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Abiotic formation of organoiodine compounds by manganese dioxide induced iodination of dissolved organic matter☆

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ABSTRACT

Iodination of dissolved organic matter (DOM) initiated by manganese oxide may represent an important source of organoiodine compounds (OICs) for iodide-containing waters. Here, Suwannee River natural organic matter was selected as model DOM, the OICs formation in simulated freshwater samples from iodinated DOM induced by manganese oxide (δ-MnO_2) was investigated at different pHs and concentrations of iodide and δ-MnO_2 by using negative ion electrospray ionization coupled with Fourier transform ion cyclotron resonance mass spectrometry (ESI-FT-ICR MS). While no OIC was observed in DOM control samples without δ-MnO_2, hundreds of OICs were detected in the presence of δ-MnO_2, suggesting the enhanced role of δ-MnO_2 played in DOM iodination. The relative abundance was defined as the value of dividing the peak intensity of OICs by the highest m/z peak intensity constantly occurred in each mass spectrum, and selected as a parameter for partly reflecting the real level of OICs. The relative abundance of most OICs were around or greater than 1%, and several OICs with higher relative abundance were identified as diiodo-5-hydroxy-4-cyclopentene-1,3-dione, diiodomethane and diiodoacetic acid. The numbers of the formed OICs increased with the increase concentrations of iodide/δ-MnO_2 and the decrease of pH, and nearly all OICs formed at lower levels of iodide/δ-MnO_2 and/or higher pH were overlapped by that at higher levels of iodide/δ-MnO_2 and/or lower pH, indicating the reliability of FT-ICR MS analysis techniques and data processing method. The OICs were formed mainly from the iodination of typical lignin-like and tannin-like compounds, as well as the precursor compounds with higher relative abundance through substitution reactions. Our findings demonstrate that the OICs formation by δ-MnO_2-initiated DOM iodination should receive more attention and the concentration, exact structure and toxicity of the OICs need to be further investigated.

1. Introduction

Iodide is present in various natural water sources worldwide. The concentrations of iodine in source waters and ground waters are in the range of 0–100 μg L^{-1} (Moran et al., 2002; Richardson et al., 2008). High levels of iodide can be found in municipal wastewaters from domestic sources such as food and urine (Below and Kahlert, 2001; Shishehbore et al., 2010). During oxidative treatment processes of drinking water, iodide can be oxidized to reactive iodine species (RIS) such as iodine (I_2) and hypoiodous acid (HOI) (Pan et al., 2016; Pan and Zhang, 2013; Ye et al., 2013). Iodide can also be oxidized to form RIS in natural processes. For example, enzymes and natural chemical oxidants such as ozone could lead to the conversion of iodide to RIS (Itoh et al., 1997; Wang et al., 2014). Photochemically induced reactive oxygen species such as HO· and the triplet state of dissolved organic matter (DOM) have been proposed as important oxidants for oxidizing the iodide to RIS (Keppler et al., 2000; Martino et al., 2009; Méndez-Díaz et al., 2014; Moore and Zafiriou, 1994). RIS, once formed, can then react with DOM to form iodinated organic compounds (OICs) (Méndez-Díaz et al., 2014). OICs formed in drinking waters and natural processes have increasingly aroused concerns since the first

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identification of iodoform and other iodinated compounds, due to their significantly higher toxicity than chlorinated and brominated analogues (Hua and Reckhow, 2007; Yang et al., 2014).

Manganese (IV) oxides are the second most important oxidants after iron oxide in the Earth's crust, because of its abundance and high redox potential. Similar to iron oxides, manganese oxides are widely distributed as suspended particles in surface waters, soils and sediments (Post, 1999). Because of the higher redox potential, manganese oxides participate in various chemical reactions involving oxidation, reduction and scavenging (sorption, precipitation) processes. Therefore, manganese oxides have been used to remove contaminants in water treatment and attracted considerable attention. Manganese oxides have been reported as adsorbant for DOM (Bernard et al., 1997) and removing water disinfection products (Colthurst and Singer, 1982). Manganese oxides are also known to contribute to the reactions of organic compounds especially DOM, resulting in the production of low molecular weight organic compounds through adsorption and electron transfer (Sunda and Kieber, 1994). The oxidation of iodide to iodine and iodate has also attracted considerable attention, as this reaction is thermodynamically possible in acidic, neutral and even in alkaline environments, depending on the concentrations of manganese oxides and I_2/I^- ratios (Allard et al., 2009; Truesdale et al., 2001). This means that OICs can be generated when manganese oxides are available for iodide in natural environments and used in the treatment of iodide-containing waters (Gallard et al., 2009). However, currently only a small part of OICs formed in MnO_2-I^--DOM system (mainly iodomethane, iodoform, iodoacetic acid) were identified, due in part to the complexity of DOM and difficulties in separating the iodinated products. Probing the composition, structure and distribution of various OICs formed in MnO_2-I^--DOM system is valuable in drinking water production, wastewater treatment and natural water environments.

Very recently, electrospray ionization coupled with Fourier transform ion cyclotron resonance mass spectrometry (ESI-FT-ICR MS) has emerged as a powerful tool to characterize the molecular composition of DOM (Lv et al., 2016; Shakeri Yekta et al., 2012; Stubbins and Dittmar, 2015; Stubbins et al., 2010), the products of chlorinated, brominated, and iodinated DOM (Gonsior et al., 2015; Xu et al., 2013; Zhang et al., 2014). The primary aim of this study was thus to utilize ultra-high resolution mass spectrometry to supply a basis concerning the potential of manganese oxides/I^-/DOM system in forming the various unknown and novel iodinated compounds in natural water environments and water treatment processes. To this end, Suwannee River natural organic matter (SRNOM) and synthetic birnessite (δ-MnO_2) were selected as model DOM and manganese oxide for batch experiments of DOM iodination under different experimental conditions (pH, concentrations of manganese oxides and iodide), and the products were characterized by ESI-FT-ICR MS.

2. Material and methods

2.1. Chemicals and manganese dioxide

Suwannee River natural organic matter (SRNOM) was purchased from the International Humic Substances Society (2R101N). Methanol (Optima grade) was purchased from Fisher Scientific Company (Shanghai, China). Sodium iodide (Guaranteed reagent) was obtained from Sigma-Aldrich (Saint Louis, America). Other reagents of analytical grade were purchased from Sinopharm Chemical Reagent Co. Ltd. (Beijing, China). Ultrapure water (18.2 MΩ) was provided by a Milli-Q purification system (Millipore, USA).

Manganese dioxide (δ-MnO_2) was prepared according to the procedure given by Pretorius (Pretorius and Linder, 2001). Briefly, 100 mL of 14 mM $KMnO_4$ and 29 mM KOH were added dropwise to 900 mL of 21 mM $Mn(NO_3)_2$. The precipitate was formed immediately and the solution was continuously stirred for 1 h at 400 rpm. The formed MnO_2 particles were allowed to settle and excess supernatant was decanted. The MnO_2 was washed with ultrapure water several times until a supernatant conductivity less than 2 μS cm^{-1}. Finally, the MnO_2 suspensions were stored in a refrigerator and diluted to appropriate concentrations as needed. Scanning electron microscopy (SEM) images (Fig. S1) showed this synthesized MnO_2 consists of variously sized nano- and microparticles and pores. The surface area of MnO_2 particles was measured by Brunauer-Emmett-Teller (BET) analyses to be approximately 300 m^2 g^{-1}. Powder X-ray diffraction analysis was conducted with X' pert PRO instrument (PANalytical, Netherlands) using CuKα radiation and continuous scanning from 5° to 90° at 0.026° sec^{-1}, and showed the peaks of synthesized MnO_2 at $d = 2.4$ Å and $d = 1.4$ Å (Fig. S1), which was a diagnostic feature for synthetic δ-MnO_2 (Pretorius and Linder, 2001; Villalobos et al., 2003). The low peak intensities and lack of low angle diffraction at 001 ($d = 7.2$ Å) and ($d = 3.5$–3.6 Å) reflections indicated that the synthesized MnO_2 was a poorly crystalline hexagonal birnessite, which had a relatively small number of randomly stacked sheets per diffracting particle (Villalobos et al., 2003).

2.2. Experimental procedures

The experiments were conducted in 250 mL amber bottles in darkness at room temperature (23 ± 2 °C). The reaction bottles were continuously stirred at 300 rpm on a magnetic stir plate during experiment courses. The solutions were buffered at 5.5, 7 and 8.5 with 5 mM phosphate to evaluate the effect of pH. Reactions were induced by adding 1.5 mL of 500 mg C L^{-1} NOM and certain volume of 50 mM sodium iodide to 248 mL suspensions containing a given mass of δ-MnO_2 and buffer. The effect of δ-MnO_2 and I^- level on the formation of DOM iodination was studied by employing 0.01 g L^{-1} and 0.1 g L^{-1} of δ-MnO_2, 0.2 μM and 1.0 μM, respectively. Reactions were stopped after 24 h by immediately filtering the suspensions with 0.45 μm membrane filters and extracting targeted compounds with solid phase extraction (SPE) procedure. The control experiments without δ-MnO_2 and without δ-MnO_2 and I^- were conducted in the same procedure in the dark.

2.3. Analytical methods

For the analysis of products of iodinated NOM, 125 mL samples were extracted according to an established SPE procedure using Agilent Bond Elute PPL cartridges (1 g per 6 mL) (Dittmar et al., 2008; Méndez-Díaz et al., 2014). Briefly, the samples were acidified to pH 2 with hydrochloric acid and pumped through the cartridges at a flow rate of ~5 mL min^{-1}. The cartridges were rinsed with 10 mL of methanol (MS grade) prior to use. Cartridges were then rinsed with ultrapure water acidified with hydrochloric acid, dried with a stream of N_2, and eluted with two cartridge volumes of methanol (MS grade). The eluent was subsequently freeze-dried under vacuum at −105 °C by using freeze drier (Bench Top Pro ZL8, Virtis, US) and kept at −20 °C in refrigerator. The extraction efficiencies for DOM compounds using this SPE method were around 60%.

These extracts were diluted in 1 mL of methanol/water (v/v, 1:1) and analyzed with a 15 T FT-ICR-MS (Bruker SolariX) with electrospray ionization in the negative ion mode. The samples were continuously injected into the electrospray source at 120 μL h^{-1} using a syringe pump, and each sample was measured triple. The ESI needle voltage was set to −3.8 kV. For M 32-bit data points were