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Spectroscopic examination of effects of iodide on the chloramination of natural organic matter

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ABSTRACT

This study examined reactions of NOM with chloramine in the presence of varying iodide concentrations using *in situ* methods of absorbance and fluorescence. The data showed that the consumption of iodide during chloramination could be quantified by the differential absorbance of NOM at 225 nm. Examination of the kinetics of iodide consumption demonstrated the presence of two different reaction stages corresponding to the engagement of fast and slow reactive site in NOM. Interactions between the fast site and chloramine in the presence of iodide did not show specific effects of the incorporation of iodine compared to that of chlorine but the engagement of the slow site caused changes of NOM fluorophores and chromophores specific to iodine. Comparison of changes of the slope of log-processed NOM absorbance spectra ($S_{325-350}$) and decreases of NOM fluorescence intensity showed the presence of heavy atom effects whose extent was proportional to the incorporation of iodine in the organic substrate. The data also indicated that the engagement of the slow site was accompanied by the formation of intermediate species whose nature remains to be elucidated.

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1. Introduction

To comply with THMs and HAAs regulatory limits, many drinking water utilities use chloramine as a secondary disinfectant. Despite the consistent decrease of concentrations of THMs, HAAs and selected other disinfection byproducts (DBPs) in the presence of chloramine, chloramination of waters that contain background iodide results in the formation of iodine-containing disinfections by-products (I-DBPs) that have been determined to be more cytotoxic and genotoxic

than their brominated or chlorinated analogues (Plewa et al., 2004; Krasner et al., 2006; Richardson et al., 2007, 2008).

The formation of I-DBPs during NOM chloramination is a result of the oxidation of iodide by monochloramine to active iodine species, notably hypoiodous acid (HOI), I_2 and I_3^- . These compounds react readily with natural organic matter (NOM). In the case of chlorination, the formation of HOI and other iodine species is suppressed due to a rapid oxidation of iodide to IO_2^- and IO_3^- anions which do not interact with NOM (Bichsel and von Gunten, 1999; Hua and Reckhow, 2007b; Allard et al., 2013).

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Prior studies have addressed many aspects of I-DBP generation, for instance effects of pH, pre-treatment of NOM prior to its chloramination and, in some extent, effects of NOM properties on the kinetics and speciation of I-THMs (Bichsel and von Gunten, 1999, 2000; Duirk et al., 2011; Jones et al., 2011, 2012). Some of these studies have observed higher I-THM yields in waters with higher SUVA values while others have determined the occurrence of higher formation of I-THMs in NOM fractions with lower molecular weights and higher hydrophilicities (Hua and Reckhow, 2007a; Kristiana et al., 2009).

Prior studies have also shown that the incorporation of iodine in NOM depends on the pH, redox potential (which defines the conversion of iodide to reactive iodine species) and NOM properties (Moulin et al., 2001; Schwehr et al., 2009; Shimamoto et al., 2011; Choung et al., 2013; Xu et al., 2013). However, the intrinsic complexity of NOM makes it a challenge to ascertain *ex situ* the nature of iodine uptake by NOM and quantify important mechanisms of iodine incorporation, for instance the formation of intermediates that may play a critically important role in the generation of I-DBPs (Ding and Zhang, 2009; Pan and Zhang, 2013).

These aspects of interactions between NOM and iodine can be tracked by means of monitoring changes of NOM chromophores or/and fluorophores that are affected by a range of reversible and irreversible NOM reactions, notably its reactions with disinfecting agents and oxidants, protons and metal cations (Korshin et al., 2009; Yan and Korshin, 2014; Yan et al., 2014a, 2014b). Quantitation of changes of NOM chromophores and fluorophores induced by these reactions can be done using several parameters such as differential absorbance at 272 nm (ΔA_{272}) or other wavelengths, differential log-transformed absorbance at 350 nm ($D \ln A_{350}$) and slope of log-transformed NOM absorbance spectra in the range 350–400 nm ($S_{350-400}$), position of the half maximum of the fluorescence intensity $\lambda_{0.5}$ and change of fluorescence intensity ratio of $\Delta(I_{500}/I_{400})$ (Korshin et al., 2007; Roccaro et al., 2009; Yan et al., 2014a).

In this study, these methods were used to examine changes of chromophores and fluorophores in allochthonous aquatic NOM (exemplified by Nordic Reservoir natural organic matter, NNOM) induced by its chloramination in the presence of variable iodide concentrations. The objective of this research was to explore interactions between NOM and iodine in the presence of chloramine and determine whether effects induced by the incorporation of iodine in NOM are similar to those associated with the incorporation of chlorine and whether interactions of iodine with NOM is accompanied by the formation of intermediates possibly specific to the NOM/ $\text{NH}_2\text{Cl}/\text{I}^-$ system.

2. Materials and methods

2.1. Reagents and solution preparation

All solutions were prepared using reagent-grade chemicals and Milli-Q water. A 1000 mg L⁻¹ (as Cl₂) free chlorine stock was prepared from 5% sodium hypochlorite solution (JT Baker) and stored in aluminum foil-covered glass stoppered flasks.

The chlorine stock solution was standardized using the DPD colorimetric method (Standards Method 4500-CL G) (Eaton et al., 2005). A 500 mg L⁻¹ (as dissolved organic carbon, DOC) Nordic Reservoir NOM stock solution was prepared by dissolving a requisite amount of Nordic Reservoir NOM powder purchased from the International Humic Substances Society (IHSS). 0.3 mol L⁻¹ phosphate buffer stock solution was made by dissolving monobasic dihydrate and dibasic anhydrous salts (from JT Baker). Sodium chloride ($\geq 99.0\% \text{NaCl}$) (from Sigma–Aldrich) was dissolved to make a 1 mol L⁻¹ stock solution. The concentration of sodium sulfite (Fisher Scientific) stock solution used as a quenching agent was 0.14 mol L⁻¹. Concentrations of potassium iodide (JT Baker) and ammonium chloride (JT Baker) in the respective stock solutions were 1.53 g L⁻¹ and 3 g L⁻¹, respectively.

2.2. Experimental procedures

All iodination experiments were carried out at pH 7 in the presence of 0.0075 mol L⁻¹ phosphate buffer and 0.001 mol L⁻¹ NaCl. The concentration of NNOM was 5 mg L⁻¹ (as DOC) in all cases. Iodide concentrations were 0, 0.1, 0.2, 0.5, 1, 2, 3, and 4 mg L⁻¹. Chloramination was performed with a 7.5 mg L⁻¹ (as Cl₂) initial monochloramine dose. The Cl₂/N ratio was 7.5 (mg L⁻¹ Cl₂)/2.2 (mg L⁻¹ N) which corresponds to a 0.67 Cl₂/N ratio of molar concentrations of chlorine and ammonia. Contact times were 0, 5, 10, 30, 60, 90, 120, and 240 min. At these contact times, 40 mL solution aliquots were taken, quenched with sodium sulfite and analyzed as described below.

2.3. Analytical methods

DOC concentrations were measured with a Shimadzu TOC-VCH analyzer. Absorbance spectra were measured with a Perkin Elmer Lambda 18 instrument using a 5 cm cell. Wavelengths were scanned from 600 nm to 200 nm. The instrument baseline was set up with DI water before each set of measurements. Fluorescence spectra were acquired using a Perkin Elmer LS-50B fluorimeter with a 1 cm rectangular quartz cell. Conventional (2D) emission spectra were acquired with a 320 excitation wavelength, with emission wavelengths 340–600 nm. 3D excitation emission matrixes (EEM) were generated using a 240–275 nm range of excitation wavelengths with a 5 nm increment. The range of emission wavelengths in these measurements was 270–600 nm. The spectra were processed to correct for non-specific Raman scattering which was measured using DI water. In 3D EEM measurements, all data for emission wavelengths less or equal to that of the excitation were excluded. The data for emission wavelengths exceeding or equal to the double of the excitation wavelengths were excluded as well.

2.4. Data processing and deconvolution

Processing of absorbance spectra of chloraminated NNOM was done as described in previous studies (Yan and Korshin, 2014; Yan et al., 2014a, 2014b). The differential absorbance spectra and differential log-transformed absorbance spectra were calculated using the equations (1) and (2), respectively:

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