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The occurrence of disinfection by-products in municipal drinking water in China's Pearl River Delta and a multipathway cancer risk assessment

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HIGHLIGHTS

- The occurrence of DBPs in 155 samples in three cities was investigated.
- The median THM and HAA levels were 17.7 and 8.6 μg/L, respectively.
- HANs, HKs, CH, and TCNM occurred at low concentrations.
- The cancer risk from mutipathway exposure to THM and HAA was estimated.

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ABSTRACT

Disinfection byproducts were measured in the finished drinking water from ten water treatment plants in three Chinese cities — Guangzhou, Foshan and Zhuhai. A total of 155 water samples were collected in 2011 and 2012. The median (range) of trihalomethane (THM) and haloacetic acid (HAA) levels were 17.7 (0.7–62.7) μg/L and 8.6 (0.3–81.3) μg/L, respectively. Chloroform, dichloroacetic acid and trichloroacetic acid were the dominant species observed in Guangzhou and Foshan water, while brominated THMs predominated in water from Zhuhai. Haloacetonitriles, haloketones, chloral hydrate and trichloronitromethane were usually detected at levels ranging from unquantifiable (<0.2 μg/L) to 12.2 μg/L (choral hydrate). THMs and HAAs showed clear seasonal variations with the total concentrations higher in winter than in summer. Correlations among DBP levels varied, with the strongest linear correlation observed between chloroform and chloral hydrate levels ($R^2 = 0.77$). The risk of cancer from ingestion, inhalation and dermal contact exposure to THMs was estimated. $CHCl_2Br$ contributed the highest percentage of the cancer risk from ingestion pathway and $CHCl_3$ contributed the highest of cancer risk from inhalation pathway.

1. Introduction

Chlorine is the most commonly used disinfectant in water treatment, and its widespread use has effectively reduced the incidence of waterborne diseases such as typhoid, cholera, hepatitis and gastrointestinal illness (Morris and Levine, 1995). However, unintended disinfection by-products (DBPs) are formed during chlorination from the reaction between chlorine and natural organic matter in raw water (Uyak et al., 2008; WHO, 2004). DBPs are ubiquitous contaminants of concern in drinking water since human exposure has been associated with cancer and adverse reproductive outcomes (Hertzberg et al., 2007; Villanueva et al., 2012). Among these DBPs, trihalomethanes (THMs) and haloacetic acids (HAAs) are two major classes on a weight basis in chlorinated drinking water (Richardson, 2003). To protect human health, the stage II DBP rules in the United States set the maximum contamination levels (MCLs) for THMs at 80 μg/L and for HAA5 (the sum of monochloro-, dichloro-, trichloro-, monobromo-, and dibromoacetic acid) at 60 μg/L on a local running annual average basis (USEPA, 1998, 2006). They are also regulated in the drinking water standards of the World Health Organization (WHO) and Chinese national standards.

Besides THMs and HAAs, DBPs, including haloacetonitriles (HANs), chloral hydrate (CH), haloketones (HKs) and trichloronitromethane (TCNM) were also observed in chlorinated or chloraminated water (Nieuwenhuijsen et al., 2000; Wei et al., 2010). Nitrogen-containing DBPs (N-DBPs) such as HANs and TCNM have been shown to be more genotoxic and cytotoxic than THMs and HAAs (Plewa et al., 2008). Moreover, brominated DBPs are more toxic and carcinogenic than their chlorinated analogs (Plewa et al., 2008). The concentration of brominated DBPs can be higher in bromide-rich waters such as sources with seawater intrusion or other brackish waters. Ultimately,

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the formation of DBPs depends on the source water, the type of treatment and the type of disinfectant used. For example, waters with high contents of natural organic matter and pH tended to form more THMs during chlorination (Kitis et al., 2001). Hydrophobic organic matter generated more THMs than hydrophilic organic matter during chlorination (Lu et al., 2009). Waters after advanced treatment, such as ozonation and carbon adsorption, tended to form less THM and HAA (Korshin et al., 1997; Siddiqui et al., 1997). Free chlorine generated higher quantities of THM and HAA than preformed monochloramine did (Yang et al., 2007).

The Pearl River Delta is one of the most developed and densely populated areas in China. With the rapid development of industry and agriculture, raw water quality has been degraded due to increasing discharges of industrial and domestic wastewater. Advanced treatment processes such as ozonation, activated carbon adsorption and ultrafiltration have been applied in some water treatment plants in the delta but the occurrence of THMs, HAAs and other DBPs is of great concern in that area.

In this study, the occurrence of DBPs in drinking water from ten water treatment plants in three cities in the region (Guangzhou, Foshan, and Zhuhai) was investigated. Their speciation and seasonal variation were of special interest. Based on the occurrence of DBPs in the area, cancer risks from three exposure pathways to THMs (ingestion of drinking water, inhalation and dermal contact) were estimated.

2. Materials and methods

2.1. Sample collection

Guangzhou, the capital of Guangdong province, is the third largest city in China and the largest in southern China, with an area of about 20,000 km^2 and a population of 12.78 million (from the 2010 census). Located along the Pearl River about 120 km north–northwest of Hong Kong, Guangzhou is a key national transportation hub and trading port, and was identified as a Beta World City in the global city index in 2008. Foshan has an area of about 3840 km^2 and a population of 6.1 million. Zhuhai is a coastal city with an area of about 7653 km^2 and a population of 2.8 million. In this study, samples were collected from the distribution systems of 10 water treatment plants, six of which serve Guangzhou (GZ1 to GZ6), two Foshan (FS1 and FS2), and two Zhuhai (ZH1 and ZH2). The sampling locations are shown in Fig. S1, and the treatment scheme of each plant is described in Table S1 in the Supporting information. Samples were drawn at 3 or 4 sites served by each plant. The temperature, pH, residual chlorine and chloramine level of samples were listed in Table S2 in the Supporting information. Water samples were collected on July 7, July 23 and December 11 of 2011 and on January 13, 2012. A total of 155 samples were collected for this study. Because bromide and DOC concentrations were not analyzed in the four sampling campaigns, a fifth sampling campaign was made on November 15, 2012. The concentrations of bromide and DOC were analyzed and the result was also shown in Table S2.

The DBPs investigated were chloroform ($CHCl_3$), bromodichloromethane ($CHCl_2Br$), dibromochloromethane ($CHClBr_2$), bromoform ($CHBr_3$), monochloroacetic acid (MCAA), dichloroacetic acid (DCAA), trichloroacetic acid (TCAA), monobromoacetic acid (MBAA), dibromoacetic acid (DBAA), tribromoacetic acid (TBAA), bromochloroacetic acid (BCAA), bromodichloroacetic acid (BDCAA), and dibromochloroacetic acid (DBCAA). There were also four HANs – trichloroacetonitrile (TCAN), dichloroacetonitrile (DCAN), bromochloroacetonitril (BCAN) and dibromoacetonitrile (DBAN) – two haloketones (HKs) (1,1-dichloropropanon (1,1-DCP) and 1,1,1-trichloropropanone (1,1,1-TCP)), chloral hydrate (CH) and trichloronitromethane (TCNM). There were thus four THMs, nine HAAs, four HANs, two haloketones plus chloral hydrate and trichloronitromethane.

155 samples were collected in pre-cleaned 40 mL amber glass bottles with PTFE septa, sealed and stored at 4 °C before analysis. All of the glassware was washed with detergent and rinsed with tap water and then with ultrapure water before sampling. It was then dried at 150 °C for 2–3 h. Prior to shipment to the field, ammonium chloride was added to the amber glass bottles to quench any chlorine residuals in the sample. Tap water was allowed to flush for 5 min before sampling. The samples filled the bottles just to overflowing without flushing out the ammonium chloride. Four samples were collected from each sampling location, two for THM and volatile DBP analysis and another two for HAA analysis. pH and temperature were also recorded. Field blanks, which accompanied the samples to the sampling sites, were used to determine any background contamination.

2.2. Reagents

All of the DBP standards, including a mixed standard containing HANs, HKs and TCNM, a THM mixture standard, a mixed standard of nine HAAs, chloral hydrate, and internal and surrogate standards were obtained from Supelco (USA). Methyl–tert butyl ether was obtained from Sigma (USA).

2.3. Analytical methods

Analyses for THMs, HANs, TCNM, HKs and CH 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 silica capillary column (30 m × 0.25 mm I.D. with 0.25 μm film thickness, J&W Scientific). The GC temperature program consisted of an initial temperature of 35 °C for 6 min, ramping to 100 °C at 10 °C/min and holding for 5 min, ramping to 200 °C at 20 °C/min and holding for 2 min. Analyses of HAAs were based on USEPA Method 552.2. The GC temperature program consisted of an initial temperature of 35 °C for 10 min, ramping to 60 °C at 5 °C/min, ramping to 75 °C at 2 °C/min and holding for 2 min, ramping to 135 °C at 20 °C/min, ramping to 200 °C at 5 °C/min and holding for 5 min. The minimum reporting limit (MRL) for all compounds except the HAAs was 0.2 μg/L. The MRLs for the HAAs ranged from 0.4 to 2 μg/L for different species. The percentage recovery for the extraction procedures ranged from 94% to 109%.

2.4. Cancer risk analysis

Based on the measured THM levels, an exposure assessment was conducted to evaluate the potential THM uptake via oral ingestion, inhalation and dermal absorption. The source of exposure, exposure pathways, and the magnitude, duration, and frequency of exposure to contaminants for each receptor group were identified based on the lifestyle of the citizens in the area and the behavior and characteristics of the THMs in the tap water. Cancer slope factors were used to estimate any carcinogenic effects.

The cancer risk from ingestion was estimated as

$$\text{Cancer risk from THM ingestion} = CDI_{oral} \times PF_{oral} \quad (1)$$

where PF_{oral} is the potential factor or slope factor of a THM specie ($[mg/kg/day]^{-1}$) and CDI_{oral} is the chronic daily ingestion of that specie (mg/kg/day).

$$CDI_{Oral} = (CW \times IR \times EF \times ED)/(BW \times AT) \quad (2)$$

where CW represents the THM concentration in drinking water (mg/L); IR is the drinking water ingestion rate (L/day); EF is the exposure frequency (days/year); ED is the exposure duration, which was assumed to be 74 years for males and 78 years for females based on Chinese population data (National Bureau of Statistics of China, 2004); BW is body