



Using fluorescence-parallel factor analysis for assessing disinfection by-product formation and natural organic matter removal efficiency in secondary treated synthetic drinking waters

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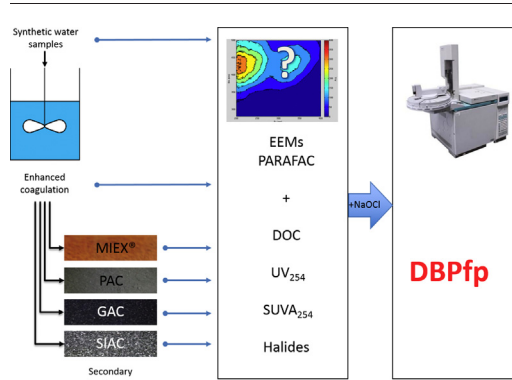
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HIGHLIGHTS

- Suwannee river NOM comprised 2 humic-like and 2 protein-like fluorescence components.
- The adsorptive water treatments studied had variable DBP precursor removal capacity.
- Fluorescence (EEM) was a better surrogate for DBP formation than DOC or UV₂₅₄.
- Most DBPs studied correlated well with humic-like component 1.

GRAPHICAL ABSTRACT



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ABSTRACT

Parallel factor (PARAFAC) analysis of fluorescence excitation-emission matrices (EEMs) was used to investigate the organic matter and DBP formation characteristics of untreated, primary treated (enhanced coagulation; EC) and secondary treated synthetic waters prepared using a Suwannee River natural organic matter (SR-NOM) isolate. The organic matter was characterised by four different fluorescence components; two humic acid-like (C1 and C2) and two protein-like (C3 and C4). Secondary treatment methods tested, following EC treatment, were; powdered activated carbon (PAC), granular activated carbon (GAC), 0.1% silver-impregnated activated carbon (SIAC), and MIEX® resin. Secondary treatments were more effective at removing natural organic matter (NOM) and fluorescent DBP-precursor components than EC alone. The formation of a suite of 17 DBPs including chlorinated, brominated and iodinated trihalomethanes (THMs), dihaloacetonitriles (DHANs), chloropropanones (CPs), chloral hydrate (CH) and trichloronitromethane (TCNM) was determined after chlorinating water sampled before and after each treatment step. Regression analysis was used to investigate the relationship between peak component fluorescence intensity (F_{MAX}), DBP concentration and speciation, and more commonly used aggregate parameters such as DOC, UV₂₅₄ and SUVA₂₅₄. PARAFAC component 1 (C1) was in general a better predictor of DBP formation than other aggregate parameters, and was well correlated ($R \geq 0.80$) with all detected DBPs except dibromochloromethane (DBCM) and dibromoacetonitrile (DBAN). These results indicate that the fluorescence-PARAFAC approach could provide a robust analytical tool for predicting DBP formation, and for evaluating the removal of NOM fractions relevant to DBP formation during water treatment.

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1. Introduction

Natural organic matter (NOM) is a complex heterogeneous mixture of organic compounds from a mixture of terrestrial and aquatic sources, consisting of aromatic, aliphatic, phenolic, and quinonic structures with varying molecular sizes and properties, present in all natural waters (Swietlik and Sikorska, 2006). The complexity and diversity of NOM characteristics presents challenges for drinking water treatment since NOM in the source water can decrease the efficiency of disinfectants and lead to the formation of toxic disinfection by-products (DBPs) (Richardson et al., 2007). To effectively remove NOM and minimise NOM-derived DBP formation in DWTPs, an understanding of the specific NOM characteristics of source waters is required (Parsons et al., 2004).

Conventional analysis of NOM has focused on aggregate measurements due primarily to the heterogeneous nature and analytical complexities associated with characterising NOM fractions (Fellman, 2008). The most commonly used surrogates to predict DBP formation are ultraviolet (UV_{254}) absorbance, dissolved organic carbon (DOC) and specific UV absorbance ($SUVA_{254}$) (Ates et al., 2007). UV_{254} absorbance (Korshin et al., 1997; Li et al., 1998), $SUVA_{254}$ (Kitis et al., 2002) and DOC, (White et al., 2003) have all been correlated with the formation of chlorinated DBPs. While UV_{254} absorbance and $SUVA_{254}$ generally correlated well with trihalomethane (THM) and haloacetic acid (HAA) formation in high DOC concentration waters (>3 mg/L), NOM moieties responsible for DBP formation in low- $SUVA_{254}$ waters do not absorb UV light at 254 nm (Ates, 2008), so alternative techniques are required.

Fluorescence spectroscopy is a rapid and sensitive technique, which can provide valuable information on NOM character together with an indication of its reactivity and treatability. Unlike aggregate parameters typically used in DWTPs, fluorescence spectroscopy provides a measure of the specific composition, structure and functional groups of the NOM investigated (Chen et al., 2002; Bridgeman et al., 2011; Leenheer and Croué, 2003). Three-dimensional fluorescence excitation-emission matrices (EEMs) have been widely used to identify the sources, optical nature, structures and chemical behaviour of NOM in many water types, including river, dam, marine, drinking and waste water (Coble, 1996; Fu et al., 2010).

The main methods used to characterise the fluorescent signals emitted by the fluorophores detected in EEMs are peak picking (Coble, 1996), fluorescence indices (McKnight et al., 2001), fluorescence regional integration (Chen et al., 2003) and, more recently, parallel factor (PARAFAC) analysis (Stedmon et al., 2003). PARAFAC analysis provides more information about the fluorophores identified in the EEMs than other methods (Baghoth et al., 2011). PARAFAC analysis separates arrays of EEMs into components, characterised by common excitation-emission signatures. Numerous studies (Pifer and Fairey, 2012; Lyon et al., 2014; Bridgeman et al., 2011) have extracted individual components from NOM samples, which have been attributed to protein-like, fulvic-like or humic-like fluorophores.

Some studies have used PARAFAC analysis to assess the fate of NOM across engineered systems including drinking water and wastewater treatment processes (Ishii and Boyer, 2012). Research suggests that NOM removal treatments have different removal efficiencies for different PARAFAC components (Baghoth et al., 2011). As individual fluorophores may correlate with the formation of specific DBPs (Pifer and Fairey, 2012; Lyon et al., 2014; Johnstone et al., 2009; Hao et al., 2012; Hua et al., 2010), the PARAFAC approach could identify NOM components resistant to removal and thereby assist in optimising the performance of drinking water treatment processes aimed at removing NOM and minimising toxic DBP formation. While biologically activated carbon (BAC) (Baghoth et al., 2011) and MIEX® treatments have previously been assessed with PARAFAC (Pifer et al., 2014), several other treatment options such as powdered activated carbon (PAC), granular activated carbon (GAC) and silver-impregnated activated carbon

(SIAC) have not been investigated. MIEX®, GAC and SIAC have the additional benefit of providing some bromide removal along with NOM removal, thereby potentially decreasing brominated DBP formation, as well as chlorinated DBP formation, in the finished (chlorinated) water (Sharma et al., 2014).

In this study, fluorescence EEMs, PARAFAC analysis, and chlorine DBP formation potential tests were used to investigate organic matter and chlorinated/brominated DBP characteristics of untreated, primary (enhanced coagulation; EC) treated and secondary treated synthetic waters made using a Suwannee River NOM (SR-NOM) isolate. Secondary treatment methods, following EC treatment, were: PAC, GAC, 0.1% SIAC or MIEX® resin. The purpose of this study was to use PARAFAC analysis to (1) assess the characteristics of NOM and preferential removal of components by various water treatment options, (2) identify the impact of treatment on chlorinated/brominated DBP formation, and (3) determine the accuracy of PARAFAC analysis and more conventional aggregate measurements as DBP precursor surrogate parameters.

2. Materials and methods

2.1. Reagents

Chemicals were purchased from the following suppliers – Accustandard: mixed standard of trichloromethane (TCM), bromodichloromethane (BDCM), dibromochloromethane (DBCM), tribromomethane (TBM), 2.0 mg/mL in methanol; 1,2-dibromopropane, 5 mg/mL in methanol; mixed standard of dichloroacetonitrile (DCAN), trichloroacetonitrile (TCAN), bromochloroacetonitrile (BCAN), dibromoacetonitrile (DBAN), 1,1-dichloropropanone (1,1-DCP), 1,1,1-trichloropropanone (1,1,1-TCP), CH, trichloronitromethane (TCNM), 1 mg/mL in acetone. Orchid Cellmark (Canada): dichloriodomethane (DCIM) (95%), chlorodiiodomethane (CDIM) (90–95%), bromochloriodomethane (BCIM) (95%), dibromiodomethane (DBIM) (95%) and bromodiiodomethane (BDIM) (90–95%). Acros organics: phosphate buffers (Na_2HPO_4 and KH_2PO_4) (99%), ascorbic acid (ACS grade). Sigma-Aldrich: $Al_2(SO_4)_3 \cdot 18H_2O$ (98%), NaOCl ($\geq 4\%$), $MgSO_4$ ($\geq 99.5\%$), $CaSO_4 \cdot 2H_2O$ (98%), $NaHCO_3$ (99.7–100.3%), methyl *tert*-butyl ether (MtBE) ($\geq 99.8\%$), NaBr ($\geq 99.0\%$). ThermoFisher: NaCl (99.95%). Merck: HCl (32%), KI (99.5%). Chem-supply: NaOH ($\geq 98\%$). Malcron chemicals: sodium sulfate (anhydrous) 99.7%. Suwannee river (whole) NOM isolate was purchased from the International Humic Substances Society (batch number 1R101N). Commercial DPD test kits (HACH) were used for the analysis of free chlorine (method 8021). Norit 18 × 40AG1 (0.1% Ag) SIAC and Norit GCN1840 GAC was donated by Cabot Norit, Amersfoort, The Netherlands. Used, regenerated, MIEX® resin was obtained from a South Australian water treatment plant (WTP). Norit W35 PAC was purchased from Sigma-Aldrich.

2.2. Synthetic water samples

Synthetic water samples of varied water quality characteristics were prepared by dosing ultrapure water (Sartorius Arium 611UV) with SR-NOM (International Humic Substances Society) to give a DOC concentration of 4.40, 9.97 and 14.44 mg/L (Table 1). Stock solutions of standard SR-NOM were prepared daily from the freeze-dried solids and sonicated for 1 h before use to ensure rehydration. Sodium bromide was added at concentrations of 100 $\mu\text{g/L}$, 450 $\mu\text{g/L}$, or 800 $\mu\text{g/L}$ (as Br^-), and sodium iodide was added at concentrations of 4 $\mu\text{g/L}$, 18 $\mu\text{g/L}$, or 32 $\mu\text{g/L}$ (as I^-). These halides were dosed to samples of each DOC concentration level as a combined, proportional concentration, *i.e.*, low Br^- /low I^- , medium Br^- /medium I^- , and high Br^- /high I^- was dosed to each of the three DOC levels. Multiple levels of halide and NOM concentration were used to ensure a range of Br:DOC ratios in the samples, therefore a range of speciation and concentration of individual DBPs should be formed upon disinfection. Sodium chloride was

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