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Occurrence of nitrogenous and carbonaceous disinfection byproducts in drinking water distributed in Shenzhen, China

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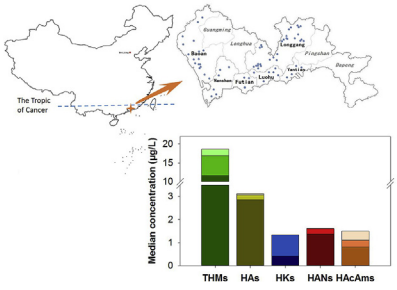
HIGHLIGHTS

- The occurrence of 17 C- and N-DBPs was investigated in drinking water in Shenzhen, South China.
- The level of haloacetamides was 0.1−3.1 μg/L and that of trihaloacetaldehydes was 0.1−11.4 μg/L.
- 12-month sampling results indicated the seasonal variation with highest levels in spring.
- Trihalomethane levels can be used as indicator of haloacetonitriles and haloacetamides levels.

GRAPHICAL ABSTRACT



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ABSTRACT

A 12-month sampling program was conducted throughout a drinking water distribution system in Shenzhen and the data from 251 samples provide a comprehensive picture of the spatial and seasonal variability of 17 species disinfection by-products (DBPs) in a city with subtropical monsoon climate. The carbonaceous disinfection by-product (C-DBPs) included four trihalomethanes (THMs), three trihaloacetaldehydes (THAs) and two haloketones (HKs). Their median concentrations over the entire period were 19.9 μg/L, 3.4 μg/L and 1.4 μg/L, respectively. The nitrogenous DBPs (N-DBPs) monitored were four haloacetonitriles (HANs) and four haloacetamides (HAcAms). Their median levels were 2.0 μg/L and 1.5 μg/L, respectively. Low levels of brominated DBP species (bromine substitution factors $\leq$ 0.5) were observed. The BSF of each DBP class followed the trend: THMs $\approx$ DHAcAms > DHANs > THAs. All the DBP concentrations showed clear seasonal variations with the highest average concentrations in spring. Correlation analyses showed that the THMs and CH levels in Shenzhen drinking water could be used as statistical indicators of the levels of unregulated N-DBPs ($0.4 < r < 0.7$, $p < 0.5$). The results supplement the database of DBP occurrence in drinking water in China, and provide an important reference data set for DBP occurrence in cities with a subtropical monsoon climate around the world.

1. Introduction

To prevent waterborne diseases and maintain the microbial stability of distributed water, a chemical disinfectant, usually chlorine, must be used in water treatment. However, disinfection

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byproducts (DBPs) are generated by the reaction between the disinfectant and organic matter with increasing concentrations along the distribution system (Shanks et al., 2013). The occurrence of DBPs is an important concern since some DBPs are considered toxic and potentially carcinogenic (Richardson et al., 2007).

Trihalomethanes (THMs) and haloacetic acids (HAAs) are the most prevalent DBPs, and their levels are regulated in the drinking water standards of many countries. Chloral hydrate (CH) is the next most prevalent DBP found in drinking water, followed by haloketones (HKs) (Wang et al., 2015), but the occurrence of other trihaloacetaldehydes (THAs) has only occasionally been reported (Koudjonou et al., 2008). Recently, nitrogenous DBPs (N-DBPs) such as haloacetonitriles (HANs) and haloacetamides (HAcAms) have become topics of particular concern because they are reportedly more cytotoxic and genotoxic than regulated carbonaceous DBPs (C-DBPs), such as THMs and HAAs (Muellner et al., 2007; Plewa et al., 2008).

Although various studies have reported the occurrence of certain C-DBPs and N-DBPs in drinking water distribution systems in different regions around the world (Chang et al., 2010; Wei et al., 2010; Gan et al., 2013; Shanks et al., 2013; Guilherme and Rodriguez, 2014; Uyak et al., 2014), little information is available about the presence of THAs and HAcAms within distribution networks (Koudjonou et al., 2008; Bond et al., 2015; Kosaka et al., 2016). The temporal and spatial variations in HAcAms levels in distributed water have not been reported.

In this study, a survey was conducted to document the occurrence, speciation and seasonal and spatial variability of these emerging DBPs in an urban drinking water distribution system. It was conducted in Shenzhen, a major city in Guangdong Province, southern China, located immediately north of Hong Kong. Samples were collected from tap water throughout the city for about a year and the C-DBP levels attributable to THAs, THMs and HKs were measured along with the N-DBP levels attributable to HAcAms and HANs. Shenzhen has a subtropical monsoon climate with high temperature and humidity and intense insolation for much of the year. According to a government report for 2015, Shenzhen's population was 10, 778, 900 and the metropolitan area covered more than 19 million km^2. The drinking water distribution system was therefore extensive. Accordingly, the results of the survey are intended to improve knowledge about the occurrence of DBPs in drinking water in China as a resource for setting future DBP standards and for water quality management. The observations provide an important reference data set relevant to DBP occurrence in the drinking water systems of large communities with a subtropical monsoon climate around the world.

2. Materials and methods

2.1. Materials

A suite of 17 DBPs, including nine C-DBPs (four THMs, three THAs and two HKs) and eight N-DBPs (four HANs and four HAcAms) were investigated in this study (Table 1). The DBP standards, including a mixed standard containing HANs and HKs, a THM mixture standard and a CH standard, and internal and surrogate standards were obtained from Supelco (USA). DCAcAm and TCAcAm standards were obtained from Alfa Aesar (USA). Standards of BDCAcAl, DBCAcAl, BCAcAm and DBAcAm were obtained from Cansyn (Canada). Methyl-tertbutyl ether (MTBE) was obtained from Sigma (USA) and used as extracting solvent. Anhydrous sodium sulphate (Na_2SO_4) and ascorbic acid were purchased from J&K (China).

2.2. Sample collection

The sampling locations are shown in Fig. S1. Water samples were collected from January to November of 2015. Samples were collected in 60 mL amber glass vials with PTFE septa. All of the glassware were washed with ultrapure water (Millipore, U.S) and ashed (400 °C for 2–3 h) before use. Two set of sampling vials were collected from each sampling points. One was for all target compounds analysis using ascorbic acid as dechlorinating agent and the other set was collected for dissolve organic carbon (DOC) analysis. The pH of samples was adjusted to around 5.0 by adding phosphate butter to prevent degradation of DBPs. Field blanks, which accompanied the samples to the sampling sites, were used to determine any background contamination. Tap water was collected in sampling vials to just overflowing (head-space free) after 5 min flush. Samples were shipped back to laboratory in coolers with ice-bags and stored at 4 °C before use. DBPs extraction and analysis were according to method USEPA 551.1. All the samples were extracted within 24 h and analyzed within 7 days. A total of 251 samples were collected and analyzed in this survey. Because of the unavailability of corresponding DBP standards, brominated THA concentrations were only measured for the 122 samples collected after July 2015 and HAcAms concentration was measured in the 132 samples collected after April 2015. There were 251 concentrations measured for the other DBPs.

2.3. Analytical methods

The THMs, THAs, HANs and HKs analysis were carried out with a gas chromatograph (Agilent 7890) with an electron capture detector using USEPA Method 551.1. The column was an HP-5 fused

Table 1
The targeted DBPs with abbreviations used and their detection limit.

Compound	Abbreviation	Detection limit (μg/L)	Compound	Abbreviation	Detection limit (μg/L)
C-DBPs			**N-DBPs**		
Trihalomethanes	**THMs**		**Haloacetonitriles**	**HANs**	
Trichloromethane	TCM	0.19	Dichloroacetonitrile	DCAN	0.06
Bromodichloromethane	BDCM	0.10	Bromochloroacetonitrile	BCAN	0.07
Dibromochloromethane	DBCM	0.04	Dibromoacetonitrile	DBAN	0.06
Tribromomethane	TBM	0.04	Trichloroacetonitrile	TCAN	0.12
Trihaloacetaldehydes	**THAs**		**Haloacetamides**	**HAcAms**	
Chloral hydrate	CH	0.07	Dichloroacetamide	DCAcAm	0.22
Bromodichloroacetaldehyde	BDCAcAl	0.05	Bromochloroacetamide	BCAcAm	0.12
Dibromochloroacetaldehyde	DBCAcAl	0.05	Dibromoacetamide	DBAcAm	0.12
Haloketones	**HKs**		Trichloroacetamide	TCAcAm	0.11
1,1- dichloropropanone	DCP	0.05			
1,1,1-trichloropropanone	TCP	0.06			