



# Identifying unknown by-products in drinking water using comprehensive two-dimensional gas chromatography–quadrupole mass spectrometry and *in silico* toxicity assessment



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## HIGHLIGHTS

- A method of GC×GC-qMS along with QSAR Toolbox was developed for analysis of DBPs.
- More than 500 compounds were tentatively identified in each water sample.
- A total of 170 DBPs in different disinfected water samples were identified.
- 58 DBPs were found to be actually or potentially genotoxic.

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## ABSTRACT

Improvements in extraction and detection technologies have increased our abilities to identify new disinfection by-products (DBPs) over the last 40 years. However, most previous studies combined DBP identification and measurement efforts with toxicology to address concerns on a few expected DBPs, making it difficult to better define the health risk from the individual DBPs. In this study, a nontargeted screening method involving comprehensive two-dimensional gas chromatography–quadrupole mass spectrometry (GC × GC-qMS) combined with OECD QSAR Toolbox Ver. 3.2 was developed for identifying and prioritizing of volatile and semi-volatile DBPs in drinking water. The method was successfully applied to analyze DBPs formed during chlorination, chloramination or ozonation of the raw water. Over 500 compounds were tentatively identified in each sample, showing the superior performance of this analytical technique. A total of 170 volatile and semi-volatile DBPs representing fourteen chemical classes were then identified, according to the criteria that the DBP was presented in the duplicate treated samples. The genotoxicity and carcinogenicity of the DBPs were evaluated using Toolbox, and 58 DBPs were found to be actual or potential genotoxicants. The accuracy of the compound identification was determined by comparing 47 identified compounds with commercially available standards. About 90% (41 of the 47) of the compounds that were automatically identified using the library were correct. The results show that GC×GC-qMS coupled with a quantitative structure–activity relationship model is a powerful and fast nontargeted screening technique for compounds. The method and results provide us a new idea for identification and prioritization of DBPs.

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## 1. Introduction

Drinking water disinfection processes have been used since the end of the 19th century to reduce the incidence of water-borne diseases and have been one of the greatest advances in public health protection. However, chlorine, chloramines and ozone, which are widely used as chemical disinfectants in drinking water treatment, can react with natural organic matter (NOM), inorganic

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materials and anthropogenic contaminants in water to form disinfection by-products (DBPs). Because DBPs vary in molecular weight, volatility and polarity, no one single analytical method exists for extracting and identifying them all. Various analytical methods were thus developed for identifying specific groups of DBPs. Early on, gas chromatography–mass spectrometry (GC–MS) was successfully used to identify a number of previously unidentified DBPs (Cavanagh et al., 1992; Collette et al., 1994; Richardson et al., 2000b; Taguchi, 2001; Zou et al., 2002). Liquid chromatography (LC)–MS was later used to try to uncover highly polar carbonyl DBPs that may have been missed by earlier GC–MS studies (Kempter and Karst, 2000; Kempter et al., 2000; Richardson et al., 2000a; Zwiener et al., 2002). LC–MS/MS and ultraperformance LC (UPLC)–MS/MS have recently been increasingly used to identify highly polar DBPs (Kadmi et al., 2014; Pan and Zhang, 2013; Pan et al., 2016; Qin et al., 2010; Ripollés et al., 2011; Wu et al., 2014; Zhao et al., 2006, 2010). Because DBPs are typically present at low levels, samples are usually extracted and concentrated into an organic solvent prior to measurement by analytical techniques. Concentration methods that are commonly used include solid phase extraction, solid phase microextraction, liquid–liquid extraction, and XAD resin extraction (Richardson, 2011). Improvements in the areas of extraction, separation, and detection technologies as well as instrumentation are enhancing our ability to identify new DBPs in drinking water. It is therefore certain that more DBPs that may affect human health will continue to be detected in drinking water.

Nontargeted analytical techniques are unconstrained by preconceived notions of chemicals of concern and are becoming increasingly important in the analysis of complex mixtures (Myers et al., 2014). Recently, nontargeted techniques, such as comprehensive two-dimensional gas chromatography (GC × GC), have been successfully applied to characterize organic compounds in various complex samples (da Cunha et al., 2013; Dugo et al., 2014; Hoh et al., 2012; Myers et al., 2014; Santos et al., 2014; Ubukata et al., 2015). It has also been shown in a number of reviews that better separation efficiencies, more reliable qualitative and quantitative analyses, and more information on the whole sample and its components can be achieved using GC × GC than by using one-dimensional GC (Adahchour et al., 2008; Murray, 2012). However, GC × GC has only been used to analyze a limited number of target chemicals, such as estrogens, volatile organic compounds, certain emerging contaminants, drug residues and pesticides, in aqueous matrices (Gomes et al., 2013; Gunatilake et al., 2014; López et al., 2013; Lacina et al., 2013; Purcaro et al., 2011). It is thus expected that analyzing drinking water samples by nontargeted GC × GC will allow volatile and semi-volatile DBPs that were previously unresolved using traditional one-dimensional GC to be identified.

As increasing numbers of DBPs have been identified by the developed analytical methods, more and more studies have combined DBP identification and measurement efforts with toxicology to address concerns related to the potential health effects of DBP exposure (Lyon et al., 2014; Plewa et al., 2008; Pressman et al., 2010; Richardson et al., 2008; Simmons et al., 2008; Wei et al., 2013; Yang et al., 2014). However, it should be noted that these studies were just focused on the environmentally realistic complex mixtures of DBPs or a few expected or representative DBPs, making it difficult to better define the public health risk from the individual DBPs identified in drinking water. It would be therefore beneficial to find effective ways of prioritizing future DBP research before expensive toxicological tests and occurrence monitoring studies are initiated. The quantitative structure–activity relationship (QSAR) method, in which a computer-based technique is used to predict the toxicity of a chemical solely from its molecular attributes, is such a method. A small number of QSAR–DBPs studies have been

published about the toxicities of the hundreds of DBPs actually found in drinking water (Liu and Zhang, 2014; Moudgal et al., 2000; Woo et al., 2002; Yang and Zhang, 2013). The “OECD QSAR Toolbox” application (<http://www.qsartoolbox.org/>) is an open-source application, which is intended to be used by the governments, chemical industry and toxicologists to fill gaps in toxicity data needed for assessing the hazards posed by chemicals (Benigni et al., 2013; Fuat-Gatnik and Worth, 2010; Low et al., 2013). The Toolbox contains databases with results from experimental studies, a library of QSAR models, which is able to quickly estimate missing experimental values by read-across (i.e. extrapolating data for untested chemicals from the available toxicity data for structurally similar chemicals) (Benigni et al., 2013).

Therefore, attempts were made in the study presented here to combine DBP identification and toxicology to comprehensively characterize DBPs in drinking water and provide the potential for further investigating the DBPs in the future. A quick nontargeted screening method involving GC × GC–quadrupole MS (qMS) combined with OECD QSAR Toolbox Ver. 3.2 was developed to allow unknown volatile and semi-volatile DBPs produced during different raw-water disinfection processes to be identified and prioritized.

## 2. Materials and methods

### 2.1. Materials

The analytical standards listed in Supporting Information (SI) Table S1 were purchased from AccuStandard (New Haven, USA), Alfa Aesar (Ward Hill, USA), TCI (Tokyo, Japan), J&K Scientific (Beijing, China) and Acros (Belgium). High-performance LC-grade methyl *tert*-butyl ether was purchased from Thermo Fisher Scientific (Waltham, USA). Ultrapure water (18.2 MΩ cm) was prepared by a Milli-Q purification system (Millipore, USA). Analytical grade sodium hypochlorite (NaClO) and ammonium chloride (NH<sub>4</sub>Cl) were purchased from Sinopharm Chemical Reagent Co. (Beijing, China). Monochloramine stock solutions were prepared daily by slowly adding NaClO to a rapidly stirred NH<sub>4</sub>Cl solution that had been adjusted to pH 8 with sodium hydroxide. A Cl:N molar ration of 1:1.2 was used to avoid dichloramine formation resulting from local excess of hypochlorite (Mitch and Sedlak, 2002). Anhydrous sodium sulfate (99.5%, guaranteed reagent, Sinopharm Chemical Reagent, Beijing) was heated at 450 °C for at least 4 h, allowed to cool naturally, and then stored in desiccators.

### 2.2. Chlorination, chloramination, and ozonation experiments

The raw water that was used in the disinfection experiments was collected from the inlet of a drinking water treatment plant in Beijing City. The water samples were filtered through a 0.45-μm glass fiber filter (Millipore, USA), and then stored at 4 °C until use (within 2 days). The water quality data were: dissolved organic carbon (DOC) = 6.3 mg/L, NO<sub>3</sub>-N = 6.3 mg/L, NO<sub>2</sub>-N = 0.4 mg/L, bromide = 394 μg/L, pH = 8.2.

Chlorination and chloramination experiments were conducted at room temperature (~21 °C) under headspace-free conditions in 4 L amber glass bottles shielded from light for 48 h. A relatively high free chlorine or pre-formed monochloramine was dosed with a Cl<sub>2</sub>/DOC ratio of 5 mg/mg on the basis of previous study (Tian et al., 2013), with minor modifications to ensure that the chlorine or chloramine reacted thoroughly with the NOM and other constituents of the water. For the ozonation experiment, water sample was treated with ozone at a dose of 1 mg O<sub>3</sub>/mg C as the previous studies (Chuang et al., 2013; Hua and Reckhow, 2013; Yang et al., 2012). Ozonation was conducted by bubbling an ozone and

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