Science of the Total Environment 517 (2015) 246–258

Contents lists available at ScienceDirect

Science of the Total Environment

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

Seasonal evaluation of the presence of 46 disinfection by-products throughout a drinking water treatment plant

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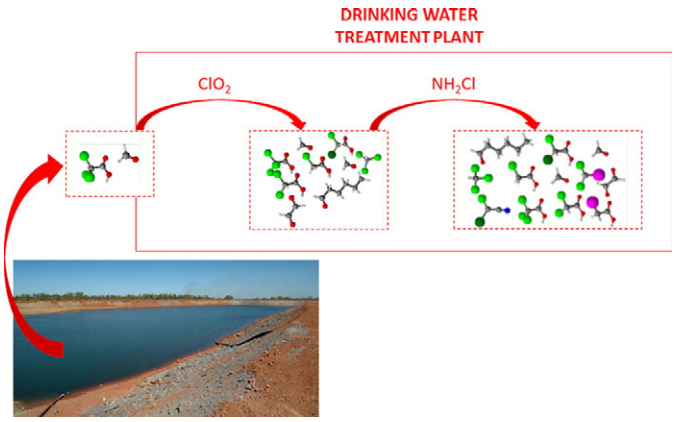
HIGHLIGHTS

- Occurrence of 46 regulated and non-regulated DBPs through a DWTP was investigated.
- A systematic study on both spatial and seasonal occurrence of the DBPs was performed.
- Pre-oxidation with ClO_2 and NH_2Cl caused the formation of up to 16 species.
- The formation of DBPs was higher in the warmer seasons.
- The concentration of the detected DBPs increased along the network.

GRAPHICAL ABSTRACT



ARTICLE INFO

Article history:
Received 2 December 2014
Received in revised form 19 February 2015
Accepted 19 February 2015
Available online 11 March 2015

Editor: D. Barcelo

Keywords:
Trihalomethanes
Halonitromethanes
Haloacetonitriles
Haloacetic acids
Aldehydes
Drinking water treatment plant
Chlorine dioxide/chloramination

ABSTRACT

In this work, we studied a total of 46 regulated and non-regulated disinfection by-products (DBPs) including 10 trihalomethanes (THMs), 13 haloacetic acids (HAAs), 6 halonitromethanes (HNMs), 6 haloacetonitriles (HANs) and 11 aldehydes at different points in a drinking water treatment plant (DWTP) and its distribution network. Determining an increased number of compounds and using accurate, sensitive analytical methodologies for new DBPs can be useful to overcome some challenges encountered in the comprehensive assessment of the quality and safety of drinking water. This paper provides a detailed picture of the spatial and seasonal variability of DBP concentrations from raw water to distribution network. Samples were collected on a monthly basis at seven different points in the four seasons of a year to acquire robust data for DBPs and supplementary quality-related water parameters. Only 5 aldehydes and 2 HAAs were found in raw water. Chlorine dioxide caused the formation of 3 new aldehydes (benzaldehyde included), 5 HAAs and chloroform. The concentrations of DBPs present in raw water were up to 6 times higher in the warmer seasons (spring and summer). The sedimentation process further increased their concentrations and caused the formation of three new ones. Sand filtration substantially removed aldehydes and HAAs (15–50%), but increased the levels of THMs, HNMs and HANs by up to 70%. Chloramination raised the levels of 8 aldehydes and 7 HAAs; also, it caused the formation of monoiodoacetic acid, dibromochloromethane, dichloroiodomethane and bromochloroacetonitrile. Therefore, this treatment increases the levels of existing DBPs and leads to the formation of new ones to a greater extent than does chlorine

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http://dx.doi.org/10.1016/j.scitotenv.2015.02.070

dioxide. Except for 5 aldehydes, the 23 DBPs encountered at the DWTP exit were found at increased concentrations in the warmer seasons (HAAs by about 50% and THMs by 350%).

1. Introduction

Water disinfection has been used to improve the hygienic quality of drinking water by removing waterborne bacterial pathogens since the early twentieth century (Krasner et al., 2006; Richardson et al., 2007). Chlorine is the most widely used disinfectant for this purpose by virtue of extremely high efficiency and relatively low cost. However, studies conducted in the 1970s revealed that chlorination generated potentially harmful disinfection by-products (DBPs) (Hrudey and Charrois, 2012). Since then, several hundred DBP species have been identified and new ones continued to emerge as more accurate and precise analytical methods with determination capabilities at the trace level have become available (Richardson, 2012). Drinking water frequently contains the following types of DBPs in addition to trihalomethanes (THMs) and haloacetic acids (HAAs): haloacetonitriles (HANs), haloketones (HKs), trichloronitromethane (chloropicrin, CP), trichloroacetaldehyde (chloral hydrate, CH) (Nikolaou et al., 2004; Golfinopoulos and Nikolaou, 2005a; Wei et al., 2010), *N*-nitrosamines (Jurado et al., 2012), aldehydes (Papageorgiou et al., 2014) and carboxylic acids (Jurado et al., 2014). The presence of nitrogenous disinfection by-products (N-DBPs) including nitrosamines, cyanogen halides, haloacetamides, halonitromethanes (HNMs) and HANs in drinking water is of concern due to their high genotoxicity and cytotoxicity compared with regulated DBPs (Bond et al., 2011). Moreover, to reduce regulated DBPs, chloramination has been proposed as alternative to chlorination but this disinfection process increases certain N-DBPs. The impact of the water treatment processes on N-DBP formation has been reviewed (Bond et al., 2011). Several studies have revealed potentially harmful effects on health in more than two hundred halogenated and non-halogenated DBPs (Moudgal et al., 2000; Woo et al., 2002; Richardson et al., 2007). This has led the United States Environmental Protection Agency to regulate acceptable levels for the most prevalent DBPs in chlorination process as the total concentration of four THMs and five HAAs to 80 μg/L and 60 μg/L, respectively (US EPA, 2003). Also, the European Union has regulated the total concentration of THMs to 100 μg/L after 2008 (Directive 98/83/EC, 1998), but has so far established no regulatory limit for HAAs or other DBPs. A review about the occurrence, genotoxicity and carcinogenicity of regulated and emerging DBPs in drinking water has been performed for 85 DBPs, 11 regulated and 74 non-regulated (Richardson et al., 2007). These 74 include HNMs, HANs, iodo-acids, halo-acids, iodotrihalomethanes, halomethanes, halofuranones, haloamides, aldehydes and nitrosamines. This study identified three categories of DBPs according to their toxicological characteristics of human carcinogens. In general, the brominated BDPs are both more genotoxic and carcinogenic than are chlorinated compounds, and iodinated DBPs were the most genotoxic of all but have not been tested for carcinogenicity (Richardson et al., 2007).

Some authors have suggested that the formation of DBPs should be prevented at any rate because once formed, they are difficult to remove by treatments commonly used in drinking water production (Kim et al., 2005). Rodriguez et al. (2007a) found a reduction in DBP potentials and degradation of HAAs at points with a high bioactivity such as the rapid sand filtration unit. Also, Chuang et al. (2011) conducted sand column laboratory studies to explore the association between HAA biodegradation and the chlorine concentration; and Tubić et al. (2010) used a pilot-scale system to assess the performance of ozone, H_2O_2/O_3 and GAC in an overall treatment to reduce DBP precursors such as natural organic matter. Some studies on DBP formation and evolution in water distribution systems have shown HAAs and THMs to differ in spatial behaviour (Rodriguez et al., 2007a; Chuang et al., 2011; Waseem and Mohsin, 2011). A survey of DBP occurrence in US was conducted at 12 drinking water treatment plants (DWTPs). In addition to regulated DBPs, more than 50 DBPs were studied to obtain occurrence information for new DBPs for prioritising future health effect studies (Krasner et al., 2006). This interesting study was carried out with different disinfectants (chlorine, ozone, chlorine dioxide and chloramines) but the sampling point was only taken in the plant effluent. Other studies have documented the formation of halogenated DBPs including THMs, HAAs, HKs, HANs, CP and CH in water treatment plants in various cities (Lebel et al., 1997; Cancho et al., 1999; Golfinopoulos and Nikolaou, 2005a, 2005b; Mercier-Shanks et al., 2013; Wei et al., 2013). The first studies about these halogenated DBPs that involved sampling raw water and distribution system were carried out in the 1990s and involved sampling raw water and the distribution systems of three DWTPs using different disinfectants over a period of one year (Lebel et al., 1997), in addition to a DWTP using chlorination and ozonation (Cancho et al., 1999). The results for the four DWTPs were similar. Thus, chlorination caused the formation of halogenated DBPs; THM levels varied all year long by effect of changes in water temperature and break-point conditions; HAAs formed and evolved differently from THMs; HANs were formed at all stages of the process and completely adsorbed in the GAC filters; HKs and CH were detected at concentrations below 1 μg/L and also adsorbed in the GAC filters; and no CP was formed during the process (Cancho et al., 1999). Golfinopoulos and Nikolaou (2005a, 2005b) conducted a more extensive study at four conventional DWTPs in Athens; although they detected no DBP in raw water, they encountered all DBP categories in all chlorinated samples within the DWTP and its distribution network in all sampling periods for 10 years.

A detailed picture of the spatial and temporal variability of non-regulated DBPs (4 HANs, CP and 2 HKs) in a drinking water distribution network was recently provided by Mercier-Shanks et al. (2013). In a recent survey, a total of 4 THMs and 9 HAAs including iodoform (IF) and iodoacetic acid (IAA) were detected in drinking waters from 13 DWTPs in Shangai (Wei et al., 2013). The survey, however, focused mainly on the influence of water characteristics (8 different parameters) and disinfection treatments in the presence of IF and IAA. Neale et al. (2012) used in vitro bioanalytical tools and quantified halogen-specific adsorbable organic halogens to examine the formation of DBPs in a DWTP. Papageorgiou et al. (2014) studied the presence and fate of carbonyl compounds as ozonation by-products at a DWTP for one year. They detected up to 14 DBPs at concentrations in the region of 70 μg/L after ozonation and found them to have been removed by about 75% in the treated water.

Some natural waters are cocktails of chemical and microbial contaminants that require appropriate processing to remove various kinds of potentially harmful substances including DBPs. Although several authors have investigated DBP occurrence in the recent years, very few studies have considered their formation from alternative disinfectants than chlorine. The objectives of this study included, namely: (i) the application of sensitive and reliable analytical methods based on the principles of the Green Chemistry for measuring a large number of regulated and non-regulated DBPs including 10 THMs, 13 HAAs, 6 HNMs, 6 HANs and 11 aldehydes in a DWTP treated sequentially with chlorine dioxide and chloramines; (ii) the effect of source water and treatment conditions on their formation (7 sampling points); (iii) the influence of the combination of chlorine dioxide and chloramination as an atypical disinfection method on DBP occurrence; (iv) and the effect of seasonal changes on DBP concentrations. The study involved sampling water at the DWTP on a monthly basis for each season. The selection of the 46 DBPs was based on their toxicological relevance and frequency in treated water.