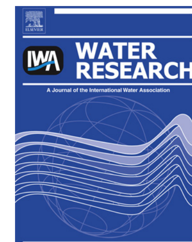
Available online at www.sciencedirect.com

ScienceDirect

journal homepage: www.elsevier.com/locate/watres



Critical analysis of commonly used fluorescence metrics to characterize dissolved organic matter

Julie A. Korak [a], *Aaron D. Dotson* [b], *R. Scott Summers* [a], *Fernando L. Rosario-Ortiz* [a,*]

[a] Department of Civil, Environmental and Architectural Engineering, 428 UCB, University of Colorado – Boulder, Boulder, CO 80309, USA

[b] Civil Engineering Department, ENGR 201, University of Alaska Anchorage, Anchorage, AK 99508, USA

ARTICLE INFO

Article history:
Received 29 July 2013
Received in revised form 14 October 2013
Accepted 18 November 2013
Available online 27 November 2013

Keywords:
Dissolved organic matter
Fluorescence
Peak picking
Fluorescence index

ABSTRACT

The use of fluorescence spectroscopy for the analysis and characterization of dissolved organic matter (DOM) has gained widespread interest over the past decade, in part because of its ease of use and ability to provide bulk DOM chemical characteristics. However, the lack of standard approaches for analysis and data evaluation has complicated its use. This study utilized comparative statistics to systematically evaluate commonly used fluorescence metrics for DOM characterization to provide insight into the implications for data analysis and interpretation such as peak picking methods, carbon-normalized metrics and the fluorescence index (FI). The uncertainty associated with peak picking methods was evaluated, including the reporting of peak intensity and peak position. The linear relationship between fluorescence intensity and dissolved organic carbon (DOC) concentration was found to deviate from linearity at environmentally relevant concentrations and simultaneously across all peak regions. Comparative analysis suggests that the loss of linearity is composition specific and likely due to non-ideal intermolecular interactions of the DOM rather than the inner filter effects. For some DOM sources, Peak A deviated from linearity at optical densities a factor of 2 higher than that of Peak C. For carbon-normalized fluorescence intensities, the error associated with DOC measurements significantly decreases the ability to distinguish compositional differences. An in-depth analysis of FI determined that the metric is mostly driven by peak emission wavelength and less by emission spectra slope. This study also demonstrates that fluorescence intensity follows property balance principles, but the fluorescence index does not.

© 2013 Elsevier Ltd. All rights reserved.

1. Introduction

Dissolved organic matter (DOM) is comprised of a wide range of compounds that originate from terrestrial or aquatic sources as well as from anthropogenic inputs, such as wastewater effluent (Leenheer, 2009). Composition is spatially and temporally dependent and associated with source material variation and environmental transformation processes (e.g., redox and photochemical processing). DOM is highly heterogeneous and is often characterized by bulk parameters (e.g., dissolved organic carbon (DOC), light absorption/fluorescence, aromaticity, hydrophobicity and functional groups) (Leenheer, 2009).

* *Corresponding author*. Tel.: +1 303 492 7607.
E-mail address: Fernando.rosario@colorado.edu (F.L. Rosario-Ortiz).

0043-1354/$ – see front matter © 2013 Elsevier Ltd. All rights reserved.
http://dx.doi.org/10.1016/j.watres.2013.11.025

Fluorescence spectroscopy measures the fraction of DOM that both absorbs and emits light, and the fluorescent DOM fraction is often associated with aromaticity (Senesi et al., 1991). Observed fluorescence can be a function of individual fluorophores contributing superimposed signals or a function of intramolecular charge-transfer mechanisms between interacting fluorophores (Del Vecchio and Blough, 2004).

1.1. *Application of fluorescence spectroscopy for DOM characterization*

Fluorescence spectroscopy has been used extensively to characterize differences in DOM signatures in natural systems (Hudson et al., 2007; Fellman et al., 2010). Recently, fluorescence has been applied to engineered treatment systems to characterize DOM changes (Win et al., 2000; Cheng et al., 2004; Swietlik and Sikorska, 2004; Allpike et al., 2005; Beggs et al., 2009; Dwyer et al., 2009; Kraus et al., 2010; Baghoth et al., 2011; Beggs and Summers, 2011; Bieroza et al., 2011; Beggs et al., 2013). Early applications of fluorescence included two-dimensional emission, excitation and synchronous scans and focused on spectral peak intensity and positions. Analysis of two-dimensional scans also led to the development of indices such as the fluorescence index (FI) and humification index (HIX) (Zsolnay et al., 1999; McKnight et al., 2001; Ohno, 2002). Recent analysis of DOM fluorescence has focused on the use of three dimensional excitation-emission matrices (EEMs), as illustrated in Fig. 1. Peak picking methods have driven a significant portion of quantitative fluorescence analysis (Coble, 1996). Furthermore, parallel factor analysis (PARAFAC) has been used to decompose EEMs into components, but relies on collecting large datasets of EEMs (Stedmon et al., 2003; Stedmon and Bro, 2008; Murphy et al., 2013).

A wide range of metrics has been used to analyze EEMs. The simplest EEM characterization method is qualitative observation of the presence or absence of regional intensity (Bu et al., 2010). A fluorescence regional integration (FRI) method was developed that sums all intensities within a region (Chen et al., 2003; Zhou et al., 2013). Peak picking is a quantitative method that records the peak intensities within pre-defined regions of interest. Common peak regions relevant to freshwater include two humic-like (A, C) and two heterocyclic nitrogen/polyphenolic/protein-like peaks (B, T) and are outlined in Table S-1 (Coble, 1996; Leenheer, 2009). Peak picking has been executed using two distinct methods. The first method reports the intensity of a stationary point (fixed wavelength) within each region of interest (Leenheer, 2009; Lønborg et al., 2010; Murphy et al., 2010; Romera-Castillo et al., 2011). The second approach is to define a region of interest and systematically extract the maximum intensity within the region even though the location of the maximum may vary between samples and replicates (Senesi et al., 1991; Wang et al., 2009; Beggs and Summers, 2011; Bieroza et al., 2011; Esparza-Soto et al., 2011; Guéguen and Cuss, 2011; Yang et al., 2013). This method will be referred to as an "algorithm-based" approach herein. Many studies that employ this method also record the excitation and emission wavelength at which the maximum is located and use this information to infer changes in DOM composition (Del Vecchio and Blough, 2004; Wang et al., 2009; Bieroza et al., 2011; Esparza-Soto et al., 2011; Yang et al., 2013). Furthermore, much in the same way as specific UV absorbance (SUVA) has been used to characterize DOM (Weishaar et al., 2003), carbon-normalized peak intensities (intensity divided by DOC), have been used to characterize fluorescence per unit DOC, often termed specific intensities (Alberts et al., 2002; Alberts and Takács, 2004; Cheng et al., 2004; Jaffe et al., 2004; Allpike et al., 2005; Cumberland and Baker, 2007; Hudson et al., 2007; Wu et al., 2007; Dwyer et al., 2009; Fellman et al., 2010; Beggs and Summers, 2011; Fleck et al., 2013).

FI has been correlated to DOM aromaticity and is often used as a surrogate for DOM origin, i.e., allochthonous or autochthonous (Win et al., 2000; McKnight et al., 2001; Cheng et al., 2004; Swietlik and Sikorska, 2004; Allpike et al., 2005; Beggs et al., 2009; Dwyer et al., 2009; Kraus et al., 2010; Baghoth et al., 2011; Beggs and Summers, 2011; Bieroza et al., 2011; Beggs et al., 2013). FI was originally defined for fulvic acids isolated from a range of DOM sources, but has since been applied to whole water analyses (McKnight et al., 2001; Beggs et al., 2009; Kraus et al., 2010; Beggs and Summers, 2011). FI was initially defined as a ratio of emission intensities at 450 nm and 500 nm when excited at a wavelength of 370 nm (Coble, 1996; McKnight et al., 2001). The 450 nm point was chosen because it was between the peak emission for Pony Lake and Suwannee River end members. The 500 nm index represented the point where emission intensity for microbial end members was half of its maximum intensity. Due to instrument specific corrections that shift the emission maxima to longer wavelengths by about 15 nm (red-shifted), the indices for FI were modified to the ratio of 470 nm–520 nm (Cory et al., 2010).

Past work has made great advances in standardizing the procedures by which EEMs are collected, corrected and

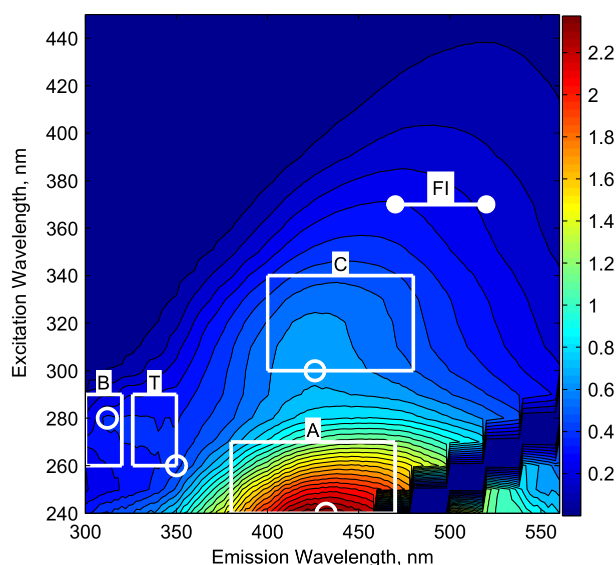


Fig. 1 – Excitation emission matrix for BEM. Intensity is presented in Raman units (RU). Boxes outline the four peak regions (A, B, C and T) with labels above. Hollow circles indicate the location of the peak intensity in each region. The two points used in the I_{470}/I_{520} Fluorescence Index (FI) metric are represented by filled circles connected by a line at an excitation of 370 nm.

Download English Version:

https://daneshyari.com/en/article/4481713

Download Persian Version:

https://daneshyari.com/article/4481713

Daneshyari.com