WATER RESEARCH 59 (2014) 80–89

Available online at www.sciencedirect.com

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Critical evaluation of spectroscopic indices for organic matter source tracing via end member mixing analysis based on two contrasting sources

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ARTICLE INFO

Article history:
Received 3 January 2014
Received in revised form
7 April 2014
Accepted 9 April 2014
Available online 18 April 2014

Keywords:
Absorption spectroscopy
Fluorescence spectroscopy
EEM-PARAFAC
Solution chemistry
End member mixing analysis
Source discrimination

ABSTRACT

Despite the wide use of absorption and fluorescence spectroscopy for tracking the sources of dissolved organic matter (DOM), there are limited studies on evaluating their source discrimination capabilities at variable solution chemistry (pH, NaCl, Ca^{2+}, and DOM concentration). For this study, we compared the applicability of several well-known spectroscopic indices via end member mixing analysis based on two contrasting DOM sources (Suwannee River fulvic acid and an algal DOM). The absorption coefficients and the intensities of fluorescent components from parallel factor analysis (PARAFAC) showed linear relationships with increasing algal carbon fraction in the mixture of the two DOMs. In contrast, although they still behaved conservatively, spectral ratio indices such as spectral slopes, ratios of PARAFAC components, humification index, and fluorescence index changed in nonlinear patterns with the mixing ratios. The indices based on PARAFAC results exhibited strong discrimination capabilities, as indicated by high susceptibility to the changes in DOM sources relative to the analytical precision. While variable NaCl concentrations had limited effects, most fluorescence indices were considerably affected by other solution chemistry such as pH, Ca^{2+}, and DOM level. Our study demonstrated that the applicability of the source discrimination indices should be critically examined especially in the environments with notable changes in the solution chemistry. The solution chemistry effects could be minimized by adjusting samples to a constant condition prior to the measurements or otherwise the effects should be fully taken into account in interpreting the field observations.

1. Introduction

Absorption and fluorescence spectroscopy have been widely used for characterizing dissolved organic matter (DOM) and discriminating the sources in both natural environments and engineered systems (Blough and Del Vecchio, 2002; Leenheer and Croue, 2003; Coble, 2007; Henderson et al., 2009; Ishii and Boyer, 2012). In particular, fluorescence excitation emission matrices combined with parallel factor analysis (EEM-PARAFAC) have been popularly used for identifying individual fluorescent components in a recently growing number of DOM studies (Stedmon et al., 2003; Stedmon and Bro, 2008). The absorption coefficients and fluorescence intensities, as

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http://dx.doi.org/10.1016/j.watres.2014.04.018
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quantitative parameters, are often suggested as surrogates for a variety of organic matter content proxies such as dissolved organic carbon (DOC; Spencer et al., 2012; Yang et al., 2013a), biochemical oxygen demand (BOD), chemical oxygen demand (COD; Henderson et al., 2009; Hur and Cho, 2012), lignin-derived phenols (Osburn and Stedmon, 2011), and amino acids (Jorgensen et al., 2011). A large variability of DOM constituents and their spectroscopic properties across wastewater, soils, rivers, groundwater, lakes, rainwater, and the oceans provides a basis for using the spectroscopic proxies to keep track of various DOM sources (Hur et al., 2006; Inamdar et al., 2011; Fichot et al., 2013). Commonly used quality indices are the absorption spectral slope and slope ratio (S and S_R, respectively; Helms et al., 2008), carbon specific UV absorbance (ε_{280} or $SUVA_{254}$; Chin et al., 1994; Weishaar et al., 2003), fluorescence index (FI; McKnight et al., 2001), humification index (HIX), biological index related to recent autochthonous contribution (BIX; Huguet et al., 2009), and the relative abundance of different fluorescent components (Baker et al., 2008; Fellman et al., 2010; Hur et al., 2011a).

In the use of absorption and fluorescence spectroscopy for tracing DOM sources, it is critical to obtain the knowledge concerning the conservative mixing behaviors of spectroscopic indices because it helps identify possible effects of biogeochemical processes in field. For example, Stedmon and Markager (2003) revealed that the absorption spectral slope did not follow a linear behavior in the conservative mixing of two different types of chromophoric DOM (CDOM). They explained much observational data in the estuarine and coastal environments based on the nonlinear behavior of the index. The theoretical mixing lines for S and S_R also exhibited nonlinear patterns in the Delaware Estuary (Helms et al., 2008). These examples show that some spectroscopic quality indices may change nonlinearly under conservative mixing and that such nonlinear changes do not necessarily indicate nonconservative behaviors (i.e. with additions or removals due to biogeochemical processes). Thus, it is important to examine comprehensively the mixing behaviors of widely used spectroscopic indices for a controlled system, in which different DOM end members are physically mixed together in known content ratios. In addition, the source discrimination capability of a particular index is likely to be dependent on its sensitivity to the changes in the DOM sources as well as its analytical precision, which has not yet been compared for various known spectroscopic indices.

The other important issue regarding spectroscopic applications for DOM source tracing is the susceptibilities of the indices to the solution chemistry such as pH, ionic strength, concentrations of the major cations (e.g., Ca^{2+}), and the DOM concentration, which may vary greatly in aquatic systems. There are some prior studies showing the effects of solution chemistry, which primarily focused on absorption coefficients and fluorescence intensities (Mobed et al., 1996; Westerhoff et al., 2001; Patel-Sorrentino et al., 2002; Sheng and Yu, 2006; Baker et al., 2007; Spencer et al., 2007; Hartland et al., 2010; Deng et al., 2012; Yan et al., 2013). However, a comprehensive study is required to explore the applicability of spectroscopic indices for source tracing in contrasting environments, especially for the EEM-PARAFAC components and the quality indices whose responses to solution chemistry are much less known. This investigation could offer a better interpretation of the spectroscopic responses in the fields where the solution chemistry largely varies (e.g., Yang et al., 2012), and it could also provide valuable information for optimizing the measurement conditions in the field.

Therefore, our study aimed to: (1) examine the patterns of spectroscopic properties changing during the controlled mixing processes of two typical end members (Suwannee River fulvic acid (SRFA) and an algal DOM), (2) assess the effects of solution chemistry on widely used spectroscopic indices during the mixing, and (3) evaluate their applicability for source tracing in the environments with a large variability of solution chemistry. The source of SRFA is dominated by terrestrial plant and soil organic matter, while the algal DOM originates from the phytoplankton collected during a severe algal bloom. These two typical end members, therefore, are well representative of allochthonous and autochthonous organic matter, respectively, of which their mixtures are typically found in many aquatic environments.

2. Material and methods

2.1. *Preparation of samples*

SRFA was purchased from the International Humic Substance Society (IHSS). The powder was dissolved in Milli-Q water and filtered through a cellulose acetate filter with a pore size of 0.2 μm. The filtrate was diluted to a concentration of 0.90 mgC L^{-1} for a SRFA working solution. Phytoplankton was collected and concentrated using plankton net with a pore size of 20 μm during a severe algal bloom event at the Seungchon dam reservoir in Korea. The sample was freeze dried, ground, dissolved in Milli-Q water, and shaken at 2000 rpm in dark for 24 h. The solution was then centrifuged at 8000 rpm, and the supernatant was filtered through 0.2 μm cellulose acetate filters. The filtrate was diluted to a concentration of 0.99 mgC L^{-1} to obtain an algal DOM working solution.

To examine the changes in the spectroscopic parameters with different ratios of the two DOM end members, the working solutions of SRFA and algal DOM were mixed at a series of volume ratios of 0/1, 1/9, 1/3, 1/1, 3/1, 9/1 and 1/0, respectively. The mixing experiment was carried out in triplicate, and the mean analytical precisions were 1.4%–4.2% for the absorption parameters and 0.4%–3.0% for all fluorescence parameters used for this study.

To assess changing pH effects, the pH of the working solutions was adjusted to 3.0 or 9.0 with 0.1 M HCl or 0.1 M NaOH. The solutions were then mixed at a series of the same ratios for the spectroscopy measurements. The results were compared with those of the previous mixing experiment at pH 5.7. To test the effects of ionic strength, NaCl was added to the working solutions at 0.26 M or 0.46 M, and the same procedures were taken to prepare the mixing solutions. For the Ca^{2+} studies, a 300 mM $CaCl_2$ solution was spiked into the SRFA and algal DOM working solutions to obtain 3.0 mM $CaCl_2$ of the solutions, of which pH was adjusted to 3.0, 5.7, or 9.0. A series of the DOM mixtures in 1.5 mM $CaCl_2$ at pH 3.0 were prepared as well for comparison. To study the effects of DOM concentrations, algal DOM and SRFA solutions of ~10 mg C L^{-1} were prepared