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Occurrence and variability of iodinated trihalomethanes concentrations within two drinking-water distribution networks☆,☆☆

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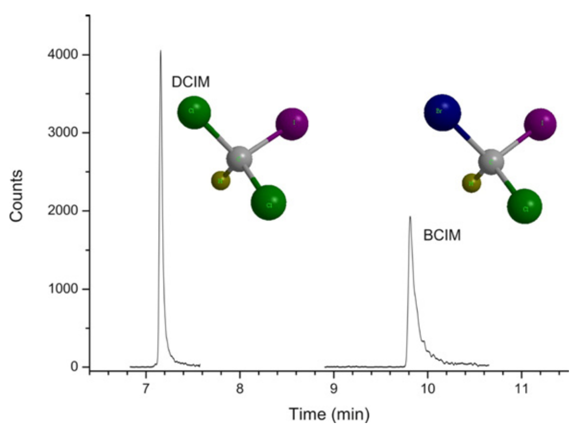
HIGHLIGHTS

- Iodinated trihalomethanes were studied in two water distribution systems.
- Low levels of iodinated trihalomethanes in tap water
- Large variability of iodinated trihalomethanes within the water distribution system

GRAPHICAL ABSTRACT



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ABSTRACT

Non-iodo-containing trihalomethanes (TTHM) are frequently detected in chlorinated tap water and currently regulated against their carcinogenic potential. Iodinated THM (ITHM) may also form in disinfected with chlorine waters that are high in iodine content, but little is known about their magnitude and variability within the drinking-water pipe distribution network of urban areas. The main objective of this study was to determine the magnitude and variability of ITHM and TTHM levels and their corresponding daily intake estimates within the drinking water distribution systems of Limassol and Nicosia cities of Cyprus, using tap samples collected from individual households ($n = 37$). In Limassol, mean household tap water ITHM and TTHM levels was 0.58 and 38 μg L^{-1}, respectively. Dichloroiodomethane (DCIM) was the dominant species of the two measured ITHM compounds accounting for 77% of total ITHM and in the range of 0.032 and 1.65 μg L^{-1}. The range of DCIM concentrations in Nicosia tap water samples was narrower (0.032 – 0.848 μg L^{-1}). Mean total iodine concentration in tap water samples from the seaside city of Limassol was 15 μg L^{-1} and approximately twice to those observed in samples from the mainland Nicosia city. However, iodine concentrations did not correlate with the

Abbreviations: DBP, Disinfection by-product; THM, Trihalomethanes; HAA, Haloacetic acid; NOM, Natural organic matter; TCM, Trichloromethane (chloroform); BDCM, Bromodichloromethane; DBCM, Dibromochloromethane; TBM, Tribromomethane (bromoform); DCIM, Dichloroiodomethane; BCIM, Bromochloroiodomethane; TTHM, Total Trihalomethanes; ITHM, Iodinated Trihalomethanes; CHO, Chinese Hamster Ovaries (ToxTest); CDI, Chronic Daily Intake; U.S. EPA, United States Environmental Protection Agency.

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ITHM levels. The calculated chronic daily intake rates of ITHM were low when compared with those of TTHM, but because of their widespread occurrence in tap water and their enhanced mammalian cell toxicity, additional research is warranted to assess the magnitude and variability of human ITHM exposures.

1. Introduction

Trihalomethanes (THM) is a frequently-occurring class of disinfection by-products (DBP), and it has been historically regulated in disinfected (chlorinated) tap water (Nieuwenhuijsen et al., 2000). Halogenated THM typically form upon water disinfection comprising of chlorinated-(chloroform), or mixtures of chloro/bromo-, or iodinated-THM compounds (Richardson et al., 2007). Upon oxidation of dissolved iodide during water treatment, hypoiodous acid (HOI) may form, which may react with natural organic matter (NOM) producing iodinated trihalomethanes (ITHM) (Bichsel and Von Gunten, 2000; Richardson et al., 2007). The first report on the occurrence of ITHM in drinking-water was published in the 1970s (Brass et al., 1977). Hydrophobic and high-molecular mass NOM, with high aromatic carbon content was found to readily react with chlorine towards the formation of non-iodine THM, while iodine and bromine have been observed to be more reactive with hydrophilic and low-molecular mass NOM, forming brominated and iodinated DBPs (Hua and Reckhow, 2007a, 2007b). Based on their carcinogenic potency, the four non-iodo THM are currently regulated in the EU, i.e., chloroform, bromodichrolomethane, dibromochloromethane and bromoform, and their sum is known as total trihalomethanes (TTHM) (European Council Directive 98/83/EC, 1998). When TTHM were assessed for cytotoxicity in chronic Chinese hamster ovaries (CHO) assays, toxicity speciation showed bromoform > dibromochloromethane > bromodichloromethane > chloroform, suggesting the influence of bromine atoms in enhancing the overall cytotoxicity of THMs (Plewa et al., 2008). Compared to chloro- and bromo-THMs, ITHM were found to be even more cytotoxic, but not genotoxic, with the exception of chlorodiiodomethane (Richardson et al., 2008). This order of toxicity correlated well with the leaving tendency of the halogens in S_N2 reactions with iodo-groups being much better substitution groups than bromo- and chloro-groups (Richardson et al., 2008).

The water levels of dissolved bromide and iodide may also affect both the concentration and speciation of formed THM (Villanueva et al., 2012; Richardson et al., 2008). For example, it was shown that the formation of total organic iodine (TOI) from chloramination of the hydrophobic acid fraction of river water samples, increased in a linear fashion with increasing iodide concentration, while holding the bromide levels constant (Kristiana et al., 2009). Other factors that may also influence the magnitude of formation of ITHM are: i) pH (increase in pH from 6 to 8 favored the formation of THM and vice versa) (Liang and Singer, 2003, Hansen et al., 2012), ii) water temperature; higher temperatures favored the formation of THM (Richardson, 2003, Zhang et al., 2013), iii) the disinfection practice; chloramination favored the formation of ITHM (Krasner et al., 2006, Richardson et al., 2008), iv) the residence time of drinking water in the distribution system and v) the characteristics of the water distribution system such as its age, pipe material type and the presence of re-chlorination reservoir stations (Legay et al., 2010). Kinetic studies observed that the formation of ITHM was highly dependent upon the disinfection method used. Chlorination was found to favor the formation of chlorinated and brominated THM rather than ITHM due to the oxidation of hypoiodous acid to iodate, occurring at a fast rate when chlorine was used for disinfection (Jones et al., 2011). When chloramination was used as the main disinfection process, the oxidation of hypoiodous acid to iodate was much slower (Jones et al., 2011) and because monochloramine hardly oxidizes bromide (Criquet et al., 2012) the formation of ITHM was enhanced. Apart from the disinfection method, the presence of iodide and the pH may also influence the formation and speciation of ITHM (Jones et al., 2012a, 2012b, Cancho et al., 2000).

Occurrence of ITHM in various water resource matrices was reported, for example, in wastewater effluents (Gong and Zhang, 2015), water treatment plants (Cancho et al., 2000; Serrano et al., 2015), desalination units (Le Roux et al., 2015), drinking water treatment plants (Plewa et al., 2004; Krasner et al., 2006; Richardson et al., 2008; Jeong et al., 2012; Ding et al., 2013a, 2013b; Wei et al., 2013a, 2013b). Brief information on literature reporting ITHMs in various water resources is presented in Table 1. However, to our best knowledge, no study is available on monitoring ITHMs spatially along drinking water distribution systems and in kitchen tap water at household level. Drinking-water supply in Cyprus originates from surface water behind dams and it is supplemented with post-chlorinated reverse osmosis treated seawater in periods of high water demand (spring, summer). Cyprus, is characterized by elevated average TTHM levels in its tap water (range: 3–130 μg L^{-1}, Mean (SD): 65 (24) μg L^{-1}) (Charisiadis et al., 2015). Being a Mediterranean island, Cyprus' seaside urban areas may be subject to high dissolved iodide levels in source water acting as precursors for ITHM formation. The seaside city of Limassol was chosen along with the mainland city of Nicosia, which is one hour away from the coast. No data is currently available on the magnitude and variability of ITHM in the region of the Eastern Mediterranean and particularly for the magnitude and variability of water ITHM levels within the distribution network of a city. This study also systematically collected all studies of quantitative ITHM analyses in tap water around the globe through a systematic literature search. The main objective of this study was to determine the magnitude and variability of ITHM and TTHM levels within the drinking water distribution systems of Limassol and Nicosia cities and their corresponding daily intake estimates, using drinking-water samples collected from individual households, after obtaining residents' written informed consent. The relative contribution of each of the three routes (ingestion, dermal absorption and inhalation) of exposure to the daily intake estimates for ITHM and TTHM was also assessed, based on their water concentrations found in water, and the corresponding frequency of water use activities, such as, drinking tap water, bathing and showering as recorded with questionnaire data.

Gas chromatography (GC) has been the choice of instrumentation for analysis of volatile and semi-volatile ITHMs in various water matrices. For example, ITHMs were detected and quantified using GC coupled with electron capture detection (Bichsel and Von Gunten, 2000; Krasner et al., 2006; Hua and Reckhow, 2007a, 2007b; Jones et al., 2012a, 2012b) and GC coupled with mass spectrometry detection (Plewa et al., 2004; Richardson et al., 2008; Duirk et al., 2011). Polar and semi-polar ITHMs in water matrices were analyzed with liquid chromatography coupled with mass spectrometry detection (Ding and Zhang, 2009; Ding et al., 2013a, 2013b; Gong and Zhang, 2015). Analytical method parameters and instrumentation used in representative studies are presented in Table 1. We applied GC coupled to a tandem mass spectrometer (MS/MS) for the analysis of TTHMs and ITHMs in drinking water samples collected at household level along two different drinking water distribution systems in two major cities of Cyprus. Out of the six ITHM (iodoform-IF, dichloroiodomethane-DCIM, bromochloroiodomethane-BCIM, chlorodiiodomethane-CDIM, dibromoiodomethane-DBIM, bromodiiodomethane-BDIM), we quantified two viz., dichloroiodomethane (DCIM) and bromochloroiodomethane (BCIM) because (i) these are the most frequently occurring