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Distribution and relevance of iodinated X-ray contrast media and iodinated trihalomethanes in an aquatic environment

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HIGHLIGHTS

- Iodinated X-ray contrast media (ICM) distribution in the waters of China was investigated.
- Relevance of ICM and I-DBPs in the surface water and DWTPs was investigated.
- Some ICM were strongly correlated with iodinated trihalomethanes (I-THMs).
- ICM were transformed to I-THMs during chlorination and ozonization processes in DWTPs.
- ICM was an important source for I-THMs formation in the real aquatic environment.

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ABSTRACT

Distribution and relevance of iodinated X-ray contrast media (ICM) and iodinated disinfection byproducts (I-DBPs) in a real aquatic environment have been rarely documented. In this paper, some ICM were proven to be strongly correlated with I-DBPs through investigation of five ICM and five iodinated trihalomethanes (I-THMs) in surface water and two drinking water treatment plants (DWTPs) of the Yangtze River Delta, China. The total ICM concentrations in Taihu Lake and the Huangpu River ranged from 88.7 to 131 ng L^{-1} and 102–252 ng L^{-1}, respectively. While the total I-THM concentrations ranged from 128 to 967 ng L^{-1} in Taihu Lake and 267–680 ng L^{-1} in the Huangpu River. Iohexol, the dominant ICM, showed significant positive correlation ($p < 0.01$) with $CHCl_2$ in Taihu Lake. Iopamidol and iomeprol correlated positively ($p < 0.01$) with some I-THMs in the Huangpu River. The observed pronounced correlations between ICM and I-THMs indicated that ICM play an important role in the formation of I-THMs in a real aquatic environment. Characteristics of the I-THM species distributions indicated that I-THMs may be transformed by natural conditions. Both DWTPs showed negligible removal efficiencies for total ICM (<20%). Strikingly high concentrations of total I-THMs were observed in the finished water (2848 ng L^{-1} in conventional DWTP and 356 ng L^{-1} in advanced DWTP). Obvious transformation of ICM to I-THMs was observed during the chlorination and ozonization processes in DWTPs. We suggest that ICM is an important source for I-DBP formation in the real aquatic environment.

1. Introduction

Iodinated X-ray contrast media (ICM) derived from 2, 4, 6-triiodobenzoic acid with carboxyl and hydroxyl groups (Table S1 in Supplementary data), are widely used to enhance imaging of organs, surrounding tissues, and blood vessels (Perez and Barcelo, 2007). To reduce its adverse influence on health, ICM are designed to be inert with high hydrophilicity, making ICM recalcitrant to conventional wastewater treatment (Echeverria et al., 2013), so it is ultimately released into the aquatic environment (Zemann et al., 2014). Although the intrinsic toxicity of ICM is low due to their high ionic strength and osmolarity (Kim et al., 2015), some ICM can be transformed to low-molecular weight DBPs, I-THMs and iodoacetic acid, and high-molecular weight DBPs by oxidization, and some of these have shown potential mutagenicity and cytotoxicity (Magdeburg et al., 2014; Wendel et al., 2014). Recently, ICM have been reported to be a source of carcinogenic iodinated disinfection by-products (I-DBPs) in drinking water (Ye

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et al., 2014). I-DBPs are the by-products of the oxidization process among disinfectants, iodide and natural organic matter (NOM), including iodinated trihalomethanes (I-THMs), iodoacetic acids, iodoacetonitrile, iodoacetamides, iodoacetaldehyde, and iodophenolic compounds, and these are more cytotoxic and genotoxic than their chlorinated and brominated analogues due to high nucleophilicity (Plewa et al., 2004; Zhang et al., 2012). In addition, Yang and Zhang (2013) found that iodinated phenols showed higher developmental toxicity than other halogenated analogues when they were evaluated by marine polychaete *Platynereis dumerilii*. Though I-DBP concentrations in drinking water are typically lower than chlorinated and brominated DBPs, they still pose a potential human health concern, especially in coastal cities and places with a high concentration of iodide and other iodinated compounds. Moreover, I-DBPs cause taste and odour problems in drinking water, especially for CHI_3 with an organoleptic threshold concentration of 1 μg L^{-1} (Hansson et al., 1987). Therefore, it is of great importance to investigate the occurrence and distribution of ICM and I-DBPs in the aquatic environment and drinking water sources.

The distribution of ICM in the aquatic environment has only been documented in a few places, such as Europe, USA and Jordan (Duirk et al., 2011; Seitz et al., 2006; Zemann et al., 2014). These studies found up to 680,000 ng L^{-1} of iopromide (IOP) in treated wastewater, 2700 ng L^{-1} of iopamidol (IOD) in drinking water treatment plants (DWTPs), 36,000 ng L^{-1} of IOD in groundwater, and 78,000 ng L^{-1} of IOD in surface water (Duirk et al., 2011; Zemann et al., 2014). For I-DBPs, it was reported that sum iodoacids was up to 1100 ng L^{-1} in DWTPs. In contrast, I-THMs ($CHCl_2I$ and CHBrClI) was found to be up to 7800 ng L^{-1} in DWTPs and 848 ng L^{-1} in household tap water in the USA (Duirk et al., 2011; Ioannou et al., 2016). No data are currently available on the magnitude and variability of ICM in the aquatic environment of China; information about the occurrence and distribution of I-DBPs in the natural aquatic environment are still scare (Ding et al., 2013; Luo et al., 2014), especially in regards to ICM and I-DBPs. The iodide oxidation product HOI and I_2 can react with NOM and may form I-DBPs (Bichsel and Gunten, 2000). Duirk et al. (2011) also reported that ICM may be another iodine source. The iodine atom on the ICM benzene ring may be slowly oxidized by disinfectants to HOI, which then reacts with NOM to form I-DBPs (Duirk et al., 2011). However, direct evidence of ICM in the formation of I-DBPs in the aquatic environment must still be confirmed.

Huangpu River and Taihu Lake provide two of most important drinking water sources of the Yangtze River Delta, which is a highly industrialized area in China. Huangpu River is a tributary of the Yangtze River Estuary, running through 11 districts of Shanghai. Taihu Lake is one of five large freshwater lakes in China. It is located in the lower reaches of the Yangtze River Delta across Zhejiang, Jiangsu, Shanghai. In recent decades, an increased population and industrial development have contributed to a great amount of sewage to be discharged into rivers and lakes, leading to serious damage of the ecological system and watershed. In this paper, the Huangpu River and Taihu Lake were chosen as case studies to analyse the distribution of ICM and I-THMs. The main factors (including dissolved organic carbon (DOC), I^-, Br^- and ICM) that might influence the formation of I-THMs in the real aquatic environment were also investigated. In addition, ICM removal and I-THM formation were compared in conventional DWTP and advanced DWTP. This study not only identifies the distribution of ICM and I-THMs in an aquatic environment but also confirms that ICM were a source of I-THM formation in the real aquatic environment.

2. Materials and methods

2.1. Chemicals and reagents

All chemicals used in this investigation were at least of analytical grade. Iopamidol (IOD, 99.0%), iomeprol (IOM, 96.0%), iopromide (IOP, 98.0%), iohexol (IOX, 96.0%) and diatrizoate (DTZ, 92.0%) standards were obtained from Dr. Ehrenstorfer (Augsburg, Germany). Isotope internal standard IOX-d_5 for ICM and 1, 2-dibromopropane for I-THMs were purchased from Toronto Research Chemicals (North York, Canada). $CHCl_2I$ (97.82%), $CHBrI_2$ (95.03%), $CHClI_2$ (97.21%), $CHBr_2I$ (96.27%) were purchased from CanSyn Chem. Corp. (Toronto, ON, Canada), along with CHI_3 (99%) from Sigma-Aldrich (Steinheim, Germany), 2-dibromopropane from o2si Smart Solutions (Charleston, SC, USA). HPLC-grade methanol, acetonitrile and methyl *tert*-butyl ether (MtBE) were purchased from Merck (Darmstadt, Germany). Formic acid, anhydrous Na_2SO_4 and Na_2SO_3 were purchased from CNW Technologies GmbH (Duesseldorf, Germany). Ultrapure water was obtained from a Milli-Q purification system (18.2 Ω, Millipore, Billerica, MA, USA).

2.2. Sampling

Details of the sampling of Taihu Lake (9 sites) and Huangpu River (11 sites) are shown in Fig. 1. For Pudong DWTP (PDWTP), the treatment processes include pre-chlorination, sedimentation, sand filtration and chloramination, while Yangshupu DWTP (YDWTP) included pre-chlorination, sedimentation, sand filtration, ozonation, biological-activated carbon and chloramination (Fig. S1 in Supplementary data). To compare the conventional treatment process and advanced treatment process, especially for the oxidization process, we chose raw water, pre-chlorination, sites before disinfection and finished water as sampling sites. Water samples of 2 L were collected and then immediately quenched by anhydrous Na_2SO_3 (20 mg), stored in amber glass containers under 4 °C during transportation and in laboratory, all within two days during February 2015. Before pretreatment and concentration, all samples were filtered through 0.7 μm glass fibre filters (GF/F, Whatman, England), and samples for ICM detection were adjusted to pH 3.2.

2.3. Analytical methods

Dissolved organic carbon (DOC) was measured by a Shimadzu TOC-VCSH analyser (Shimadzu, Kyoto, Japan), with a limit of detection (LOD) of 0.1 mg C L^{-1}. Br^- and I^- were analysed using ICS-1000 ion chromatography (Dionex, Sunnyvale, CA, USA) equipped with a conductivity detector in 35 °C, combined with an anion exchange column AS22 under 30 °C and both of their LODs were 0.015 mg L^{-1}. The concentrations of DOC, Br^-, and I^- in the sampling sites of Taihu Lake, Huangpu River, PDWTP and YDWTP are shown in Table S2 in Supplementary data. The method for ICM measurement was based on our previous research (Li et al., 2015). Isotope internal standard IOX-d_5 (final concentration of 20 ng L^{-1} in the sample) was added to the acidified samples. Then, the samples were enriched by a combination of LiChrolute EN (Merck, Darmstadt, Germany) and ENVI-Carb (Supelco, Bellefonte, PA, USA) solid phase extraction cartridges. Finally, the concentrated samples were quantified by an ACQUITY TQ UPLC-MS/MS system (Waters, Milford, MA, USA) equipped with a BEH Shield RP_{18} column (18 mm × 2.1 mm, 1.7 μm, Waters, Milford, MA, USA). The LODs were 0.4–1.9 ng L^{-1}, and recoveries were 84.8%–108.6%. The analysis of I-THMs were performed with liquid-liquid extraction through methyl *tert*-butyl ether (MtBE) by using EPA method 551.1 and analysed by gas chromatography (GC) (GC-7890A, Agilent, Santa Clara, CA, USA) equipped with an electron capture detector