Environ Chem Lett (2007) 5:73–77
DOI 10.1007/s10311-006-0085-7

ORIGINAL PAPER

Fluorescence fingerprints to monitor total trihalomethanes and *N*-nitrosodimethylamine formation potentials in water

Bin Hua · Kristen Veum · Amod Koirala · John Jones · Thomas Clevenger · Baolin Deng

Received: 20 March 2006 / Accepted: 25 July 2006 / Published online: 19 September 2006
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Abstract Water samples from 56 lakes of Missouri, USA, were analysed for their fluorescence excitation/emission matrix (EEM) spectroscopy and the formation potentials of total trihalomethanes (TTHM) and *N*-nitrosodimethylamine (NDMA). Comparing the excitation/emission matrix fingerprints with trihalomethanes formation revealed that water with higher fluorescence intensity generally exhibited higher trihalomethanes formation potential. Moreover, waters with fluorescence centre at excitation: 290–310 nm/emission: 330–350 nm were related to high *N*-nitrosodimethylamine and trihalomethanes formation potentials. The results suggest that excitation/emission matrix fingerprints could be used as surrogate parameters for monitoring trihalomethanes and *N*-nitrosodimethylamine formation potentials.

Keywords Fluorescence spectroscopy · Excitation/emission matrix · Disinfection by-products

Introduction

A major issue of water quality management is to identify appropriate parameters for rapid and cost-effective monitoring of water. UV absorbance at 254 nm, for example, has been used as a surrogate indicator for total organic carbon (TOC) and total trihalomethane (TTHM) formation potentials (Edzwald et al. 1985). However, as the method only collects information at a single absorption wavelength, its application has been limited.

Recent developments in excitation/emission matrix (EEM) fluorescence spectroscopy and synchronous fluorescence spectroscopy allow for the resolution of various fluorescence components including petroleum hydrocarbons, pesticides, landfill leachate, and sewage, and thus could potentially be used as fingerprints for water quality characterization and source identification (Reynolds and Ahmad 1997; Galapate et al. 1998; Baker 2005; Christensen et al. 2005). For environmental water samples, fluorescence is ubiquitous and normally derived from two types of organic matter: (i) a humic acid-like fluorescence which occurs at 420–450 nm from excitation at 230–260 and 320–350 nm; and (ii) a protein- or amino acid-like fluorescence with maxima between 300–305 nm and 340–350 nm from excitation at 220 and 275 nm, respectively (Coble et al. 1990; Mopper and Schultz 1993; Tipping et al. 1997; Baker 2001; Yan et al. 2000). Applications of fluorescence spectroscopy, including mean positions of the fluorescence maxima and the ratio of tryptophan (type ii) to fulvic-like (type i) fluorescence, were used successfully to distinguish different sources of water (Yan et al. 2000; Baker, 2001; Ahmad and Reynolds 1995, Reynolds 2003a, b). Recently, concerns have been raised over the TTHM and *N*-nitrosodimethylamine (NDMA) formation potentials of source waters. TTHM are a group of disinfection by-products formed when chlorine or other halogenated disinfectants are used to control pathogens in water. Several of these halogenated disinfection by-products have been shown to be carcinogenic and may also have adverse reproductive and developmental effects. NDMA, another probable human carcinogen, was first found in 1998 in a drinking water well from northern California and subsequently

B. Hua · A. Koirala · T. Clevenger · B. Deng (✉)
Department of Civil and Environmental Engineering, University of Missouri,
Columbia, MO 65211, USA
e-mail: Dengb@missouri.edu

K. Veum · J. Jones
Department of Fisheries & Wildlife Sciences, University of Missouri,
Columbia, MO 65211, USA

detected in many other locations. An action level of 10 ng/l was set in 2002 by the California Department of Health Services, based on the discovery of NDMA as a by-product of chlorination and chloramination of drinking water.

The methods currently used to measure TTHM and NDMA formation potentials are extremely tedious (see the Experimental section below). The fluorescence fingerprints, however, may potentially serve as surrogate parameters for monitoring TTHM formation potentials (Nakajima et al. 2002). Likely, fluorescence could also be used for monitoring NDMA formation potentials. In this paper, TTHM and NDMA formation potentials were assessed for water samples from 56 lakes in Missouri, USA, and the correlations between the formation potentials and the fluorescence EEM fingerprints were examined. The results suggest that EEM fingerprints could be used as surrogate parameters for monitoring TTHM and NDMA formation potentials.

Experimental

Epilimnetic surface water samples were collected from 56 Missouri lakes between 27 July 2004 and 18 August 2004 in 500 ml amber glass bottles with TFE-lined screw caps. Samples were stored on ice until reaching the laboratory then refrigerated in the dark until analysis. Samples for dissolved organic carbon (DOC) and TTHM formation potential analysis were filtered with pre-washed 0.45 μm membrane filters within 24 h of collection.

DOC analysis was preformed using the wet oxidation-persulfate method on a Tekmar-Dohrmann Phoenix 8000 TOC Analyser. Filtrate was acidified immediately after filtration (pH$<$2) and analysed in triplicate within 14 days.

A 7-day, reactivity-based chlorine demand incubation was employed for TTHM formation potential. Samples were dosed with a chlorine solution providing a free chlorine residual of 1.0 ppm ($\pm$0.4 ppm) at the end of the incubation. The incubation was conducted at a pH of 8.0 ($\pm$0.2) and a temperature of 20 °C in the dark. Post incubation, samples were neutralized with sodium thiosulfate and stored head-space free in 40 ml glass vials with Teflon-lined septa caps (Veum 2006).

TTHM analysis was performed within 14 days using a non-compliance, wet-chemistry, colorimetric method based on the Fujiwara method and adapted as detailed by Veum (2006). The standard gas chromatography/mass spectroscopy were not used due to time and cost constraints. Individual species of THM were not resolved using this method and thus results were given as total trihalomethane-4 (chloroform, bromoform, dichlorobromomethane and dibromochloromethane), with a linear response range of 0–200 ppb and a detection limit of $\sim$6 ppb. Samples were analysed in triplicate and absorbance was measured at 515 nm in a 5 cm quartz cell on a Spectrogenesys II spectrophotometer.

NDMA formation potential was assessed by adding 1 mM NH_2Cl to 50 ml water sample in a brown bottle, and letting the sample react in dark for 7 days at room temperature. The produced NDMA was then measured with solid-phase extraction (SPE)-GC/MS-SIS (Varian Saturn GC/MS 2000/Ion trap detector) according to the following procedure: (i) adsorption of NDMA to Ambersorb 572 for 1 h with shaking; (ii) vacuum filtration of the sample; (iii) air dry of the Ambersorb 572 in a hood following sample transfer to a 2 ml vial; (iv) extraction of NDMA from Ambersorb 572 with dimethyl chloride; and (v) GC/MS-SIS analysis of NDMA using NDMA-d6 as the internal standard, and methanol as chemical ionization gas. The system was equipped with 60 m $\times$ 0.32 mm ID, 1.6 μm film thickness, J&W Scientific RTX-VRX column. The initial column temperature was 35 °C. It was raised to 140 °C at 20 °C/min and then to 200 °C at 50 °C/min, and held for 5 min.

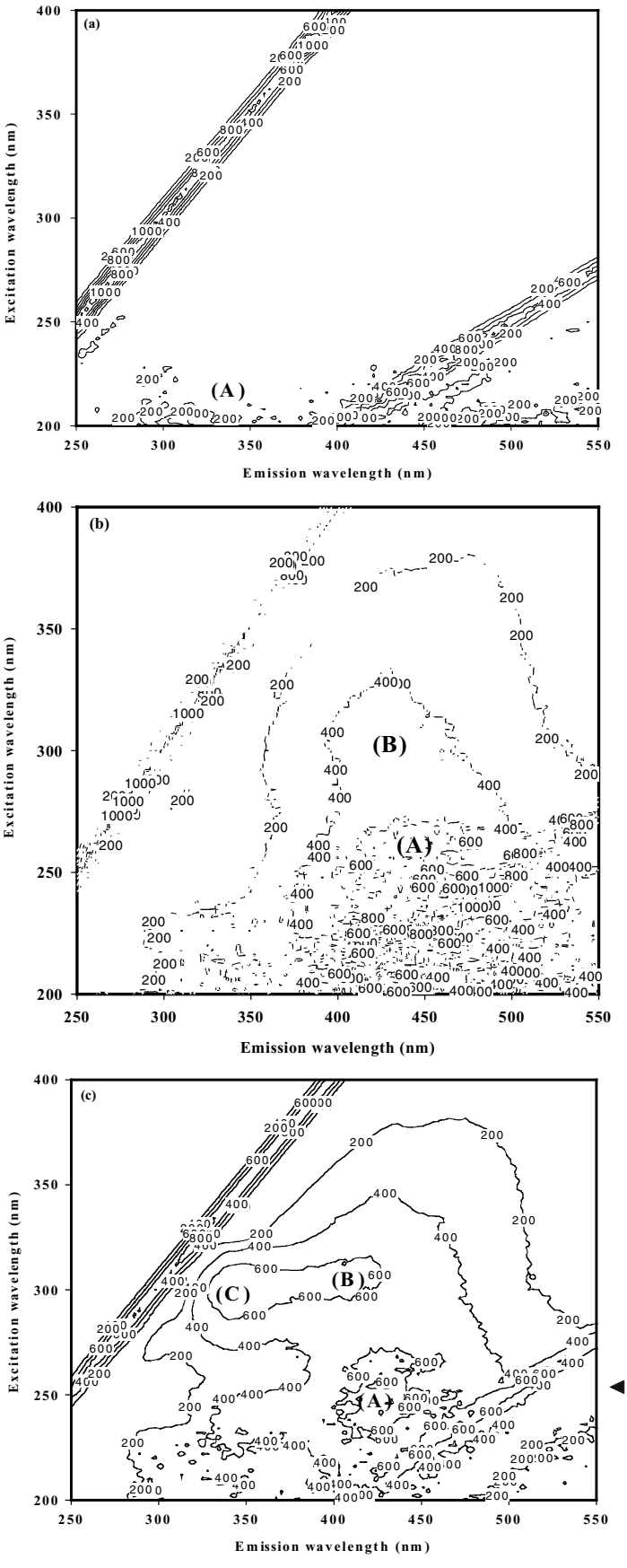
Fluorescence measurements were performed on Hitachi F-4500 Spectrograph (Hitachi Co.). Samples were held in a standard 1 cm quartz cuvette and the lamp voltage was held constant at 700 V for all experiments. Fluorescence spectra were then collected by scanning emission spectra at a range of excitation wavelengths as EEM, in which emission spectra were gathered from 250 to 550 nm in 3 nm steps, while the excitation wavelengths were stepped in 2 nm from 200 to 400 nm.

Results and discussion

Fluorescence spectra for the water samples from the 56 Missouri lakes exhibit three distinct fingerprints, as shown in Fig. 1. Comparison of the fluorescence patterns with NDMA and TTHM formation potentials reveals that the waters with higher fluorescence intensity also exhibit higher TTHM formation potentials. Moreover, waters with fluorescence centre in the range of excitation: 290–310 nm/emission: 330–350 nm are positively related to high NDMA and TTHM formation potentials.

Fingerprints of lake waters in Missouri, USA

EEM for the waters from the 56 Missouri lakes can be divided into three groups in terms of their fluorescence fingerprints as illustrated in Fig. 1. Rayleigh scatters appearing in the EEM as diagonal lines should be ignored during the spectrum interpretation because they were not resulted from fluorophores in the water. Group I, consisting of eight lakes, has low fluorescence intensity (Fig. 1a). The fluorescence peaks in this group are located in a not-so-well-defined narrow



region of excitation: 200–240 nm/emission: 250–450 nm. Group II comprises 39 lakes (Fig. 1b). Although the fluorescence intensity changes greatly among these lake waters, the fluorescence patterns of these waters are similar. Specifically, there are two main fluorescence centres in the spectra: a fluorescence centre at excitation: 210–260 nm/emission: 300–480 nm; and a fluorescence centre at excitation: 280–320 nm/emission: 390–460 nm. Group III includes nine lakes with medium to high fluorescence intensity (Fig. 1c). The most distinctive feature in this group is the presence of a fluorescence centre in a narrow range of excitation: 290–310/emission: 330–350 nm. In addition, there are two other fluorescence centres at excitation: 210–260 nm/emission: 300–480 nm and excitation: 280–320 nm/emission: 390–460 nm.

Correlation between fluorescence fingerprints and DOC

Three groups of lake waters with different fluorescence fingerprints have shown different concentrations of dissolved organic carbon (DOC): higher DOC is normally found in the waters with higher fluorescence intensity and broader fluorescence centres. Specifically, for the waters in Group I, the DOC is very low, ranging from 1.8 mg/l (Clearwater Lake) to 4.3 mg/l (Lake Nehai Tonkyea) (Fig. 2). This group also has low fluorescence intensity and no well-defined fluorescence centres. DOC in Groups II and III is appreciably higher, ranging from 3.5 to 12.2 mg/l. More intense and well-defined fluorescence centres can be defined as having been just discussed (Fig. 1b, c).

Correlation between fluorescence fingerprints and TTHM and NDMA formation potentials

As illustrated in Fig. 2, Group I waters generally have the lowest TTHM and NDMA formation potentials; Group III waters usually have greater TTHM and NDMA formation potentials; while Group II waters have comparable TTHM formation potential to Group III waters but somewhat lower NDMA formation potential in most lakes. Waters with higher fluorescence intensity possess higher TTHM formation potential. The data also suggest that the fluorescence centre C in Group III has a larger impact on NDMA formation

◀ **Fig. 1** Representative fluorescence fingerprints from each of the three groups of Missouri lake waters (numbers on the contour lines represent fluorescence intensities. The two diagonal straight lines in the upper and lower parts of the spectra come from the first and second-order Rayleigh scatters). (a) Clearwater Lake from Group I with undefined fluorescence centre (A). (b) Longbranch Lake from Group II with two fluorescence centres (**A**), (**B**). (**c**) Hazel Hill Lake from Group III with three fluorescence centres (**A**), (**B**), (**C**)

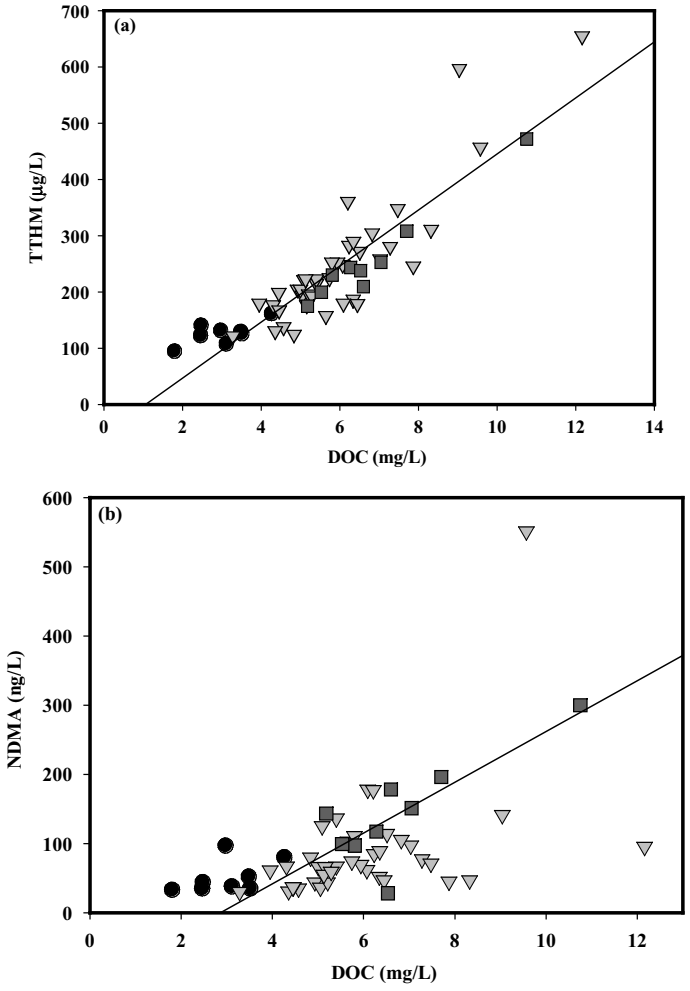


Fig. 2 DOC, TTHM and NDMA formation potentials for three groups of lake waters ((**a**) DOC vs. TTHM formation potential (*circles* TTHM for Group I; *triangles* TTHM for Group II; *squares* TTHM for Group III; *straight line* linear regression for the data). (**b**) DOC vs. NDMA formation potential (*circles* NDMA for Group I; *triangles* NDMA for Group II; *squares* NDMA for Group III; *straight line* linear regression for the data of Group III)

potential than the centres A and B. Waters with this fluorescence centre are always associated with high NDMA formation potential with only one exception, Manito Lake. Nakajima et al. (2002) similarly found that the fluorescence emission from certain TTHM precursors was much higher than that of the overall DOC, particularly in the wavelength range of 250–265 nm/325–480 nm, and that these precursors contribute to a much larger degree to the fluorescence than the other dissolved organic matter (DOM). Quantitatively, a reasonably good linear correlation between TTHM formation potential and DOC exists ([TTHM] (μg/l) = 49.8[DOC] (mg/l) − 53.2; with $R^2 = 0.79$) ([ ] denotes concentration). This agrees with our general understanding that natural organic materials are TTHM precursors. In comparison, there is essentially no correlation between NDMA formation potential and DOC when all the lakes are considered. If the samples from Group III alone are analysed, a weak correlation could be identified with [NDMA] (ng/l) = 36.6[DOC] (mg/l) − 104.5 ($R^2 = 0.63$).

Conclusion

In summary, three types of fluorescence EEM fingerprints exist among 56 lakes in Missouri, USA. It was found by comparing the fluorescence fingerprints with NDMA and TTHM formation potentials that water with higher fluorescence intensity generally exhibited high TTHM formation potential. In addition, waters with fluorescence centre in the range of excitation: 290–310 nm/emission: 330–350 nm were normally associated with high NDMA and TTHM formation potentials. The results suggest that fluorescence EEM fingerprints could be used as surrogate parameters for monitoring TTHM and NDMA formation potentials.

Acknowledgements We greatly appreciate Ms. Xiaoyan Qin for sharing the data on NDMA for the lake waters. Financial supports from the Superfund program of Missouri Department of Natural Resources and Missouri Water Resources Centre for this research are gratefully acknowledged.

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