOIDS ON POLLUTANT TRANSPORT IN GROUNDWATER. *Environ. Sci. Technol.* **1990**, *24*, (8), 1214-1223.

19. Schlautman, M. A.; Morgan, J. J., EFFECTS OF AQUEOUS CHEMISTRY ON THE BINDING OF POLYCYCLIC AROMATIC-HYDROCARBONS BY DISSOLVED HUMIC MATERIALS. *Environ. Sci. Technol.* **1993**, *27*, (5), 961-969.

20. Backhus, D. A.; Golini, C.; Castellanos, E., Evaluation of fluorescence quenching for assessing the importance of interactions between nonpolar organic pollutants and dissolved organic matter. *Environ. Sci. Technol.* **2003**, *37*, (20), 4717-4723.

21. Woodhead, R. J.; Law, R. J.; Matthiessen, P., Polycyclic aromatic hydrocarbons in surface sediments around England and Wales, and their possible biological significance. *Mar. Pollut. Bull.* **1999**, *38*, (9), 773-790.

22. Santos, F. J.; Galceran, M. T., The application of gas chromatography to environmental analysis. *Trac-Trends Anal. Chem.* **2002**, *21*, (9-10), 672-685.

23. USEPA Website; http://water.epa.gov/drink/contaminants/basicinformation/benzo-a-pyrene.cfm.

24. European Comission, Council Directive 98/83/EC; *Off. J. Eur. Commun.* 1998, L330, 32.

25. Gauthier, T. D.; Shane, E. C.; Guerin, W. F.; Seitz, W. R.; Grant, C. L., FLUORESCENCE QUENCHING METHOD FOR DETERMINING EQUILIBRIUM-CONSTANTS FOR POLYCYCLIC AROMATIC-HYDROCARBONS BINDING TO DISSOLVED HUMIC MATERIALS. *Environ. Sci. Technol.* **1986**, *20*, (11), 1162-1166.

26. Doll, T. E.; Frimmel, F. H.; Kumke, M. U.; Ohlenbusch, G., Interaction between natural organic matter (NOM) and polycyclic aromatic compounds (PAC) - comparison of fluorescence quenching and solid phase micro extraction (SPME). *Fresenius J. Anal. Chem.* **1999**, *364*, (4), 313-319.

27. MacKenzie, K.; Georgi, A.; Kumke, M.; Kopinke, F. D., Sorption of pyrene to dissolved humic substances and related model polymers. 2. Solid-phase microextraction (SPME) and fluorescence quenching technique (FQT) as analytical methods. *Environ. Sci. Technol.* **2002**, *36*, (20), 4403-4409.

28. Revchuk, A. D.; Suffet, I. H., Ultrafiltration separation of aquatic natural organic matter: Chemical probes for quality assurance. *Water Res.* **2009**, *43*, (15), 3685-3692.

29. Rosario-Ortiz, F. L.; Snyder, S.; Suffet, I. H., Characterization of the polarity of natural organic matter under ambient conditions by the polarity rapid assessment method (PRAM). *Environ. Sci. Technol.* **2007**, *41*, (14), 4895-4900.

30. Marhaba, T. F.; Van, D.; Lippincott, L., Rapid identification of dissolved organic matter fractions in water by spectral fluorescent signatures. *Water Res.* **2000**, *34*, (14), 3543-3550.

31. Holbrook, R. D.; Breidenich, J.; DeRose, P. C., Impact of reclaimed water on select organic matter properties of a receiving stream-fluorescence and perylene sorption behavior. *Environ. Sci. Technol.* **2005**, *39*, (17), 6453-6460.

32. Ramos, E. U.; Meijer, S. N.; Vaes, W. H. J.; Verhaar, H. J. M.; Hermens, J. L. M., Using solid-phase microextraction to determine partition coefficients to humic acids and bioavailable concentrations of hydrophobic chemicals. *Environ. Sci. Technol.* **1998**, *32*, (21), 3430-3435.

33. Lee, S.; Gan, J.; Liu, W. P.; Anderson, M. A., Evaluation of K-d underestimation using solid phase microextraction. *Environ. Sci. Technol.* **2003**, *37*, (24), 5597-5602.
34. Rebhun, M.; Meir, S.; Laor, Y., Using dissolved humic acid to remove hydrophobic contaminants from water by complexation-flocculation process. *Environ. Sci. Technol.* **1998**, *32*, (7), 981-986.

35. Mackay, D.; Shiu, W. Y., AQUEOUS SOLUBILITY OF POLYNUCLEAR AROMATIC-HYDROCARBONS. *J. Chem. Eng. Data* **1977**, *22*, (4), 399-402.

36. Miller, M. M.; Wasik, S. P.; Huang, G. L.; Shiu, W. Y.; Mackay, D., RELATIONSHIPS BETWEEN OCTANOL WATER PARTITION-COEFFICIENT AND AQUEOUS SOLUBILITY. *Environ. Sci. Technol.* **1985**, *19*, (6), 522-529.

37. Hawthorne, S. B.; Grabanski, C. B.; Miller, D. J.; Kreitinger, J. P., Solid-phase microextraction measurement of parent and alkyl polycyclic aromatic hydrocarbons in milliliter sediment pore water samples and determination of K-DOC values. *Environ. Sci. Technol.* **2005**, *39*, (8), 2795-2803.

38. Yan, M.; Wang, D.; Shi, B.; Wang, M.; Yan, Y., Effect of pre-ozonation on optimized coagulation of a typical North China source water. *Chemosphere* **2007**, *69*, (11), 1695-1702.

39. Owen, D. M., NOM CHARACTERIZATION AND TREATABILITY (VOL 87, PG 46, 1995). *J. Am. Water Work Assoc.* **1995**, *87*, (4), 148-148.

40. Chandrakanth, M. S.; Amy, G. L., Effects of ozone on the colloidal stability and aggregation of particles coated with natural organic matter. *Environ. Sci. Technol.* **1996**, *30*, (2), 431-443.

41. DeBano, L. F., The role of fire and soil heating on water repellency in wildland environments: a review. *J. Hydrol.* **2000**, *231*, 195-206.

42. Rosario-Ortiz, F. L.; Gerringer, F. W.; Suffet, I. H., Application of a novel polarity method for the characterization of natural organic matter during water treatment. *J. Water Supply Res Technol.-Aqua* **2009**, *58*, (3), 159-169.

43. Chin, Y. P.; Aiken, G. R.; Danielsen, K. M., Binding of pyrene to aquatic and commercial humic substances: The role of molecular weight and aromaticity. *Environ. Sci. Technol.* **1997**, *31*, (6), 1630-1635.

44. Tanaka, S.; Oba, K.; Fukushima, M.; Nakayasu, K.; Hasebe, K., Water solubility enhancement of pyrene in the presence of humic substances. *Anal. Chim. Acta* **1997**, *337*, (3), 351-357.

45. MacDonald, B. C.; Lvin, S. J.; Patterson, H., Correction of fluorescence inner filter effects and the partitioning of pyrene to dissolved organic carbon. *Anal. Chim. Acta* **1997**, *338*, (1-2), 155-162.

46. Scurfiel.G; Nicholls, P. W., AMINO-ACID COMPOSITION OF WOOD PROTEINS. *J. Exp. Bot.* **1970**, *21*, (69), 857-&.

47. Rosario-Ortiz, F. L.; Snyder, S.; Suffet, I. H., Analysis of polarity fractionated dissolved organic matter using 3-D fluorescence excitation-emission matrix spectroscopy. *Abstr. Pap. Am. Chem. Soc.* **2007**, *233*, 444-444.

48. Weishaar, J. L.; Aiken, G. R.; Bergamaschi, B. A.; Fram, M. S.; Fujii, R.; Mopper, K., Evaluation of specific ultraviolet absorbance as an indicator of the chemical composition and reactivity of dissolved organic carbon. *Environ. Sci. Technol.* **2003**, *37*, (20), 4702-4708.

C. Chapter 3:

Research Paper 2

Understanding the Interaction of Trihalomethanes and Dissolved Organic Matter in Raw and Treated Drinking Water

C.1 Abstract

Disinfection is required to make pathogen inactive in drinking water to protect human health. However, disinfection by-products (DBPs) (e.g. trihalomethanes, THMs) formed through reactions between disinfectants like chlorine and dissolved organic matter (DOM) cause health risks to humans. Water treatment agencies are facing more pressure to decrease DBPs concentrations from more stringent regulations on drinking water quality. Understanding the relationship between DOM characteristics and DBPs formation will help water treatment agencies reduce DBPs by optimize water treatment processes. Characteristics of DOM were measured for: 1) size distribution 2) polarity and 3) UV and fluorescent chemical functionality. Trihalomethanes formation potential (THMFPs) was determined as a DBPs measure.

As some other studies, DOM in terms of total organic carbon (TOC) and the aromatic structure of DOM measured as UV absorbance and Specific UV Absorbance (SUVA) were found to highly correlate with THMFP. The results showed that THMFP had positive and high

correlation with TOC concentration of bulk water samples ($R^2 = 0.85$), UV_{254} ($R^2 = 0.88$), and SUVA ($R^2 = 0.68$). This study shows for the first time that in addition, TOC concentration of > 10 kDa ($R^2 = 0.77$), 10 - 5 kDa ($R^2 = 0.79$) fractions; and UV_{254} of > 10 kDa ($R^2 = 0.63$), 10 - 5 kDa ($R^2 = 0.72$), 5 - 1 kDa ($R^2 = 0.56$), and < 1 kDa fractions ($R^2 = 0.71$) also correlated to THMFP indicating larger molecular weight fractions of DOM and aromatic structure of DOM within each size fraction produce most of the THMs.

In order to comply with more stringent DBPs regulations, water treatment agencies should decrease total DOM, but more specifically should develop approaches to remove larger MW size fractions and aromatic structure of DOM during different water treatment processes.

C.2 Introduction

Dissolved organic matter (DOM) is ubiquitous in the aquatic environment at mg C/L concentrations. DOM is composed of heterogeneous combination of aromatic and aliphatic organic compounds which contain nitrogen, oxygen, and sulfur functional groups coming from microbial decomposition in waterways and on land and runoff into waterways (Chen et al. 2003). The components of DOM have been classified as humic acids, fulvic acids, humin, amino acids, proteins, sugars, and polysaccharides (Thurman 1985, Krasner et al. 1996, Stevenson 1994). The transformation of DOM is important in water treatment processes because DOM is one of the main components to cause disinfection by-products (DBPs) formation (Thurman 1985, Krasner et al. 1996, Amy et al. 1990, Zhang and Minear 2002, Singer 1999) and membrane fouling (Lee et al. 2004, Taniguchi et al. 2003, Amy and Cho 1999).

DOM can form disinfection byproducts such as trihalomethanes (THMs) and haloacetic acids (HAAs) (Christman et al. 1983) which are associated with health risks to humans. For example, DBPs have been correlated to bladder and colon cancers, low birth weight, spontaneous abortion, and intrauterine growth retardation (Nieuwenhuijsen et al. 2000, Richardson et al. 2007, Villanueva et al. 2007). Because of the potential adverse effects of DBPs on human health, DBPs concentrations in drinking water are regulated. In the United States, two main DBPs, trihalomethanes (THMs) and haloacetic acids (HAAs), are regulated at 80 μg/L for total THMs ($CHCl_3$, $CHBrCl_2$, $CHClBr_2$, and $CHBr_3$) and 60 μg/L for five HAAs species. More stringent the stage 2 Disinfection D)/DBP Rule has been applied to reduce peak total THMs and HAAs concentration by changing the compliance monitoring locations implemented under Stage 1 D/DBP Rule and revising the method of determining compliance (USEPA 1998). In the European Union, total THMs are also regulated at 100 μg/L and chloroform at 30 μg/L (Lin et al. 2006).

There are three methods that can control the level of DBPs in drinking water: (1) treatment to remove DBPs after formation, (2) treatment to remove DBPs precursors, and (3) change in oxidation/disinfection strategies (Keith et al. 1995, Tanju et al. 2008). Removal of the main precursor of DBPs, DOM, before disinfection is the most effective and feasible method to decrease DBPs (Keith et al. 1995, Tanju et al. 2008). Removal mechanisms include separation such as coagulation/flocculation, activated carbon adsorption, membrane filtration, and ion exchange; and transformation such as ozonation (Cordelia et al. 2001). Therefore, understanding the relationship between DOM characteristics and DBPs formation potential is necessary to help water treatment agency to remove DOM more efficiently.

The objective of this study is to enable researchers to better understand the relationships between DOM and THMFP in raw and treated drinking water as well as during unit treatment processes. Trihalomethanes (THMs) measured as THM formation potential (THMFP) were compared to the changes of DOM. The data then can be used to optimize water treatment processes for THMFP control while maintaining disinfection control. New methods of DOM characterization are studied at ambient pH and ionic strength for polarity, size and chemical characterization. These include: ultrafiltration (UF) for size distribution (Revchuk and Suffet 2009), the polar rapid assessment method (PRAM) for polarity characterization (Rosario-Ortiz et al. 2007a), and fluorescence excitation-emission matrix (EEM) and fluorescence regional integration (FRI) for chemical functionality (Chen et al. 2003), DOC, UV absorbance at 254 nm and specific UV_{254} absorbance (SUVA) for aromatic structures.

Chow et al. (2005) reviewed the correlations between characteristics of DOM by three common fractionation techniques: (1) XAD fractionation, (2) UF, and (3) size exclusion chromatography (SEC) and THMFP. Chou et al. (2005) concluded that the hydrophobic fraction isolated by XAD and 10-1 kDa molecular weight fractioned by UF/SEC were the main precursors of THMs (Chow et al. 2005). Researches also indicate that UV_{254}, DOC, and SUVA are still the main surrogate parameters for estimating THMFP even though these cannot represent all the reactivity of DOM to form THMs (Chow et al. 2005, Ceraso 1987, Edzwald et al. 1985). Chow et al. (2005) also suggested using UF or SEC methods without adding acids, bases or any other harsh chemicals for fractionating DOM. Similarly, Baghoth et al. (2011) also mentioned drinking water treatment plants require less laborious, time consuming, and pretreatment DOM characterization methods (Baghoth et al. 2011). New methods of DOM characterization applied in this study are all done at in-situ conditions without changing samples and can be done within 2 hours and thus can offer valuable and timely information to drinking water treatment plants.

C.3 Experimental Section

Sample Preparation

The reference DOM studied was from the Suwannee River in Florida purchased from International Humic Substances Society for testing. Na_2HPO_4 and KH_2PO_4 (Fisher Scientific) were used as phosphate buffer to adjust Suwannee River DOM (SRDOM) (pH =5.2 to be pH 7.6 (Adjusted SRDOM [ASRDOM]) and conductivity 668 us/cm to be similar to natural water conditions. Forest Fire Water Sample (FFWS) were prepared by leaching dry ash of leaves and branches from Santa Barbara (collected at N +34° 27' 18.05", W -119° 43' 41.03"). Water samples from treatment process were collected from Soldier Canyon Filtration Plant (SCFP) in Colorado (influent water) and the following California plants: Castaic Lake Water Agency (CLWA) in Santa Clarita, Long Beach Water Department (LBWP) and Weymouth Water

Treatment Plant (The Metropolitan Water District of Southern California, MWD). The samples represent the water after each treatment process. The water quality parameters for this study are listed in Table 1.

All samples were filtered through 0.7 µm glass fiber membranes (Whatman Corp., Sanford, ME) prior to any analysis procedure to remove filterable organic matter and microorganisms which may consume DOM. All membranes were baked for 24 hours at 100 °C and rinsed with Milli-Q water before use to reduce leaching of organics from the membranes during filtration.

Ultrafiltration

DOM was size fractionated by ultrafiltration (UF) through Millipore YM (regenated cellulose, negatively charged) 1000 (1k), 10000 (10k) molecular weight cut off (MWCO), and PB (polyethersulfone, negatively charged) 5000 (5k) MWCO membranes (Millipore Corp., Billerica, MA) that are recommended for the size characterization of DOM (Revchuk and Suffet 2009). To reduce leaching of DOC, membranes were soaked three times in deionized water (30 min per time), from Milli-Q Plus water system,(Millipore Corp., Bedford, MA) and then in 5% NaCl solution over night. UF was performed in Millipore solvent-resistant stirred cells (XFUF 076 01). The final step was to rinse the membranes with 100 ml DI water just before filtration. 200 ml of bulk solution was added to the cell and 100 ml was filtered through under 55 psi nitrogen gas. Each membrane was discarded after one use. Fractions were analyzed by a

Shimadzu TOC 5050 Analyzer and a Shimadzu UV-1700 Pharmaspec UV-Vis spectrophotometer (Shimadzu Corp. Columbia, MD). All samples were completed in duplicate.

Polarity Rapid Assessment Method

DOM polarity was identified by the polar rapid assessment method (PRAM) under ambient water quality conditions without any pretreatment (Rosario-Ortiz et al. 2007a, Rosario-Ortiz et al. 2007b). Analysis takes into account the effect of pH and ionic strength on the structure of DOM under ambient conditions. Solid phase extraction (SPE) cartridges were cleaned by passing Milli-Q water to remove UV absorbing impurities. Parallel SPE cartridges with different sorbent polarities were used to adsorb DOM. The SPE cartridges include C18 (non-polar, hydrophobic), Diol (polar, hydrophilic), and NH2 (weak anion exchanger, negative charge). Ambient sample flow through each SPE cartridge was maintained at 1.2 mL/min for 8 min using a syringe pump (KD Scientific, Model 100, Holliston, MA). Effluent was collected from 4 to 8 minutes after initial breakthrough, and the absorbance at 254 nm was measured (UV 1700 Pharma Spec, Shimadzu) to get retention coefficient. The RC is defined as 1-(C_{max}/C_o) in percentage, where C_{max} is the maximum absorbance of the samples after breakthrough and C_o is the absorbance of the original sample. PRAM experiments were performed in triplicate. The effluent was also analyzed by fluorescence spectroscopy to record the excitation emission matrix (EEM).

Fluorescence Spectroscopy

Fluorescence spectroscopy, a highly sensitive and rapid method for the identification of DOM characteristics, was used to obtain the excitation-emission matrix (EEM) (Marhaba et al. 2000). The five regions represent aromatic proteinaceous compounds I and II, fulvic acids, microbial by-products, and humics (Chen et al. 2003). EEM spectroscopy was measured by fluorescence spectrophotometer (Varian, R3896, Palo Alto, CA). Using parameters were modified from Holbrook, et al. (Holbrook et al. 2005). Excitation wavelengths spanned from 220 to 470 nm in 5 nm increments, and the emission wavelengths spanned from 280 to 580 nm in 4 nm increments using an integration time of 0.1s and a bandwidth of 10 nm.

The fluorescence intensities of spectra were normalized by Raman peak, which was measured daily at pair excitation-emission wavelengths of 350 and 397 nm in deionized water (DI water) (Milli-Q water) and described as intensity unit (IU). All data were obtained by Matlab (version 7.4.0.287, R2007a, Natick, MA) to exclude the water-scattering peaks from Raleigh and Raman scattering (Marhaba et al. 2000).

Adjusted EEMs were quantified by the fluorescence regional integration (FRI) method to quantify and analyze fluorescence EEM spectra based on the integration of the total surface and subsequent divisions of the surface into five regions (Chen et al. 2003). Table 2 lists the regions and their associated excitation and emission regions.

Powdered Activated Carbon

The powdered activated carbon (PAC) adsorbent used in this research was HYDRODARCO B (Norit Americas Inc., USA), which is produced by steam activation of lignite coal. This PAC was chosen because it removes the precursors of trihalomethanes (THMs) and major contributors to color and taste caused by tannins and humic acids effectively (http://www.norit.com/files/documents/HDB-rev8.pdf). A PAC dose of 20 mg C/L was used in 1500 ml raw water samples of LBWD and MWD. Adsorption time was set 24 hours to ensure the adsorption reaches equilibrium. During the adsorption, stir bars were used for mixing. In 2-L beakers that were covered by Al foil to prevent evaporation and reaction with light. After the PAC adsorption, samples were filtered through 0.7 μm glass fiber membranes (Whatman Corp., Sanford, ME) to remove PAC prior to any analyses.

Trihalomethanes

Traihalomethanes (THMs) were measured as a formation potential in this study. All samples were chlorinated according to Standard Method 5710 B for THMFP under 25 ± 2 °C for 7 days. Chlorine residuals in the THMFP procedure were quenched by sodium sulfite (Na_2SO_3) before THMs analysis. The THMs analysis was performed in MWH laboratories, Monrovia, CA.

C.4 Results and Discussion

Size Characterization by Ultrafiltration

Figure 1 is the molecular size fractions of DOM for four source waters- SRDOM, ASRDOM, FFWS and SCFP. The DOM for SRDOM and ASRDOM was mainly composed of 10 -5 kDa fraction. The sum of >10 kDa and 10 -5 kDa fraction percentages were up to 80% for both SRDOM and ASRDOM, indicating that the DOM of Suwannee River was dominated by higher molecular weight DOM. Moreover, > 10 kDa fraction of SRDOM (pH=5.2) was about 10% higher than ASRDOM (pH=7.6) because higher hydrogen ion concentration appear to make the molecular size of the humic materials increase (Carter and Suffet 1982). Similarly, the > 10 kDa fraction of FFWS was over 40%. In contrast, the size fractions of SCFP were with the majority 10 -1 kDa and the least > 10 kDa. The UF results indicate that different source water will have different size fraction distributions.

Figure 2 is the UF analysis of CLWA and LBWD process waters. For CLWA process waters, the main fraction of DOM in raw was 10 -5 kDa. After ozonation process, the 10 -5 kDa fraction decreased and the lower molecular weight fractions- 5 -1 kDa,< 1 kDa, increased. Ozonation process has been known to facilitate the coagulation process by destabilizing and aggregating the particles in the water (Chandrakanth and Amy 1996). In CLWA, ozonation transformed DOM components from higher MW fractions into lower MW fractions to reduce the electrostatic barriers of particles to coagulate. Therefore, after coagulation, the size fractions of > 10 kDa and 10 -5 kDa increased to approximate 80%. CLWA treatment processes mainly removed 10 -5 kDa fraction of DOM and increased 5 -1 kDa fraction. Other researches have also shown ozone to decrease the MW of DOM (Yan et al. 2007, Owen 1995). For LBWD process waters, the raw water DOM was dominated by > 10 kDa fraction and 5 -1 kDa and < 1 kDa fractions were less than 20%. The DOM components after coagulation were composed of 20% - 30% for each different size fractions. The result indicates that most > 10 kDa DOM fraction decreased to smaller fractions by coagulation in LBWD. For MWD water, comparing raw and treated water, the raw water DOM was dominated by > 10 kDa fraction (42%). MWD treatment processes mainly removed 10 -5 kDa fraction (from 23% to 0%) of DOM and increased 5 -1 kDa fraction which was similar to CLWA processes result. > 10 kDa and < 1 kDa fractions stayed similarly throughout the processes (data were not showed here). Figure 4 also shows that different water sources and water treatment processes would have different DOM size fraction distributions.

PRAM Analysis

Figure 3 is the PRAM analysis of four source waters. It is obviously that for all samples, the retention coefficients (RCs) for the anionic ion exchanger [NH_2 solid phase extraction (SPE) cartridges] were significantly higher than neutral C18 and hydrophilic Diol SPE cartridges. The NH_2 RCs for all samples were from 60% to 80% indicating that DOM components in either DOM standard (SRDOM and ASRDOM) or natural source waters going into the water treatment plants had significant negative charge characteristic. Under ambient conditions, DOM was dominated by negative charges as a result of deprotonation of phenolic and carboxylic functional groups (Stevenson 1994). The NH_2 RCs of ASRDOM (pH=7.6) and SRDOM (pH=5.2) were 78% and 61%, respectively. The negative charge DOM portions of ASRDOM increase was due to more deprotonation of acid groups at higher pH condition. The C18 RC of FFWS was about 10% and higher than the DOM standard, SRDOM and ASRDOM. The higher C18 RC of FFWS indicated more hydrophobic components and might be due to the effect of fire on organic matter. Hydrophobic substances can be generated by the heating of decomposing plant organisms and mineral soil (DeBano 2000). Therefore, the DOM of FFWS would be more hydrophobic because FFWS was made by leaching of ashes and burnt materials from a forest fire.

Figure 4 is the PRAM analysis of CLWA and LBWD process waters. For both CLWA and LBWD process waters, the RCs of NH_2 cartridge decreased following the treatment processes indicating some removal of DOM through the process. For both CLWA and LBWD treatment processes, overall NH_2 RCs decreased about 30% which was similar to the result of Rosario-Ortiz et al. (Rosario-Ortiz et al. 2009). Similar results were also obtained in MWD samples. The RC_s of NH_2 for MWD decreased from 60% for raw water to 45% for treated water.

In CLWA process samples, Figure 4 shows that ozonation significantly decreased both RC_s of C18 and Diol which represent non-polar and polar fractions of DOM, respectively. The ozonation process might decrease the non-polar fractions by adding oxygen atoms and thus transform DOM to be more polar fractions. Then ozone continued to break down polar fractions to become smaller molecules. After coagulation, the non-polar and polar fractions of DOM increase might be due to the charge neutralization of coagulation process from negative charge fractions. The results also match the phenomenon observed in UF analysis of CLWA samples (ozonation decreased DOM size and coagulation increased DOM size). For LBWD samples, the raw water sample which was from groundwater had the highest NH_2 RC of 96% among all samples in this study. Moreover, after coagulation the NH_2 RC decrease was as the reduction of negatively charge in CLWA, showing the charge neutralization mechanism of coagulation. The non-polar components of DOM remained approximate 10% throughout the treatment process. However, the polar components increased before and after the treatment process.

Fluorescence Regional Integration (FRI) Analysis

This research used a fluorescence spectrophotometer to identify the characteristics of the DOM composition of all water samples according the method of Chen et al. (Chen et al. 2003). Figure 5 shows FRI results of each treatment process from CLWA and LBWD. Fulvic acids and humic acids were the main components of DOM after all the different treatment process waters, and percentages range were from 40% to 47% and 21% to 27% for CLWA; 48% to 53% and 18% to 22% for LBWD, respectively. High fulvic and humic acids inputs indicate of terrestrially derived source. The FRI results of MWD raw and treated water also showed the same relationships. Also, coagulation decreased fulvic acids in CLWA and fulvic and humic acids in LBWD indicating coagulation process is the critical processes to control DOM composition. The reason for this is that fulvic and humic acids have higher molecular weight and more negative charges, thus coagulation can be more efficient to remove fulvic and humic acids.

Changes of THMs Distribution in Raw and Treated Waters

Because of different components and characteristics (e.g. size, polarity, and chemical components) of DOM, the ability of DOM to generate THMs will be different. As a result, different water sources, different treatment process waters, and even different samples of different sampling time will have different THMFP.

Table 1 includes all THMs distribution in raw and treated waters tested in this study. The results showed that DOM standard from IHSS- SRDOM and ASRDOM and FFWS had much higher THMFP than other surface and treated drinking water. In addition, ASRDOM generated more THMs (950 μg/L) than SRDOM (720 μg/L) due to higher pH condition in ASRDOM. Previous study has also shown that lower pH values in the water can effectively control and decrease THMs formation (Hu et al. 2010). For process water in CLWA and LBWD, THMs decreased 31% and 44% for CLWA and LBWD, respectively, by removing DOM and changing DOM characteristics.

Changes of DOM Characteristics and THMFP after PAC Treatment

Powdered activated carbon (PAC) is one of the most effective methods to adsorb DOM and thus can decrease THMFP during the drinking water process. This study applied PAC treatment at dose 20 mg/L to treat LBWD and MWD raw water samples to understand the effects of PAC on DOM characteristics and its effect on THMFP.

Figure 6 presents the FRI result of LBWD and MWD raw water before and after 20 mg/L treatment. In LBWD samples, fulvic acids decreased 49%, humic acids decreased 40%, aromatic proteins I and II decreased 22% to 60%, and Microbial by-products did not have removal. In MWD samples, fulvic acids decreased 45%, humic acids decreased 33%, aromatic proteins I and II decreased 9% to 53%, and Microbial by-products decreased 28%. The results indicate that PAC used in this study adsorbs DOM effectively. However, site specific adsorption behaviors between PAC and DOM were apparent. In addition, in LBWD, DOM shows it has more microbial by-products present after PAC adsorption of other components. This phenomena also occurred in the previous study that the aromatic proteins fluorescence of these molecules could occur after fulvic and humic acids adsorbed by SPE cartridges (Rosario-Ortiz et al. 2007c).

In figure 7, the RC of NH2 anion exchanges cartridge decreased from 96% to 88% and 60% to 51%, C18 decreased from 12% to 10% and 13% to 8%, and Diol increased from 0% to 8% and 5% to 11%, respectively.

In Figure 8 for LBWD raw water, the % fractions of 5 - 1 kDa and < 1 kDa decreased to zero after 20 mg C/L adsorption and thus increased the % fractions of > 10 kDa and 10 - 5 kDa based upon a measure of DOC. The result shows that PAC adsorbed small fractions (< 5 kDa) of DOM of LBWD raw water very effectively and thus changed size fractions distribution. For MWD raw water, PAC mainly removed >10 kDa and some < 1 kDa fractions and thus led to increase of 10 - 5kDa and 5 - 1 kDa fractions. These waters act completely different to PAC. This is why PAC has to be tested on a site specific basis (Suffet 1981).

Figure 9 presents DOM size fraction changes after PAC adsorption in TOC (mg C/L) unit. As the result of Figure 9 for LBWD, smaller fractions (5 – 1 kDa and < 1 kDa) of DOM that are not absorbed at UV_{254} and more aliphatic in nature were all adsorbed by PAC. However, the amount of 10 - 5 kDa remained the same and the amount of > 10 kDa decreased indicating that PAC might specifically remove DOM with size fractions smaller than 5 kDa and larger than 10 kDa in LBWD by DOC. In MWD raw water adsorption experiment, for TOC concentration, > 10 kDa decreased from 1.1 to 0 mg C/L and < 1 kDa decreased from 0.8 to 0.4 mg C/L; 10 - 5 kDa and 5 - 1 kDa fractions did not change significantly considering the errors after PAC treatment. The UF size fractions distribution in terms of TOC (mg C/L) after PAC treatment was similar to the results of LBWD raw water that PAC mainly removed > 10 kDa and < 1 kDa fractions by DOC.

Figure 10 and 11 were the results of LBWD and MWD UF size fractions analysis in terms of % change of UV_{254} and UV_{254} absorbance (cm^{-1}) by measuring UV_{254} of different fractions. Figure 10 showed that even though UV_{254} which is only part of TOC concentration were measured, the % UF size fractions behaved similarly to measuring the TOC in percentage (Figure 8), especially for LBWD. Nonetheless, in LBWD raw waters adsorption, although UF size fractions for 10 - 5 kDa, 5 - 1 kDa and < 1 kDa measured by UV_{254} absorbance showed similar trend as measured by TOC (Figure 9 and 11), > 10 kDa fraction showed differently between these two measuring methods. After LBWD raw water treated by PAC, > 10 kDa fraction in terms of TOC decreased, but > 10 kDa fraction in terms of UV_{254} increased indicating that although PAC adsorbed and removed some > 10 kDa TOC concentration, the main DOM removed was not primarily aromatic.

For UV_{254} absorbance analysis, MWD results were not similar as LBWD results. In MWD raw water, PAC removed > 10 kDa, 10 - 5 kDa and < 1 kDa. In LBWD, PAC removed 10-5 kDa, 5 – 1 kDa, and < 1 kDa. It showed although the DOM removal mechanism by PAC for different size by TOC was similar between two different raw water sources, the removal mechanisms for different structures of DOM in different raw waters were different. Furthermore, comparing Figure 9 and 11, it is likely that in MWD raw water, after PAC treatment, 10 - 5 kDa fraction was mainly composed of non-aromatic structure DOM and 5 - 1 kDa fraction was mostly composed of aromatic structure DOM due to different changes ratio between TOC concentration and UV_{254} absorbance.

Figure 12 showed the changes of TOC (mg C/L), SUVA (L/mg/mg) and UV_{254} (cm^{-1}) of LBWD and MWD raw water samples before and after 20 mg C/L PAC treatment. It is obviously that total DOM contents decreased in terms of TOC for both LBWD and MWD raw waters. For both LBWD and MWD, 20 mg C/L PAC adsorbed about 1 mg C/L DOM (2.6 to 1.7 for LBWD and 2.6 to 1.6 for MWD). In terms of percentage of TOC, after treatment LBWD kept 65% and MWD kept 62% DOM. In addition, UV_{254} decreased to 74% and 61% of the original value for LBWD and MWD after PAC treatment, indicating that PAC removed some aromatic parts of DOM in the waters. However, SUVA increased in LBWD samples but did not change significantly in MWD after PAC treatment indicating the site specificity of DOM. Therefore, different water sources have different extent of PAC adsorption and thus cause different SUVA values even though PAC decreased TOC and UV_{254} contents. Previous study also showed the same trend that UV_{254} and DOC concentration decreased by increasing dose of PAC reacted with surface water (Szlachta and Adamski 2009). In conclusion, even though PAC effectively removed DOM contents in terms of TOC and UV_{254}, different size fractions behaved differently during the treatment and need to be monitored.

In Table 1, for THMs removal, PAC at dose 20 mg C/L can remove 22% and 26% for LBWD and MWD, respectively. The relationships between DOM characteristics and THMFP through drinking water processes and after PAC treatment will be discussed in the following section.

The Correlations between THMs and DOM Characteristics

This research examined the correlations between THMFP in terms of total THMs and DOM characteristics by linear regression and R-squared values to understand which factors might affect THMFP. All water samples including after PAC treatment were analyzed for THMFP. The correlations between THMFP and DOM characteristics are listed in Table 3. The results showed that THMFP hads a positive and high correlation with TOC concentration of bulk water samples ($R^2 = 0.85$), UV_{254} ($R^2 = 0.88$), and SUVA ($R^2 = 0.68$); TOC concentration of > 10 kDa ($R^2 = 0.77$), 10 - 5 kDa ($R^2 = 0.79$) fractions; and UV_{254} of > 10 kDa ($R^2 = 0.63$), 10 - 5 kDa ($R^2 = 0.72$), and < 1 kDa fractions ($R^2 = 0.71$). THMFP also had positive but moderate correlation with UV_{254} of 5 - 1 kDa ($R^2 = 0.56$). Other parameters were poorly correlated ($R^2 < 0.45$). All the correlations were shown in Figure 13.

The results indicate the THMFP was mainly from total DOM contents of samples and specifically aromatic structures of DOM. Other studies also presented that high UV_{254}, SUVA and aromaticity of DOM tend to form more THMs (Chow et al. 2005, Chang et al. 2001, Wei et al. 2008) and fulvic acids were the main components to form THMs (Reckhow et al. 1990). However, fulvic acids did not show very high correlation in this study ($R^2 = 0.24$).

For different size fractions, THMs had higher correlations with the TOC for > 10 kDa, 10 - 5 kDa. Similarly, THMs were stronger correlated with UV_{254} for > 10 kDa, 10 - 5 kDa and moderate correlated with < 5 - 1 kDa. The results showed that DOM with high molecular weight and more aromatic structures can generate more THMs. Kristiana et al. (2010) also indicated larger molecular weight fractions of DOM produced higher concentration of DBPs (I. Kristiana 2010). In addition, UV_{254} for < 1 kDa also had high correlation compared to other fractions. It indicated that within the size fraction smaller than 1 kDa, DOM with aromatic structure was the main formers of THMs. Previous studies regarding DOM and THMs formation showing that hydrophobic fraction and the fraction with molecular weight of 10 - 1 kDa have been implicated as the main source of THMs precursors also supported this study's results (Chow et al. 2005, Wu 2000).

Analysis of THMs after PAC Treatment

For LBWD raw water, the THMs concentration before and after PAC treatment were 180 and 100 μg/L. After PAC dose 20 mg C/L treatment, the bulk TOC concentration decreased from 2.6

to 1.7 mg C/L, bulk UV_{254} decreased from 0.097 to 0.072 cm^{-1}. TOC for > 10 kDa fraction decreased from 1.3 to 1.1 mg C/L, and UV_{254} for 10 - 5 kDa, 5 - 1 kDa, and < 1 kDa decreased from 0.023 to 0.021, 0.019 to 0.003, 0.009 to 0.002, respectively.

For MWD raw water, the THMs concentration before and after PAC treatment were 110 and 81 µg/L. After PAC dose 20 mg C/L treatment, the bulk TOC concentration decreased from 2.6 to 1.6 mg C/L, bulk UV_{254} decreased from 0.048 to 0.029 cm^{-1}, and bulk SUVA decreased from 1.9 to 1.8 L/mg/m, respectively. Also, TOC for > 10 kDa fraction decreased from 1.1 to < the detection limit, and UV_{254} for > 10 kDa, 10 - 5 kDa, and < 1 kDa decreased from 0.014 to 0.006, 0.018 to 0.009, 0.010 to 0.004, respectively. The results were identical to the correlations between THMFP and DOM characteristics.

Following the decrease of bulk TOC and UV_{254} of sample, and TOC for > 10 kDa, UV_{254} for different size fractions, THMFP also decreased due to these parameters of DOM having positive correlations with THMFP. Furthermore, Chang et al. (2001) and Wei et al. (2008) also reported that lower molecular weight of organic substance (average molecular weight < 1 kDa) contributed the most of DBPs (Chang et al. 2001, Wei et al. 2008). In this study, 5 – 1 kDa and < 1 kDa fractions of LBWD decreased and < 1 kDa fraction of MWD decreased after PAC treatment which might lead to decrease in THMs.

Implication of THMs Analysis

The result showed that PAC used in this study might be suitable to remove DOM for LBWD and MWD raw water. The reason is that PAC can remove total DOM content (TOC concentration) and aromatic contents of DOM which are the precursors of THMs and thus decrease THMFP.

Understanding the characteristics of DOM of raw water and throughout treatment processes can give effective information to water treatment agency. It is very important for water treatment agency to treat water effectively and simultaneously keep water safer to use. Decreasing THMFP by removing specific characteristics of DOM can help to decrease operation cost and match more stringent DBPs regulation and to operate treatment processes more efficiently. In order to have lower THMs, water treatment should remove TOC and aromatic contents of DOM as more as possible and particularly remove DOM size fractions of > 10 kDa and 10 - 5 kDa fractions.

C.5 Conclusions

Integrating all results of UF, PRAM, FRI analysis, this study had the following conclusions. DOM was mainly composed of fulvic and humic acids according to the Flourescence Method as expected. In general, fulvic and humic acids were with negative charges and of higher molecular weight. Following the water treatment processes, THMs decreased as DOM was removed. DOM characteristics are definitely changed after treatment.

The results showed that THMs had positive and high correlation with TOC concentration of bulk water samples ($R^2 = 0.85$), UV_{254} ($R^2 = 0.88$), and SUVA ($R^2 = 0.68$); TOC concentration of > 10 kDa ($R^2 = 0.77$), 10 - 5 kDa ($R^2 = 0.79$) fractions; and UV_{254} of > 10 kDa ($R^2 = 0.63$), 10 - 5 kDa ($R^2 = 0.72$). Therefore, higher DOM concentration, DOM with more aromatic structures, and DOM with > 10 kDa, 10 – 5 kDa size fractions have ability to produce more THMs.

PAC appears to be an effective method to control THMs. Explore the relationship between characteristics of DOM and DBPs can offer valuable knowledge to guide water agencies towards optimization of water treatment processes and obtain higher water quality. The monitoring protocol and analysis methods of this research should be applied to other unit operations and water treatment plants to continue disentangle the complexities of DOM effects on DBPs formation and removal in drinking water.

C.6 Figures

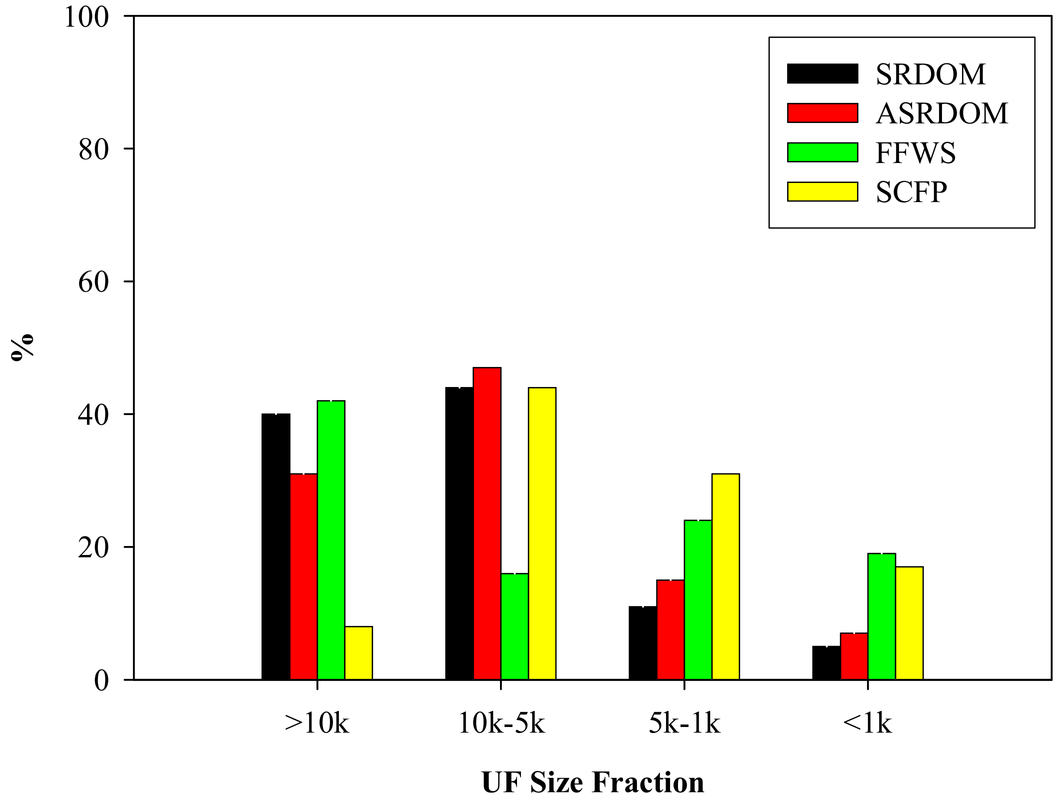

Figure 1. UF analysis of four source waters.

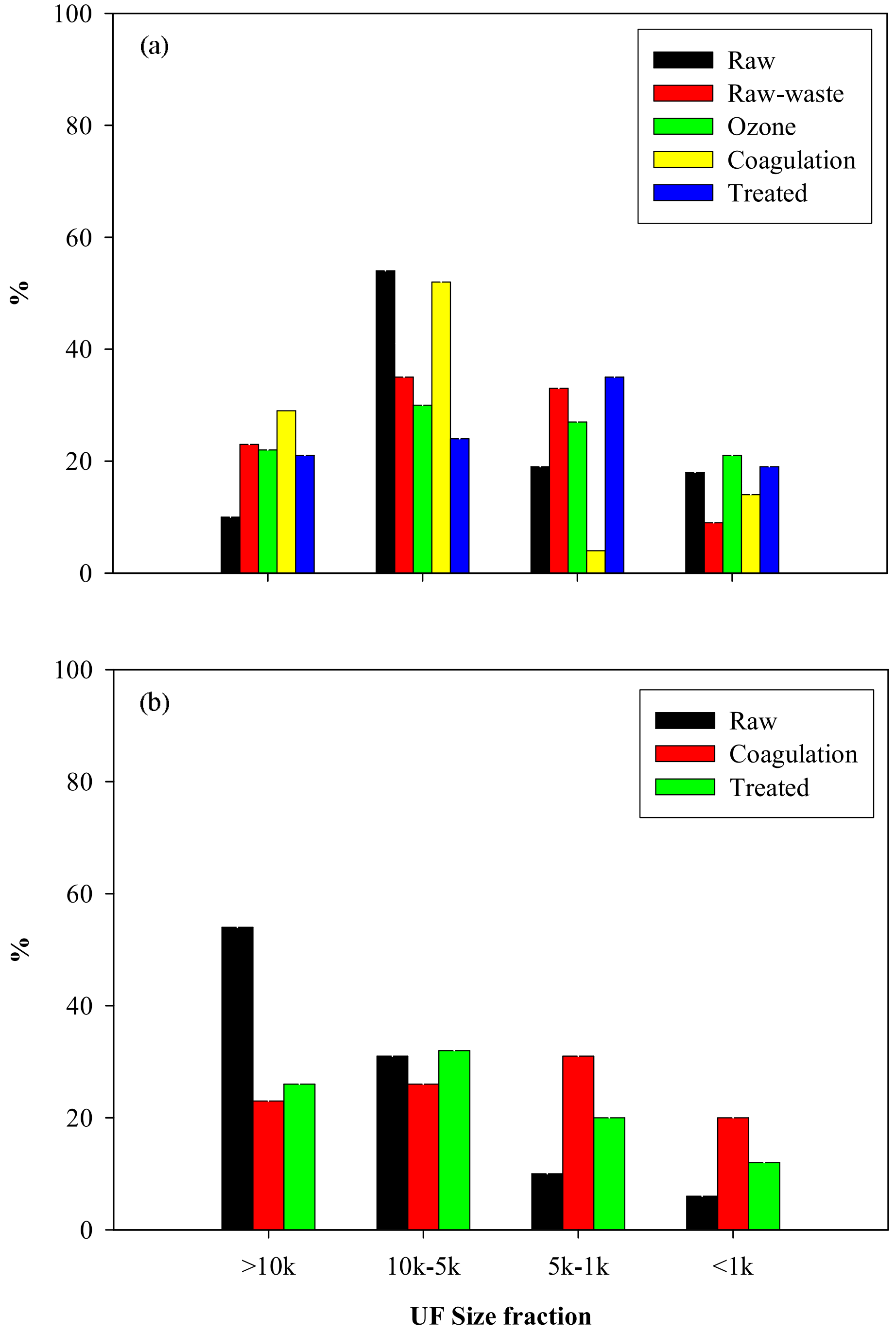

Figure 2. UF analysis of process waters of (a) CLWA, (b) LBWD.

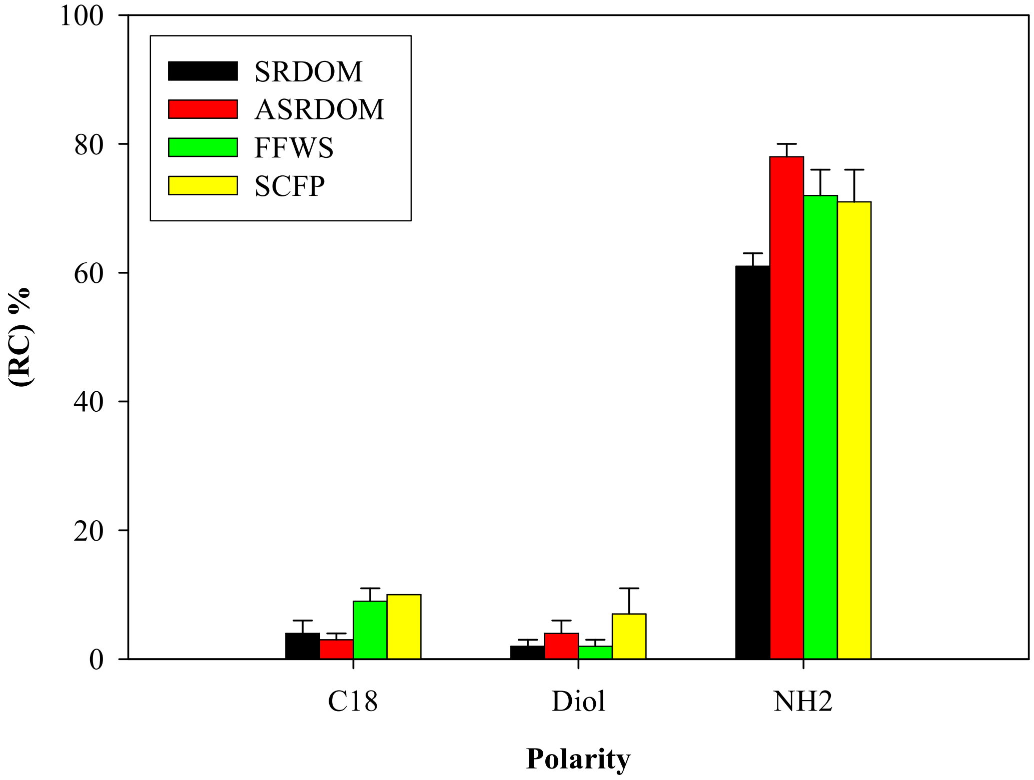

Figure 3. PRAM analysis of four source waters.

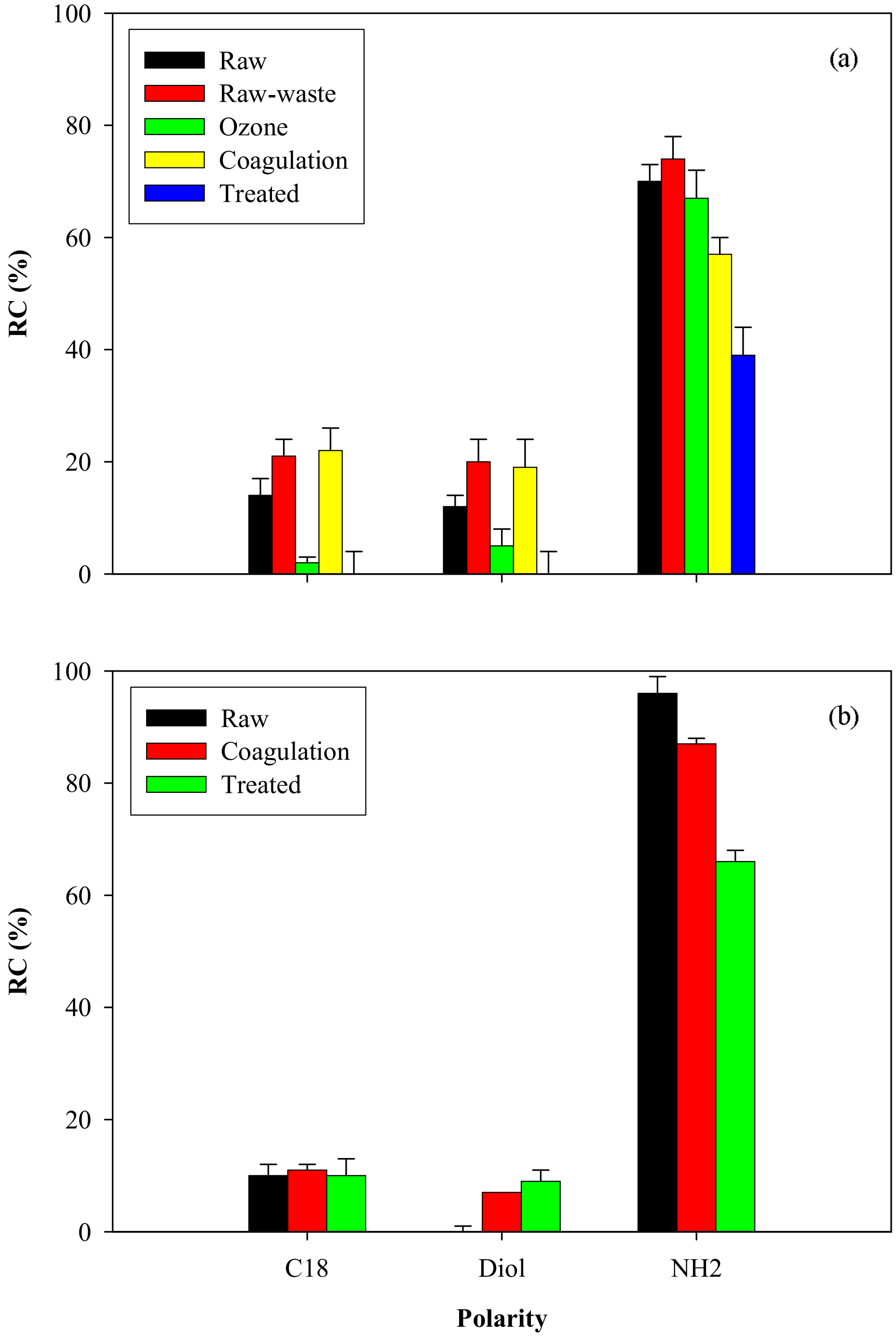

Figure 4. PRAM analysis of process waters of (a) CLWA, (b) LBWD.

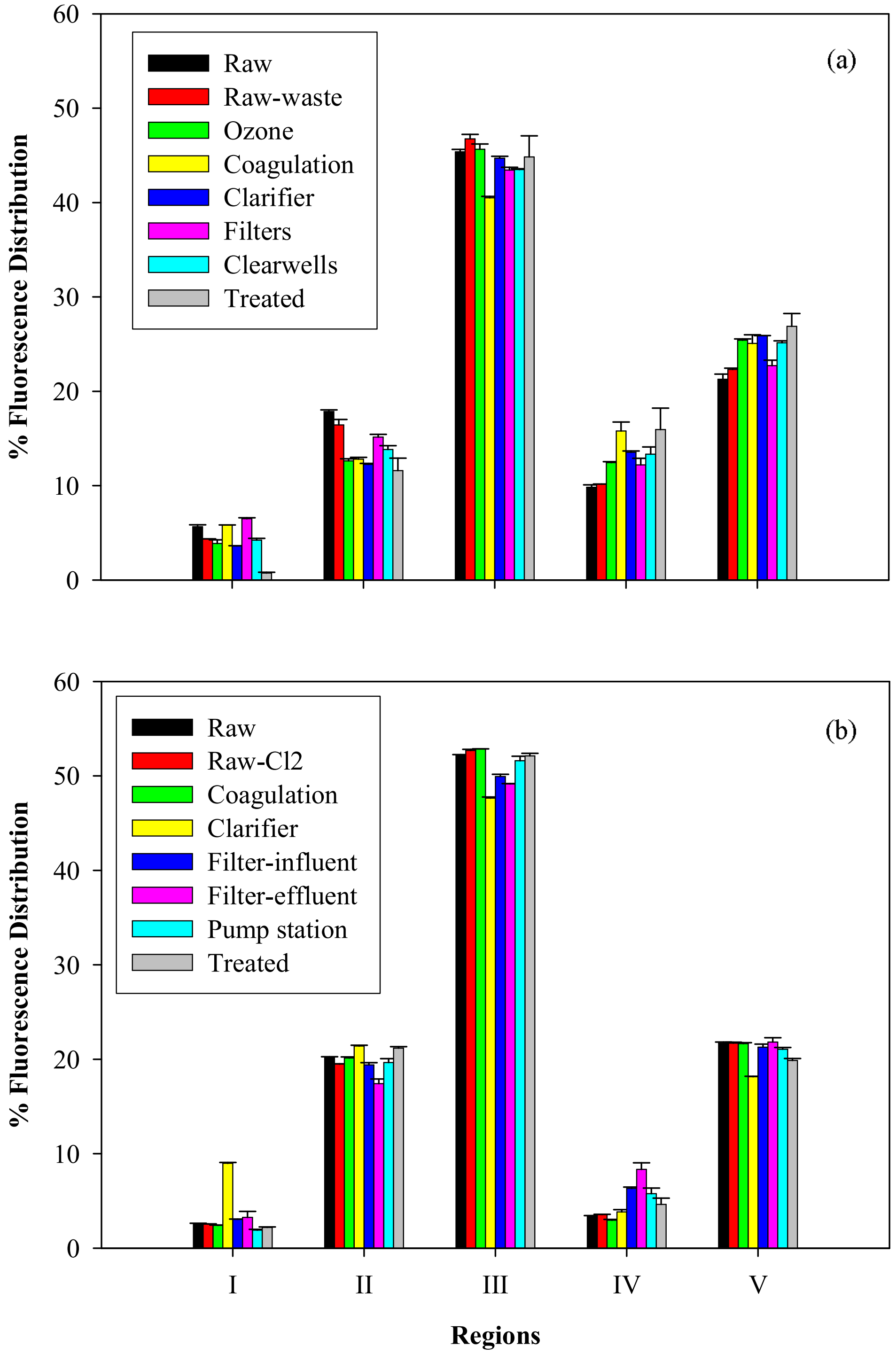

Figure 5. FRI results of each treatment process of (a) CLWA and (b) LBWD.

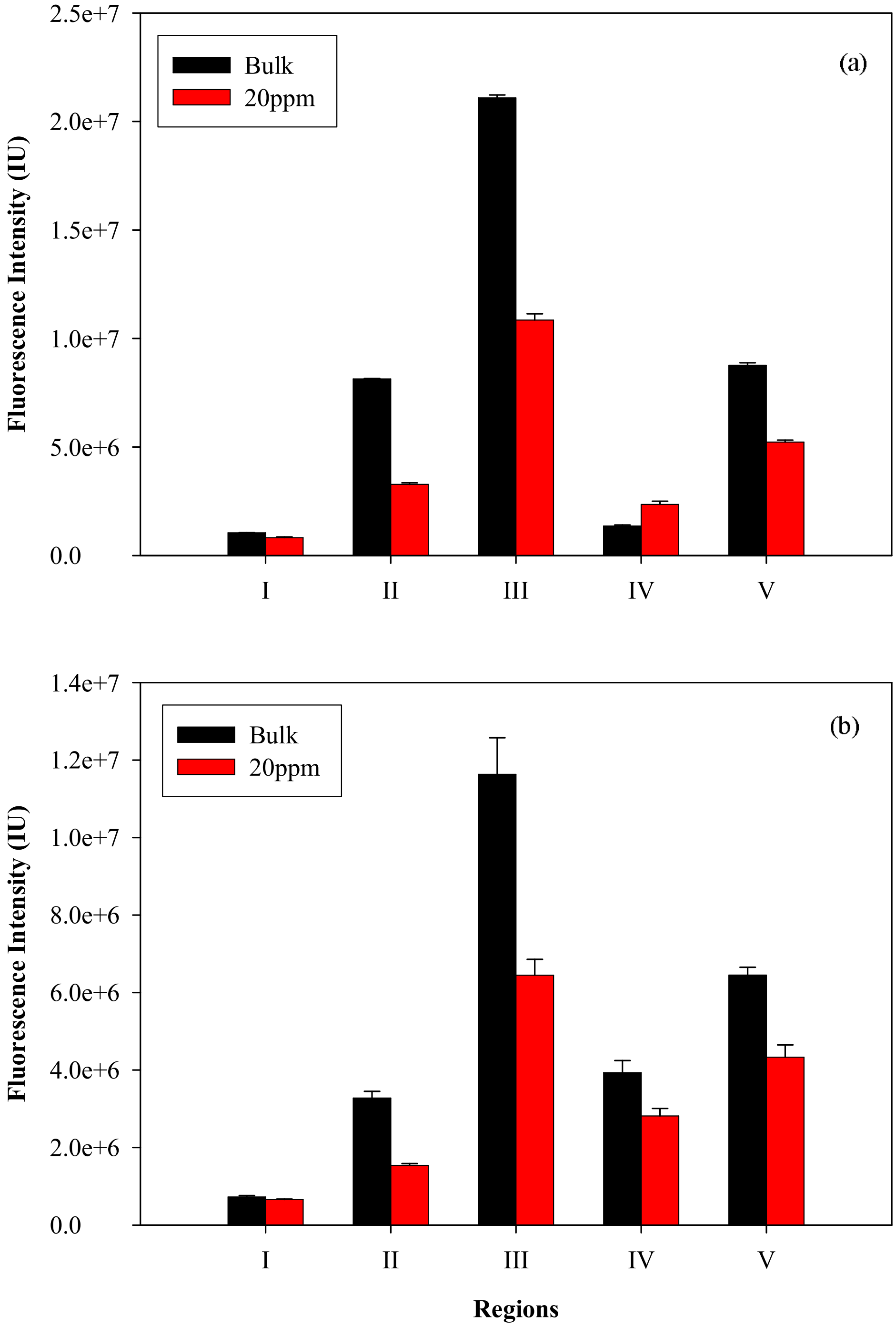

Figure 6. FRI results of PAC dose 20 mg C/L reacted with (a) LBWD and (b) MWD raw water.

(IU: Intensity Unit)

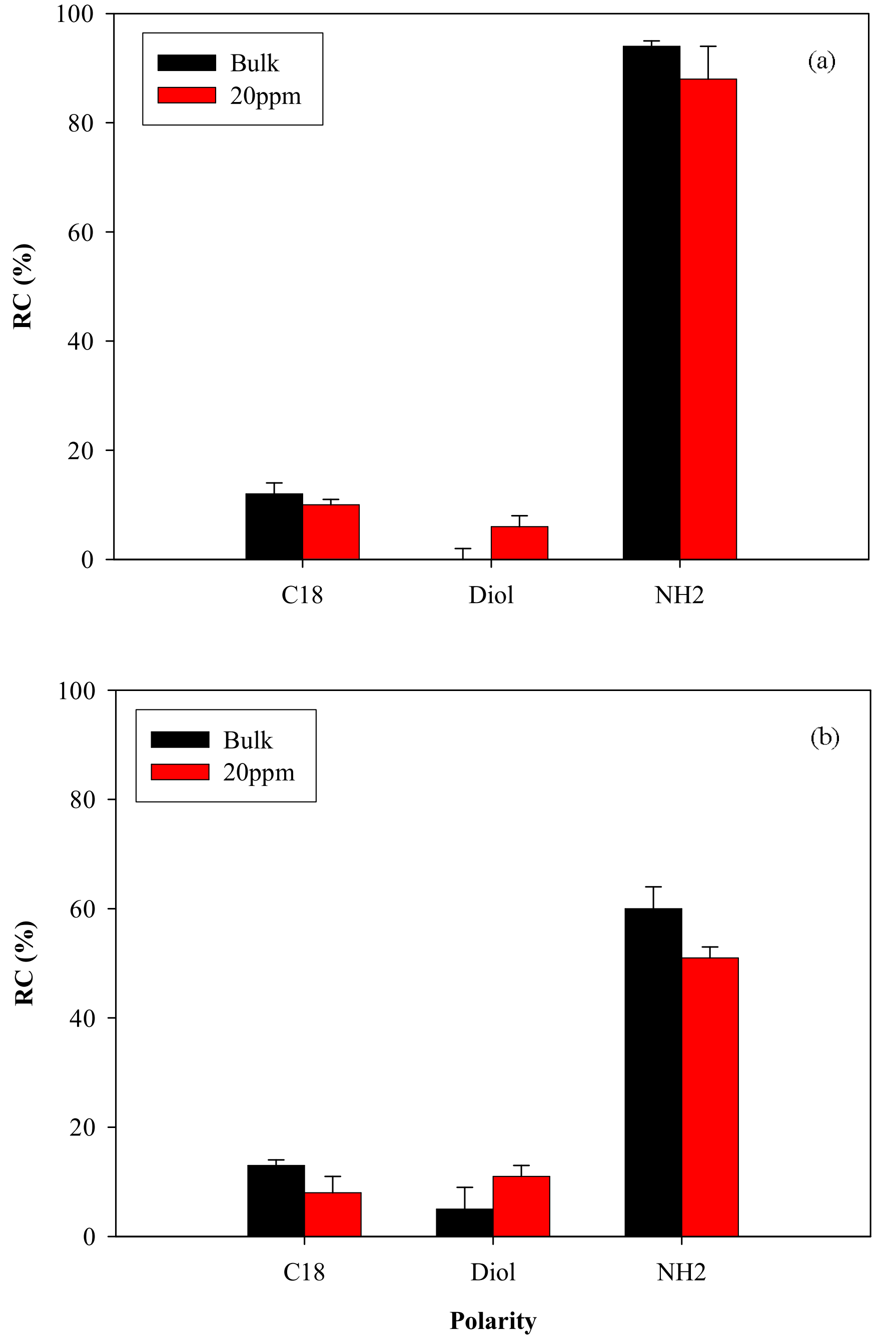

Figure 7. PRAM analysis of PAC dose 20 mg C/L reacted with (a) LBWD and (b) MWD raw water.

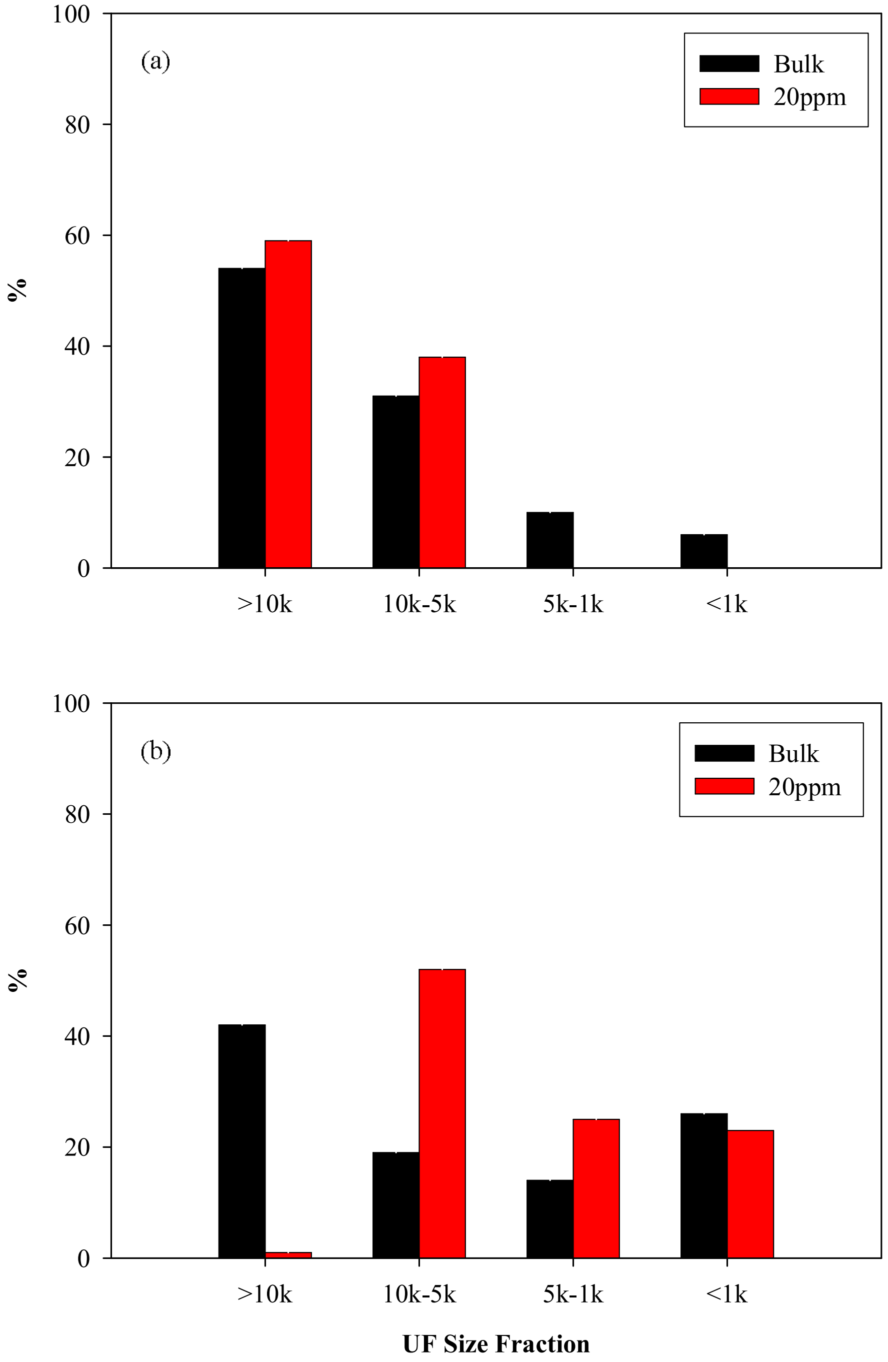

Figure 8. UF analysis in percentage by TOC of PAC dose 20 mg/L reacted with (a) LBWD and (b) MWD raw water.

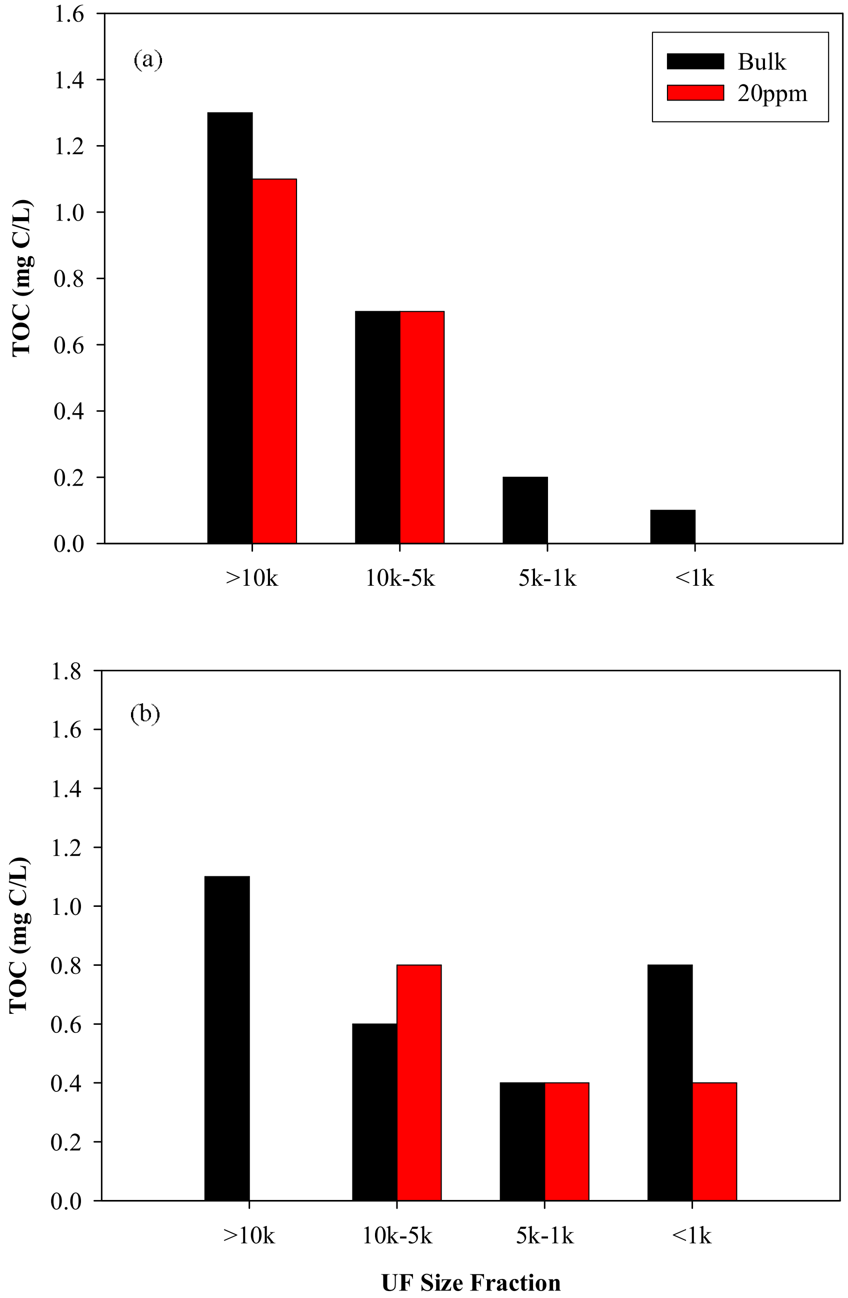

Figure 9. UF analysis in mg C/L by TOC of PAC dose 20 mg/L reacted with (a) LBWD and (b) MWD raw water.

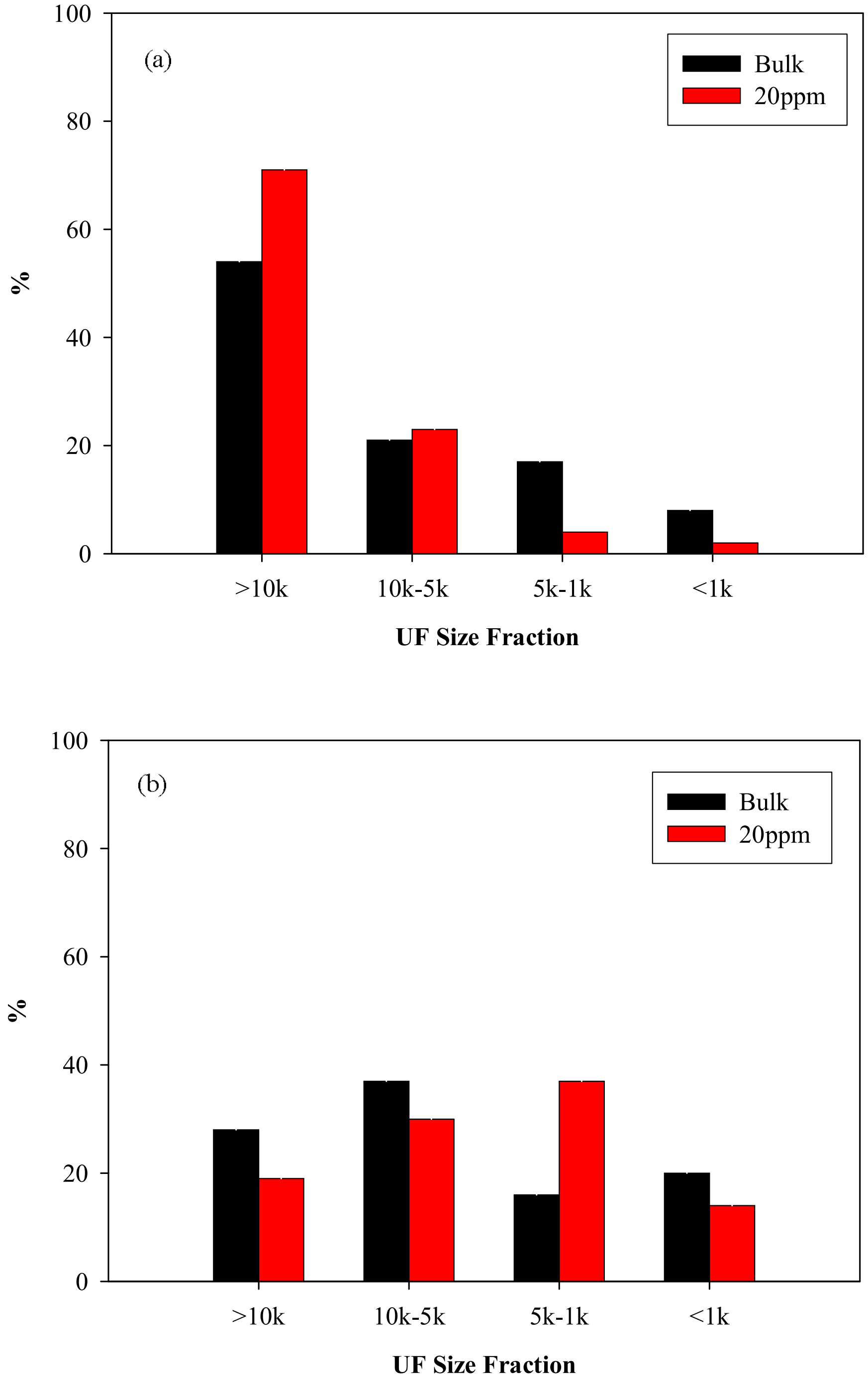

Figure 10. UF analysis in % by UV_{254} absorbance of PAC dose 20 mg/L reacted with (a) LBWD and (b) MWD raw water.

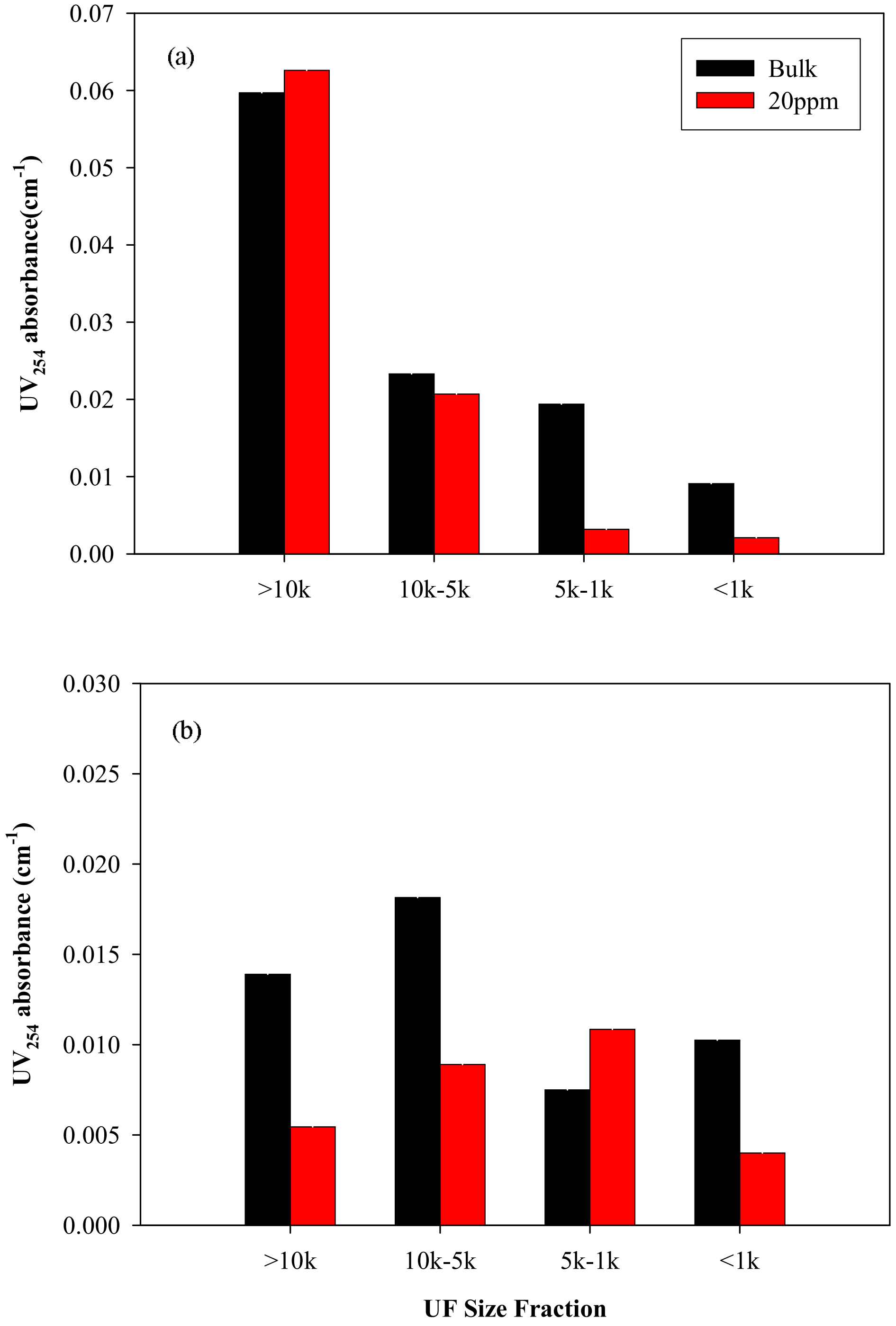

Figure 11. UF analysis in cm^{-1} by UV_{254} absorbance of PAC dose 20 mg/L reacted with (a) LBWD and (b) MWD raw water.

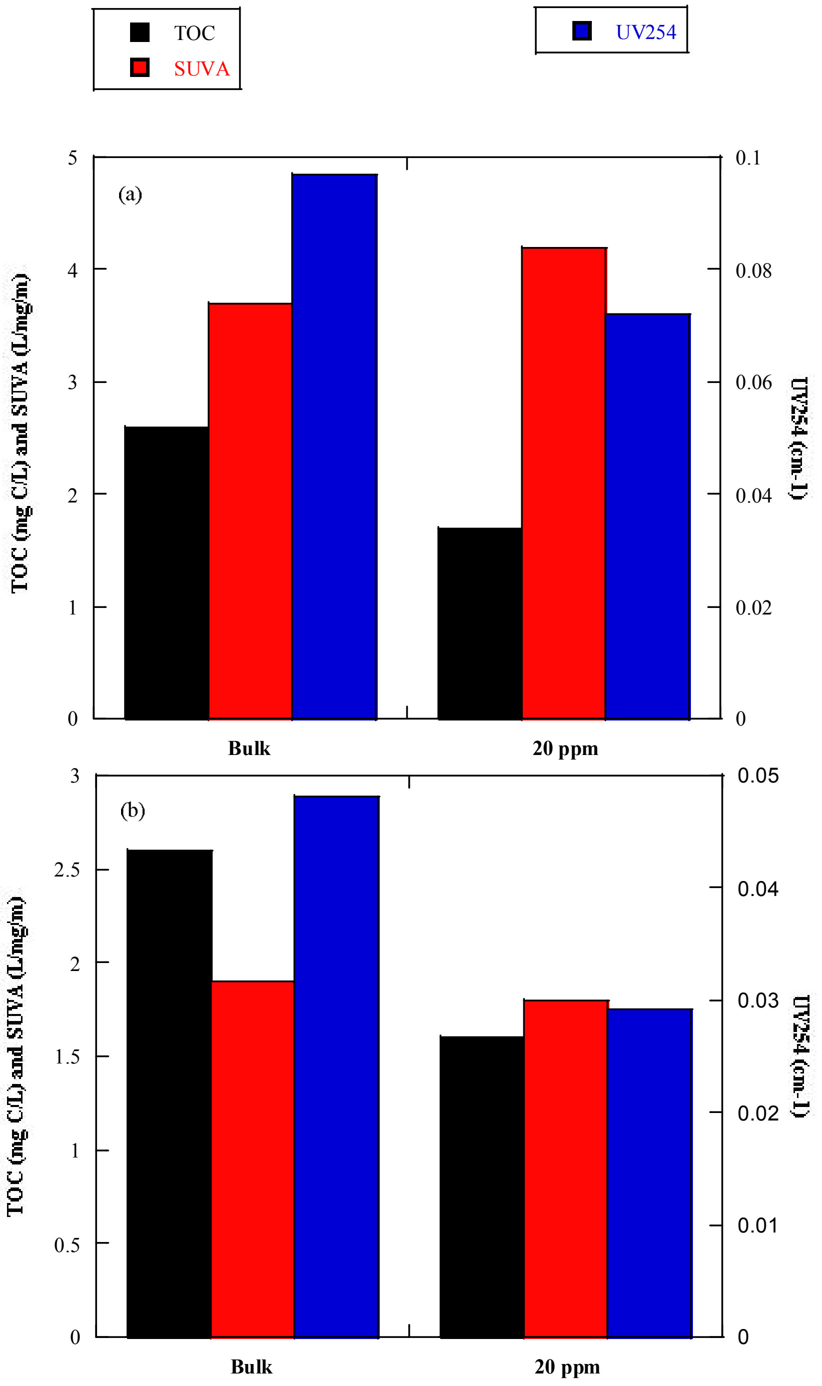

Figure 12. Changes of TOC, SUVA and UV_{254} before and after 20 ppm PAC reacted with (a) LBWD and (b) MWD raw water.

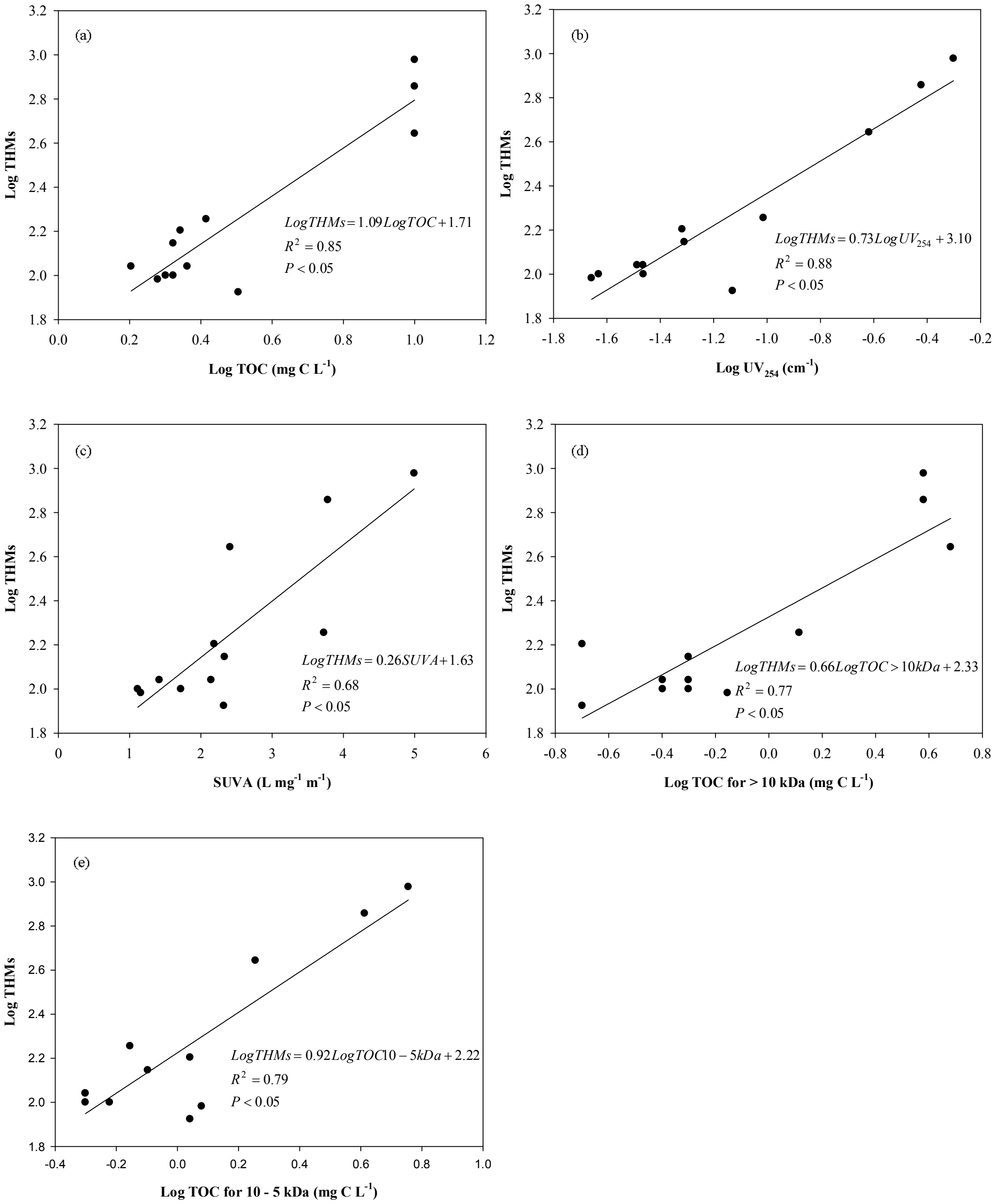

Figure 13-1. The linear regression curves between THMs and DOM characteristics (a) bulk TOC concentration (mg C/L), (b) bulk UV$_{254}$ (cm^{-1}), (c) bulk SUVA (L/mg/m), (d) TOC concentration for > 10 kDa fraction (mg C/L), (e) TOC concentration for 10 – 5 kDa fraction (mg C/L).

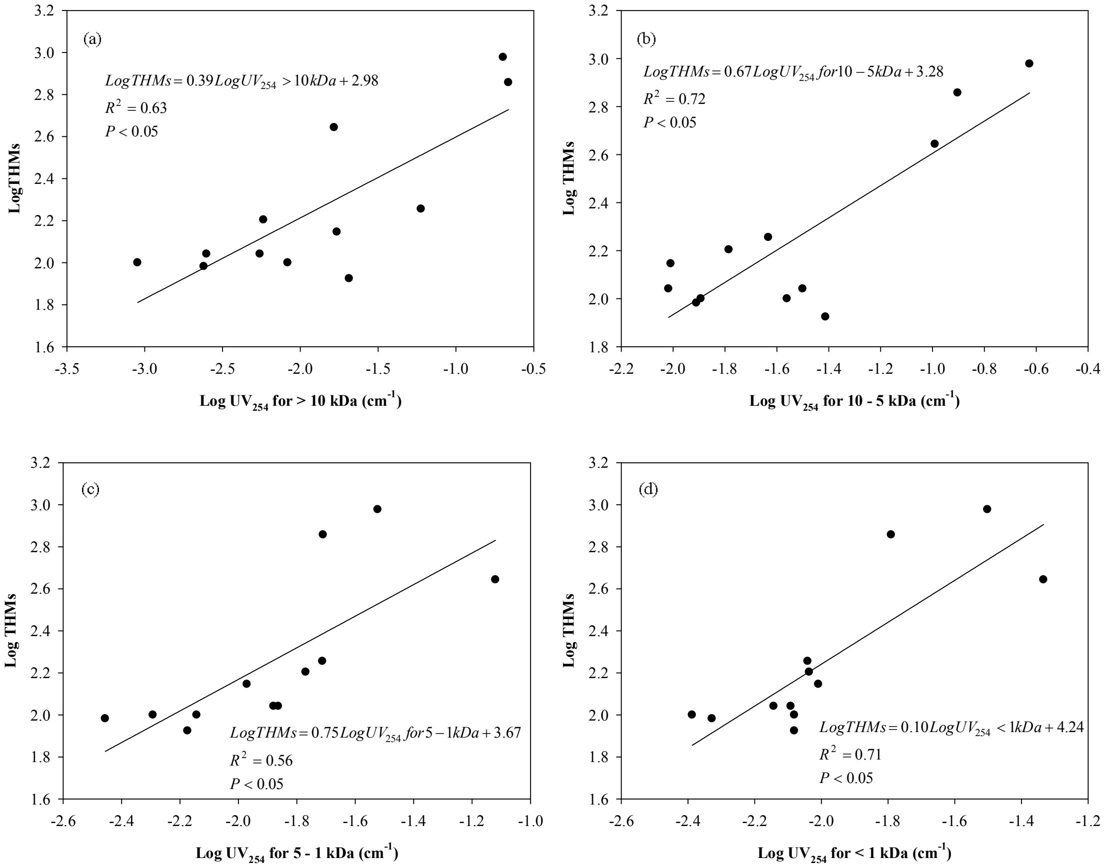

Figure 13-2. The linear regression curves between THMs and DOM characteristics (a) UV_{254} for > 10 kDa fraction (cm^{-1}), (b) UV_{254} for 10 – 5 kDa fraction (cm^{-1}), (c) UV_{254} for 5 - 1 kDa fraction (cm^{-1}), (d) UV_{254} for < 1 kDa fraction (cm^{-1}).

C.7 Tables

Table 1. Water quality parameters and THMs distribution in raw, treated, and after PAC (20 mg C/L) treatment waters.

samples	TOC (mg L^{-1})	UV$_{254}$ (cm^{-1})	SUVA (L mg^{-1} m^{-1})	pH	Conductivity (us cm^{-1})	THMs (µg L^{-1})
SRDOM	10.0	0.378	3.8	5.2	49	720
ASRDOM	10.0	0.499	5.0	7.6	425	950
FFWS	10.0	0.241	2.4	7.2	668	440
SCFP	3.2	0.074	2.3	7.5	114	84
CLWA						
Raw	2.2	0.048	2.2	8.0	300	160
Raw-waste	2.1	0.049	2.3	8.2	290	140
Ozone	2.1	0.023	1.1	7.9	290	100
Coagulation	1.9	0.022	1.1	8.0	284	96
Treated	2.3	0.033	1.4	8.1	271	110
LBWD						
Raw	2.6	0.123	3.8	8.5	378	180
Coagulation	1.6	0.034	2.1	8.0	385	110
Treated	2.0	0.034	1.7	8.2	418	100
Raw+PAC	1.7	0.072	4.2	8.7	380	140
MWD						
Raw	2.6	0.048	2.6	8.5	861	110
Treated	2.3	0.034	2.3	8.3	873	120
Raw+PAC	1.6	0.029	1.8	8.5	450	81

Table 2. Characterization of DOM and location of FRI regions (Chen et al. 2003)

Region	Characterization of DOM	Excitation Range (nm)	Emission Range (nm)
I	Aromatic proteins I	220-250	280-332
II	Aromatic proteins II	220-250	332-380
III	Fulvic acids	220-250	380-580
IV	Microbial by-products	250-470	280-380
V	Humic acids	250-470	380-580

Table 3. Correlations between Log THMs and DOM characteristics

Parameters	**unit**	**Relationship**	**R^2**
TOC	mg L^{-1}	+	**0.85**
UV_{254}	cm^{-1}	+	**0.88**
SUVA	L mg^{-1} m^{-1}	+	**0.68**
TOC for > 10 kDa	mg L^{-1}	+	**0.77**
TOC for 10-5 kDa	mg L^{-1}	+	**0.79**
UV_{254} for > 10 kDa	cm^{-1}	+	**0.63**
UV_{254} for 10-5 kDa	cm^{-1}	+	**0.72**
UV_{254} for 5-1 kDa	cm^{-1}	+	**0.56**
UV_{254} for < 1 kDa	cm^{-1}	+	**0.71**

C.8 References

Amy, G. and Cho, J. (1999) Interactions between natural organic matter (NOM) and membranes: Rejection and fouling. Water Science and Technology 40(9), 131-139.

Amy, G.L., Thompson, J.M., Tan, L., Davis, M.K. and Krasner, S.W. (1990) EVALUATION OF THM PRECURSOR CONTRIBUTIONS FROM AGRICULTURAL DRAINS. Journal American Water Works Association 82(1), 57-64.

Baghoth, S.A., Sharma, S.K. and Amy, G.L. (2011) Tracking natural organic matter (NOM) in a drinking water treatment plant using fluorescence excitation-emission matrices and PARAFAC. Water Research 45(2), 797-809.

Carter, C.W. and Suffet, I.H. (1982) BINDING OF DDT TO DISSOLVED HUMIC MATERIALS. Environmental Science & Technology 16(11), 735-740.

Ceraso, J. (1987) Development of a Surrogate Parameter to Determine the Trihalomethane Formation Potential of Two Reservoirs. Jour. New England Water Work Assn. 101(12), 382-291.

Chandrakanth, M.S. and Amy, G.L. (1996) Effects of ozone on the colloidal stability and aggregation of particles coated with natural organic matter. Environmental Science & Technology 30(2), 431-443.

Chang, C.Y., Hsieh, Y.H., Lin, Y.M., Hu, P.Y., Liu, C.C. and Wang, K.H. (2001) The effect of the molecular mass of the organic matter in raw water on the formation of disinfection by-products. Journal of Water Supply Research and Technology-Aqua 50(1), 39-45.

Chen, W., Westerhoff, P., Leenheer, J.A. and Booksh, K. (2003) Fluorescence excitation - Emission matrix regional integration to quantify spectra for dissolved organic matter. Environmental Science & Technology 37(24), 5701-5710.

Chow, A.T., Gao, S. and Dahlgren, R.A. (2005) Physical and chemical fractionation of dissolved organic matter and trihalomethane precursors: A review. Journal of Water Supply Research and Technology-Aqua 54(8), 475-507.

Christman, R.F., Norwood, D.L., Millington, D.S., Johnson, J.D. and Stevens, A.A. (1983) IDENTITY AND YIELDS OF MAJOR HALOGENATED PRODUCTS OF AQUATIC FULVIC-ACID CHLORINATION. Environmental Science & Technology 17(10), 625-628.

Cordelia J. Hwang, S.W.K., Michael J. Sclimenti, Gary L. Amy, Eric Dickenson, Auguste Bruchet, Celine Prompsy, Gisele Filippi, Jean-Philippe Croue, David Violleau (2001) Polar NOM: Characterization, DBPs, Treatment, AWWA Research Foundation and American Water Works Association, Denver, CO.

DeBano, L.F. (2000) The role of fire and soil heating on water repellency in wildland environments: a review. Journal of Hydrology 231, 195-206.

Edzwald, J.K., Becker, W.C. and Wattier, K.L. (1985) SURROGATE PARAMETERS FOR MONITORING ORGANIC-MATTER AND THM PRECURSORS. Journal American Water Works Association 77(4), 122-132.

EPA (1998) National primary drinking water regulations: disinfectants and disinfection byproducts. Final Rule. Federal Register, Wednesday, December 16, 1998, pp. 60390-69476.

Holbrook, R.D., Breidenich, J. and DeRose, P.C. (2005) Impact of reclaimed water on select organic matter properties of a receiving stream-fluorescence and perylene sorption behavior. Environmental Science & Technology 39(17), 6453-6460.

Hu, J., Song, H. and Karanfil, T. (2010) Comparative Analysis of Halonitromethane and Trihalomethane Formation and Speciation in Drinking Water: The Effects of Disinfectants, pH, Bromide, and Nitrite. Environmental Science & Technology 44(2), 794-799.

Keith E. Dennett, A.A., Anne Studstill, Thomas F. Moran, and Joseph P. Gould (1995) Humic Substance Removal and Minimization of Trihalomethanes by Ferric Chloride Coagulation, AWWA Research Foundation and American Water Works Association, Denver, CO.

Krasner, S.W., Croue, J.P., Buffle, J. and Perdue, E.M. (1996) Three approaches for characterizing NOM. Journal American Water Works Association 88(6), 66-79.

Kristiana, I, Allpike, B.P., Joll, C. A., Heitz, A. and Trolio, R. (2010) Understanding the behaviour of molecular weight fractions of natural organic matter to improve water treatment processes. Water Science and Technology 10.1, 59-68.

Lee, N.H., Amy, G., Croue, J.P. and Buisson, H. (2004) Identification and understanding of fouling in low-pressure membrane (MF/UF) filtration by natural organic matter (NOM). Water Research 38(20), 4511-4523.

Lin, Y.L., Chiang, P.C. and Chang, E.E. (2006) Reduction of disinfection by-products precursors by nanofiltration process. Journal of Hazardous Materials 137(1), 324-331.

Marhaba, T.F., Van, D. and Lippincott, L. (2000) Rapid identification of dissolved organic matter fractions in water by spectral fluorescent signatures. Water Research 34(14), 3543-3550.

Nieuwenhuijsen, M.J., Toledano, M.B., Eaton, N.E., Fawell, J. and Elliott, P. (2000) Chlorination disinfection byproducts in water and their association with adverse reproductive outcomes: a review. Occupational and Environmental Medicine 57(2), 73-85.

Norit Website; http://www.norit.com/files/documents/HDB-rev8.pdf.

Owen, D.M. (1995) NOM CHARACTERIZATION AND TREATABILITY (VOL 87, PG 46, 1995). Journal American Water Works Association 87(4), 148-148.

Reckhow, D.A., Singer, P.C. and Malcolm, R.L. (1990) CHLORINATION OF HUMIC MATERIALS - BY-PRODUCT FORMATION AND CHEMICAL INTERPRETATIONS. Environmental Science & Technology 24(11), 1655-1664.

Revchuk, A.D. and Suffet, I.H. (2009) Ultrafiltration separation of aquatic natural organic matter: Chemical probes for quality assurance. Water Research 43(15), 3685-3692.

Richardson, S.D., Plewa, M.J., Wagner, E.D., Schoeny, R. and DeMarini, D.M. (2007) Occurrence, genotoxicity, and carcinogenicity of regulated and emerging disinfection by-products in drinking water: A review and roadmap for research. Mutation Research-Reviews in Mutation Research 636(1-3), 178-242.

Rosario-Ortiz, F.L., Snyder, S. and Suffet, I.H. (2007a) Characterization of the polarity of natural organic matter under ambient conditions by the polarity rapid assessment method (PRAM). Environmental Science & Technology 41(14), 4895-4900.

Rosario-Ortiz, F.L., Snyder, S.A. and Suffet, I.H. (2007b) Characterization of dissolved organic matter in drinking water sources impacted by multiple tributaries. Water Research 41(18), 4115-4128.

Rosario-Ortiz, F.L., Gerringer, F.W. and Suffet, I.H. (2009) Application of a novel polarity method for the characterization of natural organic matter during water treatment. Journal of Water Supply Research and Technology-Aqua 58(3), 159-169.

Rosario-Ortiz, F.L., Snyder, S. and Suffet, I.H. (2007c) Analysis of polarity fractionated dissolved organic matter using 3-D fluorescence excitation-emission matrix spectroscopy. Abstracts of Papers of the American Chemical Society 233, 444-444.

Singer, P.C. (1999) Humic substances as precursors for potentially harmful disinfection by-products. Water Science and Technology 40(9), 25-30.

Suffet, I.H.a.M., I.H. (1981) Activated Carbon Adsorption of Organics from the aqueous phase, Ann Arbor Science Publisher Inc., The Butterworth Group.

Stevenson, F.J. (1994) Humus Chemistry, Genesis Composition, Reaction., John Wiley & Sons, New York.

Szlachta, M. and Adamski, W. (2009) Application of Adsorption on Powdered Active Carbon for the Removal of Dissolved Organic Substances from Surface Water. Ochrona Srodowiska 31(2), 61-66.

Taniguchi, M., Kilduff, J.E. and Belfort, G. (2003) Modes of natural organic matter fouling during ultrafiltration. Environmental Science & Technology 37(8), 1676-1683.

Tanju Karanfil, S.W.K., Paul Wsterhoff, Yuefeng Xie (2008) Disinfection By-Products in Drinking Water: Occurence, Formation, Health Effects, and Control. Tanju Karanfil, S.W.K., Paul Wsterhoff, Yuefeng Xie (ed), ACS Division of Environmental Chemistry, Inc., Washtington, DC.

Thurman, E.M. (1985) Organic Geochemistry of Natural Waters., Dr. W. Junk Publishers., Dordrecht, The Netherlands: Martinus Nijhoff, Netherlands.

Villanueva, C.M., Cantor, K.P., Grimalt, J.O., Malats, N., Silverman, D., Tardon, A., Garcia-Closas, R., Serra, C., Carrato, A., Castano-Vinyals, G., Marcos, R., Rothman, N., Real, F.X., Dosemeci, M. and Kogevinas, M. (2007) Bladder cancer and exposure to water disinfection by-products through ingestion, bathing, showering, and swimming in pools. American Journal of Epidemiology 165(2), 148-156.

Wei, Q.S., Wang, D.S., Wei, Q., Qiao, C.G., Shi, B.Y. and Tang, H.X. (2008) Size and resin fractionations of dissolved organic matter and trihalomethane precursors from four typical source waters in China. Environmental Monitoring and Assessment 141(1-3), 347-357.

Wu, W.W.C., P.A.; Davis, W.M.; Delfina, J.J.; Powell, D.H. (2000) Natural Organic Matter and Disinfection By-Products: Characterization and Control in Drinking Water. S.E. Barrett, S.W.K., G.L. Amy (ed), pp. 109-121, American Chemical Society, New York, NU.
Yan, M., Wang, D., Shi, B., Wang, M. and Yan, Y. (2007) Effect of pre-ozonation on optimized coagulation of a typical North China source water. Chemosphere 69(11), 1695-1702.

Zhang, X.G. and Minear, R.A. (2002) Characterization of high molecular weight disinfection byproducts resulting from chlorination of aquatic humic substances. Environmental Science & Technology 36(19), 4033-4038.

D. Chapter 4:

Research Paper 3

Bioavailability of Hydrophobic Organic Pollutants after Powdered Activated Carbon Treatment of Drinking Water

D.1 Abstract

Hydrophobic organic pollutants (HOPs), such as polycyclic aromatic hydrocarbons (PAHs) from automobile exhausts and dissolved organic matter (DOM) are ubiquitous in the aquatic environment. The interaction between DOM and HOPs minimizes the bioavailability of HOPs and their potential health effects. Powdered activated carbon (PAC) is one of the most effective methods to adsorb DOM as well as HOPs and thus decreases trihalomethanes (THMs) and HOPs during drinking water processes, respectively. This research studied the effect of PAC on the interaction of DOM-HOPs and the effect of THM removal during PAC drinking water treatment. This study found PAC changed the DOM size, polarity and chemical components distribution of the DOM and decreased DOC, UV_{254} and SUVA values. PAC can effectively remove TOC, UV_{254}, DOM size fractions smaller than 5 kDa and some larger than 10 kDa DOM that would affect THMFP removal. Surprisingly, PAC did not change the binding ability of DOM to interact with HOPs during this water treatment study. The PAC treatment used in this study might be an effective method to control both THMs and hazard potential of HOPs through

removing specific DOM characteristics. Various DOM characteristics behave differently during the treatment and need to be monitored.

D.2 Introduction

Hazardous hydrophobic organic pollutants (HOPs) are defined as those compounds with a log octanol-water partition coefficient over five. Polycyclic aromatic hydrocarbons (PAHs) represent such a group of hydrophobic compounds that include over 100 different chemicals. PAHs are primarily generated from incomplete fossil fuel burning, oil spills, and other industrial processes (1). The U.S. Environmental Protection Agency (U.S. EPA) has listed 16 PAHs as priority pollutants in the aquatic environment due to their levels of toxicity and potential carcinogenicity (2). The U.S. EPA sets the maximum contaminant level in drinking water at 200 ng/L for benzo(a)pyrene (3). The European Union Directive 98/83/EC sets the maximum total concentration of four PAHs (benzo(b)fluoranthene, benzo(k)fluoranthene, benzo(ghi)perylene, and indeno(1,2,3-cd)pyrene) at 100 ng/L in drinking water, and at 10 ng/L for benzo(a)pyrene (4).

Dissolved organic matter (DOM) is functionally defined as < 0.45 um in size. In this study we used a non-organic glass membrane filter of < 0.7 um to define DOM. DOM is a mixture of anionic macromolecules and submicron colloids. Chemically, DOM is a heterogeneous mixture of aromatic and aliphatic organic compounds containing nitrogen, oxygen, and sulfur functional groups stemming from decomposing organisms and biological activity in waters (5-7). Drinking water sources contain DOM at 1 to > 10 mg C/L (7). Aquatic DOM components are classified to be humic substances, hydrophilic acids, carboxylic acids, amino acids, carbohydrates, and hydrocarbons (7). DOM transformation is a very important issue in water treatment processes because DOM is one of the main causes of disinfection byproducts (DBPs) (7-11) and membrane fouling (12-14). DOM also has the ability to associate (bind or sorb) with HOPs such as PAHs in natural waters which can enter drinking water treatment plant (15-17). The association of HOPs and DOM occurs primarily as a linear association between a bound and free PAH. This binding behavior is primarily described by a binding equilibrium constant, K_{DOM}:

$$\text{PAH (soluble, free)} + \text{DOM} \overset{K_{DOM}}{\Longleftrightarrow} \text{PAH} - \text{DOM (bound)} \quad (1)$$

The free soluble form is hazardous because it is bioavailable. The bound form is not bioavailable.

The free and bound PAH can change during water treatment due to DOM oxidation (e.g. chlorination or ozonation), coagulation, and sorption (e.g., powdered activated carbon [PAC] adsorption). The binding increases the overall solubility of HOPs in water by facilitating their sorption to DOM, and therefore, potentially enhances their transport (15-17). Simultaneously as this occurs, DOM can form disinfection byproducts (DBPs) such as trihalomethanes (THMs) that are also potential carcinogens for humans.

Powdered activated carbon can be used to remove organic compounds from water such as PAHs. PAC can also adsorb DOM and is one of the most effective technologies to control DBPs such as THMs and haloacetic acids (HAAs). This DOM is commonly called the THM formation potential (THMFP). PAC is relatively cost effective, does not require large capital expenditure, and only needs to be applied when water quality notably worsens (18). The extent of THMFP reduction by PAC is mainly dependent on the type of PAC and the type of DOM in the source water treated (18, 19). However, the effect of PAC on the interaction between HOPs with DOM is not clear. Furthermore, the relationship between specific characteristics of DOM and THMFP and the interaction of DOM and HOPs need to be disentangled. Understanding the behavior of DOM sub-fractions to form DBPs as well as interact with HOPs to form DOM-HOPs complexes before and after PAC treatment can help minimize any potential drinking water hazard from either interaction.

The objective of this study is understand how PAC treatment affects the interactions of DOM-HOPs and the formation of THMFPs to enable water treatment processes to minimize both problems and produce the best quality drinking water.

D.3 Experimental

Sample Preparation

The Long Beach Water Department (LBWD) and Weymouth Water Treatment Plant (The Metropolitan Water District of Southern California, MWD) provided raw water samples from their treatment plants for this study. The water quality parameters for this study are listed in supporting information (Table S1).

All samples were filtered through 0.7 μm glass fiber membranes (Whatman Corp. Sanford, ME) prior to any analysis procedure to remove filterable organic matter and microorganisms which may consume DOM. All membranes were baked for 24 hours at 100 ^{o}C and rinsed before use to reduce leaching of organics from the membranes during filtration.

Fluorescence Quenching to Determine Sorption Coefficient of DOM (K_{DOM})

The sorption coefficient of DOM ($K_{DOM\,(P)}$) was determined by fluorescence quenching (FQ). Perylene a non-toxic PAH was used as a probe for other PAHs. Perylene was diluted in methanol to a 4 mg/L perylene stock solution and stored in an amber bottle at 4 ^{o}C. Stock solution was diluted to 0.3 μg/L perylene and added to DOM diluted samples to a final concentration of three-fourths of the reported solubility of 0.4 μg/L in water (20). To control for the loss of perylene from adsorption to the cuvette walls, 12 measurements were made at defined time points (2 minute intervals) to allow for extrapolation to initial conditions. Experiments were performed in a dimmed environment to prevent the photodegradation of perylene. This study assumed partitioning of PAHs between water and DOM was fast compared to the adsorption of PAHs to the cuvette wall. Sorption behavior can be modeled by:

$$PAH_d \underset{k_{-w}}{\overset{k_w}{\Leftrightarrow}} PAH - wall \qquad (2)$$

where PAH$_d$ is the dissolved portion of the total PAH concentration, PAH-wall is the portion adsorbed on the wall, and k$_w$ and k$_{-w}$ are first-order forward and backward rate constants for wall adsorption.

Fluorescence intensity can be obtained by

$$F = \frac{k_{-w}F_0'}{k_w + k_{-w}} + \frac{k_w F_0'}{k_w + k_{-w}} e^{-(k_w + k_{-w})t} \qquad (3)$$

where F$_0$' is the free PAH intensity at time zero. Nonlinear curve-fitting program (SigmaPlot) was used to get F$_0$', k$_w$, and k$_{-w}$. K$_{DOM}$ values were determined by the Stern-Volmer equation which can be described as

$$\frac{F_0}{F} = 1 + K_{DOM}[DOM] \qquad (4)$$

where F$_0$ and F are the fluorescence intensities in the absence and presence of DOM. [DOM] is the concentration of DOM measured as mg C/L (21). The percentage of bound PAH can be determined by equation 5 (22):

$$\%bound = \frac{K_{DOM}\left[DOM\right]}{1 + K_{DOM}\left[DOM\right]} \times 100 \qquad (5)$$

All measurements of fluorescence intensities were obtained by a fluorescence spectrophotometer (Varian, R3896) at an excitation-emission wavelength pair of 434 and 467 nm. Absorbance values at 434 and 467 nm were corrected for inner filtering effects (IFEs) which were usually below 1.2 by UV-Vis spectrophotometer (Shimadzu UV-1700) (23).

The relationship between C_{total} to C_{free} can be expressed as:

$$\frac{C_{bound}}{[DOM]} = \frac{C_{total} - C_{free}}{[DOM]} = K_{DOM}C_{free} \qquad (6)$$

where C_{total} and C_{bound} are the total and bound PAH concentrations (w/v). Rearranging equation 6 provides

$$\frac{C_{total}}{C_{free}} = 1 + K_{DOM}[DOM] \qquad (7)$$

Therefore, K_{DOM} can be obtained by plotting C_{total}/C_{free} against the concentration of DOM with a y-axis intercept set to 1.

Trihalomethanes

THMs were measured as a formation potential in this study. All samples were chlorinated according to Standard Method 5710 B (Trihalomethanes Formation Potential, THMFP) under 25 ± 2 ^{o}C for 7 days. Chlorine residuals in samples were quenched by sodium sulfite (Na_2SO_3) before THMs analysis. The final THMs formed was analyzed in MWH laboratories (Monrovia, California).

Powdered Activated Carbon

The adsorbent used in this research was HYDRODARCO B powered activated carbon (Norit Americas Inc., USA), which is produced by steam activation of lignite coal. This PAC was chosen because it effectively removes the precursors of trihalomethanes (THMs) and major contributors to color (18). PAC doses of 5, 10, 15, 20 and 25 mg C/L were chosen to be added into 200 ml raw water samples from LBWD and MWD to do preliminary tests. Due to the large volume needed for ultrafiltration (UF) analysis, PAC dose 20 mg/L was used to react with another set of raw water samples from LBWD and MWD to understand the changes of size fractions after PAC treatment (1500 ml raw water samples). Adsorption time was set 24 hours to ensure the reaction reach equilibrium; all tests were held in the dark at 20 ± 2 ^{o}C. During the adsorption, stir bars were added to make the solution homogeneous and beakers were covered by foil to prevent evaporation and reaction with light. After the PAC adsorption, samples were filtered through 0.7 μm glass fiber membranes (Whatman Corp., Sanford, ME) to remove PAC prior to any analysis.

DOM Characterization

DOM characteristics were measured according to “Standard Methods for the Examination of Water and Wastewater” (2012) (24) for: 1) total concentration of organic carbon by dissolved organic carbon (Method 5310B), 2) aromaticity by UV absorbance and specific UV absorbance (SUVA) (Method 5910), 3) size distribution by ultrafiltration (UF) (25), 4) polarity by polarity rapid assessment method (PRAM) (26), and 5) UV and fluorescent chemical DOM components by UV spectrometer and fluorescence excitation-emission matrix (EEM) and fluorescence regional integration (FRI) (5). More details of UF, PRAM, and FRI were described in the supporting information.

D.4 Results and Discussion

Change of DOC and UV and SUVA after PAC Treatment

Figure 1 showed the changes of TOC (mg C/L), SUVA (L/mg/mg) and UV_{254} (cm^{-1}) of LBWD and MWD raw water samples before and after the addition of 20 mg/L PAC treatment. The TOC decreases for both LBWD and MWD raw waters by about 65%: 2.6 to 1.7 mg C/L for LBWD and 2.6 to 1.6 mg C/L for MWD, respectively. In addition, UV_{254} decreased to 74% and

61% of the original value for LBWD and MWD after PAC treatments, respectively. This indicates that PAC removed some aromatic parts of DOM in the waters. However, SUVA increased in LBWD samples but did not change significantly in MWD after PAC treatment, indicating site specificity of DOM. Szlachta and Adamski (2009) also showed the same trend that UV_{254} and DOC concentration decreased by increasing the dose of PAC reacted with surface water (27).

Figure 2 shows the relationship of PAC adsorption and DOM in LBWD and MWD raw water. X represents the amount of DOM adsorbed on PAC and m represents the amount of PAC. C_e represents the equilibrium concentration of DOM in the water in terms of mg/L of PAC. In this study, the adsorption results matched the Freundlish isotherm with high correlation ($R^2 = 0.95$ and $R^2 = 0.98$ for LBWD and MWD, respectively). Previous researchers have showed that the adsorption behavior of activated carbon for organic substances usually follows the Freundlich model (28, 29).

The Freundlish isotherm equations for this study for LBWD and MWD respectively are:

$$Log\frac{x}{m} = 1.79 Log C_e - 2.26 \quad (8)$$

and

$$Log\frac{x}{m} = 3.01 Log C_e - 2.27 \quad (9)$$

The Freudlich isotherm can be used to determine the minimum PAC usage, x for any desirable level of PAC treatment quantified as C_e for LBWD and MWD raw water. From the isotherms, the PAC can adsorb more DOM from MWD raw water than from the raw water at LBWD.

Changes of DOM Size Fractions after PAC Treatment

This study chose a PAC dose of 20 mg/L for UF analysis due to large volumes of samples needed for UF analysis (1.2 liters for duplicate analysis). The size fraction results of LBWD and MWD were presented from Figure 3 to Figure 6. Figure 3 and 4 present the results measured by TOC in % and mg C /L. Figure 5 and 6 present the results measured by UV_{254} absorbance in % and absorbance values. Figure 3 shows that for LBWD raw water, the percentage fractions of 5 - 1 kDa and < 1 kDa decreased to zero after 20 mg/L of PC is added as measured by TOC in %. This increased the percentage fractions of > 10 kDa and 10 - 5 kDa left in solution as measured by TOC in %. In LBWD, PAC appears to adsorb smaller fractions (< 5kDa) instead of larger size fractions of DOM.

The UF data of MWD raw water treated by 20 mg/L of PAC showed completely different results by TOC in % analysis. PAC mainly removed >10 kDa and some < 1 kDa fractions and thus led to increase of 10 - 5kDa and 5 - 1 kDa fractions in MWD.

Figure 4 shows that for LBWP raw water, smaller fractions (5 – 1 kDa and < 1 kDa) of DOM were all adsorbed by PAC. However, the amount of 10 - 5 kDa remained the same and the amount of > 10 kDa decreased indicating that PAC might specifically remove DOM with size fractions smaller than 5 kDa and larger than 10 kDa in LBWD.

In the MWD raw water adsorption experiment, for TOC concentration, > 10 kDa was completely adsorbed and < 1 kDa decreased from 0.8 to 0.4 mg C/L; 10 - 5 kDa increased from 0.6 to 0.8 mg C/L, and 5 - 1 kDa fractions did not change after PAC treatment. The UF size fractions distribution in terms of TOC (mg C/L) after PAC treatment was similar to the results of LBWD raw water that PAC mainly removed > 10 kDa and < 1 kDa fractions.

Figure 5 and 6 were the results of LBWD and MWD UF size fractions analysis in terms of percentage and UV_{254} absorbance (cm^{-1}) by measuring UV_{254} of different fractions. Figure 5 showed that even though UV_{254} is only part of TOC concentrations, the percentage UF size fractions behaved similarly as measuring TOC in percentage (Figure 3), especially for LBWD. Nevertheless, in LBWD raw waters adsorption, although UF size fractions for 10 - 5 kDa, 5 - 1 kDa and < 1 kDa measured by UV_{254} absorbance (Figure 6) showed similar trend as measured by TOC (Figure 4), > 10 kDa fraction showed differently between these two measuring methods. After LBWD raw water treated by PAC, the > 10 kDa fraction in terms of TOC decreased, however, the > 10 kDa fraction in terms of UV_{254} increased indicating that although PAC adsorbed and removed some > 10 kDa TOC concentration, the main DOM removed was not an aromatic structure.

For UV_{254} absorbance analysis, MWD results were not similar to the LBWD results. In MWD raw water, PAC removed > 10 kDa, 10 - 5 kDa and < 1 kDa. However, in LBWD, PAC removed 10-5 kDa, 5 – 1 kDa, and < 1 kDa fractions. This showed although DOM removal mechanism for different size by TOC of PAC was similar between two different raw water sources, the removal mechanisms for different structures of DOM in different raw waters were different. Furthermore, comparing Figure 4 and 6, it is likely that MWD raw water's 10 - 5 kDa fraction was mainly composed of non-aromatic structure DOM and the 5 - 1 kDa fraction was mostly composed of aromatic after PAC treatment due to different changes of the ratios between TOC concentration and UV_{254} absorbance. The effect of adding 20 mg/L PAC to LBWD and MWD raw waters for UF size fractions is listed in Table 1. The numbers represent the ratios (%) increased or decreased after 20 mg/L PAC treatment compared to raw waters.

In summary, even though PAC effectively removes the DOM from the bulk samples as measured by TOC and UV_{254}, the size fractions behaved differently during the treatment and need to be monitored.

Changes of Flourescence after PAC Treatment

Figure 7 shows the FRI results of different doses of PAC added to LBWD and MWD raw water samples. For LBWD raw water, as the PAC dose increased from 5 to 25 mg/L, the fulvic acids decreased from 28% to 54%, humic acids decreased from 10% to 39% and the aromatic proteins

II decreased from 49% to 70%. Aromatic proteins I and microbial by-products were not removed. Similar adsorption reaction results were presented in MWD raw water. As the PAC dose increased from 5 to 25 mg/L the fulvic acids decreased from 28% to 65%, humic acids decreased from 22% to 58%, and the aromatic proteins II decreased from 57% to 72%. Also at MWD, aromatic proteins I had a removal rate up to 37% and the microbial by-products had a removal rate up to 49%. The results showed that removal of fulvic acids, humic acids, and aromatic protein II can likely result in increase of microbial by-products in LBWD. The more polar microbial by-products that are primarily amino acids such as tyrosine might be too polar to be adsorbed to PAC in LBWD. This group can now be observed as the other DOC material is removed.

Figure 8 presents the FRI result of LBWD and MWD raw water before and after a 20 mg/L PAC treatment. In LBWD samples, fulvic acids decreased 49%, humic acids decreased 40%, aromatic proteins I and II decreased 22% to 60%, and microbial by-products increased 73%. In MWD samples, fulvic acids decreased 45%, humic acids decreased 33%, aromatic proteins I and II decreased 9% to 53%, and microbial by-products decreased 28% after a 20 mg/L PAC treatment. Thus, PAC does remove fulvic and humic acids and aromatic proteins II fractions more efficiently from LBWD and MWD.

The overall results indicate that PAC used in this study adsorbs DOM effectively. However, site specific adsorption behaviors between PAC and DOM were apparent between LBWD and MWD waters. In addition, in LBWD, DOM shows it has more microbial by-products present after PAC adsorption of other components. Apparently, the fluorescent signal was not able to be seen when the other components were present. This phenomenon also occurred in previous study when the aromatic proteins fluorescence was observed after fulvic and humic acids were adsorbed by SPE cartridges (C18, Diol, and NH2) during PRAM analyses (30, 31) and removed by UF membranes (10k, 5k, and 1k MWCO membranes) (30).

Changes of DOM Polarity after PAC Treatment

Figure 9 displays the results of PRAM polarity analysis as the PAC dose increased from 5 to 25 mg/L, for LBWD raw water. The DOC decreased from 3.2 to 2.5 mg C/L. The RC of NH_2 type weak anion exchange (negative charge) decreased from 92% to 82% and the RC of Diol increased from 0% to 40% by increasing PAC doses. The RC of C18 ranged from 7% to 21%. The results showed that PAC can effectively remove DOM and decrease the negative charge components. Another set of experiments by adding 20 mg/L PAC only to LBWD and MWD raw waters was presented in Figure 10. Figure 10 shows that the RC of NH_2 weak anion exchange SPE is decreased from 96 % to 88% and 60% to 51%, C18 decreased from 12 to 11% and 13 to 8 % and Diol increased from 0 to 8% and 5 to 11%, respectively. Figure 9 and 10 illustrate that, by decreasing the negative charges and non-polar fractions, polar fractions increased. However, PAC dose might need to remain above 20 mg/L to ensure non-polar removal of DOM.

Analysis of K_{DOM} after PAC Treatment

Log K_{DOM} values of LBWD raw water and after PAC adsorption (PAC dose: 20 mg/L), were all 5.8. For MWD raw water test, after PAC dose 20 mg/L treatment, the Log K_{DOM} value also did not significantly change either (from 5.0 to 4.9) (Table 2). This result indicated that PAC used in this study might be suitable to remove DOM for LBWD and MWD raw water and simultaneously keep higher Log K_{DOM} to produce water that have less hazardous potential from the free concentrations of HOPs.

Raw water samples of LBWD still had the same Log K_{DOM} values after PAC removed DOM and thus continued to keep the ability to bind with HOPs and make HOPs less bioavailable. Previous results showed that Log K_{DOM} values had higher correlation with bulk SUVA (74%), and moderate correlation with bulk UV_{254} (50%), the amount of fulvic acids components (58%), TOC concentration of 10 - 5 kDa (44%), UV_{254} for > 10 kDa (54%) and 10 -5 kDa (46%) fractions (30). For the PAC adsorption experiments of LBWD raw water, Log K_{DOM} values were better correlated with bulk SUVA, the 10 - 5 kDa size fraction concentration and UV_{254} for > 10 kDa because SUVA increased and other two parameters stayed the same following PAC adsorption. In contrast, although fulvic acids, TOC and UV_{254} decreased after PAC adsorption, these parameters did not significantly affect K_{DOM} values. For MWD raw water, the reason that Log K_{DOM} values did not change significantly after PAC treatment might be that Log K_{DOM} value had more correlation with bulk SUVA, 10 - 5 kDa fraction concentration, and UV_{254} in 5 -1 kDa fraction in this case.

FRI, TOC, UV_{254} and K_{DOM} Analysis of Different Size Fractions of MWD Raw Water before and after PAC Treatment

In order to further understand the changes of K_{DOM} and DOM characteristics, this study also analyzed different size fractions components by FRI, TOC, UV_{254} and K_{DOM}. For size fractions > 10 kDa, > 5 kDa and > 1 kDa, analysis was performed for water samples called retentate which represents the part retained above each different size membranes. On the other hand, for size < 10 kDa, < 5 kDa and < 1 kDa, analysis was performed for water samples called filtrate which represents the part filtered through each different size membranes. Figure 11 shows the FRI results of different size fractions of MWD raw water sample before and after 20 ppm PAC treatment. The trend of size distributions for aromatic proteins II, microbial byproducts and humic acids remained similar before and after PAC treatment. Aromatic proteins I and fulvic acids showed more variation across size fractions. For fulvic acids, the factor which might lead to higher K_{DOM} (30), after PAC treatment, > 10 kDa, > 5 kDa, < 5 kDa, > 1 kDa and < 1 kDa decreased 13%, 16%, 19%, 3% and 39%, respectively. Only < 10 kDa increased 7% after PAC treatment. For aromatic proteins I, < 5 kDa and < 1 kDa increased significantly after PAC treatment.

Figure 12 represents TOC and UV_{254} distributions in different size fractions. For TOC, < 10 kDa and < 5 kDa increased, other fractions decreased after PAC treatment. For UV_{254} analysis, all absorbance decreased after PAC treatment. However, UV_{254} of < 5 kDa stayed almost the same after treatment.

This study also tested the K_{DOM} values of > 5 kDa and < 5 kDa size factions before and after PAC treatment. The results show that after PAC treatment, Log K_{DOM} value increased slightly from 4.6 to 4.7 for > 5 kDa and decreased from 4.9 to 4.3 for < 5 kDa. This confirms the finding that in MWD, K_{DOM}'s lack of significant change was due to more binding with 10 – 5 kDa fractions. Furthermore, in Figure 11, fulvic acids within < 10 kDa fraction was the only component increased after PAC treatment. In Figure 12, TOC for < 10 kDa also increased after PAC treatment. These DOM parameters all indicate that K_{DOM} remained similar before and after PAC treatment in MWD water.

Analysis of THMs after PAC Treatment

In order to explore the effect of PAC treatment on water quality, this study also examined the trihalomethane formation potential (THMFP) in terms of total THMs concentration to further understand the changes of K_{DOM} and THMFP before and after PAC treatment. As shown in Table 3, in LBWD, THMs concentration decreased from 180 to 140 μg/L. For MWD raw water, the THMs concentration before and after PAC treatment were 110 and 81 μg/L, respectively. This finding suggests that PAC 20 mg/L can remove THMs from raw water with DOC concentration 2.6 mg C/L around 22% to 26% in this study. After PAC dose 20 mg C/L treatment, the bulk TOC concentration decreased from 2.6 to 1.7 mg C/L and 2.6 to 1.6 mg C/L, bulk UV_{254} decreased from 0.097 to 0.072 and 0.048 to 0.029 cm^{-1} for LBWD and MWD, respectively. Also, TOC for > 10 kDa, 5 – 1 kDa and < 1 kDa fractions all decreased for both

LBWD and MWD after PAC treatment. UV_{254} absorbance decreased in 10 – 5 kDa, 5 – 1 kDa, and < 1 kDa fractions for LBWD, and decreased in > 10 kDa, 10 – 5 kDa and < 1 kDa fractions for MWD. Previous studies have demonstrated that high UV_{254}, SUVA and aromaticity of DOM tend to form more THMs (32-34). Furthermore, Hsu and Suffet (2012) (30) also found that THMFP had higher correlations with TOC (85%), UV_{254} (88%), SUVA (68%), TOC of > 10 kDa (77%), 10-5 kDa (79%); and UV_{254} of > 10kDa (63%), 10-5 kDa (72%), 5-1 kDa (56%), and < 1kDa (71%). In addition, Chang et al. (2001) and Wei et al. (2008) reported that lower molecular weight of organic substance (average molecular weight < 1 kDa) contributed the majority of DBPs (33, 34). Kristiana et al. (2010) also found low molecular weight DOM fractions produced significant amounts of DBPs (35). From the results obtained here is that PAC removes DOM (as TOC and UV_{254} absorbance) which represent THMs precursors and aromatic parts of DOM and thus leads to decreasing THMs.

Implication of K_{DOM} and THMs Analysis

The result showed that PAC used in this study might be suitable to remove DOM for LBWD and MWD raw waters. The reason is that PAC can effectively remove total DOM content (TOC concentration), some fractions of DOM, aromatic contents of DOM and some portion of fulvic acids and non-polar parts of DOM which might be the precursors of THMs and thus decrease THMs formation. On the contrary, raw water samples of LBWD and MWD still had the same K_{DOM} values after PAC removing DOM and thus continued to keep the ability to bind with HOPs and make HOPs less bioavailable.

Understanding the characteristics of DOM and its effect on raw water and throughout treatment processes provides important information to water treatment agencies. Keeping water having higher K_{DOM} and decreasing THMFP can decrease the damage from HOPs, attack of terrorists or accidental spill events. It can also help to decrease the operating cost of treatment and match more stringent DBPs regulation by removing DOM effectively and more specifically. Comparing the results between K_{DOM} and THMs in this study, in order to reach the goal that water can have high K_{DOM} and low THMs, water treatment should remove TOC of DOM and more specifically remove TOC for size fractions of > 10 kDa, 5 - 1 kDa and < 1 kDa, and UV_{254} for smaller size fractions.

Integrating all results, PAC used in this study might be able to adsorb more fulvic and humic acids and aromatic proteins II. Following the adsorption of fulvic and humic acids and aromatic proteins II, DOM might release more microbial by-products. In addition, PAC can remove non-polar and negative charge parts of DOM while increasing polar parts.

PAC appears to be an effective method to control both THMs and hazard potential of HOPs through removing specific DOM characteristics. After PAC treatment, this study found that THMs decreased, but on the other hand K_{DOM} values did not change significantly. Our findings suggest that PAC can decrease THMs by removing DBPs precursors while allowing other DOM to have more binding ability to reduce HOPs bioavailability.

Exploring the relationship between characteristics of DOM and HOPs and THMs can offer valuable knowledge to guide water agencies towards optimization of water treatment processes and to obtain better water quality. The monitoring protocol and analysis methods of this research should be applied to other unit operations and water treatment plants to continue to disentangle the complexities of DOM effects on pollutants formation and removal in drinking water.

D.5 Figures

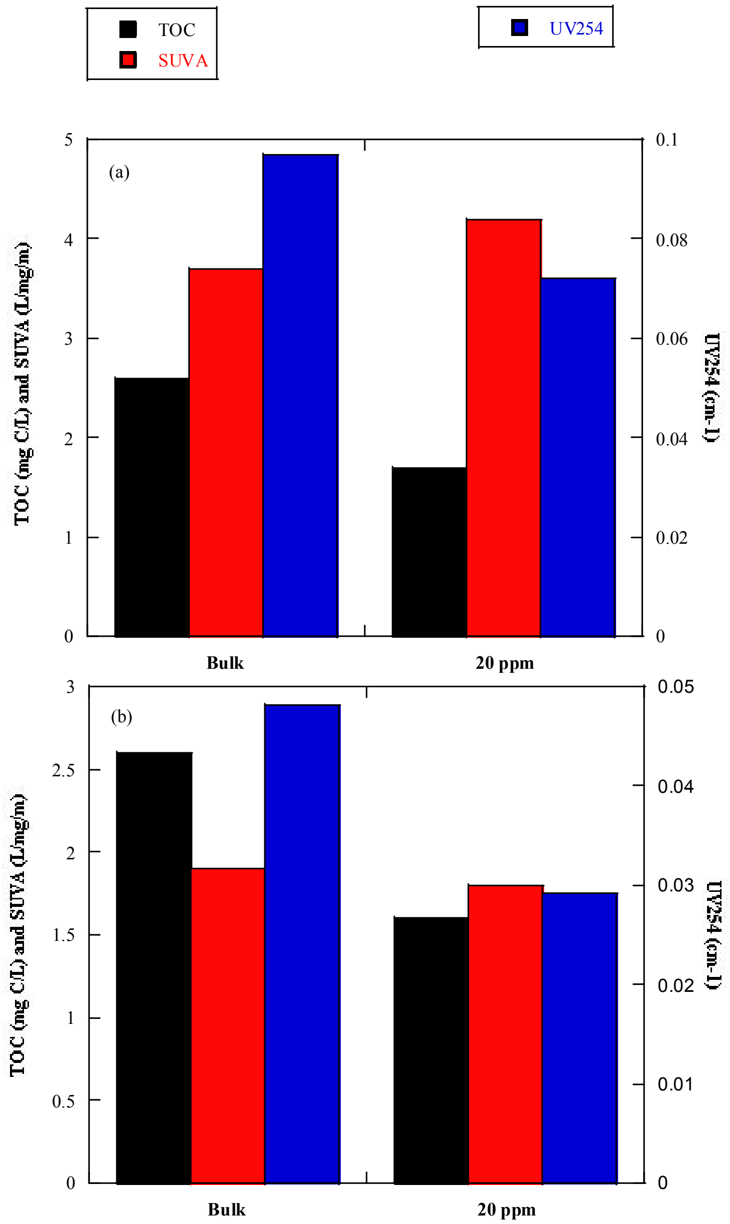

Figure 1. Changes of TOC, SUVA and UV_{254} before and after 20 ppm PAC reacted with (a) LBWD and (b) MWD raw water.

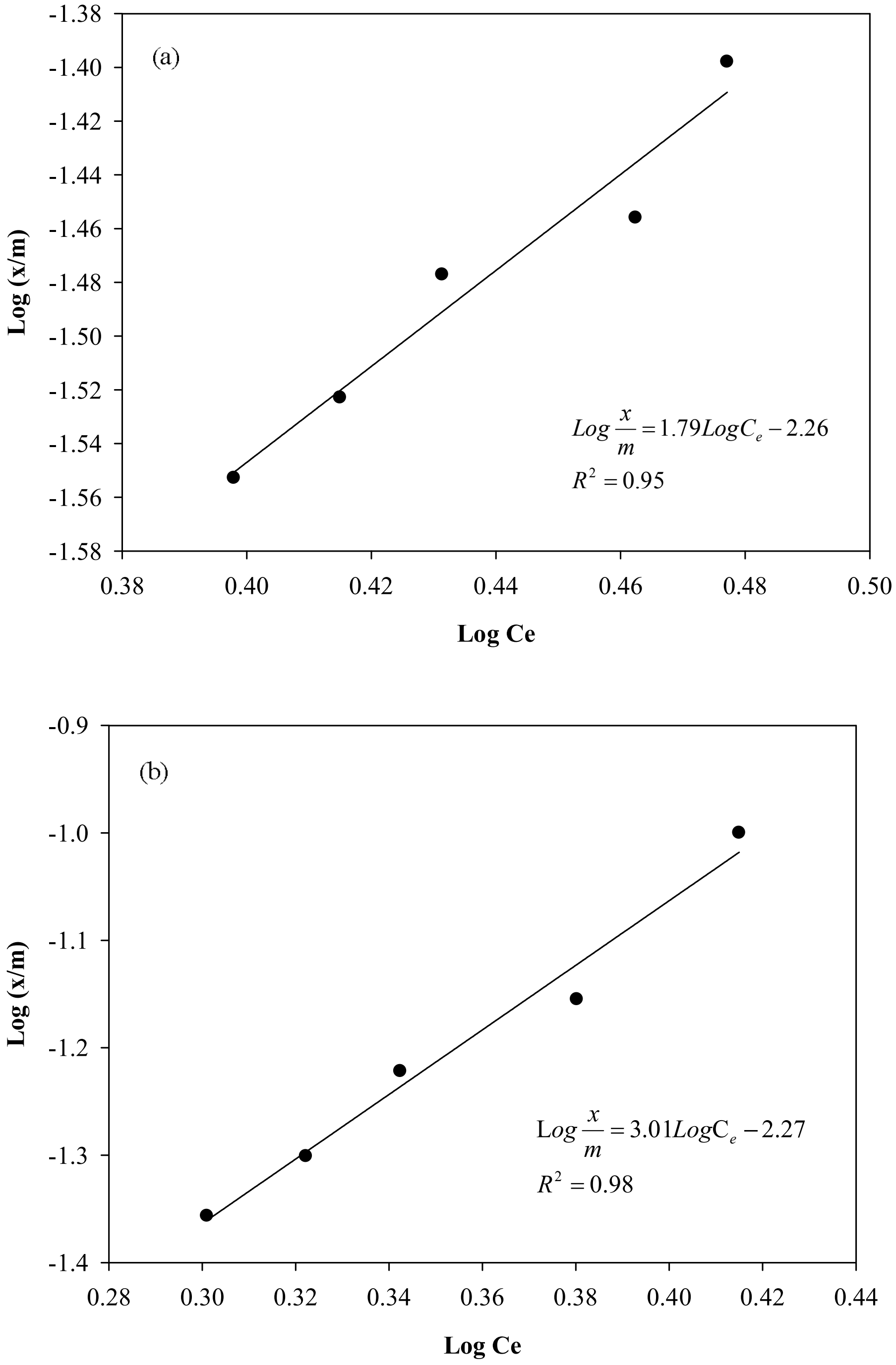

Figure 2. Freundlish isotherm of different doses of PAC reacted with (a) LBWD and (b) MWD raw water.

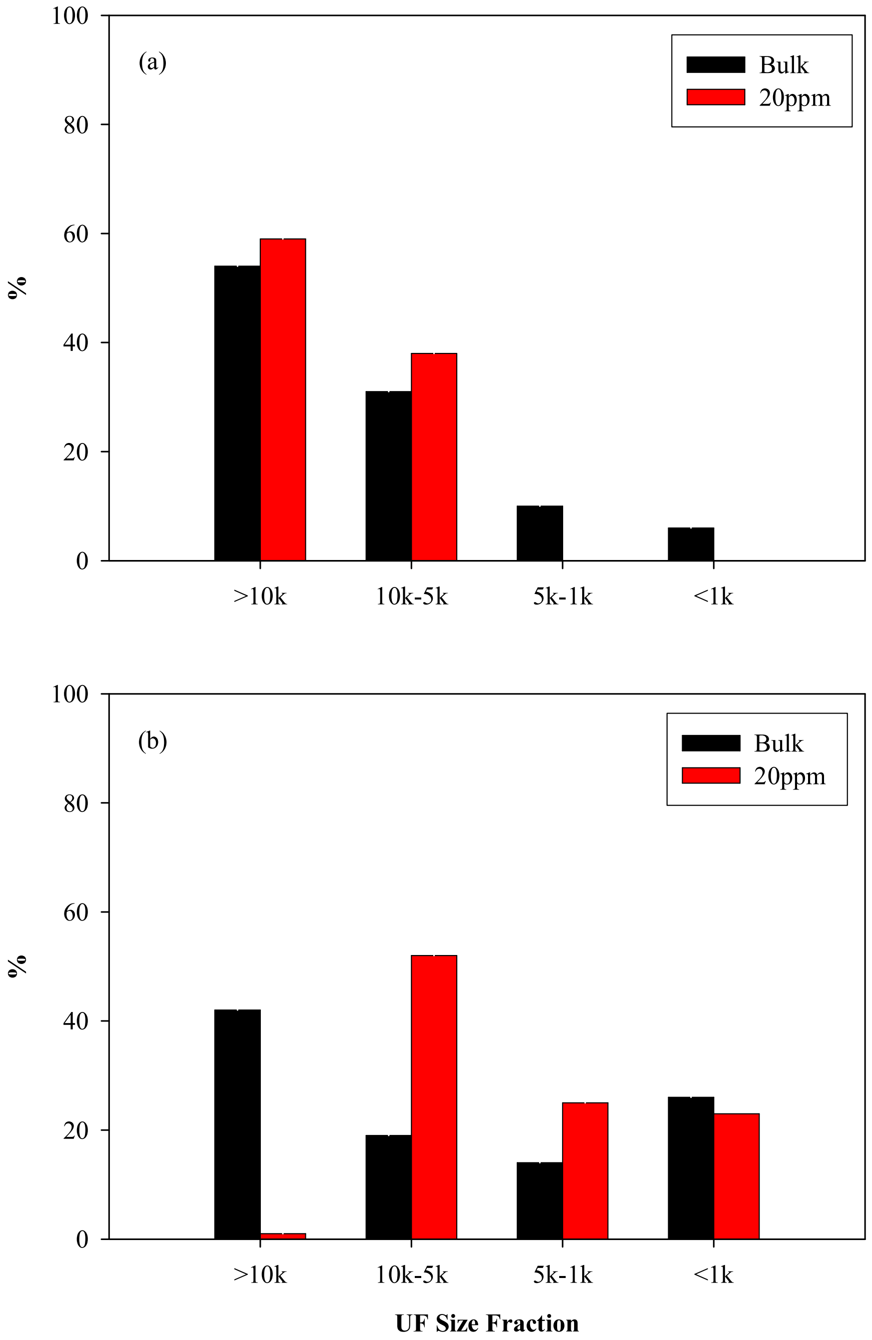

Figure 3. UF analysis in percentage by TOC of PAC dose 20 mg/L reacted with (a) LBWP and (b) MWD raw water.

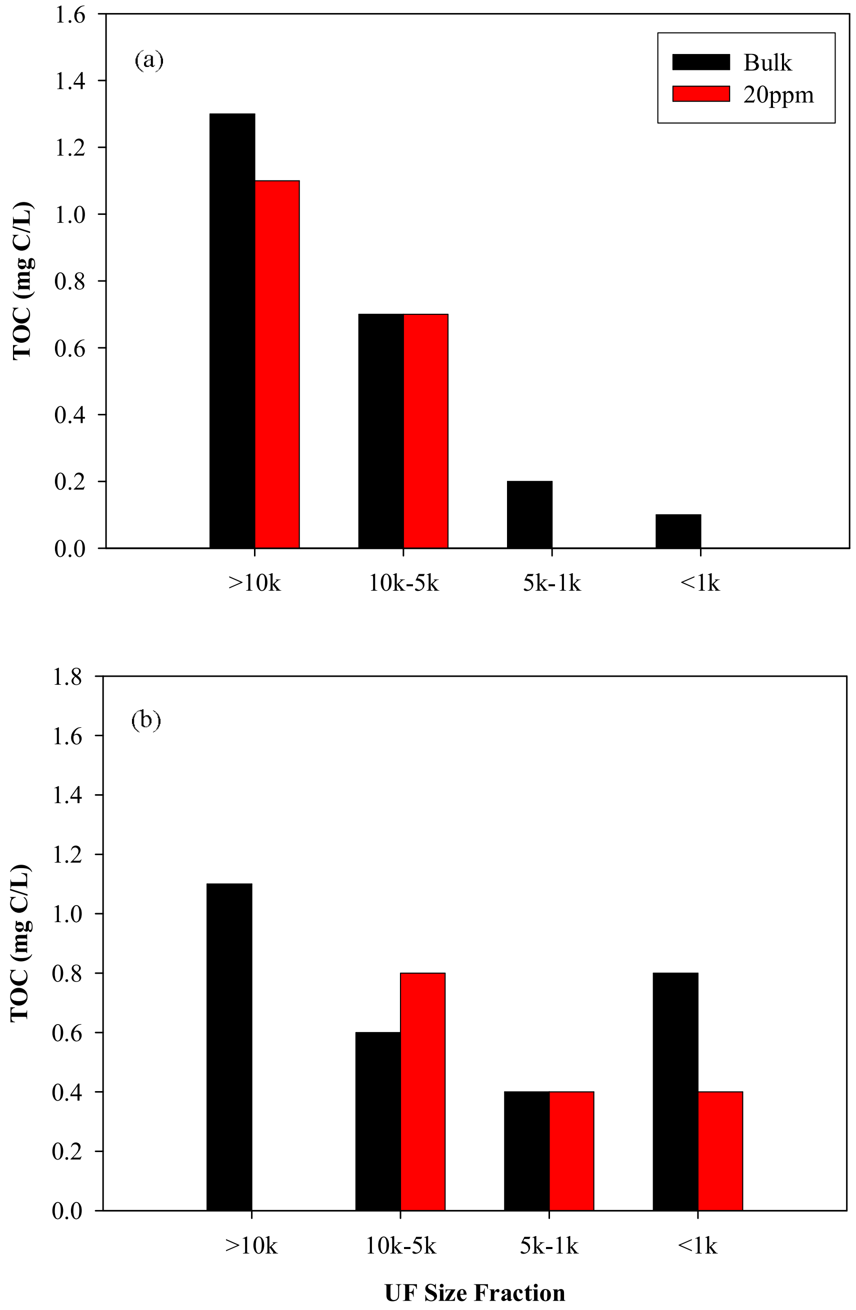

Figure 4. UF analysis in mg C/L by TOC of PAC dose 20 mg/L reacted with (a) LBWD and (b) MWD raw water.

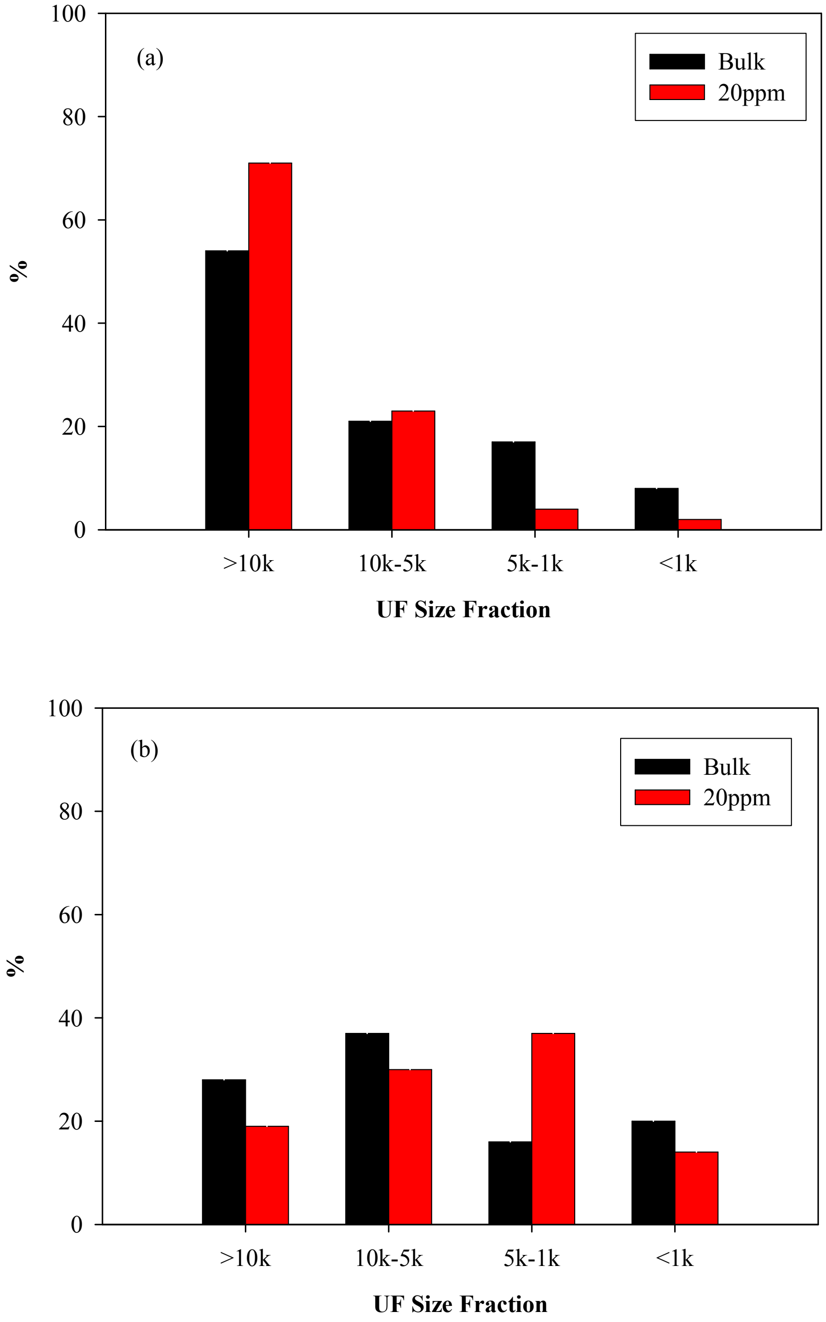

Figure 5. UF analysis in % by UV_{254} absorbance of PAC dose 20 mg/L reacted with (a) LBWD and (b) MWD raw water.

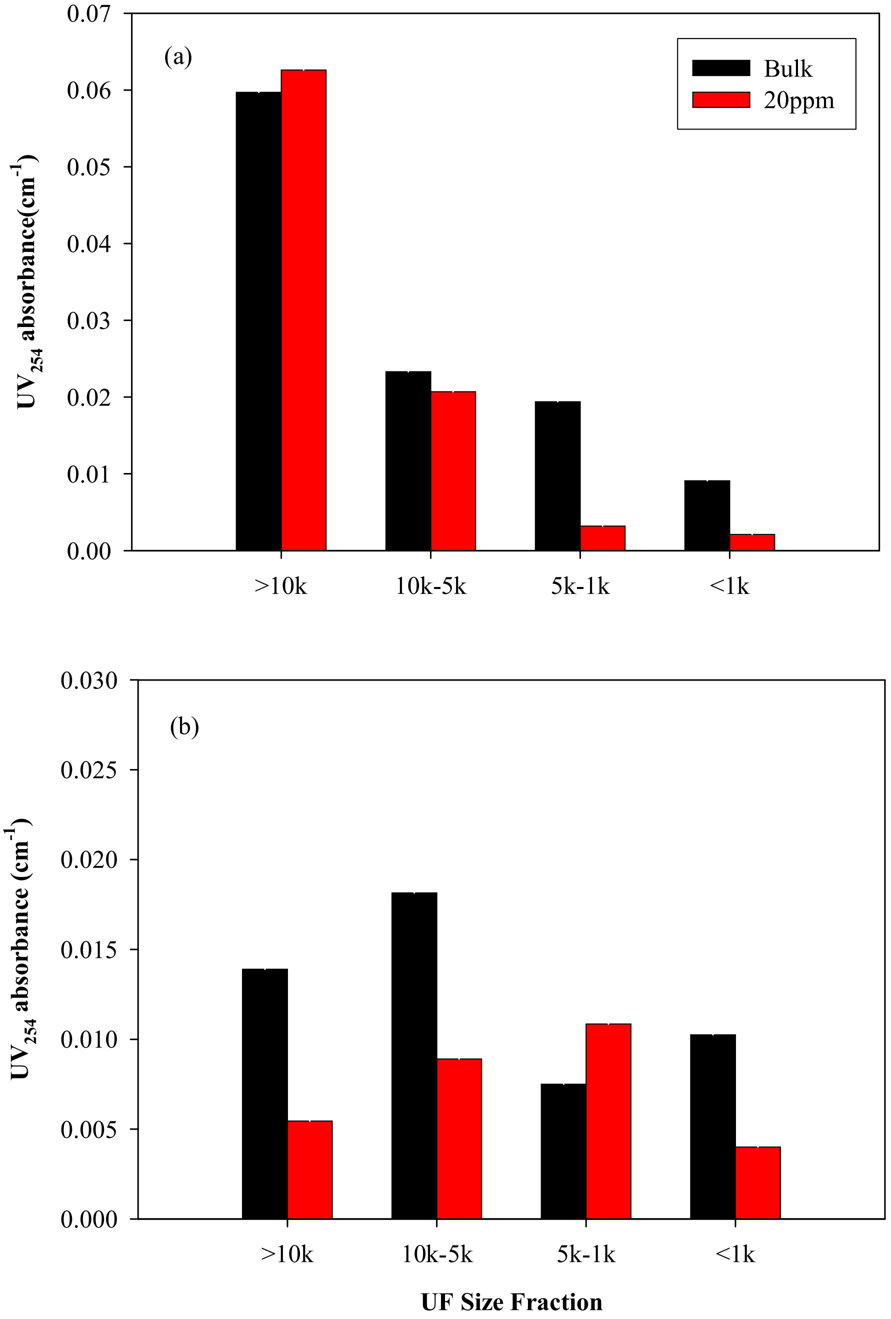

Figure 6. UF analysis in cm^{-1} by UV$_{254}$ absorbance of PAC dose 20 mg/L reacted with (a) LBWD and (b) MWD raw water.

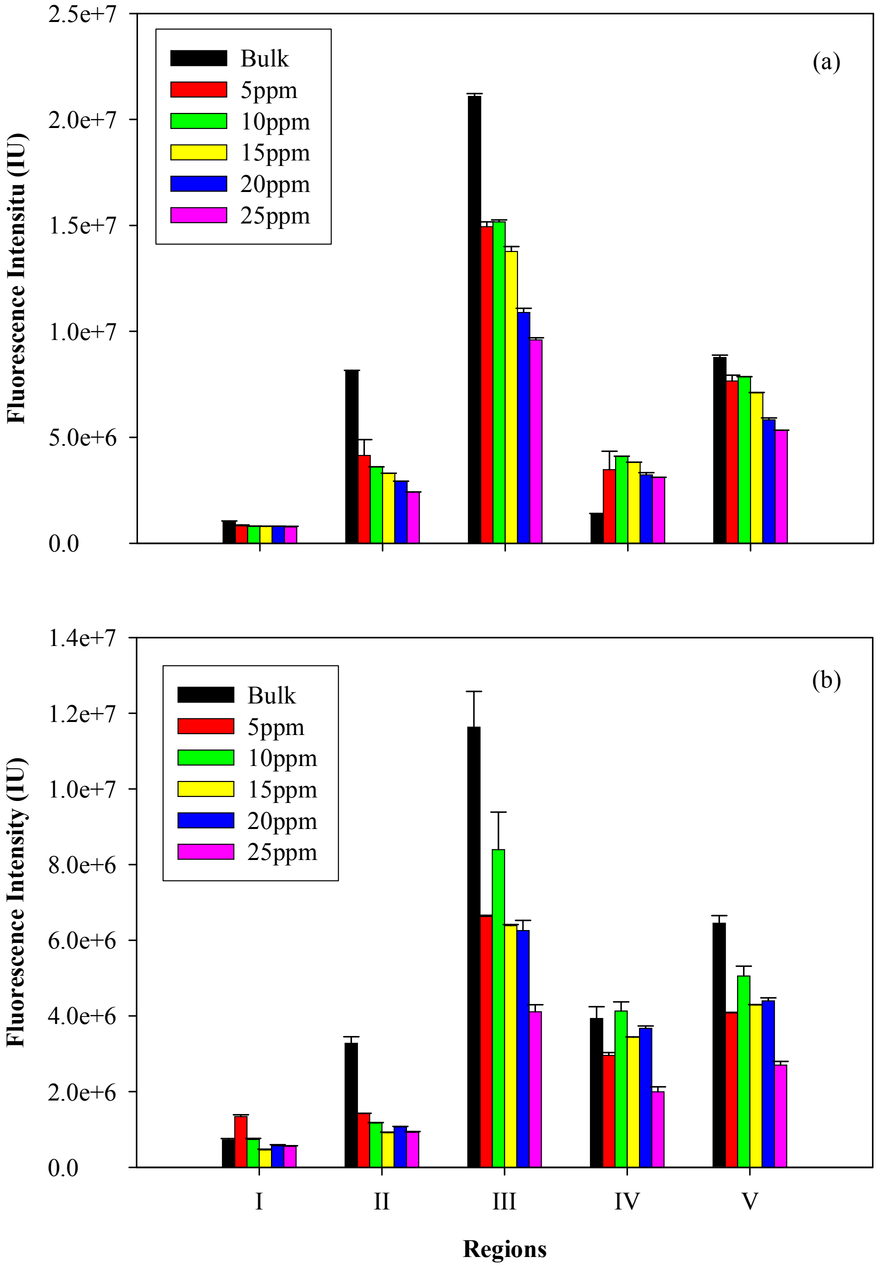

Figure 7. FRI results of different doses of PAC reacted with (a) LBWD and (b) MWD raw water. (IU: Intensity Unit)

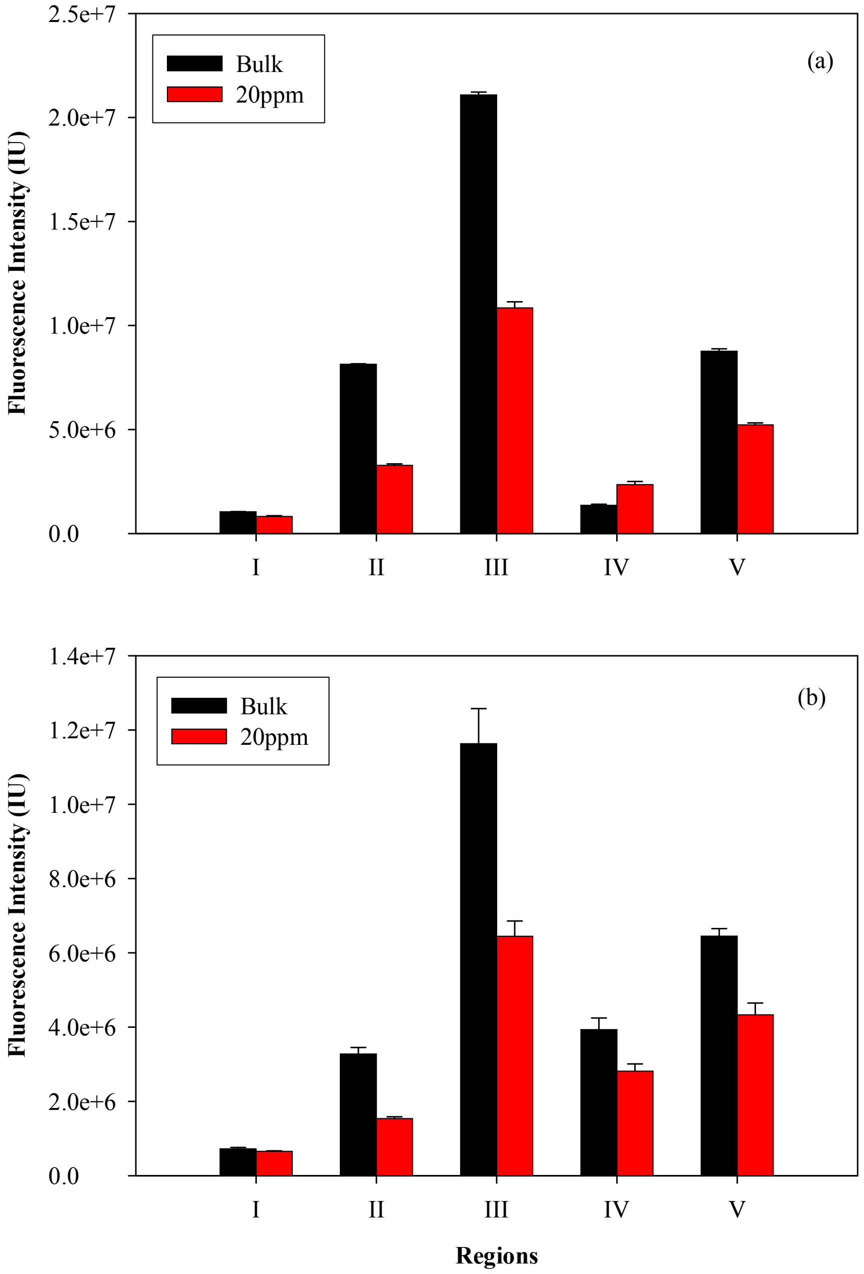

Figure 8. FRI results of PAC dose 20 mg C/L reacted with (a) LBWD and (b) MWD raw water. (IU: Intensity Unit)

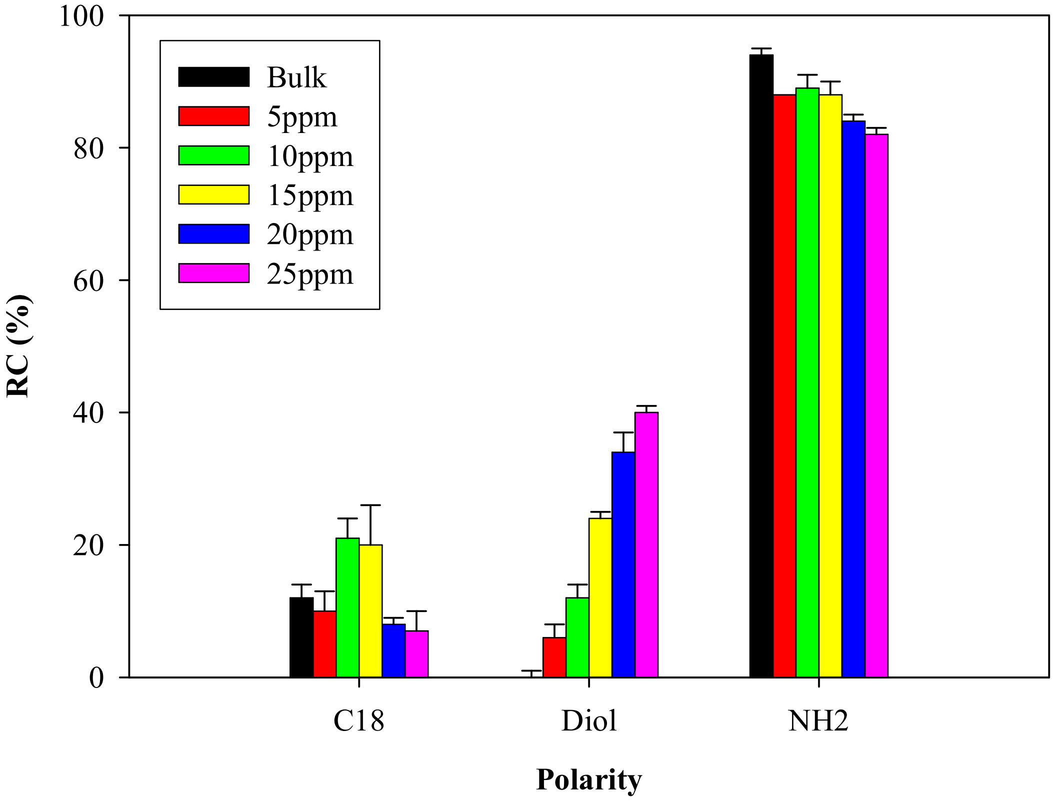

Figure 9. PRAM analysis of different doses of PAC reacted with LBWD raw water.

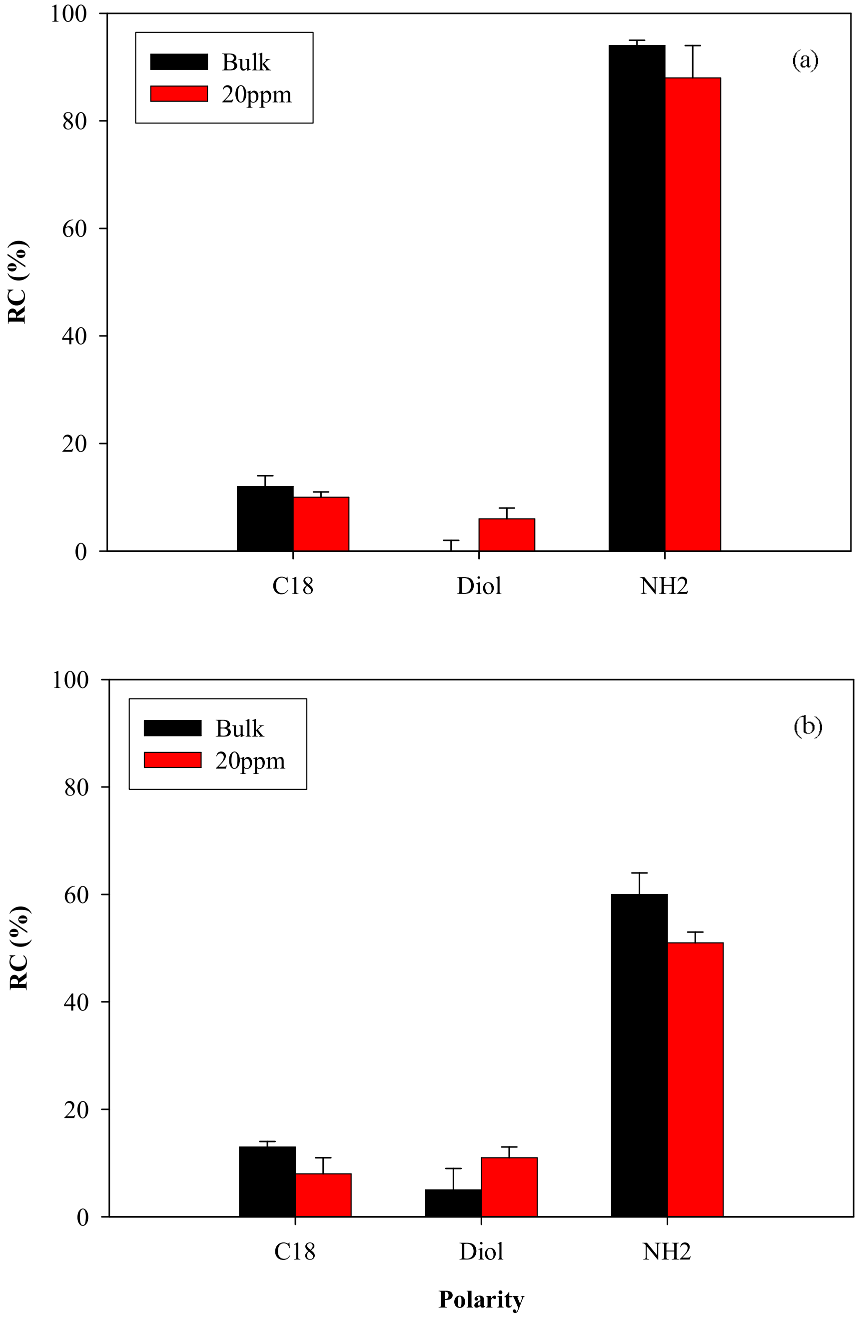

Figure 10. PRAM analysis of PAC dose 20 mg C/L reacted with (a) LBWD and (b) MWD raw water.

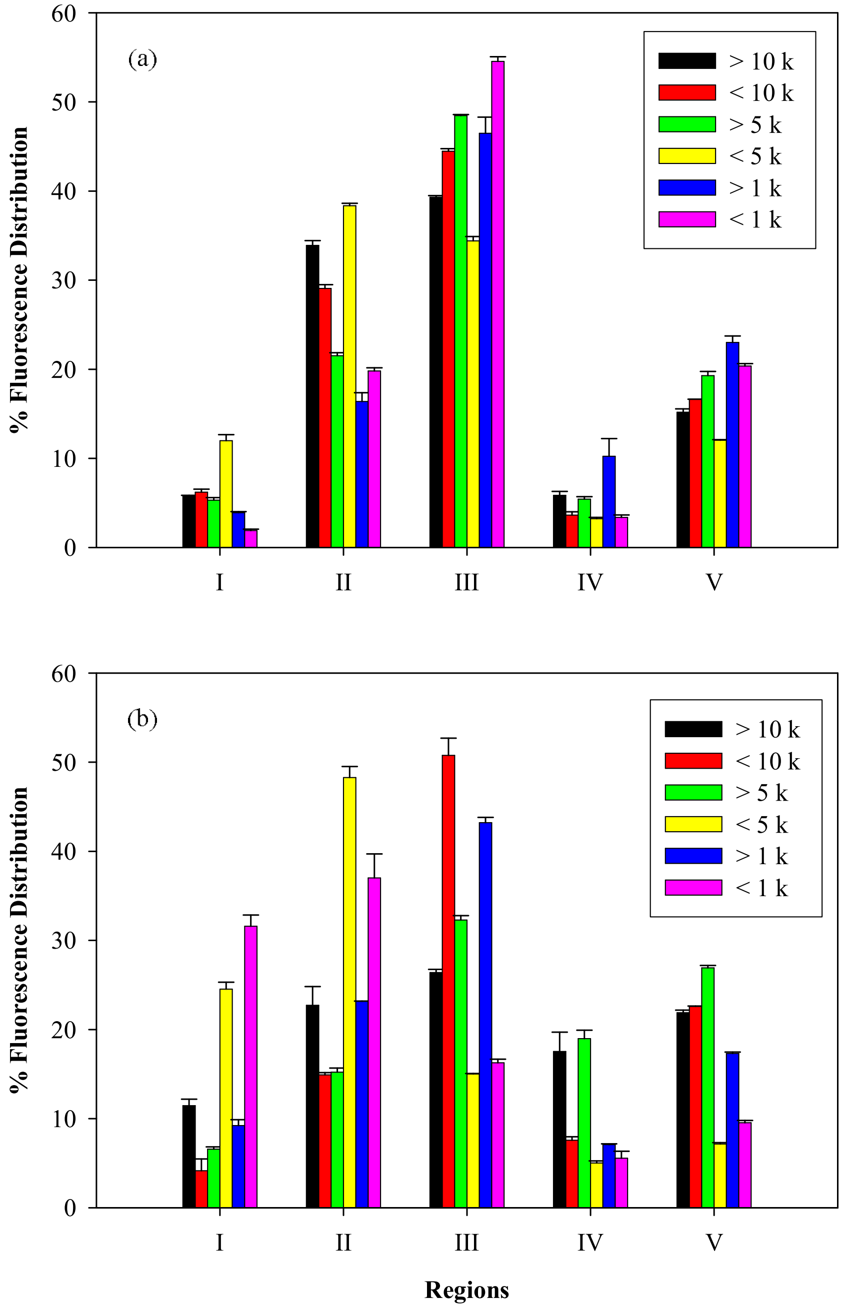

Figure 11. FRI results of different size fractions of MWD raw water sample (a) before and (b) after 20 ppm PAC treatment

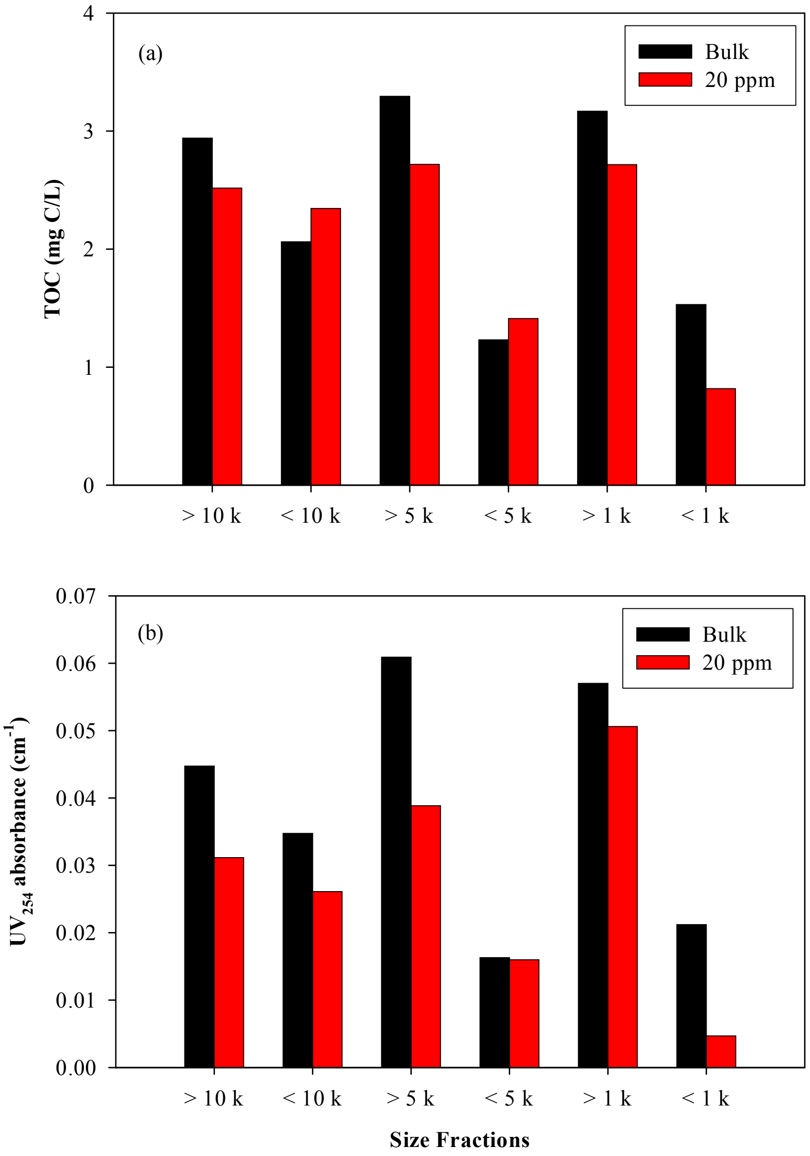

Figure 12. (a) TOC (mg C/L) and (b) UV_{254} (cm^{-1}) results of different size fractions of MWD raw water sample before and after 20 ppm PAC treatment

D.6 Tables

Table 1. The Effect of Adding 20 mg/L PAC to Raw Waters - UF Size Fractions Analysis

		Size Fractions			
Raw Waters	**TOC & UV$_{254}$**	**> 10 kDa**	**10-5 kDa**	**5-1 kDa**	**< 1 kDa**
LBWD	TOC by %	↑9%	↑23%	↓100%	↓100%
	TOC by mg C/L	↓15%	−0%	↓100%	↓100%
	UV$_{254}$ by %	↑31%	↑10%	↓76%	↓75%
	UV$_{254}$ by cm^{-1}	↑5%	↓11%	↓84%	↓77%
MWD	TOC by %	↓98%	↑174%	↑79%	↓12%
	TOC by mg C/L	↓100%	↑33%	−0%	↓50%
	UV$_{254}$ by %	↓32%	↓19%	↑131%	↓30%
	UV$_{254}$ by cm^{-1}	↓61%	↓51%	↑45%	↓61%

Note: The numbers represent the ratios (%) increased or decreased after 20 mg/L PAC treatment compared to raw waters.

↑: increase; ↓: decrease; −: no change.

Table 2. TOC, Log K_{DOM}, and THMs analysis for LBWD and MWD after 20 mg C/L PAC treatment

	LBWD			MWD		
	TOC (mgC/L)	Log K_{DOM}	THMs (μg/L)	TOC (mgC/L)	Log K_{DOM}	THMs (μg/L)
Raw	2.6	5.8	180	2.6	5.0	110
Raw + PAC	1.7	5.8	140	1.6	4.9	81

D.7 Supporting Information

Experimental

Ultrafiltration

DOM was size fractionated by ultrafiltration (UF) was completed by the method of Revchuk and Suffet (25) through Millipore YM (regenerated cellulose, negatively charged) 1,000 (1k), 10,000 (10k) molecular weight cut off (MWCO), and PB (polyethersulfone, negatively charged) 5,000 (5k) MWCO membranes (Millipore Corp., Billerica, MA). To reduce leaching of DOC, membranes were soaked three times (30 min each time) in deionized (DI) water (Milli-Q Plus water system, Millipore Corp., Bedford, MA) and then in 5% NaCl solution over night. UF was performed in Millipore solvent-resistant stirred cells (XFUF 076 01). The final step was to rinse the membranes with 100 ml DI water right before filtration. 200 ml of bulk solution was added to the cell and 100 ml was filtered under 55 psi nitrogen gas. Each membrane was discarded after one use. Fractions were analyzed for DOC by a Shimadzu TOC 5050, Total Organic Carbon Analyzer and UV_{254} by a Shimadzu UV-1700, Pharmaspec UV-Vis spectrophotometer (Shimadzu Corp. Columbia, MD). All samples were completed in duplicate.

Polarity Rapid Assessment Method

DOM polarity was identified by the polar rapid assessment method (PRAM) under ambient water quality conditions without any pretreatment (26). Analysis takes into account the effect of pH and ionic strength on the structure of DOM under ambient conditions (26). Solid phase extraction (SPE) cartridges were cleaned by passing Milli-Q water to remove UV absorbing impurities. Parallel SPE cartridges with different sorbent polarities were used to adsorb DOM. The SPE cartridges include C18 (non-polar, hydrophobic), Diol (polar, hydrophilic), and NH2 (weak anion exchanger, negative charge). Ambient sample flow through each SPE cartridge was maintained at 1.2 mL/min for 8 min using a syringe pump (KD Scientific, Model 100, Holliston, MA). Effluent was collected from 4 to 8 minutes after initial breakthrough, and the absorbance at 254 nm was measured (UV 1700 Pharma Spec, Shimadzu) to get retention coefficient. The RC is defined as 1-(C_{max}/C_o) in percentage, where C_{max} is the maximum absorbance of the samples after breakthrough and C_o is the absorbance of the original sample. PRAM experiments were performed in triplicate. The effluent was also analyzed by fluorescence spectroscopy to record the excitation emission matrix (EEM).

Fluorescence Spectroscopy

Fluorescence spectroscopy, a highly sensitive and rapid method for the identification of DOM characteristics, was used to obtain the excitation-emission matrix (EEM) (36). The five regions represent aromatic proteinaceous compounds I and II, fulvic acids, microbial by-products, and humics (5). EEM spectroscopy was measured by fluorescence spectrophotometer (Varian, R3896, Palo Alto, CA) using parameters as were modified from Holbrook, et al. (37). Excitation wavelengths spanned from 220 to 470 nm in 5 nm increments, and the emission wavelengths spanned from 280 to 580 nm in 4 nm increments using an integration time of 0.1s and a bandwidth of 10 nm.

The fluorescence intensities of spectra were normalized by Raman peak, which was measured daily at pair excitation-emission wavelengths of 350 and 397 nm in deionized water (DI water) (Milli-Q water) and described as intensity unit (IU). All data were obtained by Matlab (version 7.4.0.287, R2007a, Natick, MA) to exclude the water-scattering peaks from Raleigh and Raman scattering (23).

Adjusted EEMs were quantified by the fluorescence regional integration (FRI) method to quantify and analyze fluorescence EEM spectra based on the integration of the total surface and subsequent divisions of the surface into five regions (5). Table S2 lists the regions and their associated excitation and emission regions.

Table S1. Water quality parameters for samples

Raw water sample	**TOC** **(mg L^{-1})**	**UV_{254}** **(cm^{-1})**	**SUVA** **(L mg^{-1} m^{-1})**	**pH**	**Conductivity** **(us cm^{-1})**
LBWD	2.6	0.097	3.7	8.5	378
MWD	2.6	0.048	1.9	8.5	861

Table S2. Characterization of DOM and location of FRI regions (18).

Region	Characterization of DOM	Excitation Range (nm)	Emission Range (nm)
I	Aromatic proteins I	220-250	280-332
II	Aromatic proteins II	220-250	332-380
III	Fulvic acids	220-250	380-580
IV	Microbial by-products	250-470	280-380
V	Humic acids	250-470	380-580

D.8 References

1. Woodhead, R. J.; Law, R. J.; Matthiessen, P., Polycyclic aromatic hydrocarbons in surface sediments around England and Wales, and their possible biological significance. *Mar. Pollut. Bull.* **1999,** *38*, (9), 773-790.

2. Santos, F. J.; Galceran, M. T., The application of gas chromatography to environmental analysis. *Trac-Trends Anal. Chem.* **2002,** *21*, (9-10), 672-685.

3. USEPA Website; http://water.epa.gov/drink/contaminants/basicinformation/benzo-a-pyrene.cfm. In USEPA, Ed.

4. European Comission, Council Directive 98/83/EC; *Off. J. Eur. Commun.* 1998, L330, 32.

5. Chen, W.; Westerhoff, P.; Leenheer, J. A.; Booksh, K., Fluorescence excitation - Emission matrix regional integration to quantify spectra for dissolved organic matter. *Environ. Sci. Technol.* **2003,** *37*, (24), 5701-5710.

6. Stevenson, F. J., *Humus Chemistry, Genesis Composition, Reaction.* 2nd ed.; John Wiley & Sons: New York, 1994.

7. Thurman, E. M., *Organic Geochemistry of Natural Waters.* Dr. W. Junk Publishers.: Dordrecht, The Netherlands: Martinus Nijhoff, Netherlands, 1985.

8. Krasner, S. W.; Croue, J. P.; Buffle, J.; Perdue, E. M., Three approaches for characterizing NOM. *J. Am. Water Work Assoc.* **1996,** *88*, (6), 66-79.

9. Amy, G. L.; Thompson, J. M.; Tan, L.; Davis, M. K.; Krasner, S. W., EVALUATION OF THM PRECURSOR CONTRIBUTIONS FROM AGRICULTURAL DRAINS. *J. Am. Water Work Assoc.* **1990,** *82*, (1), 57-64.

10. Zhang, X. G.; Minear, R. A., Characterization of high molecular weight disinfection byproducts resulting from chlorination of aquatic humic substances. *Environ. Sci. Technol.* **2002,** *36*, (19), 4033-4038.

11. Singer, P. C., Humic substances as precursors for potentially harmful disinfection by-products. *Water Sci. Technol.* **1999,** *40*, (9), 25-30.

12. Lee, N. H.; Amy, G.; Croue, J. P.; Buisson, H., Identification and understanding of fouling in low-pressure membrane (MF/UF) filtration by natural organic matter (NOM). *Water Res.* **2004,** *38*, (20), 4511-4523.

13. Taniguchi, M.; Kilduff, J. E.; Belfort, G., Modes of natural organic matter fouling during ultrafiltration. *Environ. Sci. Technol.* **2003,** *37*, (8), 1676-1683.

14. Amy, G.; Cho, J., Interactions between natural organic matter (NOM) and membranes: Rejection and fouling. *Water Sci. Technol.* **1999,** *40*, (9), 131-139.

15. Carter, C. W.; Suffet, I. H., BINDING OF DDT TO DISSOLVED HUMIC MATERIALS. *Environ. Sci. Technol.* **1982,** *16*, (11), 735-740.

16. Chiou, C. T.; Malcolm, R. L.; Brinton, T. I.; Kile, D. E., WATER SOLUBILITY ENHANCEMENT OF SOME ORGANIC POLLUTANTS AND PESTICIDES BY DISSOLVED HUMIC AND FULVIC-ACIDS. *Environ. Sci. Technol.* **1986,** *20*, (5), 502-508.

17. Ravacha, C.; Rebhun, M., BINDING OF ORGANIC SOLUTES TO DISSOLVED HUMIC SUBSTANCES AND ITS EFFECTS ON ADSORPTION AND TRANSPORT IN THE AQUATIC ENVIRONMENT. *Water Res.* **1992,** *26*, (12), 1645-1654.

18. AWWA, Control of Organic Compounds with Powdered Activated Carbon, AWWA Research Foundation, American Water Works Assoc., 1991.

19. AWWA, Polar NOM: Characterization, DBPs, Treatment, AWWA Research Foundation, American Water Works Assoc. **2001**.

20. Mackay, D.; Shiu, W. Y., AQUEOUS SOLUBILITY OF POLYNUCLEAR AROMATIC-HYDROCARBONS. *J. Chem. Eng. Data* **1977,** *22*, (4), 399-402.

21. Gauthier, T. D.; Shane, E. C.; Guerin, W. F.; Seitz, W. R.; Grant, C. L., FLUORESCENCE QUENCHING METHOD FOR DETERMINING EQUILIBRIUM-CONSTANTS FOR POLYCYCLIC AROMATIC-HYDROCARBONS BINDING TO DISSOLVED HUMIC MATERIALS. *Environ. Sci. Technol.* **1986,** *20*, (11), 1162-1166.

22. Rebhun, M.; Meir, S.; Laor, Y., Using dissolved humic acid to remove hydrophobic contaminants from water by complexation-flocculation process. *Environ. Sci. Technol.* **1998,** *32*, (7), 981-986.

23. MacDonald, B. C.; Lvin, S. J.; Patterson, H., Correction of fluorescence inner filter effects and the partitioning of pyrene to dissolved organic carbon. *Anal. Chim. Acta* **1997,** *338*, (1-2), 155-162.

24. *Standard Methods For the Examination of Water and Wastewater*. 22 ND ed.; American Public Health Association: Washington, 2012.

25. Revchuk, A. D.; Suffet, I. H., Ultrafiltration separation of aquatic natural organic matter: Chemical probes for quality assurance. *Water Res.* **2009,** *43*, (15), 3685-3692.

26. Rosario-Ortiz, F. L.; Snyder, S.; Suffet, I. H., Characterization of the polarity of natural organic matter under ambient conditions by the polarity rapid assessment method (PRAM). *Environ. Sci. Technol.* **2007,** *41*, (14), 4895-4900.

27. Szlachta, M.; Adamski, W., Application of Adsorption on Powdered Active Carbon for the Removal of Dissolved Organic Substances from Surface Water. *Ochr. Sr.* **2009,** *31*, (2), 61-66.

28. Suffet, I. H. a. M., I.H. , *Activated Carbon Adsorption of Organics from the aqusous phase*. Ann Arbor Science Publisher Inc., The Butterworth Group: 1981; Vol. Vol. 1.

29. Faust, S. D. a. A., O.M. , *Adsorption Processes for Water Treatment*. Butterworth Publishers: 1987.

30. Hsu, M.-H., Suffet, Irwin (Mel) Understanding the Interaction of Hydrophobic Organic Pollutants and Dissolved Organic Matter in Natural and Treated Drinking Water. In Los Angeles, 2012.

31. Rosario-Ortiz, F. L.; Snyder, S.; Suffet, I. H., Analysis of polarity fractionated dissolved organic matter using 3-D fluorescence excitation-emission matrix spectroscopy. *Abstr. Pap. Am. Chem. Soc.* **2007,** *233*, 444-444.

32. Chow, A. T.; Gao, S.; Dahlgren, R. A., Physical and chemical fractionation of dissolved organic matter and trihalomethane precursors: A review. *J. Water Supply Res Technol.-Aqua* **2005,** *54*, (8), 475-507.

33. Chang, C. Y.; Hsieh, Y. H.; Lin, Y. M.; Hu, P. Y.; Liu, C. C.; Wang, K. H., The effect of the molecular mass of the organic matter in raw water on the formation of disinfection by-products. *J. Water Supply Res Technol.-Aqua* **2001,** *50*, (1), 39-45.

34. Wei, Q. S.; Wang, D. S.; Wei, Q.; Qiao, C. G.; Shi, B. Y.; Tang, H. X., Size and resin fractionations of dissolved organic matter and trihalomethane precursors from four typical source waters in China. *Environ. Monit. Assess.* **2008,** *141*, (1-3), 347-357.

35. I. Kristiana, B. P. A., C. A. Joll, A. Heitz and R. Trolio, Understanding the behaviour of molecular weight fractions of natural organic matter to improve water treatment processes. *Water Sci. Technol.* **2010,** *10.1*, 59-68.

36. Marhaba, T. F.; Van, D.; Lippincott, L., Rapid identification of dissolved organic matter fractions in water by spectral fluorescent signatures. *Water Res.* **2000,** *34*, (14), 3543-3550.

37. Holbrook, R. D.; Breidenich, J.; DeRose, P. C., Impact of reclaimed water on select organic matter properties of a receiving stream-fluorescence and perylene sorption behavior. *Environ. Sci. Technol.* **2005,** *39*, (17), 6453-6460.

E. Chapter 5:

Research Paper 4

Bioavailability of Hydrophobic Organic Pollutants in Urban Runoff

E.1 Abstract

Polycyclic aromatic hydrocarbons (PAHs), a group of the hydrophobic organic pollutants (HOPs), are commonly found in the urban runoff and toxic to biota. Dissolved organic matter (DOM) is also ubiquitous in the urban runoff. DOM can bind with HOPs in urban runoff and thus decrease the bioavailability of HOPs and affect their fate and transport. This study used the PAH, perylene, as a probe for carcinogenic HOPs, such as benzo(a)pyrene (BAP). Partition coefficients (K_{DOM}) between DOM and perylene were measured by the fluorescence quenching method. Characteristics of DOM were measured for: 1) size distribution 2) polarity and 3) UV and fluorescent chemical functionality.

The results showed that DOM characteristics vary seasonally and there is a significant difference between dry weather runoff and stormwater runoff events. Thus the relationship between DOM and HOPs in equilibrium with DOM-HOPs needs definition on a seasonal basis to understand the bioavailability of HOPs. The California "State Implementation Plan" indicates site-specific dissolved and total recoverable "metals" can be developed from direct determination of fraction

dissolved metals. The determination of free and total HOPs has not been considered. The data in this paper indicate it should be as free HOPs are bioavailable and only a part of the total is soluble. This study has defined the bioavailability by a standard test using a PAH probe and found 34 - 86 % free equivalent BaP.

The association between DOM and HOPs is not controlled by the total amount of DOM as total organic carbon but the specific mixture of DOM compounds present. The Log K_{DOM} demonstrated positive correlation with UV_{254} values in 10 - 5 kDa fractions ($R^2 = 0.72$) and UV_{254} in 10 - 5 kDa fractions in terms of percentage of total UV_{254} value ($R^2 = 0.66$). Therefore the aromatic structures in the mixture of DOM compounds appear to control the interaction of PAHs with DOM.

E.2 Introduction

Urbanization result in the transport of pollutants from urban runoff into receiving waters (1). The pollutants include disease causing microorganisms and chemical pollutants including inorganic chemicals, such as heavy metals (lead, copper, and zinc) and organic chemicals, such as polycyclic aromatic hydrocarbons (PAHs) and pesticides. The pollution of urban runoff can affect beach closure and damage biota or degrade water sources for directly potable and non-potable uses (2). In southern California, stormwater pollution from urban watersheds significantly impacts surface water quality and the mass emission of bacteria, heavy metals, and hydrophobic priority pollutants often exceed water quality standards (3).

PAHs, a group of the hydrophobic organic pollutants (HOPs), are mainly generated from incomplete combustion and are commonly found in the urban runoff (4). PAHs have been targeted to control due to their prevalence, persistency, carcinogenicity and toxicity. PAHs are on the list of priority pollutants (5). The discharge of urban runoff is managed in California by Federal Clean Water Act (CWA) and the California Porter-Cologne Water Quality Control Act (6). Under these, State Water Resources Control Board issues National Pollutant Discharge Elimination System (NPDES) permit to control pollution by regulating point sources that discharge pollutants into waters, including HOPs are regulated under these regulations.

Researches have estimated that urban runoff results in 14-36% of the total PAHs loading into aquatic ecosystems (7-8). Most quantitative studies for PAHs in urban runoff have been done completed on the particulate phase to determine mass loading because of the high water-solid partition coefficients of the PAHs (1,9,10,11). The pollution levels and the form of PAHs, in the dissolved phase of urban runoff have not been clarified.

Dissolved organic matter (DOM) is also ubiquitous in the urban runoff. DOM is defined functionally as passing a 0.45 microns filter. Chemically, DOM is a mixture of anionic macromolecules and submicron colloids. More specifically, DOM is composed of heterogeneous combination of aromatic and aliphatic organic compounds which contain nitrogen, oxygen, and sulfur functional groups coming from microbial decomposition in waterways and on land and runoff into waterways (12). The components of DOM have been classified as humic acids, fulvic acids, humin, amino acids, proteins, sugars, and polysaccharides (13). DOM decomposed by microorganisms from natural organic matter has different characteristics from site to site.

DOM has the ability to associate (bind or sorb) with HOPs, such as PAHs, in natural waters from urban runoff (14). The association of HOPs and DOM occurs primarily as a linear association between a bound and free PAH. This binding behavior is primarily described by a binding equilibrium constant, K_{DOM}:

$$\mathrm{PAH\ (soluble, free)} + \mathrm{DOM} \overset{K_{DOM}}{\Longleftrightarrow} \mathrm{PAH} - \mathrm{DOM\ (bound)} \quad (1)$$

The free soluble form is hazardous because it is bioavailable. The bound form is not, but it increases the solubility of PAHs, i.e. from sediments and enables the mobility of the PAHs pollutants in aquatic environments. Subsequently, the bound PAHs then at a location downstream equilibrate and become partially free, soluble and bioavailable. Thus, in the aquatic environment, knowing true free concentration of HOPs is necessary to effectively determine the bioavailable quantity of HOPs. Then the issue becomes what kind of DOM characteristics affect binding and the bioavailability of HOPs in urban runoff. The California “State Implementation Plan” (SIP), Section 1.4 (15) also indicates site-specific transformation of dissolved and total recoverable “metals” can be developed from direct determination of fraction dissolved metals, or development of a site-specific partition coefficient under ambient background conditions such as pH and organic carbon. The determination of free and total HOPs has not been listed in the SIP. Should this be done for HOPs as well?

The first objective of this paper is to understand how HOPs distribute between dissolved and bound DOM in urban runoff from stormwater runoff and dry weather flow. In this paper, the distribution of HOPs will be followed during four different seasons.

The second objective is to understand how specific DOM characteristics affect the distribution behavior of HOPs in the dissolved phase of runoff from stormwater runoff and dry weather flow. DOM characteristics were determined by ultrafiltration (UF), the polarity rapid assessment method (PRAM), excitation emission matrix- fluorescence regional integration (EEM-FRI), and UV_{254}, for size, polarity, chemical functionality, and molecular structures, respectively.

E.3 Experimental

Sample Collection

Samples of stormwater runoff and dry weather flow were from the storm drains within the City of Anaheim tributary to Anaheim Bay and Huntington Harbour. Stormwater runoff samples were collected in the beginning of rain events during the first hour of discharge (required in NPDES permit, NPDES NO. CA0106283[16]) to catch the “first flush” of pollutants since the first flush of runoff delivers most of the contaminants to the storm drains (17-20).

Dry weather flow samples were collected during the period from 00:00 am to 04:00 am without rain. Samples were collected in 1 gallon brown glass bottles. Grab samples were collected in less than 15 minutes required in National Pollutant Discharge Elimination System (NPDES) permit in four different seasons (NPDES NO. CA0106283 [16]). Sampling time were November, 2011 for fall, January, 2012 for winter, April, 2012 for spring, and June, 2012 for summer. The weather conditions of sampling dates are shown in Table S1 (Supporting information). There was no stormwater runoff in the summer.

Sample Preparation

Water samples were filtered through 0.7 μm glass fiber membranes (Whatman Corp, Sanford, ME) prior to any analysis to remove filterable organic matter and microorganisms that may consume DOM. Before using, membranes were baked for 24 hours at 100 °C to reduce leaching of organics during filtration. This step is to ensure that the study is only measuring the dissolved form of natural organic matter.

Water Quality

Water quality measurements were completed according to "Standard Methods for the Examination of Water and Wastewater" (21). Parameters include total organic carbon (TOC, Method 5310B), ultraviolet absorbance at 254nm (UV_{254}, Method 5910), pH (Method 4500), conductivity (Method 2510), and specific UV absorbance (SUVA) - a ratio of UV absorption to dissolved organic carbon concentration.

Ultrafiltration to Measure Size Fraction of DOM

DOM was size fractionated by ultrafiltration (UF) through Millipore YM (regenerated cellulose, negatively charged) 1,000 (1k), 10,000 (10k) molecular weight cut off (MWCO), and PB (polyethersulfone, negatively charged) 5,000 (5k) MWCO membranes (Millipore Corp., Billerica, MA) that are recommended for the size characterization of DOM (22). To reduce leaching of DOC from the UF membranes, they were soaked three times in deionized (DI) water (30 min per time), from a (Milli-Q Plus water system, (Millipore Corp., Bedford, MA) and then in 5% NaCl solution over night. UF was performed in Millipore solvent-resistant stirred cells (XFUF 076 01). The final step was to rinse the membranes with 100 ml DI water just before filtration. 200 ml of sample solution was added to the cell and 100 ml was filtered through under 55 psi nitrogen gas. Each membrane was discarded after one use. Fractions were analyzed by a Shimadzu total organic carbon (TOC) 5050 Analyzer and a Shimadzu UV-1700 Pharmaspec UV-Vis spectrophotometer (Shimadzu Corp. Columbia, MD). All samples were completed in duplicate.

Polarity Rapid Assessment Method (PRAM)

DOM polarity is identified by the polar rapid assessment method under ambient water quality conditions without any pretreatment (23). Analysis takes into account the effect of pH and ionic strength on the structure of DOM under ambient conditions. Solid phase extraction (SPE) cartridges are cleaned by passing Milli-Q water to remove UV absorbing impurities. Parallel SPE cartridges with different sorbent polarities are used to adsorb DOM. The SPE cartridges include C18 (non-polar, hydrophobic), Diol (polar, hydrophilic), and NH2 (weak anion exchanger, negative charge). The retention coefficient is defined as 1- (C_{max}/C_o) in percentages describing the specific polarity characteristics (polar, non-polar, and negative charges) retained on the cartridges, where C_{max} is the maximum UV absorbance at 254 nm of the samples after breakthrough and C_o is the UV absorbance at 254 nm of the absorbing impurities.

Fluorescence Spectroscopy

Fluorescence spectroscopy, a highly sensitive and rapid method for the identification of DOM characteristics, is used to obtain the EEM spectra (18). The five regions represent aromatic proteinous compounds I and II, fulvic acids, microbial by-products, and humic acids (12). EEM spectroscopy is measured with a fluorescence spectrophotometer using parameters modified from Holbrook, et al. (24). Excitation wavelengths span from 220 to 470 nm in 5 nm increments, and the emission wavelengths span from 280 to 580 nm in 4 nm increments using an integration time of 0.1 s and a bandwidth of 10 nm. The fluorescence intensities of spectra are normalized by Raman peak, which is measured daily at pair excitation-emission wavelengths of 350 and 397 nm in deionized water (Milli-Q water) and described in intensity units. All data are obtained by

Matlab program to exclude the water-scattering peaks from Raleigh and Raman scattering (25). Adjusted EEMs are quantified by the fluorescence regional integration method to quantify and analyze fluorescence EEM spectra based on the integration of the total surface and subsequent divisions of the surface into five regions (12). Table S2 lists the regions and their associated excitation and emission wavelengths (Supporting Information).

Fluorescence Quenching

The sorption coefficient of DOM (K_{DOM}) was determined by fluorescence quenching (FQ). Perylene was diluted in methanol to 4 mg/L perylene stock solution and stored in an amber bottle at 4 ^{o}C. Stock solution was diluted to 0.3 µg/L perylene and added to DOM diluted samples to a final concentration of three-fourths of the reported solubility 0.4 µg/L in water. To control for the loss of perylene from the cuvette system, the 12 measurements were made at defined time points (2 min intervals) to allow for extrapolation to initial conditions. Experiments were performed in a dimmed environment to prevent the photodegradation of perylene. This study assumed partitioning of PAHs between water and DOM was fast compared to the adsorption of PAHs to the cuvette wall. Sorption behavior can be modeled by:

$$PAH_d \underset{k_{-w}}{\overset{k_w}{\Leftrightarrow}} PAH - wall \qquad (2)$$

where PAH_d is the dissolved portion of the total PAH concentration, PAH-wall is the portion adsorbed on the wall, and k_w and k_{-w} are first-order forward and backward rate constants for wall adsorption. Fluorescence intensity can be obtained by

$$F = \frac{k_{-w}F_0'}{k_w + k_{-w}} + \frac{k_w F_0'}{k_w + k_{-w}} e^{-(k_w + k_{-w})t} \qquad (3)$$

where F_0' is the free PAH intensity at time zero. Nonlinear curve-fitting program (SigmaPlot) was used to get F_0', k_W, and k_{-W}. K_{DOM} values were determined by the Stern-Volmer equation which can be described as

$$\frac{F_0}{F} = 1 + K_{DOM}[DOM] \qquad (4)$$

where F_0 and F are the fluorescence intensities in the absence and presence of DOM. [DOM] is the concentration of DOM measured as mg C/L (26). The percentage of bound PAH can be determined by equation 4 (27):

$$\%bound = \frac{K_{DOM}[DOM]}{1 + K_{DOM}[DOM]} \times 100 \qquad (5)$$

All measurements of fluorescence intensities were obtained by fluorescence spectrophotometer (Varian, R3896) at an excitation-emission wavelength pair of 434 and 467 nm. Absorbance values at 434 and 467 nm were corrected for inner filtering effects (IFEs) which were usually below 1.2 by UV-Vis spectrophotometer (Shimadzu UV-1700) (25).

E.4 Results and Discussion

Water Quality Data

The water quality data for this study are listed in Table 1. The TOC concentration of urban runoff samples ranged from 6.6 mg C/L to 34.5 mg C/L which were consistently higher than studies of raw and drinking water samples (1.9-3.2 mgC/L, [28]) (1.3-7.0 mgC/L, [29]), and natural stream samples (4.4-8.2 mgC/L, [[24]]). UV_{254} varied from 0.115 to 0.793 absorbance units. SUVA varied widely from 0.7 to 12. Moreover, urban runoff samples had higher UV_{254} and SUVA than raw and drinking water samples (28).

pH and conductivity were all higher in dry weather flow. pH ranged from 7.3 to 8.4 which were within the NPDES permit limit (6.5-8.5). Conductivity in dry weather flow samples were consistently ranged from 612 to 697 us/cm. In stormwater runoff samples, conductivity fluctuated from 145 to 427 us/cm. The intensity of rain events might cause this variability.

Fluorescence Regional Integration (FRI) Analysis

This research used a fluorescence spectrophotometer to identify the characteristics of the DOM composition of all water samples according the method of Chen et al. (2003) (12). Figure 1 presents FRI results of stormwater runoff and dry weather flow. Region I, aromatic proteins I and region IV, microbial by-products, had higher content in dry weather flow than stormwater runoff. This trend is also consistent with conductivity. The reason might be rain events diluted the collected water samples. During dry weather flow conditions, microbial activity might be higher due to wash down water from washpads of food waste. The washdown water should carry a higher BOD load. Region III, fulvic acids, and Region V, humic acids, had higher content in stormwater runoff than dry weather flow indicating stormwater runoff had higher amounts of DOM from soil runoff. In addition, spring stormwater runoff had highest content of fulvic (42%) and humic acid (25%). This might be due the generation of NOM (natural organic matter) from new vegetation in the natural environment.

Furthermore, the fluorescence integration was not mainly dominated by terrestrially derived NOM in urban runoff. The total average % fluorescence distribution of aromatic proteins and microbial by-products were 52% which are microbially derived materials. Total average % fluorescence distribution of fulvic and humic acids were 48% of urban runoff. Only spring runoff samples had higher total fulvic and humic acids over 50%, especially in spring stormwater runoff, the total fulvic and humic acids were up to 67%. The fluorescence distribution behavior was different compared to previous study in raw and treated drinking waters. The average total fuvic and humic acids fluorescence distribution were 71% of different raw and treated drinking waters (28).

PRAM Analysis

PRAM results of stormwater runoff and dry weather flow were shown in Figure 2. Non-polar fractions (C18) and polar fractions (Diol) were all consistently higher in the dry weather flow. Non-polar fractions of dry weather flow were about 49% to 54% and decreased slightly from fall to summer. Non-polar fractions of stormwater runoff were about 26% to 33% and increased slightly from fall to summer. In studies of raw and drinking water, the non-polar fraction has ranged from 2 to 25% (28, 29). Non-polar fractions of dry weather flow were much higher than in natural water and treated drinking water (28, 29). Only Rosario-Ortiz et al. (29) found that non-polar fractions can be up to 53% in upper Colorado River which is dominated by snowmelt. Thus, the non-polar character of the stormwater runoff and dry weather are unique.

Polar fractions of stormwater runoff decreased slightly from fall to spring and ranged from 10% to 12%. Polar fractions of dry weather flow ranged from 20% to 34%. Previous study showed that raw and drinking water samples contained polar fractions from 2 to 20% (28, 29). Again, the polar character of the stormwater runoff and dry weather flow are unique.

Negative charge portions of dry weather flow ranged from 64% to 70%. In stormwater runoff, negative charge portions ranged from 57% to 74%. Data of negative charge portions of urban runoff samples appeared to be more consistent with less variability compared to findings in raw and drinking water as well as other natural waters where the negative charges were reported at(39%-96% [28]; 28%-80% [29]). In addition, in studies of Rosario-Ortiz et al. (2007) (29), the

Las Vegas Wash samples carrying wastewater effluent, urban runoff and groundwater presented non-polar fractions from 25 to 85%, polar fractions < 5%, and negative charges from 28% to 48% which were also lower than the findings in this study either in dry weather flow or stormwater runoff.

The results of PRAM analysis showed that polarity distributions including non-polar and polar fractions were mainly dependent on flow types. Season variations also resulted in different polarity distribution. Non-polar and polar fractions of DOM of dry weather flow appear to be uniquely higher than stormwater runoff and raw and drinking waters.

Size Characterization by Ultrafiltration

Figure 3 presents the UF results of stormwater runoff and dry weather flow measured by TOC by (a) mg C/L and by (b) %. Figure 3 (a) shows spring dry weather flow had very high <1k fraction (28.1 mg C/L) compared to other samples. All the other samples had a <1k UF fraction below 10 mg C/L. No explanation can be offered for this at this time, Only the winter samples of dry weather flow and stormwater runoff had a measurable 5k-1k fraction. Figure 3 (b) also shows that the >10k fraction from stormwater runoff was always higher than the >10 k fraction from dry weather flow in fall, winter, and spring (No stormwater runoff in summer). This might be due to that stormwater runoff had higher flow rate than dry weather flow to wash off higher molecular weight NOM.

Figure 4 shows the UF results of stormwater runoff and dry weather flow measured by UV_{254} by (a) UV_{254} absorbance and (b) UV_{254} in %. Figure 4 (a) shows that all stormwater samples had a higher UV_{254} absorbance for the > 10 kDa and < 1 kDa than dry weather flow samples. Spring stormwater runoff also had relative higher UV_{254} absorbance in the molecular weight fractions (> 5 kDa) compared to other fractions. In Figure 4 (b), the winter stormwater had highest > 10 kDa fraction (65%) and fall dry weather had highest < 1 kDa fraction (72%). Thus, the DOM distribution was different for TOC that measures all the organic carbon in a sample and UV_{254} analysis that measures the aromatic and double bond character of the TOC.

The results of UF analysis showed that size distributions of DOM were mainly dependent on flow types. Season variations also resulted in different size distribution. The variability in these samples could be ascribed to the changes in different environments such as weather and runoff footprint resulting in different sources of DOM. DOM of stormwater runoff appears to have more > 10 kDa size fractions than dry weather flow.

Using Perylene as a Hydrophobic Organic Pollutants (HOPs) Indicator

The K_{DOM} values shown in Tables 2 were determined by FQ method with perylene as a probe (28). K_{DOM} represents the ability for perylene to bind with DOM. Equation 5 was used to calculate the free concentration of perylene. As shown, the higher the K_{DOM} values of water samples represent the PAHs in the water that are potentially less hazardous because more PAHs are bound to DOM. Figure 5 shows the plots of the % bound according to equation 4 versus the

DOC concentration of DOM for a variety of values of Log K_{DOM} values from 4.0 to 6.5 from (28). The probe perylene can be used to predict the free concentration of a related cancer causing PAH, as the human carcinogen, benzo(a)pyrene by using perylene as an indicator. This is done by transferring the % free portions of perylene into % free portions of BaP according to the proportion of the hydrophobicity using relative Log K_{ow} (28).

Table 2 shows that within Anaheim area, dry weather flow contained free fraction distribution of perylene from 32% to 85% and stormwater runoff contained free fraction distribution of perylene from 28% to 58%. Birch et al. (30) also found that free fraction was 85% in roof runoff and 27% - 36% in stormwater runoff in terms of fluoranthene (Log Kow = 5.22) which was comparable to our results that stormwater runoff can bind with more HOPs than dry weather flow runoff.

In Table 2, spring stormwater runoff had the highest Log K_{DOM} and thus had the lowest free perylene (28%) and free BaP (34%) distribution. It shows that spring stormwater runoff had more ability to bind with HOPs to have higher ability to decrease hazardous potential. Only 28% HOPs in terms of perylene is bioavailable. Fall dry weather flow had the highest free Perylene (85%) and BaP distribution (86%).

Table 2 shows the data for the sample TOC, UV_{254}, SUVA, the K_{DOM} values, and free perylene and free BaP fraction (%) of dry weather flow and stormwater runoff for different seasons. The hazardous potential of % free perylene and BaP were different due to different DOM components coming from different runoff of the NOM present. For example, spring dry weather flow had highest DOC concentration presenting the most amount of DOM, however, it did not represent the highest K_{DOM} values (Log K_{DOM} = 4.6) indicating the poor binding ability of DOM. On the contrary, spring stormwater runoff had the highest binding ability (Log K_{DOM} = 5.6) but with the lowest DOC concentration. This indicates the binding ability of DOM (Log K_{DOM}) is not mainly dominated by the total amount of DOM in the water, but affected much more by different characteristics of DOM.

Spring stormwater runoff also had the highest UV_{254} and SUVA values compared to other samples. The results of Table 2 showed that within fall, winter, and spring seasons, stormwater runoff all had higher Log K_{DOM} than dry weather flow. Stormwater runoff also contained higher UV_{254} and SUVA in fall, winter, and spring. These indicate that UV_{254} and SUVA could be the main factors affecting Log K_{DOM} values within fall, winter, and spring, respectively. Stormwater runoff includes more DOM with aromatic structures and double bonds in fall, winter and spring. However, each season still had its own DOM characteristics as described in the previous sections for fluorescence, size, and polarity distribution and this affect Log K_{DOM} values as well.

The Relationship Between K_{DOM} and Different Parameters of DOC

This study examined the correlations between Log K_{DOM} values and DOM characteristics of all 7 samples of stormwater runoff and dry weather flow by linear regression and R-squared values to understand which factors might affect perylene partition behavior. The results are shown in Figure 6. By comparing all factors described in this study, Log K_{DOM} demonstrated positive correlation with UV_{254} values in 10 - 5 kDa fractions ($R^2 = 0.72$) and UV_{254} of 10 - 5 kDa fractions in percentage of total UV_{254} value ($R^2 = 0.66$).

Log K_{DOM} also had moderate correlation with sample SUVA ($R^2 = 0.53$). The correlations between Log K_{DOM} and other DOM characteristics were well below 30%. Since UV_{254} and SUVA were both relevant measures of aromaticity of DOM, binding phenomenon appears to occur on the aromatic structures and double bonds of DOM. This is also identical to the results found in Table 2. Chin et al. (1997) (31), and Tanaka et al. (1997) (32) also found DOM with higher molecular weight and aromatic content can result in higher binding ability between pyrene and DOM. Our previous studies in raw and drinking waters also showed that DOM with higher size (> 5kDa) and more aromatic contents (high SUVA and UV_{254}) can bind with perylene more efficiently (28).

Partition coefficient between DOM and perylene (K_{DOM}) had higher correlation with UV_{254} in size fraction 10 - 5 kDa of DOM in urban runoff. The result indicates DOM in urban runoff with higher molecular weight and higher content of aromaticity as indicated by UV_{254} and SUVA can bind more HOPs.

DOM characteristics showed seasonal variations and significant difference between dry weather runoff and storm events. Spring dry weather flow had highest DOC concentration, however, it did not have the highest K_{DOM} values (Log $K_{DOM} = 4.6$) (Free Bap = 42%). In contrast, spring stormwater runoff had an order of magnitude higher binding ability (Log $K_{DOM} = 5.6$) but with the lowest DOC concentration (Free BaP = 28%). This shows the binding ability of DOM (Log K_{DOM}) is not dominated by the total amount of DOM in the water, but affected much more by different characteristics of DOM such as UV_{254} and SUVA in different DOM size fractions.

Environmental Significance

HOPs, such as PAHs, are ubiquitous in the environment coming from diverse sources like pavements, atmospheric deposition, and anthropogenic spilling. The procedure developed in this study can quickly identify the bioavailability of HOPs in the dissolved phase of urban runoff. Understand the fate and transport of HOPs in urban runoff can help optimize the Toxicity Identification Evaluation (TIE) process required in the National Pollutant Discharge Elimination System (NPDES) permit by relating the toxic free PAHs from the non-toxic bound DOM-PAH complex and develop better best management practices (BMPs) to treat HOPs in urban runoff. For example, adding a specific type of DOM to water might be a possible BMP for HOPs pollution to decrease the hazardous potential in urban runoff.

The California SIP ("State Implementation Plan") (15) states that when determining the appropriate water quality-based effluent limits, the Regional Water Quality Control Board may take into account actual and seasonal variation. The SIP also indicates site-specific transformation of dissolved and total recoverable "metals" can be developed from direct determination of fraction dissolved metals, or development of a site-specific partition coefficient under ambient background conditions such as pH and organic carbon. The determination of free and total HOPs has not been listed in the SIP. The data in this paper indicate it should be as free HOPs are bioavailable and only a part of the total is soluble HOPs. This study has defined the bioavailability by a standard test using a PAH probe and found 34 - 86 % free equivalent BaP (See Table 2).

Furthermore, the bioavailability of HOPs of receiving water bodies is affected from upstream urban runoff. Estuarine bed sediments are important reservoirs for HOPs serving as both sink (through burial, degradation, or sequestration) and sources (through resuspension, molecular and colloidal diffusion, pore water advection, and bioturbation) of HOPs (33). The distribution and mobility of HOPs in estuarine sediments is determined primarily by association to NOM existing in sediments and pore water (34). Other researches also indicated aeration of anoxic estuarine sediments induced by dredging, bioturbation, or storm events may result in release of HOPs from particle-associated and dissolved organic matter and increase the concentration of the truly free-dissolved bioavailable HOPs (33-36). This study found that DOM in urban runoff of fall and winter has less ability to bind with HOPs resulting in over 50% free portion of HOPs. This means that HOPs might partition more into particulates or sediments when urban runoff moves downstream. In contrast, DOM in urban runoff of spring and summer have more ability to associate with HOPs and transport these HOPs to further downstream receiving water bodies and then equilibrate again between sediments, pore water, and particular matters. Similarly, DOM in stormwater runoff has more binding ability than dry weather flow and leads to different partition behaviors during transport. The fate and transport of HOPs in aquatic environments still depends on the real in-situ partition coefficients of organic matters between sediments, pore water, suspended sediments and runoff. Thus, this information should be considered when regulatory agencies set up water quality-based effluent limits of HOPs for NPDES permit and total maximum daily loads (TMDLs) of impaired water bodies under the Clean Water Act 303(d) list.

E.5 Figures

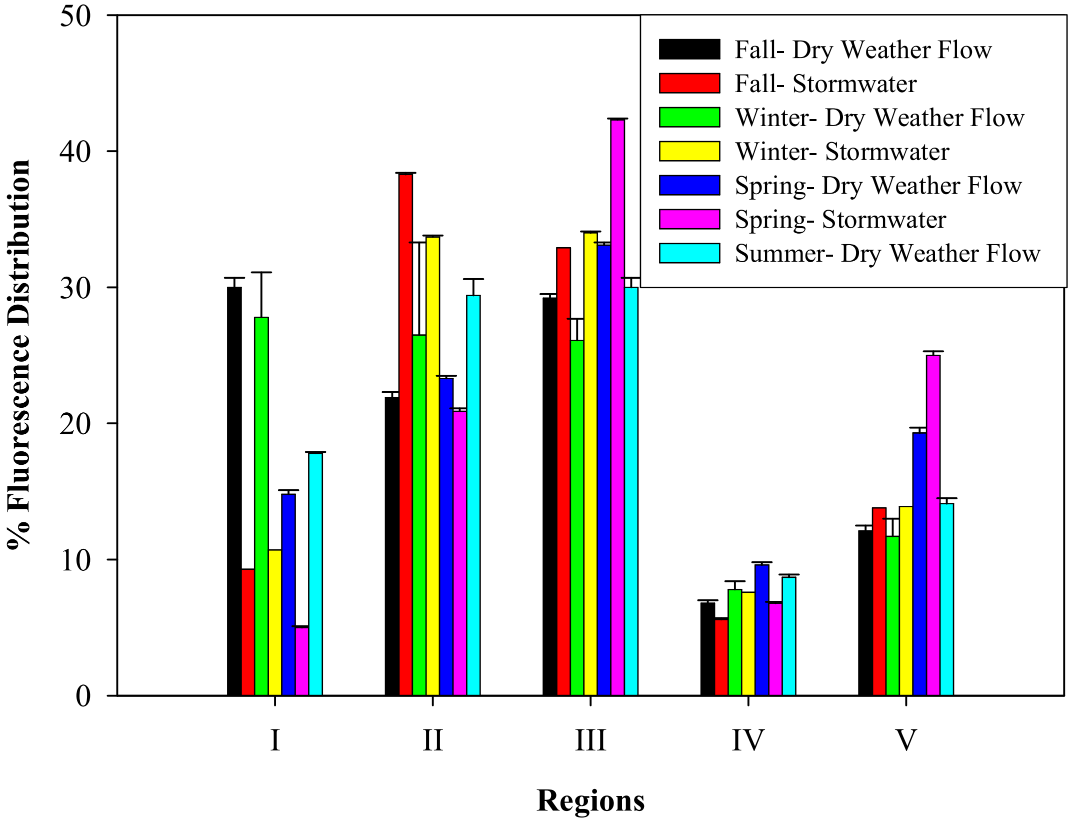

Figure 1. FRI results of stormwater runoff and dry weather flow.

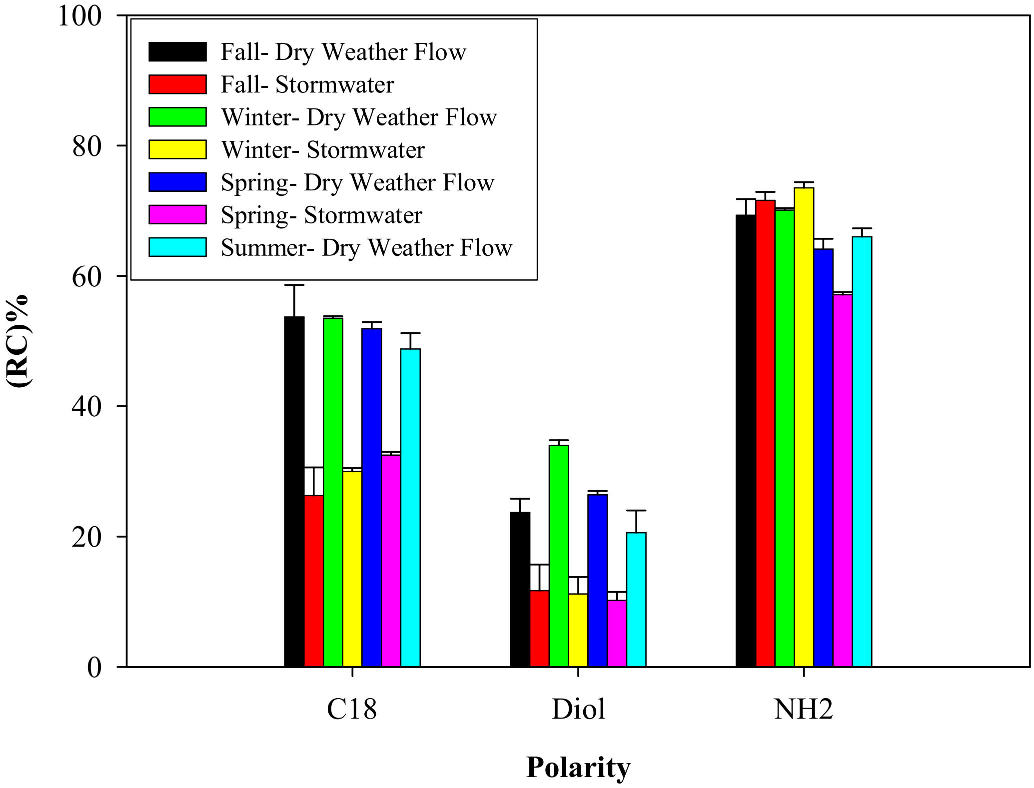

Figure 2. PRAM results of stormwater runoff and dry weather flow.

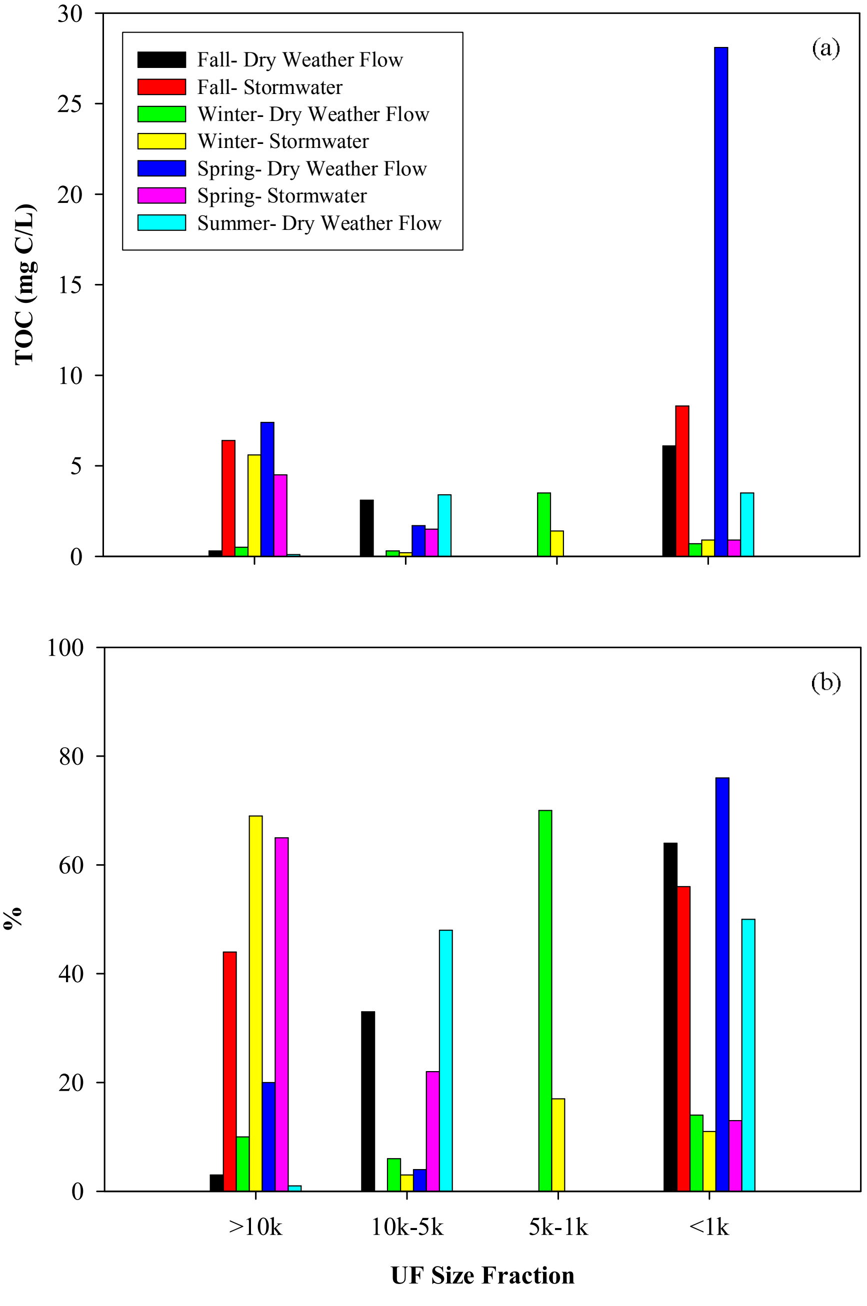

Figure 3. UF results of stormwater runoff and dry weather flow: (a) TOC in mg C/L, (b) TOC in %.

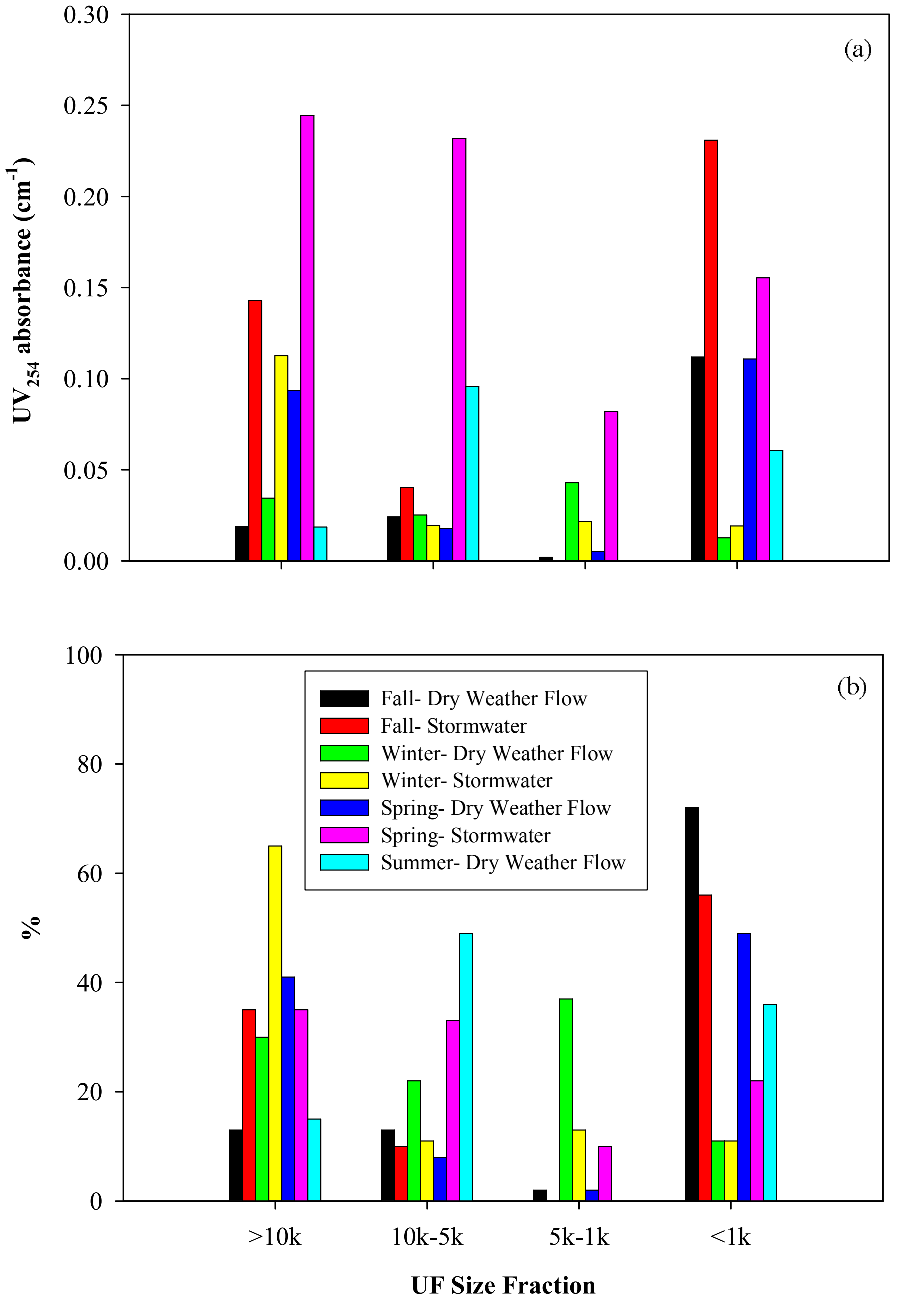

Figure 4. UF results of stormwater runoff and dry weather flow: (a) UV_{254}, (b) UV_{254} in %.

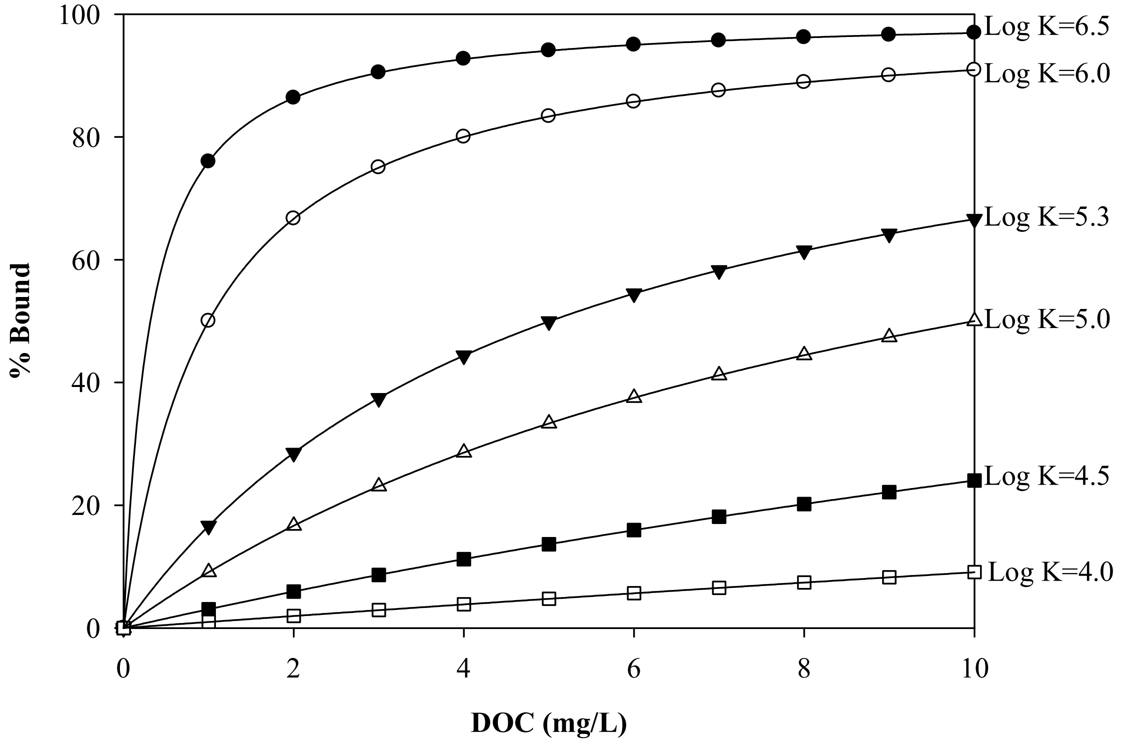

Figure 5. Data fitting results of eq 8 for a variety of values of log K (log K from 4.0 to 6.5)

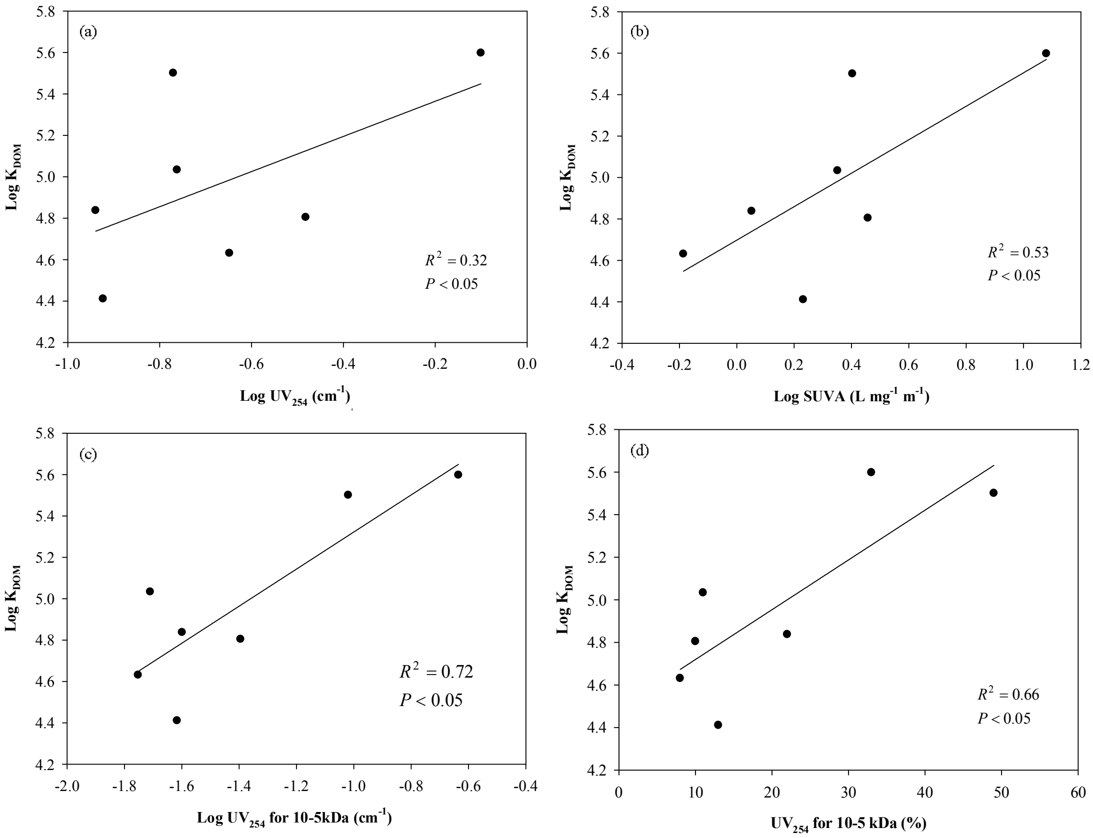

Figure 6. Correlations between Log K_{DOM} and DOM characteristics: (a) UV_{254}, (b) SUVA, (c) UV_{254} for 10-5 kDa, (d) UV_{254} for 10-5 kDa (%).

E.6 Tables

Table 1. Water quality parameters for stormwater runoff and dry weather flow samples.

Sampling Date	Season	Samples	TOC (mg L^{-1})	UV_{254} (cm^{-1})	SUVA (L mg^{-1} m^{-1})	pH	Conductivity (us cm^{-1})
11/09/2011	Fall	Dry Weather Flow	7.0	0.1194	1.7	8.4	612
11/21/2011 (0.44 in)		Stormwater runoff	11.5	0.3297	2.9	7.4	276
01/12/2012	Winter	Dry Weather Flow	10.2	0.1150	1.1	8.3	644
01/22/2012 (0.42 in)		Stormwater runoff	7.7	0.1730	2.2	7.3	145
04/05/2012	Spring	Dry Weather Flow	34.5	0.2249	0.7	7.7	621
04/11/2012 (P: 0.22 in)		Stormwater runoff	6.6	0.7934	12.0	7.6	427
06/00/2012	Summer	Dry Weather Flow	6.7	0.1697	2.5	7.7	697

Table 2. Free fraction of Perylene determined by fluorescence quenching and calculated fraction of benzo(a)pyrene (BaP) of dry weather flow and stormwater runoff runoff in different seasons.

Sampling Date	**Season**	**Samples**	**TOC (mg L^{-1})**	**UV_{254} (cm^{-1})**	**SUVA (L mg^{-1} m^{-1})**	**Log K_{DOM}**	**Free Perylene (%)**	**Free BaP (%)**
11/09/2011	Fall	Dry Weather Flow	7.0	0.1194	1.7	4.4	85	86
11/21/2011 (P: 0.44 in)		Stormwater runoff	11.5	0.3297	2.9	4.8	58	60
01/12/2012	Winter	Dry Weather Flow	10.2	0.1150	1.1	4.8	59	61
01/22/2012 (P: 0.42 in)		Stormwater runoff	7.7	0.1730	2.2	5.0	55	58
04/05/2012	Spring	Dry Weather Flow	34.5	0.2249	0.7	4.6	40	42
04/11/2012 (P: 0.22 in)		Stormwater runoff	6.6	0.7934	12.0	5.6	28	34
06/04/2012	Summer	Dry Weather Flow	6.7	0.1697	2.5	5.5	32	38

P: Precipitation

E.7 Supporting Information

Table S1. Weather conditions of sampling dates (Anaheim, CA 92803).

Sampling Date	**Season**	**Samples**	**Precipitation (in)**	**High Temp. (F)**	**Low Temp. (F)**	**Ave Temp. (F)**
11/09/2011	Fall	Dry Weather Flow	0.00	73.9	44.1	58.5
11/21/2011		Stormwater runoff	0.44	63.0	46.0	54.5
01/12/2012	Winter	Dry Weather Flow	0.00	72.0	52.0	59.6
01/22/2012		Stormwater runoff	0.42	62.1	46.9	55.6
04/05/2012	Spring	Dry Weather Flow	0.00	66.0	53.1	58.7
04/11/2012		Stormwater runoff	0.22	63.0	53.6	58.3
06/04/2012	Summer	Dry Weather Flow	0.00	69.1	64.2	62.1

Table S2. Characterization of DOM and location of FRI regions (18).

Region	Characterization of DOM	Excitation Range (nm)	Emission Range (nm)
I	Aromatic proteins I	220-250	280-332
II	Aromatic proteins II	220-250	332-380
III	Fulvic acids	220-250	380-580
IV	Microbial by-products	250-470	280-380
V	Humic acids	250-470	380-580

E.8 References

1. Makepeace, D. K.; Smith, D. W.; Stanley, S. J., URBAN STORMWATER QUALITY - SUMMARY OF CONTAMINANT DATA. *Crit. Rev. Environ. Sci. Technol.* **1995,** *25*, (2), 93-139.

2. Herngren, L.; Goonetilleke, A.; Ayoko, G. A.; Mostert, M. M. M., Distribution of polycyclic aromatic hydrocarbons in urban stormwater in Queensland, Australia. *Environmental Pollution* **2010,** *158*, (9), 2848-2856.

3. Park, M.-H.; Pincetl, S.; Stenstrom, M. K., Water quality improvement by implementation of Proposition O in the Los Angeles river watershed, California. *Water Sci. Technol.* **2008,** *58*, (12), 2271-2278.

4. Estebe, A.; Boudries, H.; Mouchel, J. M.; Thevenot, D. R., Urban runoff impacts on particulate metal and hydrocarbon concentrations in river seine: Suspended solid and sediment transport. *Water Sci. Technol.* **1997,** *36*, (8-9), 185-193.

5. Sharma, M.; Marsalek, J.; McBean, E., MIGRATION PATHWAYS AND REMEDIATION OF URBAN RUNOFF FOR PAH CONTROL. *Journal of Environmental Management* **1994,** *41*, (4), 325-336.

6. Swamikannu, X.; Radulescu, D.; Young, R.; Allison, R., A comparative analysis: storm water pollution policy in California, USA and Victoria, Australia. *Water Sci. Technol.* **2003,** *47*, (7-8), 311-317.

7. Hoffman, E. J.; Mills, G. L.; Latimer, J. S.; Quinn, J. G., URBAN RUNOFF AS A SOURCE OF POLYCYCLIC AROMATIC-HYDROCARBONS TO COASTAL WATERS. *Environ. Sci. Technol.* **1984,** *18*, (8), 580-587.

8. Menzie, C. A.; Hoeppner, S. S.; Cura, J. J.; Freshman, J. S.; LaFrey, E. N., Urban and suburban storm water runoff as a source of polycyclic aromatic hydrocarbons (PAHs) to Massachusetts estuarine and coastal environments. *Estuaries* **2002,** *25*, (2), 165-176.

9. Gonzalez, A.; Moilleron, R.; Chebbo, G.; Thevenot, D. R., Determination of polycyclic aromatic hydrocarbons in urban runoff samples from the "Le Marais" experimental catchment in Paris centre. *Polycyclic Aromatic Compounds* **2000,** *20*, (1-4), 1-19.

10. Marsalek, J.; Brownlee, B.; Mayer, T.; Lawal, S.; Larkin, G. A., Heavy metals and PAHs in stormwater runoff from the Skyway Bridge, Burlington, Ontario. *Water Quality Research Journal of Canada* **1997,** *32*, (4), 815-827.

11. Wang, X. C.; Zhang, Y. X.; Chen, R. F., Distribution and partitioning of polycyclic aromatic hydrocarbons (PAHs) in different size fractions in sediments from Boston Harbor, United States. *Mar. Pollut. Bull.* **2001,** *42*, (11), 1139-1149.

12. Chen, W.; Westerhoff, P.; Leenheer, J. A.; Booksh, K., Fluorescence excitation - Emission matrix regional integration to quantify spectra for dissolved organic matter. *Environ. Sci. Technol.* **2003,** *37*, (24), 5701-5710.

13. Krasner, S. W.; Croue, J. P.; Buffle, J.; Perdue, E. M., Three approaches for characterizing NOM. *J. Am. Water Work Assoc.* **1996,** *88*, (6), 66-79.

14. Carter, C. W.; Suffet, I. H., BINDING OF DDT TO DISSOLVED HUMIC MATERIALS. *Environ. Sci. Technol.* **1982,** *16*, (11), 735-740.

15. The California "State Implementation Plan" (SIP), Policy for Implementation of Toxics Standards for Inland Surface Waters Enclosed Bays, and Estuaries from the California State Water Resources Control Board, Section 1.4 "Calculation of Effluent Limitations" (http://www.waterboards.ca.gov/water_issues/programs/state_implementation_policy/docs/final.pdf).

16. WASTE DISCHARGE REQUIREMENTS FOR DISNEYLAND RESORT. In *ORDER NO. R8-2008-0001,* NPDES NO. CA0106283. California Regional Water Quality Control Board Santa Aana Region, 2008.

17. Li, Y. X.; Lau, S. L.; Kayhanian, M.; Stenstrom, M. K., Particle size distribution in highway runoff. *Journal of Environmental Engineering-Asce* **2005,** *131*, (9), 1267-1276.

18. Li, Y.; Lau, S.-L.; Kayhanian, M.; Stenstrom, M. K., Dynamic characteristics of particle size distribution in highway runoff: Implications for settling tank design. *Journal of Environmental Engineering-Asce* **2006,** *132*, (8), 852-861.

19. Li, Y.; Kang, J.-H.; Lau, S.-L.; Kayhanian, M.; Stenstrom, M. K., Optimization of Settling Tank Design to Remove Particles and Metals. *Journal of Environmental Engineering-Asce* **2008,** *134*, (11), 885-894.

20. Kang, J. H.; Kayhanian, M.; Stenstrom, M. K., Implications of a kinematic wave model for first flush treatment design. *Water Res.* **2006,** *40*, (20), 3820-3830.

21. *Standard Methods For the Examination of Water and Wastewater*. 22 ND ed.; American Public Health Association: Washington, 2012.

22. Revchuk, A. D.; Suffet, I. H., Ultrafiltration separation of aquatic natural organic matter: Chemical probes for quality assurance. *Water Res.* **2009,** *43*, (15), 3685-3692.

23. Rosario-Ortiz, F. L.; Snyder, S.; Suffet, I. H., Characterization of the polarity of natural organic matter under ambient conditions by the polarity rapid assessment method (PRAM). *Environ. Sci. Technol.* **2007,** *41*, (14), 4895-4900.

24. Holbrook, R. D.; Breidenich, J.; DeRose, P. C., Impact of reclaimed water on select organic matter properties of a receiving stream-fluorescence and perylene sorption behavior. *Environ. Sci. Technol.* **2005,** *39*, (17), 6453-6460.

25. MacDonald, B. C.; Lvin, S. J.; Patterson, H., Correction of fluorescence inner filter effects and the partitioning of pyrene to dissolved organic carbon. *Anal. Chim. Acta* **1997,** *338*, (1-2), 155-162.

26. Gauthier, T. D.; Shane, E. C.; Guerin, W. F.; Seitz, W. R.; Grant, C. L., FLUORESCENCE QUENCHING METHOD FOR DETERMINING EQUILIBRIUM-CONSTANTS FOR POLYCYCLIC AROMATIC-HYDROCARBONS BINDING TO DISSOLVED HUMIC MATERIALS. *Environ. Sci. Technol.* **1986,** *20*, (11), 1162-1166.

27. Rebhun, M.; Meir, S.; Laor, Y., Using dissolved humic acid to remove hydrophobic contaminants from water by complexation-flocculation process. *Environ. Sci. Technol.* **1998,** *32*, (7), 981-986.

28. Hsu, M.-H., Suffet, I.H. (Mel) Understanding the Interaction of Hydrophobic Organic Pollutants and Dissolved Organic Matter in Natural and Treated Drinking Water. In Los Angeles, 2012.

29. Rosario-Ortiz, F. L.; Snyder, S. A.; Suffet, I. H., Characterization of dissolved organic matter in drinking water sources impacted by multiple tributaries. *Water Res.* **2007,** *41*, (18), 4115-4128.

30. Birch, H.; Gouliarmou, V.; Lutzhoft, H.-C. H.; Mikkelsen, P. S.; Mayer, P., Passive Dosing to Determine the Speciation of Hydrophobic Organic Chemicals in Aqueous Samples. *Anal. Chem.* **2010,** *82*, (3), 1142-1146.

31. Chin, Y. P.; Aiken, G. R.; Danielsen, K. M., Binding of pyrene to aquatic and commercial humic substances: The role of molecular weight and aromaticity. *Environ. Sci. Technol.* **1997,** *31*, (6), 1630-1635.

32. Tanaka, S.; Oba, K.; Fukushima, M.; Nakayasu, K.; Hasebe, K., Water solubility enhancement of pyrene in the presence of humic substances. *Anal. Chim. Acta* **1997,** *337*, (3), 351-357.

33. Pedersen, J. A.; Schweitzer, L. E.; Lin, C. H. M.; Suffet, I. H., Effect of oxic state on nonpolar organic contaminant distribution, mobility, and bioavailability in estuarine sediments. *Israel Journal of Chemistry* **2002,** *42*, (1), 109-118.

34. Lin, C. H. M.; Pedersen, J. A.; Suffet, I. H., Influence of aeration on hydrophobic organic contaminant distribution and diffusive flux in estuarine sediments. *Environ. Sci. Technol.* **2003,** *37*, (16), 3547-3554.

35. Pedersen, J. A.; Gabelich, C. J.; Lin, C. H.; Suffet, I. H., Aeration effects on the partitioning of a PCB to anoxic estuarine sediment pore water dissolved organic matter. *Environ. Sci. Technol.* **1999,** *33*, (9), 1388-1397.

36. HunchakKariouk, K.; Schweitzer, L.; Suffet, I. H., Partitioning of 2,2',4,4'-tetrachlorobiphenyl by the dissolved organic matter in oxic and anoxic porewaters. *Environ. Sci. Technol.* **1997,** *31*, (3), 639-645.

F. Conclusions and Future Work

F.1 Conclusions

Hydrophobic organic pollutants (HOPs), such as polyaromatic hydrocarbons primarily from automobile exhausts and dissolved organic matter (DOM) are ubiquitous in the aquatic environment. The association between DOM and HOPs as a bound interaction of DOM-HOPs minimizes the bioavailability of free HOPs and their potential health effects. In addition, DOM is also the precursor of disinfection by-products involving the disinfection treatment processes.

It is very important to understand the relationship between free and bound HOPs, disinfection by-products, and DOM in drinking water treatment, stormwater runoff and dry weather flow of aquatic environment. This thesis explored the binding phenomenon between HOPs and DOM in raw and treated water from water treatment plants, after powdered activated carbon treatment, and in stormwater runoff and dry weather flow.

This thesis also introduced the analytical methodologies for characterizing DOM and the hazardous potential of HOPs and thus understanding their relationship. DOM characteristics were measured for: 1) total concentration of organic carbon by dissolved organic carbon (DOC), 2) aromaticity by UV absorbance and specific UV absorbance (SUVA), and 3) size distribution by ultrafiltration (UF), 4) polarity by polarity rapid assessment method (PRAM), 5) UV and fluorescent chemical components by UV spectrometer and fluorescence excitation-emission matrix (EEM) and fluorescence regional integration (FRI). Hazardous potential of HOPs was measured by fluorescence quenching determined partition coefficient K_{DOM}.

Studies have been completed and showed that monitoring both the free and bound forms of HOPs as well as disinfection by-products (such as, trihalomethanes) and their relationship to DOM during drinking water treatment processes is necessary to better understand drinking water quality and give more effective suggestions to optimize treatment processes. In addition, this work showed the relationship between DOM and HOPs in equilibrium with DOM-HOPs needs definition on a seasonal basis to understand the bioavailability of HOPs in dry weather flow and stormwater runoff events. The determination of free and total HOPs has not been considered in the California "State Implementation Plan" for water quality-based effluent limits of HOPs. A method using a standard probe- perylene has been developed to be able to evaluate these situations on a site specific basis since DOM is site specific.

Key findings of this thesis were: 1) DOM characteristics are different from site to site and affect pollutants removal and formation. 2) Bulk SUVA shows a positive correlation with Log K_{DOM} (R^2=74%). Thus, DOM with more aromatic structure can result in higher binding between HOPs and DOM. 3) DOM with higher concentration, aromaticity, and molecular weight can have more ability to form THMs. 4) Under the conditions studied, PAC (20 mg/L) is an effective method to control both THMs and the hazard potential of HOPs. 5) DOM in urban runoff with higher molecular weight and aromaticity can associate with more HOPs. As a result, the distribution of HOPs affected by DOM in urban runoff needs definition on a seasonal basis and runoff types.

Chapter 2 presented that the developed PAH probe can measure the potential amount of DOM associated PAHs and the amount of free PAHs in natural and drinking waters and thus define a standard method scale of reactivity of different DOMs. The interaction between HOPs and DOM in different environments showed the partition coefficient between DOM and perylene (K_{DOM}) had higher correlation with SUVA ($R^2 = 0.74$), and moderate correlation with UV_{254} ($R^2 = 0.50$), fluorescence distribution of fulvic acids ($R^2 = 0.58$), UV_{254} for > 10 kDa fraction ($R^2 = 0.54$), and UV_{254} for > 10 kDa fraction ($R^2 = 0.52$). The results indicate DOM in natural water and drinking water treatment process with higher molecular weight and higher content of aromaticity can bind more HOPs. Characterization of DOM and using perylene as a PAH probe can help to understand the behaviors between HOPs and DOM. It is also very important that water treatment plant operators know the possible distribution of HOPs by the monitoring program developed in this study. Then if there is a HOPs pollution event happened in the water treatment plant, the operator can response more quickly and effectively. Furthermore, by removing the specific characteristics of DOM generating DBPs and keeping the specific characteristics of DOM binding with HOPs, would have a better drinking water quality.

Chapter 3 showed that DOM was mainly composed of fulvic and humic acids according to the Flourescence Method as expected. In general, fulvic and humic acids were with negative charges and of higher molecular weight. Following the water treatment processes, THMs decreased as DOM was removed. DOM characteristics are definitely changed after treatment. The results showed that THMs had positive and high correlation with TOC concentration of bulk water samples ($R^2 = 0.85$), UV_{254} ($R^2 = 0.88$), and SUVA ($R^2 = 0.68$); TOC concentration of > 10 kDa ($R^2 = 0.77$), 10 - 5 kDa ($R^2 = 0.79$) fractions; and UV_{254} of > 10 kDa ($R^2 = 0.63$), 10 - 5 kDa ($R^2 = 0.72$). Therefore, higher DOM concentration, DOM with more aromatic structures, and DOM with > 10 kDa, 10 – 5 kDa size fractions have ability to produce more THMs.

Chapter 4 found that PAC changed the DOM size, polarity and chemical components distribution of the DOM and decreased DOC, UV_{254} and SUVA values. PAC can effectively remove TOC, UV_{254}, DOM size fractions smaller than 5 kDa and some larger than 10 kDa DOM that would affect THMFP removal. Surprisingly, PAC did not change the binding ability of DOM to interact with HOPs during this water treatment study. The PAC treatment used in this study might be an effective method to control both THMs and hazard potential of HOPs through removing specific DOM characteristics. Various DOM characteristics behave differently during the treatment and need to be monitored.

Chapter 5 presented that DOM characteristics vary seasonal and there is a significant difference between dry weather runoff and stormwater runoff events. Thus the relationship between DOM and HOPs in equilibrium with DOM-HOPs needs definition on a seasonal basis to understand the bioavailability of HOPs. The California “State Implementation Plan” indicates site-specific dissolved and total recoverable “metals” can be developed from direct determination of fraction dissolved metals. The determination of free and total HOPs has not been considered. The data in this paper indicate it should be as free HOPs are bioavailable and only a part of the total is soluble. This study has defined the bioavailability by a standard test using a PAH probe and found 34 - 86 % free equivalent BaP. The association between DOM and HOPs is not controlled by the total amount of DOM as total organic carbon but the specific mixture of DOM compounds present. The Log K_{DOM} demonstrated positive correlation with UV_{254} values in 10 - 5 kDa fractions ($R^2 = 0.72$) and UV_{254} in 10 - 5 kDa fractions in terms of percentage of total UV_{254} value ($R^2 = 0.66$). Therefore the aromatic structures in the mixture of DOM compounds appear to control the interaction of PAHs with DOM. Understand the fate and transport of HOPs in urban runoff can help optimize the Toxicity Identification Evaluation process required in the National Pollutant Discharge Elimination System (NPDES) permit by relating the toxic free PAHs from the non-toxic bound DOM-PAH complex and develop better best management practices (BMPs) to treat HOPs in urban runoff. For example, adding a specific type of DOM to water might be a possible BMP for HOPs pollution to decrease the hazardous potential in urban runoff. Furthermore, the bioavailability of HOPs of receiving water bodies is affected from upstream urban runoff. The fate and transport of HOPs in aquatic environments still depends on the real in-situ partition coefficients of organic matters between sediments, pore water, suspended sediments and runoff. Thus, this information should be considered when regulatory agencies set up water quality-based effluent limits of HOPs for NPDES permit and total maximum daily loads (TMDLs) of impaired water bodies under the Clean Water Act 303(d) list.

F.2 Future Work

The monitoring procedure developed in this thesis has been proven an effective protocol to characterize DOM and thus understand the removal and formation of pollutants affected by DOM in the aquatic environments. The analytical techniques used in this work include EEM-FRI, UF, UV_{254}, SUVA, TOC, PRAM, and FQ providing real in-situ DOM information and only need a short period of time (within an hour). Understand real in-situ DOM characteristics can help to optimize drinking water treatment processes and lower the operation cost by effectively removing selected DOM. DOM characterization in the urban runoff was found first time in this work. The procedure developed in this study can quickly identify the bioavailability of HOPs in the dissolved phase of urban runoff.

The monitoring protocol should be continued applied in the drinking water treatment plants, wastewater treatment plants, different unit operations of treatment techniques such as coagulation, activated carbon adsorption, ultrafiltration, nanofiltration, and UV disinfection to understand more details of correlations between DOM, THMFP, and association of HOPs to optimize treatment processes to decrease THMPF while keeping less hazardous potential and build an in-situ mathematic model for correlations. The monitoring protocol should also be applied in urban runoff and receiving water bodies such as rivers, creeks, estuaries, wetlands, lakes, and oceans to better understand the bioavailability of HOPs for regulations.

This work also identified when measuring K_{DOM}, there is no significant difference between SPME-GC/MS and FQ methods. Therefore, SPME and FQ can complement with each other. It means that at a site of interest, while FQ obtains K_{DOM}, SPME measures the free concentration of

HOPs. Thus, real in-situ free, bound, and total concentration of HOPs can be known easily in a short time (less than two hours). This information is very important for HOPs management in aquatic environments.

More online monitoring techniques such as online size exclusion chromatography (SEC), online TOC, online fluorescence and online UV detector for different wavelengths should be applied at sites of interest or during the treatments to better understand the correlations of different DOM characteristics such as size, polarity, and chemical functionality.