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Simultaneous assessments of occurrence, ecological, human health, and organoleptic hazards for 77 VOCs in typical drinking water sources from 5 major river basins, China

Xichao Chen [a, d], Qian Luo [a, b, *], Donghong Wang [d], Jijun Gao [c], Zi Wei [a], Zijian Wang [a, **], Huaidong Zhou [c], Asit Mazumder [b]

[a] State Key Laboratory of Environmental Aquatic Chemistry, Research Center for Eco-Environmental Sciences, Chinese Academy of Sciences, Beijing 100085, China
[b] Shenzhen Institutes of Advanced Technology, Chinese Academy of Sciences, Shenzhen 518055, China
[c] State Key Laboratory of Simulation and Regulation of Water Cycle in River Basin, China Institute of Water Resources and Hydropower Research, Beijing 100038, China
[d] Key Laboratory of Drinking Water Science and Technology, Research Center for Eco-Environmental Sciences, Chinese Academy of Sciences, Beijing 100085, China

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ABSTRACT

Owing to the growing public awareness on the safety and aesthetics in water sources, more attention has been given to the adverse effects of volatile organic compounds (VOCs) on aquatic organisms and human beings. In this study, 77 target VOCs (including 54 common VOCs, 13 carbonyl compounds, and 10 taste and odor compounds) were detected in typical drinking water sources from 5 major river basins (the Yangtze, the Huaihe, the Yellow, the Haihe and the Liaohe River basins) and their occurrences were characterized. The ecological, human health, and olfactory assessments were performed to assess the major hazards in source water. The investigation showed that there existed potential ecological risks ($1.30 \times 10 \leq RQ_{total}s \leq 8.99 \times 10$) but little human health risks ($6.84 \times 10^{-7} \leq RQ_{total}s \leq 4.24 \times 10^{-4}$) by VOCs, while that odor problems occurred extensively. The priority contaminants in drinking water sources of China were also listed based on the present assessment criteria.

1. Introduction

As the population and demand for safe drinking water increase, it is important to examine water quality and identify contaminants that occur in source water (Rowe et al., 2007), which are thought to be frequently exposed to large amounts of micropollutants originating from the discharge of anthropogenic activities and natural process (Cho et al., 2014). Volatile organic compounds (VOCs), one contaminant group of concern, could be originated from photochemical and microbial activities (Fink, 2007; Watson, 2004) and introduced to the aquatic environment by emission and combustion (Liu and Zhou, 2011). Halogenated hydrocarbons used to be thought as the most frequently detected VOCs, followed by benzene, toluene, ethylbenzene and xylene (Chary and Fernandez-Alba, 2012; Ma et al., 2014), thus they were known as common VOCs (Niri et al., 2008). The carbonyl compounds are also widely present in the aqueous environment, even more widely than common VOCs, which concentrations in river waters ranged from 0.04 to 513 μg/L (Chen et al., 2013; Dąbrowska and Nawrocki, 2013; Takeda et al., 2006). The presence of aldehydes in raw and finished water intended to be used for potable purposes is undesirable since they may cause taste and odor problems (Bao et al., 1997; Dąbrowska and Nawrocki, 2013). Especially, formation of aldehydes during pre-ozonation process and removal of this class by using coagulation/flocculation and filtration processes in drinking water treatment plants has been also reported (Papageorgiou et al., 2014). Most of selected VOCs can pose significant risk to biological systems and human health with their toxic, carcinogenic, and/or mutagenic properties at very low concentrations (Liu and Zhou, 2011; Ma et al., 2014). Other compounds, such as carbonyl compounds blamed for odor problems (Dąbrowska and Nawrocki,

* Corresponding author. Shenzhen Institutes of Advanced Technology, Chinese Academy of Sciences, Shenzhen 518055, China.
** Corresponding author.
E-mail addresses: qian.luo@siat.ac.cn (Q. Luo), wangzj@rcees.ac.cn (Z. Wang).

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2013), some biogenic VOCs 2-methylisoborneol (MIB) and goesmin have not been associated with immediate health effects yet they can have a profound effect on consumer acceptance due to their extremely low odor threshold concentrations (OTCs) (Burgos et al., 2014; Robertson et al., 2006).

Accordingly, it is essential to environmental managers to understand hazards of VOCs in source water, besides the current pollution level. Previous study for evaluating contaminants is to directly compare the measured concentrations with regulated values by China, guidelines by the World Health Organization (WHO) or maximum contamination levels (MCLs) by the US Environmental Protection Agency (USEPA) for about 20 VOCs. There are uncertainties about the safety of current regulated VOCs, and the potential health impacts of unregulated chemical contaminants are largely unknown. This is not sufficient to identify the most concerned criteria and provide complete hazard information (Liu and Zhou, 2011). To gain a more comprehensive understanding of specific hazards of individual VOC, Rowe et al. (2007) have selected candidate VOCs involving multiple criteria, including potential human cancer risks and non-cancer hazards, toxicity to and bioconcentration in aquatic organisms, physical properties and occurrence statistics, use or potential use, and so on. After that, related studies are focusing on ecological and human health risk assessments to evaluate the likelihood of adverse effects as a result of exposure to environmental contaminants (Du et al., 2013; Gao et al., 2012; Yang et al., 2014), especially the risks of natural water (Nganje et al., 2015; Zhu et al., 2015). What's more, concerns on taste and odor problems have been dramatically increased (Chen et al., 2013a,b; Sun et al., 2012, 2014; Yu et al., 2009) since the water crisis in Wuxi, China in 2007 (Guo, 2007; Yang et al., 2008). These hazardous VOCs in water sources may not only affect the aquatic ecosystem, but also cause human health risks or taste and odor problems when they provide raw water for drinking water.

The determination of candidate VOCs in water is supposed to be very limited due to the high polarity, chemical instability and volatility of these compounds (Serrano et al., 2013; Weinberg, 2009). Thus, a total of 77 target VOCs (including common VOCs, carbonyl compounds, and taste and odor compounds) in typical drinking water sources from 5 major river basins (the Yangtze River basin, the Huaihe River basin, the Yellow River basin, the Haihe River basin and the Liaohe River basin), China were investigated in the present work. Here we present simultaneous assessments of four criteria: (1) occurrence assessment, (2) ecological assessment, (3) human health risk assessment, and (4) olfactory assessment for five important source water ecosystems in China. The results will be contributed to the knowledge on potential hazards from various VOCs in major water sources in China and that these results will lead to desperately needed management of contaminant loading and corresponding policy development.

2. Materials and methods

2.1. Chemicals and reagents

A total of 77 compounds (listed in Table S1) were monitored, including 54 common VOCs, 13 carbonyl compounds and 10 taste and odor compounds. Stock standard solutions for each class of compounds were prepared in methanol and stored at 4 °C. Fresh working solutions were used as spiking solutions for preparation of the aqueous calibration standards.

2.2. Sampling

Two sampling campaigns were carried out in 5 major river basins in China, including the Yangtze River basin, the Huaihe River basin, the Yellow River basin, the Haihe River basin and the Liaohe River basin, one from July to November in 2012 and the other from July to October in 2013. Five drinking water sources (near intakes) were selected in every basin each campaign, except four in Haihe River basin. Geographical coordinates were taken at each sampling site with a handheld global positioning system (GPS) and then plotted in a map (Fig. 1). Information on the sampling sites was summarized in Table S2.

A total of 48 source water samples (24 samples during each sampling campaign) were taken to screen for 77 priority VOCs. River or reservoir samples were manually collected from water bodies at least 30 cm beneath the surface to avoid underestimation of VOCs due to the possible loss of the target analytes caused by air stripping or volatilization. Groundwater samples were taken with a pump after 2 min of pumping. Three samples in every site were filled completely without headspace in 40 mL amber vials with poly-tetra-fluoroethylene-lined caps to prevent effusion and photolysis of the analytes. We added HCl solution (1/1, *v*/*v*) to lower the pH $\leq$ 2 at the time of collection to avoid biodegradation for 54 common VOCs. Pre-addition of 50 mg $CuSO_4 \cdot 5H_2O$ as a biocide was important to inhibit bacteriological decay for 13 carbonyl compounds; and the left ones prepared for 10 taste and odor compounds. Duplicates of every sample were used for backup purposes (in case of breakage of the primary sample) and for laboratory replicates. Samples were stored at 4 °C until prepared for analyses no more than 14 days.

2.3. Analysis and quality control

The analysis of the 77 selected target analytes was performed using 3 different procedures. 54 common VOCs were analyzed using an Agilent 6890/5975N Gas Chromatograph/Mass Spectrometer (GC/MS) (Agilent Technologies Inc., Santa Clara, CA, USA) equipped with a Tekmar-3100 purge and trap (P&T) concentrator (Tekmar-Dohrmann, Mason, OH) referring to EPA Method 524.2. 13 carbonyl compounds were derivatized with PFBHA, and the oxime products were extracted by solid-phase microextraction (SPME) (Supelco, Bellefonte, PA, USA) and analyzed by GC/MS. Carbonyl compounds derivatization is modified according to the derivatization procedure described in EPA Method 556. The method for determination of 10 taste and odor compounds was developed in our previous work (Chen et al., 2013). The details of the analysis methods can be found in the Supporting information.

Solvent blanks and procedural blanks showed no detectable amounts of target compounds. The accuracies of the methods were evaluated by measuring the recoveries in matrix spikes (*R*%). *R*% was calculated as:

$$R\% = \frac{C_{\text{spiked sample}} - C_{\text{sample}}}{C_{\text{spiking standard}}} \times 100$$

The limit of detection (LOD) was estimated at a signal-to-noise ratio of 3 (S/N > 3). A summary of the main experimental conditions of methods employed in this study is shown in Table 1.

2.4. Hazards identification

In order to identify the specific hazards of the target micropollutants in source water, ecological, human health, and olfactory risk assessments were carried out for those with toxicological data or OTCs available. The models of ecological, human health, and olfactory assessments are described in the Supporting information. The related toxicological data or OTCs necessary are shown in Table S4.