Water Research 112 (2017) 129–136

Contents lists available at ScienceDirect

Water Research

journal homepage: www.elsevier.com/locate/watres

# Detection, formation and occurrence of 13 new polar phenolic chlorinated and brominated disinfection byproducts in drinking water

Yang Pan [a], Ying Wang [a], Aimin Li [a], Bin Xu [b], Qiming Xian [a], Chendong Shuang [a], Peng Shi [a], Qing Zhou [a], *

[a] State Key Laboratory of Pollution Control and Resource Reuse, School of the Environment, Nanjing University, Nanjing, 210023, China
[b] State Key Laboratory of Pollution Control and Resource Reuse, College of Environmental Science and Engineering, Tongji University, Shanghai, 200092, China

## ARTICLE INFO

*Article history:*
Received 27 October 2016
Received in revised form
16 January 2017
Accepted 20 January 2017
Available online 24 January 2017

*Keywords:*
Phenolic disinfection byproducts
Formation
Precursor
Occurrence
Drinking water

## ABSTRACT

Recently, 13 new polar phenolic chlorinated and brominated disinfection byproducts (Cl- and Br-DBPs) were identified and quantified in simulated chlorinated drinking water by adopting product ion scan, precursor ion scan, and multiple reaction monitoring (MRM) analyses using ultra performance liquid chromatography/electrospray ionization-triple quadrupole mass spectrometry (UPLC/ESI-tqMS). The 13 new DBPs have been drawing increasing concern not only because they possess significantly higher growth inhibition, developmental toxicity, and chronic cytotoxicity than commonly known aliphatic DBPs, but also because they act as intermediate DBPs that can decompose to form the U.S. EPA regulated DBPs. In this study, through MS parameter optimization of the UPLC/ESI-tqMS MRM analysis, the instrument detection and quantitation limits of the 13 new DBPs were substantially lowered to 0.42–6.44 and 1.35–16.51 μg/L, respectively. The total levels of the 13 new DBPs formed in chlorination were much higher than those formed in chloramination within a contact time of 3 d. In chlorination, the 13 new DBPs formed quickly and decomposed rapidly, and their total concentration kept on decreasing with contact time. In chloramination, the levels of the dominant species (i.e., trihalo-phenols) firstly increased and then decreased with contact time, whereas the levels of the other new DBPs were relatively low and kept on increasing with contact time. An increasing of pH from 6.0 to 9.0 decreased the formation of the 13 new DBPs by 57.8% and 62.3% in chlorination and chloramination, respectively. Gallic acid was found to be present in various simulated and real source water samples and was demonstrated to be a precursor of the 13 new DBPs with elucidated formation pathways. Furthermore, 12 of the 13 new DBPs were detected in 16 tap water samples obtained from major cities in East China, at total levels from 9.5 to 329.8 ng/L. The concentrations of the new DBPs were higher in samples with source waters containing higher bromide levels. Ozone-activated carbon treatment prior to disinfection might reduce the formation of the new DBPs since it was effective in precursor reduction.

## 1. Introduction

Bromide ubiquitously exists in natural drinking water sources globally. The reported bromide levels in water sources from the U.S., Canada, Australia, and Israel were in the range of 0.024–4.13 mg/L (Heller-Grossman et al., 1999; Magazinovic et al., 2004; Richardson et al., 2008). Chlorine is the most intensively used chemical disinfectant since it is cost-effective and efficient in killing/inactivating bacteria and pathogens. During chlorination, hypochlorous acid (HOCl) can quickly oxidize bromide to hypobromous acid (HOBr) ($k = 1550\ 1/(M \cdot s)$) (Kumar and Margerum, 1987; Deborde and von Gunten, 2008), and the resulting mixture of HOBr/HOCl may further react with natural organic matter (NOM) to generate numerous chlorinated and brominated disinfection byproducts (Cl- and Br-DBPs) (Xie, 2004; Richardson and Postigo, 2011). Chloramines are increasingly applied for disinfecting drinking water in recent years since they persist longer in distribution systems and produce less haloacetic acids and trihalomethanes (two groups of most prevalent regulated DBPs), as compared with chlorine (Diehl et al., 2000; Hua and Reckhow, 2007). In

---

* Corresponding author.
*E-mail address:* zhouqing@nju.edu.cn (Q. Zhou).

http://dx.doi.org/10.1016/j.watres.2017.01.037

chloramination, monochloramine ($NH_2Cl$) and its derivatives (e.g., HOCl) may react with bromide and NOM to generate numerous Cl- and Br-DBPs (Kristiana et al., 2009; Zhai et al., 2014).

Recently, 13 new polar phenolic Cl- and Br-DBPs were identified and quantified in simulated chlorinated drinking water by adoption of product ion scan, precursor ion scan, and multiple reaction monitoring (MRM) analyses using ultra performance liquid chromatography/electrospray ionization-triple quadrupole mass spectrometry (UPLC/ESI-tqMS) (Zhai and Zhang, 2011; Pan and Zhang, 2013a). The 13 new phenolic DBPs were divided into four groups according to their structures, i.e., three dihalo-4-hydroxybenzoic acids, three dihalo-salicylic acids, three dihalo-4-hydroxybenzaldehydes, and four trihalo-phenols. These new phenolic DBPs have been drawing increasing concern not only because they possess significantly higher growth inhibition, developmental toxicity, and chronic cytotoxicity than commonly known aliphatic DBPs (Yang and Zhang, 2013; Wang et al., 2014; Liu and Zhang, 2014), but also because they act as intermediate DBPs that can decompose to form the U.S. EPA regulated DBPs such as trihalomethanes and haloacetic acids (Zhai and Zhang, 2011; Pan and Zhang, 2013a). Regarding to their possible adverse health implications on human health, further study on their formation during various disinfection processes should be of high importance.

In previous studies, quantitation of the new phenolic DBPs was achieved using standard addition followed by the UPLC/ESI-tqMS MRM analysis, which can promote the detection of these new DBPs via allowing the specific fragmentation ions (i.e., chloride or bromide in the third quadrupole) of the target ion (i.e., molecular ion in the first quadrupole) and filtering out all the other undesirable fragmentation ions (Pan and Zhang, 2013a). With this method, the concentrations of these new DBPs in various simulated tap water samples were tentatively determined. However, during the MRM analysis of these new DBPs, uniform MS parameters were applied without optimization for each DBP, which might inhibit their efficient and accurate quantitation at trace levels. In fact, MS parameters including desolvation temperature, source temperature, capillary voltage, desolvation gas flow rate, cone gas flow rate, cone voltage, collision energy, and dwell time can all affect the MRM analysis of the new DBPs, and thus optimization of the aforementioned parameters should be necessary. IntelliStart is a specific function provided by the Waters UPLC/ESI-tqMS, and it can aid in setting up the MS hardware (e.g., mass resolution, mass calibration, and ion source) and in determining optimum ionization parameters (e.g., cone voltage, collision energy, and dwell time) for specific transitions in MRM analysis (Jones and Glover, 2016). Accordingly, it was expected that via optimization of MS parameters with IntelliStart and batch experiments, lower detection and quantitation limits for the new DBPs could be obtained.

This study was designed to optimize the UPLC/ESI-tqMS MRM parameters for better detection and quantitation of the 13 new polar phenolic Cl- and Br-DBPs, and to examine their formation in drinking water during different disinfection processes with an emphasis on their precursor and formation pathways. Moreover, the occurrence concentrations and frequencies of the 13 new DBPs were examined and compared in 16 real tap water samples obtained from drinking water treatment plants using various water sources and treatment processes in East China.

## 2. Materials and methods

### 2.1. Materials

3-Bromo-5-chlorosalicylic acid (95%) was obtained from Enamine Ltd. 3,5-Dibromo-4-hydroxybenzoic acid (98%) was obtained from Indofine Chemical Company. 2,6-Dibromo-4-chlorophenol (95%) was purchased from Fluorochem. 3,5-Dibromo-4-hydroxybenzaldehyde (98%) was obtained from Alfa Aesar. 3,5-Dichloro-4-hydroxybenzaldehyde (97%), 3,5-dichlorosalicylic acid (99%), 3,5-dichloro-4-hydroxybenzoic acid (98%), 3-bromo-5-chloro-4-hydroxybenzaldehyde (95%), 2,6-dichloro-4-bromophenol (98%), and 3,5-dibromosalicylic acid (98%) were obtained from International Laboratory USA. Gallic acid (98%), 2,4,6-tribromophenol (99%), 2,4,6-trichlorophenol (98%), and 4-hydroxybenzoic acid (≥99%) were obtained from Sigma-Aldrich. Since 3-bromo-5-chloro-4-hydroxybenzoic acid did not have commercially available standard compound, it was synthesized through the reaction of "4-hydroxybenzoic acid + bromide + chlorine" and subsequently isolated and quantified in the laboratory according to procedures provided previously (Pan and Zhang, 2013a). Each of the 13 new polar phenolic DBPs was dissolved in 1/1 (v/v) methanol/water to prepare a series of standard solutions. Standard solutions at 1 mg/L were used for MS parameter optimization of the UPLC/ESI-tqMS MRM analysis of these new DBPs. Suwannee river NOM (SRNOM, 2R101N) was obtained from the International Humic Substances Society. A NaOCl stock solution (~2350 mg/L as $Cl_2$) was prepared from a commercial reagent grade NaOCl solution and quantified by a standard method (APHA et al., 2012). Before each use, $NH_2Cl$ was generated by reacting $NH_4Cl$ and NaOCl at a ammonia/chlorine molar ratio of 1.25.

### 2.2. Preparation of simulated drinking water samples

Preparation of simulated source water was performed with ultrapure water by dosing SRNOM (3 mg/L as C), $NaHCO_3$ (90 mg/L as $CaCO_3$), and KBr (0.4 mg/L as $Br^-$). For simulated drinking water sample preparation, the simulated source water was chlorinated/chloraminated by NaOCl or $NH_2Cl$ (5 mg/L as $Cl_2$) under various pH (6.0, 7.0, 7.5, 8.0, and 9.0) for a series of contact times (1 h, 6 h, 12 h, 1 d, and 3 d). The chlorination/chloramination process was conducted without headspace in darkness at 20 °C. Afterwards, the disinfectant residual in each water sample was titrated and quenched using a 5% excess of the required amount of $Na_2SO_3$.

### 2.3. Precursor and formation pathways of the 13 new phenolic DBPs

As major components of higher plants, tannic acid and lignin have been demonstrated to be important sources for humic matter formation in raw water. Decomposition of both tannic acid and lignin can produce a variety of phenolic compounds, including gallic acid (Tan, 2003; Hua et al., 2014). To examine whether gallic acid was a precursor of these new phenolic DBPs during chlorination or chloramination, aliquots of a water solution containing gallic acid (3 mg/L as C), $NaHCO_3$ (90 mg/L as $CaCO_3$), and KBr (0.4 mg/L as $Br^-$) were dosed with NaOCl or $NH_2Cl$ (5 mg/L as $Cl_2$). To further explore formation pathways of the 13 new DBPs during chlorination of gallic acid in the presence of bromide, aliquots of a water solution containing gallic acid (3 mg/L as C), $NaHCO_3$ (90 mg/L as $CaCO_3$), and KBr (2 mg/L as $Br^-$) were chlorinated with addition of NaOCl (5 mg/L as $Cl_2$). All these chlorinated and chloraminated aliquots were stored in darkness without headspace at 20 °C for 12 h, and the disinfectant residuals were eliminated by dosing 105% of the required amount of $Na_2SO_3$.

### 2.4. Sampling and characterization of source/tap water samples

Water sampling was carried out in 16 drinking water treatment plants of eight cities (A–H) located in East China during June and July 2015. For each city, we collected two tap water samples and