Study of the pH influence on the optical properties of dissolved organic matter using fluorescence excitation–emission matrix and parallel factor analysis

Mingquan Yan^{a,*}, Qiangwei Fu^b, Dechao Li^b, Gunfa Gao^b, Dongsheng Wang^c

^a Department of Environmental Engineering, Peking University, The Key Laboratory of Water and Sediment Sciences, Ministry of Education, Beijing 100871, China

^b College of Environmental Sciences and Engineering, Chang'an University, Xi'an, Shanxi, 710064, China

^c State Key Laboratory of Environmental Aquatic Chemistry, Research Center for Eco-Environmental Sciences, CAS, POB 2871, Beijing 100085, China

ARTICLE INFO

Article history:

Received 7 November 2012

Received in revised form

31 January 2013

Accepted 28 February 2013

Available online 30 March 2013

Keywords:

Fluorescence

PARAFAC

pH

Dissolved organic matter

ABSTRACT

This study investigated the optical properties of dissolved organic matter (DOM) using the fluorescence excitation–emission matrix (EEM) method combined with parallel factor (PARAFAC) analysis. The examined DOM samples included Suwannee River fulvic acid (SRFA) and Nordic Reservoir natural organic matter (NRNOM). The optical properties of the DOM were determined from the behavior of individual groups of DOM fluorophores responding to different ionization states. The PARAFAC examination revealed that there were six independent EEM components in the SRFA that behaved differently in terms of pH influence on their fluorescence intensity. The dominant EEM peak locations ($\lambda_{\text{ex}}/\lambda_{\text{em}}$) of these components were (230, 330) nm/420 nm (Component 1), (250, 350) nm/450 nm (Component 2), (240, 340) nm/460 nm (Component 3), (220, 280) nm/380 nm (Component 4), (270, 400) nm/490 nm (Component 5), and (280, 340) nm/540 nm (Component 6). However, only four EEM components were observed in the NRNOM, which are similar to Components 1, 2, 3 and 4 in the SRFA. It can be speculated that Components 1, 2, 3 and 6 can be categorized as traditional terrestrial humic-like chromophores, while they are composed of different fractions of carboxylic-like and phenolic-like chromophores; Component 4 can be categorized as protein-like fluorophores primarily composed of carboxylic-like chromophores, and Component 5 can be categorized as a microbial humic-like component that is overwhelmingly composed of phenolic-like fluorophores. The results demonstrated that PARAFAC analysis is a promising approach for characterizing the fine functions in DOM.

© 2013 Elsevier B.V. All rights reserved.

1. Introduction

Dissolved organic matter (DOM) is ubiquitous in natural waters and is derived from plant or terrestrial (allochthonous) and algal (autochthonous) sources. DOM is a heterogeneous mixture of various molecular weight aromatic and aliphatic organic compounds that contain oxygen, nitrogen, and sulfur functional groups (e.g., carboxyl, phenol, enol, alcohol, carbonyl, amine, and thiol) [1,2]. The properties of DOM strongly affect its reactivity in both natural and engineered aquatic systems [1,3–7].

Fluorescence spectroscopy is a simple, sensitive, and nondestructive analytical technique that has the potential to provide invaluable information about the molecular structure, functionalities, and conformation and intramolecular and intermolecular interactions of DOM with proton and metal ions [1,8,9]. Early studies used single excitation and emission wavelengths, which

are typical of humic-like fluorophores [8,10–16]. Fluorescence excitation–emission matrix (EEM) spectroscopy can measure emission spectra across a range of excitation wavelengths and provide an overall view of all the features that exist within a selected spectral range. This technique has satisfactorily been used to characterize DOM in natural environments. Although the EEM spectroscopic approach has a greater density of spectral information than the traditional fluorescence approaches, it can demonstrate that quenching (or enhancement) of fluorescence intensity by proton and metal ions is quantitatively dissimilar in different regions of the fluorescence landscape [2,17–21]. The EEM landscape has been typically characterized by noting the locations of one or more peaks that correspond to the maximum fluorescence intensities (“peak picking”) [22–24]. Due to the broad nature and the lack of fine structure of the organic matter fluorescence spectra, the visual “peak picking” process is subjective in nature and may lead to erroneous conclusions because peaks commonly reflect more than one underlying fluorophore. An alternative, multiway methods, such as parallel factor (PARAFAC) analysis of the EEM sample pool, can be used to resolve mixtures

* Corresponding author. Tel.: +86 10 62755914 81; fax: +86 10 62756526.

E-mail addresses: yanmq@pku.edu.cn, yankingcn@yahoo.com (M. Yan).

of fluorescent compounds into their individual constituents by relying on the visual identification of peaks and the ratios of fluorescence in different regions of the spectrum, thereby reducing the interference problem and allowing a more accurate quantification [25–27]. Therefore, EEM in combination with PARAFAC has been used to investigate the oxidation and metal complexation processes of DOM [28–31].

Because the functionality of DOM, such as carboxylic, phenolic, alcoholic, enolic hydroxyl, carbonyl and nitrogen-, S- and P-containing functional groups, is very sensitive to pH, and the hydrolysis process of the functionalities may affect their fluorescence intensity [23]. In this paper, the optical properties of DOM were examined by investigating the influence of pH using fluorescence excitation–emission matrix and parallel factor analysis; the results of this study will provide some important information of the properties of DOM for further understanding its interaction with metals in future studies.

2. Methods and materials

2.1. Reagents and chemicals

All chemicals were AR grade unless mentioned otherwise. All solutions were prepared using Milli-Q water ($18.2 \text{ M}\Omega \text{ cm}^{-1}$, Millipore Corp., MA, USA), including 0.01, 0.1 and 1.0 mol L^{-1} of NaOH and 0.01, 0.1 and 1.0 mol L^{-1} of HClO_4 .

2.2. Samples

Suwannee River fulvic acid (SRFA, 1S101F) and Nordic Reservoir natural organic matter (NRNOM, 1R108N) were obtained from the International Humic Substances Society (IHSS). SRFA and NRNOM solutions were prepared at a concentration of 5.0 mg L^{-1} DOC in a total volume of 100 mL. To minimize hysteresis effects, the pH of the solution was cycled between 2.0 and 11.0 four times before the titration analysis. During this cycling, the pH of the solution was held at each end value for 30 min to account for the potentially slow equilibration of the DOM molecules. The background ionic strengths were established by including 0.04 M NaClO_4 as a background electrolyte (AR grade). The total dissolved organic carbon (DOC) was analyzed using a Shimadzu TOC-Vcsh carbon analyzer.

2.3. Fluorescence titration

The pH of the solutions was controlled during titrations from 3.0 to 11.0 by the addition of HClO_4 or NaOH solutions at concentrations of 1, 0.1, or 0.01 M . The containers were continuously stirred during acid and base addition and allowed to equilibrate for 15 min prior to the removal of 1 mL aliquots for fluorescence EEM analysis. The aliquots were returned to the solution before the next addition of NaOH for titration. Fluorescence EEM spectra were obtained using a Perkin-Elmer LS 50 B Luminescence spectrometer (with a 1 cm cell). The EEM fluorescence spectroscopy involved scanning and recording 40 individual emission spectra at sequential 5 nm increments at excitation wavelengths (λ_{ex}) between 220 and 415 nm. The emission wavelength (λ_{em}) range was set from 350 to 580 nm in 0.5 nm increments. The instrumental parameters were excitation and emission slits, 5 nm, and scan speed, 1200 nm min^{-1} .

2.4. PARAFAC modeling

The approach of PARAFAC modeling of the EEMs followed the procedure described in detail by Stedmon and Bro [25] and Ohno et al. [28]; only a brief description will be provided here. Essentially, PARAFAC examines a consistent series of EEM landscapes that form a

so-called three-way array of size $I \times J \times K$, where J is the number of emission wavelengths, K is the number of excitation wavelengths, and I is the number of samples, which corresponds to the fluorescence EEM spectra of the DOM samples measured at various pH values in this study. This technique provides an estimate of the number of independent fluorophores and their excitation and emission spectra, as well as the relative contributions (or concentrations) of each fluorophore in the samples.

Corrections for Raman scattering were performed by subtracting water blanks. The higher intensity Rayleigh scattering lines were removed by replacing the fluorescence intensity values with missing values in the region immediately adjacent to where the emission wavelength was equal to 1 and 2 times the excitation wavelength. The EEM spectra had a triangularly shaped region where the emission wavelength was less than that of the excitation wavelength. Because such a characteristic is not expected for DOM solutions, these data pairs were set to zero.

The PARAFAC modeling was conducted using MATLAB 2010a (Mathworks, Natick, MA) with the N-way toolbox and the DOM-Fluor toolbox [25]. A non-negativity constraint was applied to the parameters to allow only chemically and spectroscopically relevant results [25].

3. Result and discussion

3.1. Influence of pH on EEM spectra of DOMs.

The fluorescence EEM spectra at pH 3.0, 7.0, and 11.0 for SRFA and NRNOM are shown in Fig. 1. In both samples, two obvious peaks (peak A $\lambda_{\text{ex}}/\lambda_{\text{em}}=245\text{--}260 \text{ nm}/420\text{--}460 \text{ nm}$ and Peak B $\lambda_{\text{ex}}/\lambda_{\text{em}}=325\text{--}340 \text{ nm}/420\text{--}460 \text{ nm}$) could be observed in the EEM spectra at any pH value, and a relatively weak peak (peak C, $\lambda_{\text{ex}}/\lambda_{\text{em}}=325\text{--}340 \text{ nm}/450\text{--}490 \text{ nm}$) appeared at higher pH values but was not very obvious at lower pH values.

Chen et al. [2] have operationally delineated the EEM landscape into five regions (similar to an aromatic protein (two regions, I, II), fulvic acid (III), microbial byproduct (IV), and humic acid (V)), based on literature reports of the dominant EEM peak locations and analysis of DOM fractions, model compounds, and extracted biomass organic matter. Note that the dominant EEM peak location of Peak A observed in this work was in domain III, and Peaks B and C were located in domain V, these peaks can be categorized as fulvic acid-like substances (Peak A) and humic acid-like substances (Peak B and C) according to literature reports [2,21,32–35].

The fluorescence intensity of both samples clearly depends on the pH. The maximum fluorescence intensities of Peaks A, B and C for both samples at various pH values were picked up, and the results are shown in Figure S1. Not only the fluorescence intensities of the same peak in SRFA and NRNOM but also the three peaks in either sample presented different trends with changes in the pH change. This result indicates that the chemical behavior of the fluorophores in SRFA and NRNOM must be somewhat different [23], and it needs to be further studied.

To clearly demonstrate the influence of pH on the fluorescence intensity, fluorescence EEM spectra at each pH value vs. the reference were carried out to distinguish the chemical behavior of EEM. The fluorescence EEM spectra at pH 5.0, 7.0, 9.0 and 11.0 vs. that at pH 3.0 are shown in Fig. 2 for SRFA and Fig. 3 for NRNOM. Five regions, referred to as R1, R2, R3, R4 and R5, were observed in both the SRFA and NRNOM EEM spectra with changes in pH. The dominant EEM peak locations ($\lambda_{\text{ex}}/\lambda_{\text{em}}$) for these regions were 220–350 nm/350–380 nm (R1), 220–290 nm/450–550 nm (R2), 280–320 nm/400–430 nm (R3), 300–340 nm/450–530 nm (R4) and 360–415 nm/450–550 nm (R5). Although previous studies also divided these spectra into five regions, the domains of

Fig. 1. EEM landscape at various pH values. SRFA at (a) pH 3.0, (b) pH 7.0, and (c) pH 11.0 and NRNM at (d) pH 3.0, (e) pH 7.0, and (f) pH 11.0.

Fig. 2. Changes in the EEM landscape with reference pH values for SRFA. (a) pH 5.0 vs. pH 3.0; (b) pH 7.0 vs. pH 3.0; (c) pH 9.0 vs. pH 3.0; (d) pH 11.0 vs. pH 3.0.

Fig. 3. Changes in the EEM landscape with reference pH values for NRNM. (a) pH 5.0 vs. pH 3.0; (b) pH 7.0 vs. pH 3.0; (c) pH 9.0 vs. pH 3.0; (d) pH 11.0 vs. pH 3.0.

each region found in this study are clearly different from those of previous studies [2].

The division of the five regions based on the influence of pH was also inconsistent with the three peak regions shown in Fig. 1. The peaks in Fig. 1 represent the cumulative fluorophores that have similar excitation and emission wavelength responses, whereas these fluorophores exhibited different properties with changes in the pH. Note that it may not be accurate to divide the EEM landscape into five component regions, as shown in Figs. 2 and 3, instead of three component regions, as shown in Fig. 1, because the one region in Figs. 2 and 3 that have similar responses to the influence of pH may be composed of more than one component.

3.2. EEM spectra deconvoluted by PARAFAC analysis

To ascertain the behavior of the fluorophores that contributes to the EEM of both samples, the entire set of the EEM data generated using EEM spectra at various pH values was examined using PARAFAC. The PARAFAC models with 2–7 components were separately computed for the SRFA and NRNM data sets. Six PARAFAC components were determined to be present in the SRFA (Fig. 4), and four PARAFAC components were found in the NRNM (Fig. 5).

The appropriate number of components was chosen to be sufficiently high to fully describe the systematic variation in the data where the assumptions of trilinearity become invalid, i.e., where the core consistency diagnostic score becomes low and the residual analysis reaches a minimum. The core consistency diagnostic score was $> 90\%$, and the sum of squared error was $< 10^5$

for each data set; therefore, the error is acceptable [29]. The sum of the squared error is shown in Figure S2.

The EEM spectra of the SRFA were processed by numerically deconvoluting the SRFA into six EEM components, which are referred to as Component 1, Component 2, Component 3, Component 4, Component 5 and Component 6 (as shown in Table 1). The dominant EEM peak locations ($\lambda_{ex}/\lambda_{em}$) for these components were (230, 330) nm/420 nm (Component 1), (250, 350) nm/450 nm (Component 2), (240, 340) nm/460 nm (Component 3), (220, 280) nm/380 nm (Component 4), (270, 400) nm/490 nm (Component 5), and (280, 340) nm/540 nm (Component 6). The EEM spectra of the NRNM were processed into four components (Fig. 5), which are referred to as Component 1, Component 2, Component 3 and Component 4, and their dominant EEM peak locations ($\lambda_{ex}/\lambda_{em}$) were (220, 330) nm/430 nm (Component 1), (250, 340) nm/480 nm (Component 2), (230, 330) nm/430 nm (Component 3), (220, 310) nm/380 nm (Component 4).

By comparing the EEM components between the SRFA and the NRNM, it was observed that the four components in the NRNM were generally similar to those in the SRFA, corresponding to Components 1, 2, 3, and 4 in Fig. 4. The SRFA exhibited more complicated fluorophore characteristics than the NRNM. This observation may be because the SRFA is from Suwannee River and is more complicated than the NRNM, which is obtained from a reservoir. This result is supported by the data from IHSS website (Elemental Compositions and Stable Isotopic Ratios of IHSS Samples). S and P were not detected in the NRNM, whereas the amounts of S and P in the SRFA were 0.44 mg L^{-1} and $< 0.01 \text{ mg L}^{-1}$, respectively.

Fig. 4. Excitation and emission spectral loadings of the non-negatively on strained PARAFAC model components of the SRFA.

Fig. 5. Excitation and emission spectral loadings of the non-negatively on strained PARAFAC model components of NRNM.

Table 1
The summary of the components deconvoluted by PARAFAC.

	EEM peak locations ($\lambda_{\text{ex}}/\lambda_{\text{em}}$)	Category	Reference	Compounds in term of acid–base property
Component 1	(230, 330) nm/420 nm	Terrestrial humic-like	[29,30,33,35,40–42]	Both carboxylic-like and phenolic-like chromophores,
Component 2	(250, 350) nm/450 nm	Terrestrial humic-like	[29,30,33,35,40–42]	Primarily composed of carboxylic-like chromophores
Component 3	(240, 340) nm/460 nm	Terrestrial humic-like	[29,30,33,35,40–42]	Primarily composed of phenolic-like chromophores
Component 4	(220, 280) nm/380 nm	Protein-like (tryptophan and tyrosine-like)	[41,40]	Primarily composed of carboxylic-like fluorophores
Component 5	(270, 400) nm/490 nm	Microbial humic-like	[30,33,41,42]	Overwhelmingly composed of phenolic-like fluorophores
Component 6	(280, 340) nm/540 nm	Terrestrial humic-like	[29,30,33,35,40–42]	Composed of some chromophores other than carboxylic-like and phenolic-like chromophores

Fig. 6. The intensity of each component with changes in pH for SRFA. (a) Calculated by a PARAFAC analysis; (b) fluorescence intensity extracted from the corresponding location of each component maximum.

The maximum fluorescence intensity of each component can be extracted from the PARAFAC analysis, which represents the concentration of each PARAFAC component. The results for SRFA are shown in Fig. 6a. The intensities of the six components were significantly different, and they exhibited different trends with

changes in the pH. This result indicated that the components have different degrees of effectiveness at different pH values. According to Laane [36], the change in the fluorescent intensity with pH is likely due to the alteration of the molecular orbital of the excitable electrons. Because fluorescence properties depend on environmental conditions such as ionization state, it shows two acid functions due to pH change. On one hand, the fluorophore has an acid group with a pKa between 2.0 and 5.0, which corresponds to carboxylic-like functionality [37]. On the other hand, the fluorophore's structure is dependent on a phenolic-like function, which has a pKa between 8.0 and 10.0. A fluorescence analysis of model compounds has demonstrated that electron-donating functional groups (e.g., amine, hydroxyl) can also significantly increase fluorescence intensities [2]. It has been well recognized that carboxylic chromophores overwhelmingly contributed to the changes in fluorescence at pH values between 3.0 and 5.0, whereas phenolic chromophores are predominant at pH values between 8.0 and 10.0 [38].

In addition, Ghosh and Schnitzer [39] observed that the structure of humic substances varies with modifications in their environment, such as pH changes. Humic substances have a linear structure at high pH values and a coil structure when the pH decreases. A spherocolloidal configuration could mask some fluorophores inside of their structure. At higher pH values, the configuration becomes linear, and some fluorophores, which are no longer masked, can fluoresce, thereby increasing the fluorescence intensity.

The intrinsic quenching and enhancement mechanism is currently not clear. In combination with previous literature reports [29,30,33,35,40–42], it can be speculated that Component 1, 2, 3 and 6 can be categorized as traditional, terrestrial humic-like compounds, which are composed of different fractions of carboxylic-like and phenolic-like chromophores. Component 1 is composed of both carboxylic-like and phenolic-like chromophores, and the intensity of Component 1 rapidly increased at pH values between 3.0 and 5.0 and decreased in the strongly basic region. Component 2 is primarily composed of carboxylic-like chromophores, and the intensity of Component 2 rapidly increased at pH values between 3.0 and 5.0 and decreased gradually as the pH increased to 6.0. Component 3 is primarily composed of phenolic-like chromophores, and the intensity of Component 3 increased gradually as the pH increased to 9.0 and decreased in the strongly basic region. Component 6 appears to be composed of some chromophores other than carboxylic-like and phenolic-like chromophores, and the intensity of Component 6 changed very slightly with changes in the pH. Component 4 is in the excitation and emission wavelength range where protein-like fluorophores have been previously reported [40,41], and these fluorophores are similar to tryptophan and tyrosine-like compounds found in previous PARAFAC studies. Component 4 is

primarily composed of carboxylic-like fluorophores, and the intensity of Component 4 increased at pH values between 3.0 and 5.0 and decreased gradually as the pH increased to 6.0, especially in NRNOM. The fluorescence characteristics of Component 5 have not been traditionally defined [30,41], but they are similar to terrestrial/autochthonous [42] and microbial reduced quinone-like compounds (SQ2 in literature [33]). Therefore, Component 5 can be categorized as a microbial humic-like compounds; it is overwhelmingly composed of phenolic-like fluorophores, and the intensity of Component 5 increased slightly from pH 3.0 to 9.0, with an especially rapid increase in intensity at pH 8.0–9.0.

According to Fig. 4, the intensities at the peak site for each component were extracted and are shown in Fig. 6b. Compared with Fig. 6a, both the intensity values of each component and the trends of the intensity changes for each component with pH are significantly different. It is inaccurate to evaluate the degree of change of each component from the extracted intensity at its domain because the intensity at each site is the sum of the intensity of the relative component.

EEM combined with a PARAFAC analysis is a very useful tool for characterizing DOM. This technique can be extended for characterizing NOM fine functions based on the ionization state and fluorescence dependence of organic functional groups. However, the intrinsic mechanism of such quenching and enhancement is still unclear. With additional DOM characterization techniques, e.g. NEXAFS and NMR, this method may be capable of quantifying the relative concentrations of δ bonds with different electron-donating functional groups or bonded atoms containing electrons (e.g., oxygen, nitrogen, and sulfur). This possibility will be further investigated in a subsequent paper.

4. Conclusions

The following conclusions can be drawn:

- (1) PARAFAC examination revealed that there are six independent EEM components that behave differently in terms of the effects of pH on their fluorescence intensity; The dominant EEM peak locations ($\lambda_{ex}/\lambda_{em}$) of these components were (230, 330) nm/420 nm (Component 1), (250, 350) nm/450 nm (Component 2), (240, 340) nm/460 nm (Component 3), (220, 280) nm/380 nm (Component 4), (270, 400) nm/490 nm (Component 5), and (280, 340) nm/540 nm (Component 6). However, only four PARAFAC components similar to the Component 1, Component 2, Component 3 and Component 4 in the SRFA were observed in the NRNOM.
- (2) It could be speculated that Components 1, 2, 3 and 6 can be categorized as traditional terrestrial humic-like chromophores, which are composed of different fractions of carboxylic-like and phenolic-like chromophores. Component 4 is a protein-like fluorophore that is primarily composed of carboxylic-like chromophores, and Component 5 can be categorized as a microbial humic-like component that is overwhelmingly composed of phenolic-like fluorophores.
- (3) The results demonstrate that PARAFAC analysis is a promising approach for characterizing the fine functions in DOM. However, further investigations are required to reveal the properties of the EEM component in combination with additional DOM characterizing techniques.

Acknowledgments

The authors are very grateful to Prof. Gregory Korshin for his support for this research. This research was supported by the New-Star of Science and Technology supported by Beijing Metropolitan (Grant 2011009) and China Postdoctoral Science Foundation, and a China NSF (Grant 21277005) is also gratefully acknowledged.

Appendix A. Supporting information

Supplementary data associated with this article can be found in the online version at <http://dx.doi.org/10.1016/j.jlum.2013.02.052>.

References

- [1] J.A. Leenheer, J.P. Croue, *Environ. Sci. Technol.* 37 (2003) 18a–26a.
- [2] W. Chen, P. Westerhoff, J.A. Leenheer, K. Booksh, *Environ. Sci. Technol.* 37 (2003) 5701–5710.
- [3] N. Her, G. Amy, D. Foss, J. Cho, Y. Yoon, P. Kosenka, *Environ. Sci. Technol.* 36 (2002) 1069–1076.
- [4] M.Q. Yan, D.S. Wang, S.J. You, J.H. Qu, H.X. Tang, *Water Res.* 40 (2006) 3621–3627.
- [5] G.L. Amy, M.R. Collins, C.J. Kuo, P.H. King, *J. Am. Water Works Assoc.* 79 (1987) 43–49.
- [6] G. Korshin, C.W.K. Chow, R. Fabris, M. Drikas, *Water Res.* 43 (2009) 1541–1548.
- [7] M.Q. Yan, D.S. Wang, B.Y. Shi, Q.S. Wei, H.H. Qu, H.X. Tang, *J. Environ. Sci.—China* 19 (2007) 271–277.
- [8] D.K. Ryan, J.H. Weber, *Anal. Chem.* 54 (1982) 986–990.
- [9] S.E. Cabaniss, *Abstr Pap Am Chem Soc.* 199 (1990) 14–20.
- [10] D.S. Gamble, A.W. Underdown, C.H. Langford, *Anal. Chem.* 52 (1980) 1901–1908.
- [11] S.E. Cabaniss, *Environ. Sci. Technol.* 26 (1992) 1133.
- [12] M.J. Pullin, S.E. Cabaniss, *Environ. Sci. Technol.* 29 (1995) 1460.
- [13] M.U. Kumke, C. Tiseanu, G. Abbt-Braun, F.H. Frimmel, *J. Fluoresc.* 8 (1998) 309.
- [14] J.C.G. Esteves da Silva, A.A.S.C. Machado, C.J.S. Oliveira, M.S.S.D.S. Pinto, *Talanta* 45 (1998) 1155.
- [15] R.L. Cook, C.H. Langford, *Anal. Chem.* 67 (1995) 174.
- [16] D.M. Reynolds, *Water Res.* 37 (2003) 3055.
- [17] J.J. Mobed, S.L. Hemmingsen, J.L. Autry, L.B. McGown, *Environ. Sci. Technol.* 30 (1996) 3061.
- [18] S. Mounier, N. Patel, L. Quilici, J.Y. Benaim, C. Benamou, *Water Res.* 33 (1999) 1523.
- [19] C. Markager, *Mar. Chem.* 82 (2003) 239.
- [20] M. Sierra, M. Giovanela, E. Parlanti, E. Soriano Sierra, *Chemosphere* 58 (2005) 715–733.
- [21] T. Ohno, R. Bro, *Soil Sci. Soc. Am. J.* 70 (2006) 2028.
- [22] J. Luster, T. Lloyd, G. Sposito, I.V. Fry, *Environ. Sci. Technol.* 30 (1996) 1565.
- [23] N. Patel-Sorrentino, S. Mounier, J.Y. Benaim, *Water Res.* 36 (2002) 2571.
- [24] C. Plaza, G. Brunetti, N. Senesi, A. Polo, *Environ. Sci. Technol.* 40 (2006) 917.
- [25] C.A. Stedmon, R. Bro, *Limnol. Oceanogr.—Meth.* 6 (2008) 572.
- [26] R. Bro, *Chemometr. Intell. Lab. Sys.* 38 (1997) 149.
- [27] M. Bahram, R. Bro, C. Stedmon, A. Afkhami, *J. Chemometr.* 20 (2006) 99.
- [28] T. Ohno, A. Amirbahman, R. Bro, *Environ. Sci. Technol.* 42 (2008) 186.
- [29] J. Wu, H. Zhang, P.J. He, L.M. Shao, *Water Res.* 45 (2011) 1711.
- [30] Y. Yamashita, R. Jaffe, *Environ. Sci. Technol.* 42 (2008) 7374.
- [31] K.M.H. Beggs, R.S. Summers, D.M. McKnight, *J. Geophys. Res.—Biogeo.* 114 (2009).
- [32] J.H. Christensen, A.B. Hansen, J. Mortensen, O. Andersen, *Anal. Chem.* 77 (2005) 2210.
- [33] R.M. Cory, D.M. McKnight, *Environ. Sci. Technol.* 39 (2005) 8142.
- [34] G.J. Hall, K.E. Clow, J.E. Kenny, *Environ. Sci. Technol.* 39 (2005) 7560.
- [35] R.K. Henderson, A. Baker, K.R. Murphy, A. Hambly, R.M. Stuetz, S.J. Khan, *Water Res.* 43 (2009) 863.
- [36] R.W.P.M. Laane, *Mar. Chem.* 11 (1982) 395–401.
- [37] J.A. Leenheer, R.L. Wershaw, M.M. Reddy, *Environ. Sci. Technol.* 29 (1995) 393.
- [38] D.J. Dryer, G.V. Korshin, M. Fabbicino, *Environ. Sci. Technol.* 42 (2008) 6644.
- [39] K. Ghosh, M. Schnitzer, *Soil Sci. Soc. Am. J.* 45 (1981) 25.
- [40] Y. Yamashita, E. Tanoue, *Mar. Chem.* 82 (2003) 255.
- [41] P.G. Coble, *Mar. Chem.* 51 (1996) 325.
- [42] C.A. Stedmon, S. Markager, *Limnol. Oceanogr.* 50 (2005) 686.