A comparison of carbonaceous, nitrogenous and iodinated disinfection by-products formation potential in different dissolved organic fractions and their reduction in drinking water treatment processes

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ABSTRACT

Natural organic matter (NOM) fractions in the raw waters collected from the Huangpu and Yangtze rivers were separated according to their hydrophobicity and molecular weights (MWs) using resin adsorption (RA) and ultrafiltration (UF), respectively, to investigate the formation potential of carbonaceous disinfection by-products (C-DBPs), nitrogenous DBPs (N-DBPs) and iodinated DBPs (I-DBPs) after chlorination and chloramination for each fraction. The removal of C-, N- and I-DBP precursors in each process by the Minhang No. 2 and Yangshupu drinking water treatment plants (DWTPs) was also studied. After chlorination, hydrophobic NOM with MW < 1 kDa contributed the most to the formation of C-DBPs, whereas for chloramination, hydrophilic NOM with MW < 1 kDa contributed the most to the formation of C-DBPs in both raw waters and trihalomethanes (THM_4) were the dominant components. Most of the N-DBPs were formed from different NOM fractions in the Huangpu (hydrophilic and MW > 10 kDa fractions) and Yangtze (hydrophobic and MW < 1 kDa fractions) rivers after chlorination. However, after chloramination, the formation of N-DBPs was distributed relatively evenly among the three hydrophobic fractions. Additionally, N-DBP formation decreased with increasing MW for the Huangpu river, and for the Yangtze river, MW fractions > 10 kDa exhibited higher reactivity. In both rivers, the hydrophilic NOM contained the majority of I-DBP precursors. After chlorination, most of the I-DBPs came from MW fractions > 10 kDa and <1 kDa in the Huangpu and Yangtze rivers, respectively, whereas after chloramination, the MW < 1 kDa fraction was the major source in both rivers. This study also found that conventional water treatment processes could not remove DBP precursors effectively, and the control over DBP formation after chloramination was more difficult than after chlorination, especially for I-DBPs.

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1. Introduction

Disinfection by-products (DBPs) can be formed by the reaction between natural organic matter (NOM) and disinfectants/oxidants during water treatment processes [1,2]. Carbonaceous DBPs (C-DBPs), such as trihalomethanes (THMs), are widespread DBPs in chlorinated and chloraminated waters, and these DBPs have been regulated by many countries because of the potential health risks from these byproducts [3–5]. Nitrogenous DBPs (N-DBPs) can also be formed, such as haloacetonitriles (HANs) and N-nitroso-dimethylamine (NDMA). HANs were identified in the early 1980s

[6], can lead to mutagenicity in bacterial assays and can exert carcinogenic or mutagenic effects in mice [7,8], while NDMA has been classified as a probable human carcinogen by the US Environmental Protection Agency [9]. Use of alternative disinfectants, such as chloramine, is a common method to control the formation of THMs; however this can increase formation of certain N-DBPs [10]. Mammalian cell tests have shown that N-DBPs are a few orders of magnitude higher in cytotoxicity and genotoxicity than C-DBPs [5,11]. For iodide (I^-)-containing waters, I^- can be oxidized into hypoiodous acid (HOI) during oxidative drinking water treatment processes and further react with NOM to form iodated DBPs (I-DBPs) [12]. Recent mammalian cell toxicity results have also demonstrated that I-DBPs possess more cytotoxicity than their brominated and chlorinated analogues [13–16]. Although I-DBPs can be formed during chlorination and chloramination, chloramine

only oxidizes I^- to HOI without further oxidizing to iodate (IO_3^-) [12,17], which will generate more I-DBPs. In contrast, chlorination will typically decrease the formation of I-DBPs and increase the formation of IO_3^- [12,18].

To reduce the formation of DBPs, removing DBP precursors before disinfection is often considered more effective than altering the disinfection conditions or introducing other advanced technologies to remove DBPs after their formation [10,19]. NOM with complex structures and functional groups is the main organic source of DBP precursors in chlorinated or chloraminated waters [20]. Understanding the physicochemical properties of NOM in raw waters, including its hydrophobicity, molecular weight (MW) distribution and DBP formation potential (DBPFP), is crucial for water treatment [21]. Evaluating DBPFP as a function of hydrophobicity and MW of the precursors can provide insight into the implementation of better water treatment processes to control DBP formation.

Resin adsorption (RA) and ultrafiltration (UF) are two common methods for NOM separation [22,23]. Synthetic resins (e.g., XAD-8 and XAD-4) are used to separate NOM into groups with different hydrophobic behavior (e.g., hydrophobic, transphilic, and hydrophilic) [24,25]. Studies have shown that hydrophobic NOM is a more prevalent origin of DBP precursors than hydrophilic or transphilic ones [26,27]. UF is a purification method that separates solutes by their ability to penetrate through the micro-pores of a membrane along with a solvent under hydrostatic pressure, and retains and concentrates larger solutes [28]. The chemical nature of NOM can be maintained after UF without adjustments in solution chemistry, which is very important for the effective characterization of NOM [23]. The MW distribution of NOM varies from source to source and can be affected by seasonal changes [29,30]; however, many studies have shown that small molecule precursors play an important role in DBP formation [20,21,31,32].

This study aims to investigate the formation of C-, N- and I-DBPs from NOM fractions with different hydrophobicities and MW distributions after chlorination and chloramination. Raw water samples with different organic concentrations were collected from the Yangtze and Huangpu rivers. The reduction of DBPFP, including C-, N- and I-DBPs, in the effluent of each process in the Minhang No. 2 and Yangshupu drinking water treatment plants (DWTPs) was examined to evaluate the process efficiency in the removal of DBP precursors. The results of this study can provide a theoretical basis for the effective control of different DBPs in DWTPs.

2. Materials and methods

2.1. Waters

Samples of raw water and treated water after each process were collected in the same season (winter, 2012) from the Minhang No. 2 DWTP (MDWTP) and the Yangshupu DWTP (YDWTP), which are supplied by the Huangpu river and Yangtze river, respectively, in Shanghai, China. Samples were collected in polypropylene containers, transported to the laboratory on ice, filtered through 0.45 μm filters (Millipore, USA) to remove particulate matters upon arrival and then stored at 4 °C in the dark. The concentration of dissolved organic carbon (DOC), dissolved organic nitrogen (DON), UV_{254} and bromide in the raw water was 3.92 mg/L, 0.35 mg-N/L, 0.111 cm^{-1} and 17.1 μg/L, respectively, from the Huangpu river and 1.83 mg/L, 0.43 mg N/L, 0.033 cm^{-1} and 50.1 μg/L, respectively, from the Yangtze river.

2.2. Experimental procedures

A portion of the filtered water samples was acidified to pH 2 using concentrated sulfuric acid (Sigma–Aldrich, USA) for NOM

fractionation by RA. Two nonionic resins (Amberlite XAD-8 and XAD-4, USA) were thoroughly cleaned and conditioned as described by Leenheer [33] using Milli-Q water until the concentration of DOC in the permeate was less than 0.1 mg-C/L prior to the separation experiment. Water samples were passed through XAD-8 followed by XAD-4 [34], and the effluent from these two resins was collected as the hydrophilic fraction. Subsequently, 0.1 M sodium hydroxide (Sigma–Aldrich, USA) was used to elute additional fractions from XAD-8 and XAD-4 in the reverse direction. The fraction referred to as the hydrophobic NOM was retained by XAD-8, and the fraction adsorbed by XAD-4 was the transphilic fraction. The corresponding column capacity factor (k') was 50, and the flow rate was less than 30 bed-volumes/h [21], which permitted adequate adsorption to the resin. The pH of each of these collected fractions was adjusted to 7 using sulfuric acid or sodium hydroxide immediately after the separation. Control samples using ultrapure water were also analyzed under the same experimental procedures, and only trace levels of I-DBPs were observed.

Another portion of the filtered water samples was fractionated into three groups using a series of cellulose-derivative UF membranes (Millipore, USA) with MW cut-offs of 1 and 10 kDa, in dead-end stirred cells (Millipore, USA). A detailed experimental procedure was described in our previous study [35]. To prevent any leakage of organics from the membrane surface, Milli-Q water was passed through the membranes until the DOC concentration in the permeate was less than 0.1 mg-C/L prior to the separation test. High purity nitrogen (99.999%) was used to maintain the filtration pressure at 345 kPa. Control samples using ultrapure water were also analyzed under the same conditions, and only trace levels of I-DBPs were observed.

The C- and N-DBPFP experiments during chlorination and chloramination were conducted in duplicate under headspace-free conditions in 40-mL amber glass screw-cap vials with PTFE-lined septa at room temperature (25 ± 1 °C) for 7 d of contact time. Because the concentrations of I^- in the Huangpu and Yangtze rivers were below the detection limit, and concentration as high as 104 μg/L in raw water was reported in the literature [14], another set of experiment was spiked with an I^- dose of 100 μg/L to measure the formation of I-DBPs. The doses of chlorine and monochloramine (NH_2Cl) were determined as follows: Cl_2 (mg/L) = 3 × DOC (mg-C/L) + 8 × NH_3-N (mg-N/L) + 10 (mg/L) and NH_2Cl (mg/L) = 3 × DOC (mg-C/L), which can allow the reaction to approach completion [36,37]. The stock solution of chlorine (50 g/L as Cl_2) was prepared using a 5% sodium hypochlorite (NaOCl, Sigma–Aldrich, USA) solution. A NH_2Cl solution was freshly prepared by mixing aqueous ammonium chloride and NaOCl solutions at a Cl_2/N ratio of 0.8 M/M at pH 8.5. All samples were buffered using 10 mM phosphate solution and the pH was maintained at 7 by the addition of 0.01, 0.1 and 1 M H_2SO_4 or NaOH. After 7 d's reaction time, the samples were quenched using ammonium chloride (for C-DBP and N-DBP measurements) and sodium sulfite (for I-DBP measurement) and then extracted for DBP analysis. The analyzed C-DBPs include THM_4, vinyl chloride (VC) and haloketones (HKs, including dichloroacetone and trichloroacetone). The analyzed N-DBPs include haloacetonitriles (HANs, including dichloroacetonitrile, trichloroacetonitrile, bromochloroacetonitrile and dibromoacetonitrile) and chloropicrin (CP). The analyzed I-DBPs include iodoform (CHI_3), chlorodiiodomethane ($CHClI_2$), bromodiiodomethane ($CHBrI_2$), dichloroiodomethane ($CHCl_2I$), dibromoiodomethane ($CHBr_2I$), and bromochloroiodomethane ($CHBrClI$). All experimental data presented in this paper were obtained by subtracting the DBPFP from the control samples to eliminate potential interference from trace organic compounds eluting from resins and/or UF membranes, which could be responsible for the formation of DBPs.