Formation of known and unknown disinfection by-products from natural organic matter fractions during chlorination, chloramination, and ozonation

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HIGHLIGHTS

- We studied formation of newly detected DBPs from NOM fractions during disinfection.
- Substances in the HPO fraction were the main precursors for nitrogenous DBPs.
- Much more heterocyclic DBPs were formed from the HPO fraction during chlorination.
- More ketones were formed from the HPI fraction during chloramination and ozonation.

GRAPHICAL ABSTRACT
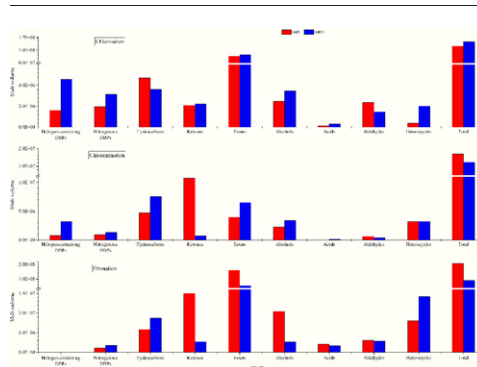
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ABSTRACT

Natural organic matter (NOM) is the main precursor of disinfection by-products (DBPs) formed during drinking water treatment processes. Previous studies of the relationships between DBP formation and NOM fractionation have mainly been focused on currently regulated DBPs and a few certain emerging DBPs. In this work, the Suwannee River NOM solution was fractionated into groups with different hydrophobicities using DAX-8 resins, and volatile and semi-volatile DBPs formed during the chlorination, chloramination and ozonation of the NOM fractions were examined by a nontargeted screening of comprehensive two-dimensional gas chromatography-quadrupole mass spectrometry procedure. The results showed that a total of 302 DBPs representing nine chemical classes were detected, of which 266 were possibly newly detected, based on library searching with NIST 08 library (using similarity and reverse values of at least 600 and 700, respectively) and linear retention indices. The characterization of DBP precursors suggests that hydrophobic (HPO) NOM contains the major fraction of precursor for the formation of nitrogenous DBPs (contributing about 60% of the total nitrogenous DBPs) during all three disinfection processes. Much larger amounts of heterocyclic DBPs were formed from the HPO fraction than from the hydrophilic fraction during chlorination. During chloramination and ozonation, 5–15 times more ketones were formed from the hydrophilic fraction than from the HPO fraction. During ozonation, more than twice the amounts of esters and alcohols were formed from the hydrophilic fraction than from the HPO fraction. Three-dimensional excitation-emission matrix spectra suggest that similar to the formation of regulated DBPs, humic acid-like substances are probably

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the precursors of halogen-containing DBPs. Relatively higher nitrogenous DBPs formation from the HPO fraction might be because of the existence of protein-like materials.

1. Introduction

The generation of disinfection by-products (DBPs) during water processing procedures is attracting increasing concern because exposure to DBPs can lead to adverse health effects (Cantor et al., 2010; Nieuwenhuijsen et al., 2000; Richardson et al., 2007; Savitz et al., 2005; Singer, 2006; Villanueva et al., 2004; Waller et al., 1998; Wei et al., 2013). Richardson (2011) reviewed DBPs in drinking water and listed >600 DBPs that have been identified either in real treatment plants or controlled laboratory studies when different disinfectants or combinations of disinfectants were used. More recently, advances in analytical methods have allowed the number of DBPs that have been detected to continually increase. For example, negative ion electrospray ionization-triple quadrupole mass spectrometry has been applied to fast selective detection of brominated DBPs and iodinated DBPs in drinking water samples (Ding and Zhang, 2009; Zhang et al., 2008). High performance and ultraperformance liquid chromatography-tandem mass spectrometry have been increasingly used to identify highly polar DBPs, including chlorinated polyphenolic and aromatic acids, aromatic halogenated DBPs, and iodinated DBPs (Gonsior et al., 2014; Pan et al., 2016a; Pan and Zhang, 2013; Pan et al., 2016b; Wu et al., 2014). Ultrahigh resolution with Fourier transform ion cyclotron resonance mass spectrometry has been used in some recent studies to determine the molecular formulas of chlorinated and brominated DBPs formed in samples of artificial and real drinking water (Lavonen et al., 2013; Zhai et al., 2014; Zhang et al., 2012; Zhang et al., 2014). Gas chromatography Orbitrap mass spectrometry has recently been applied to investigate iodine-containing disinfection by-products in disinfected waters (Postigo et al., 2016).

To control the formation of such a large number of DBPs in waterworks, removing DBP precursors before disinfection seems to be a more effective mean than altering disinfection conditions or utilizing other advanced technologies to minimize DBPs after they have been formed (Bond et al., 2011; Bond et al., 2012; Ma et al., 2013). Inorganic precursors such as bromide, iodide and nitrite play important roles in the formation of DBPs (Krasner, 2009; Kristiana et al., 2012). However, main precursors for DBPs are natural organic matter (NOM) comprising of a complex mixture of heterogeneous organic compounds (Hua and Reckhow, 2007). Therefore, formation of DBPs depend on the characteristics of NOM or its fractions. It is thus critical for researchers to isolate and fractionate NOM based on defined chemical groups, and then to examine which fractions are responsible for the generation of different DBPs identified. The most common approach is a resin fractionation procedure developed and modified to separate NOM components according to their hydrophobicity (Leenheer, 1981; Malcolm and MacCarthy, 1992; Marhaba et al., 2003; Thurman and Malcolm, 1981) and it is widely accepted in NOM fraction studies. Hua and Reckhow (2007) chlorinated NOM fractions from three surface waters, and they found that the hydrophobic (HPO) fraction was a more important source of trihalomethanes (THMs), trihaloacetic acids and total organic halogen (TOX) than the hydrophilic (HPI) or transphilic fractions for high and medium specific ultraviolet absorbance (SUVA) waters. Their observations confirmed previous studies (Kitis et al., 2002; Liang and Singer, 2003). Lin et al. (2014) fractionated two surface waters samples and determined the formation potentials of THMs, iodo-THMs, and haloacetonitriles during chlorination and chloramination. They found that more THMs tended to be formed from the HPO fraction during chlorination and from the HPI fraction during chloramination. They found that HPI NOM were potent precursors for most iodo-THMs and haloacetonitriles during chlorination. In other studies, it was found

that more N-nitrosamines formed from the HPI fraction than from the HPO and transphilic fractions during chloramination (Chen and Valentine, 2007; Wang et al., 2013), and this was attributed to higher nitrogen content in the HPI acidic and basic NOM fractions than in the HPO and transphilic fractions (Croue et al., 2000). Chu et al. (2010) investigated the formation of dichloroacetamide during the chlorination and chloramination of various polarity-based NOM fractions and found that HPI acidic NOM showed the maximum dichloroacetamide formation potential. Three-dimensional excitation-emission matrix (3D-EEM) spectra have showed that protein-like substances in the HPI acidic NOM fraction play critical roles in the dichloroacetamide formation (Chu et al., 2010). Hu et al. (2010) found that halonitromethanes yields were significantly higher from the HPI fraction than from the HPO and transphilic fractions during chlorination. Świetlik and Sikorska (2004) investigated the formation of aldehydes and carboxylic acids during ozonation and chlorine dioxide treatment of NOM fractions. They found that HPO and HPI neutrals were the main precursors for aldehydes during chlorine dioxide treatment, and that abundant aldehydes were produced from the humic acid, HPI neutral and HPI basic fractions during ozonation. The HPI basic and HPI neutral fractions were the leading precursors of carboxylic acids during ozonation but not during chlorine dioxide treatment. In this case, humic acid, HPI neutral, and HPO neutral fractions were the main responsible. Up to date, abundant knowledge has been accumulated since the first report of DBPs during disinfection processes (Rook, 1974). However, most studies have been mainly focused on currently regulated DBPs and a few certain emerging DBPs. There is still a lack of comprehensive data on the unknown volatile and semi-volatile DBPs formation from NOM fractions during different disinfection processes.

We previously developed a nontargeted method using comprehensive two-dimensional gas chromatography-quadrupole mass spectrometry (GC × GC-qMS) to screen volatile and semi-volatile DBPs in drinking water (Li et al., 2016). Therefore, the main aim of the study presented here was to use this nontargeted screening approach to examine the relationships between NOM fractions with different hydrophobicities and the formation of different chemical classes of DBPs in a much wider scope.

2. Materials and methods

2.1. Materials

A NOM solution was prepared by dissolving an aliquot of Suwannee River NOM isolate (~220 mg) (Cat. No. 1R101N, International Humic Substances Society) in Milli-Q water (1 L) and filtering it with a 0.45-μm glass fiber filter (Millipore, Billerica, MA, USA), hereby referred to as SRNOM. An *n*-alkane standard (C_7–C_{25}) solution was purchased from AccuStandard (New Haven, CT, USA). High-performance liquid chromatography-grade methyl tert-butyl ether (MTBE) was obtained from Thermo Fisher Scientific (Waltham, MA, USA). Ultrapure water (18.2 MΩ·cm) was prepared by a Milli-Q purification system (Millipore, Billerica, MA, USA). Analytical grade sodium hypochlorite (NaClO) and ammonium chloride (NH_4Cl) were purchased from Sinopharm Chemical Reagent Co. (Beijing, China). Monochloramine stock solutions were prepared daily by slowly adding NaClO to a rapidly stirred NH4Cl solution that had been adjusted to pH 8 with sodium hydroxide. A Cl:N molar ration of 1:1.2 was used to avoid dichloramine formation resulting from local excess of hypochlorite (Mitch and Sedlak, 2002). Anhydrous sodium sulfate (99.5%, guaranteed reagent, Sinopharm