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

* 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

ARTICLE INFO

Article history:
Received 9 April 2015
Received in revised form 18 June 2015
Accepted 21 June 2015
Available online 3 July 2015

Keywords:
VOCs
Drinking water sources
Ecological risk assessment
Human health risk assessment
Taste and odor

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 × 10^8/C20^RQtotals/C20^8.99/C20^4.24) but little human health risks (6.84 × 10^7/C20^RQtotals/C20^4.24) 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.

© 2015 Elsevier Ltd. All rights reserved.

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 photo-chemical 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., 2015). 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, 2013).
some biogenic VOCs 2-methylisoborneole (MIB) and goeosmin 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 bio-concentration 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 ≤ 2 at the time of collection to avoid biodegradation for 54 common VOCs. Pre-addition of 50 mg CuSO4·5H2O 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.
3. Results and discussion

3.1. Occurrence assessment

The concentrations of detected target compounds in typical drinking water sources from 5 major river basins in China are shown in Fig. 2. The box plot depicts compounds of numerical data through their six-number summaries (the minimum observation, lower quartile, medium, mean, upper quartile, and maximum observation). The six parameters were given only when they were higher than their LODs.

The concentrations of the 50 detected common VOCs above LODs varied from 0.10 to 9.18 µg L\textsuperscript{−1}, most of which were much lower than the regulated values set by China (GB5749-2006 or GB3838-2002). However, the concentrations of naphthalene ranged from 0.18 to 3.37 µg L\textsuperscript{−1}, with a median of 0.63 µg L\textsuperscript{−1} and a mean of 0.98 µg L\textsuperscript{−1}. Samples of naphthalene exceeded the regulated value of 2 µg L\textsuperscript{−1} at site 14 in 2013 (3.37 µg L\textsuperscript{−1}), at site 22 in 2013 (3.11 µg L\textsuperscript{−1}) and at site 23 in 2013 (2.90 µg L\textsuperscript{−1}).

The concentrations of hexachlorobutadiene ranged from 0.10 to 1.23 µg L\textsuperscript{−1}, with a median of 0.50 µg L\textsuperscript{−1} and a mean of 0.61 µg L\textsuperscript{−1}. Samples of hexachlorobutadiene exceeded the regulated value of 0.6 µg L\textsuperscript{−1} at site 8 in 2012 (0.93 µg L\textsuperscript{−1}), site 14 in 2013 (1.23 µg L\textsuperscript{−1}) and site 21 in 2013 (0.76 µg L\textsuperscript{−1}). Naphthalene is one of polycyclic aromatic hydrocarbons (PAHs), which was commonly detected in China (Guo et al., 2012; Liu and Zhou, 2011; Ma et al., 2014), while seldom detected in the USA (Carter et al., 2008; Moran et al., 2004; Rowe et al., 2007). For many years, naphthalene had been considered as a non-carcinogenic PAH, but in 2000, the US National Toxicology Program revealed clear evidence of the carcinogenic activity of naphthalene in rats (Preuss et al., 2003). Hexachlorobutadiene is used as solvent, heat transfer liquid, as well as hydraulic liquid. This chemical has been reported to cause kidney damage in rats and humans (Green et al., 2003). The concentrations of the compound were comparable to those measured in Greece (Nikolaou et al., 2002), but higher than those in Korea (Cho et al., 2014). The comparison to data investigated by Liu and Zhou (2011) indicated that this contaminant had been increasing in water sources in China since 2006. The frequencies of detection (FODs) (Table S4) of these contaminants ranged from 2% (bromobenzene) to 40% (1,2,4-trichlorobenzene). The top 10 most frequently detected common VOCs were 1,2,4-trichlorobenzene, toluene, m-xylene, p-xylene, o-xylene, naphthalene, 1,2-dichloropropane, bromochloromethane, ethylbenzene, and 1,2,3-trichlorobenzene, and for these compounds the FODs were above 27%. Compared to the literature (Liu and Zhou, 2011; Ma et al., 2014), toluene might be the most ubiquitous common VOC in waters of China. 1,3-Dichloropropane, 1,1,2,2-tetrachloroethane, 1,2,3-trichloropropene, and 1,2-dibromo-3-chloropropene were not found during the two campaigns.

The concentrations of the 13 detected carbonyl compounds...
Fig. 2. Box plot for the concentrations of detected VOCs in typical drinking water sources from 5 major river basins, China. 50 common VOCs (A), 13 carbonyl compounds (B), and 10 taste and odor compounds (C) were detected at least once. Among common VOCs, 1,3-dichloropropene includes cis-1,3-dichloropropene and trans-1,3-dichloropropene two isomers, and xylenes include m-xylene, p-xylene, and o-xylene three isomers.
above LODs varied from 0.01 to 34.31 µg L⁻¹. The levels of such compounds in natural water of China were higher than those (nd—1.16 µg L⁻¹) in Arno River of Italy (Bao et al., 1997) and those (nd—5.25 µg L⁻¹) in Ohta River of Japan (Takeda et al., 2006), but lower than those (0.65—133.86 µg L⁻¹) in Warta River and Bodanka River of Poland (Dąbrowska and Nawrocki, 2013). Not much has been done so far as it concerns the presence of carbonyl compounds in natural water (Dąbrowska and Nawrocki, 2013). Formaldehyde is the most studied along with acetaldehyde due to their mutagenic character and chromosomal aberrations (Serrano et al., 2013). Therefore, only formaldehyde and acetaldehyde were regulated by China. The concentrations of formaldehyde ranged from 0.30 to 34.31 µg L⁻¹, with a median of 2.09 µg L⁻¹ and a mean of 4.91 µg L⁻¹, which was much lower than the regulated value (900 µg L⁻¹). The concentrations of acetaldehyde ranged from 0.02 to 25.79 µg L⁻¹, with a median of 2.25 µg L⁻¹ and a mean of 5.32 µg L⁻¹. The concentrations of acetaldehyde at site 22 in 2013 exceeded the regulated value of 20 µg L⁻¹. The FODs of carbonyl compounds (58%—100%) indicate that they may be more widely present in natural water than common VOCs. Dąbrowska (2013) reported that formaldehyde, acetaldehyde, propanal, glyoxal, and methyglyoxal were the most frequently identified aldehydes in aquatic environment. However, we detected crotonaldehyde, pentanal, hexanal, cyclohexanone, and heptanal more frequently than formaldehyde, acetaldehyde, and propanal.

All 10 taste and odor compounds were detected in the studied source water sites, the concentrations of them above LODs ranging from 0.23 to 972.7 ng L⁻¹. The detection frequencies of them ranged between 23% (cis-3-hexenyl acetate) and 90% (MIB). In fact, almost all VOCs have various tastes and odors, but many of them do not change the organoleptic quality of the natural water because their odor threshold concentrations are usually much higher than their real concentrations (Peter, 2008). There are currently no regulations for such compounds even for the two most common MIB and geosmin. Only reference values (both are 10 ng L⁻¹) have been reported in GB5749-2006 of China, partly because they have not been associated with immediate health effects (Srinivasan and Sorial, 2011). MIB and geosmin have been identified as the most common earthy/musty compounds present in natural water system around the world, and mainly result from the metabolism and biodegradation of certain types of microorganisms, such as actinomycetes, cyanobacteria, fungi, and myxobacteria (Peng et al., 2014; Peter et al., 2009; Yu et al., 2009). Concentrations of MIB and geosmin were 0.23—28.84 ng L⁻¹ with a medium of 7.22 ng L⁻¹ and a mean of 7.75 ng L⁻¹, and 2.62—45.00 ng L⁻¹ with a medium of 12.65 ng L⁻¹ and a mean of 13.75 ng L⁻¹, respectively. Though MIB (FOD of 90%) was the most widely distributed odor-causing compounds, geosmin (FOD of 73%) was also frequently detected in this study. These results agree with others suggesting that MIB existed more widely than geosmin in source water of China (Sun et al., 2014). However, we found that the median and the mean concentrations of geosmin were higher than those of MIB, including several exceeding the reference values, but (Sun et al., 2014) detected the concentrations of geosmin lower than that of MIB. Few studies have investigated the other 8 off-flavors in large scale (Chen et al., 2013a,b).

The distributions of 3 classes of VOCs in 5 major river basins of China are summarized in Table 2. Among different river basins, the average concentrations of all 3 classes of compounds in Yellow River basin were the highest, whereas those in Haihe River basin were the lowest but carbonyl compounds. This may be explained that carbonyl compounds are so widely present in aqueous environment that the distinction in different basins were not significant. Table 2 clearly shows that Yellow River basin, Huaihe River basin, and Liaohe River basin suffered more pollution of VOCs than Yangtze River basin and Haihe River basin.

### 3.2. Ecological risk assessment

The risk quotients (RQ) estimation has been described in the Supporting information. It was widely accepted that an ecological risk is suspected when the RQ is ≥ 1 (Cho et al., 2014), so the RQs calculated for fish that were >1 are shown in Table 3. Crotonaldehyde was the only one contaminant that the RQ of which consistently exceeded 1. Although it was not regulated in China up to date, crotonaldehyde has long been regarded as an important environmental pollutant (Huang et al., 2013) since it is found ubiquitously (FOD of 98% in this study) in the environment. Crotonaldehyde is a major component of cigarette smoke and has been known as a major cause of many respiratory diseases such as chronic obstructive pulmonary disease and lung cancer (Yang et al., 2013). The RQs of xylene, n-butylbenzene, hexachlorobutadiene, heptanal, octanal, benzaldehyde, nonanal, decanal, trans,cis-2,4-heptadienal, trans,cis-2,6-nonadienal, and trans-2-decanal were higher than one in some cases, as shown in Table 3. They exhibited significant geographical differences. The risks to fish of nonanal, decanal, trans,cis-2,4-heptadienal, trans,cis-2,6-nonadienal, and trans-2-decanal occurred in some cases in all the 5 basins during both investigations. Interestingly, these contaminants together with crotonaldehyde, all belong to aldehydes. They are detected frequently, but not regulated currently in China. Many of this class of compounds are toxic and can be blamed for odor problems (Dąbrowska and Nawrocki, 2013). Therefore, they should be paid more attention to than common VOCs. The RQs of another aldehyde, heptanal, were sometimes higher than one in Yangtze River basin, Huaihe River basin, Yellow River basin, and Haihe River basin. And the RQs ≥1 of octanal occurred in Huaihe River basin, Yellow River basin, and Liaohe River basin. In addition, the risks of hexachlorobutadiene existed in the same basins as octanal. The concentrations of this compound at some sites exceeded the Chinese regulate value have discussed before. The risks of xylene, n-butylbenzene, and benzaldehyde were found only once, occurring at site 20 in 2013, at site 17 in 2013, and at site 7 in 2013, respectively. Though high concentrations may induce adverse effects or represent an ecological risk, they are not directly related to risks to the ecosystem because the ecological risk of a pollutant is induced not only by its high concentration, but also by the toxicity of the pollutant and the sensitivity of the receptor (Cho et al., 2014).

### Table 2

Concentrations of total common VOCs, total carbonyl compounds, and total taste and odor compounds in 5 major river basins.

| River basin | Sum of common VOCs (µg L⁻¹) | Sum of carbonyl compounds (µg L⁻¹) | Sum of taste and odor compounds (µg L⁻¹) |
|-------------|-----------------------------|----------------------------------|---------------------------------------|
|             | Min  | Max  | Mean | Min  | Max  | Mean | Min  | Max  | Mean |
| Yangtze River | 0.00 | 4.03 | 1.65 | 5.47 | 43.80 | 25.92 | 85.67 | 460.04 | 212.43 |
| Huaihe River | 0.00 | 22.21 | 4.10 | 4.84 | 136.06 | 30.26 | 146.11 | 1586.19 | 616.00 |
| Yellow River | 1.94 | 42.78 | 12.78 | 11.31 | 59.99 | 36.67 | 58.76 | 1708.52 | 633.36 |
| Haihe River | 0.48 | 2.75 | 1.56 | 3.68 | 94.24 | 27.01 | 10.95 | 444.11 | 160.94 |
| Liaohe River | 1.10 | 20.85 | 9.57 | 9.46 | 45.81 | 20.69 | 79.96 | 914.17 | 379.92 |
### Table 3

| Compounds                  | Yangtze River | Huaihe River | Yellow River | Haihe River | Liaohe River |
|----------------------------|---------------|--------------|-------------|-------------|--------------|
|                           | Min | Max | Mean | Min | Max | Mean | Min | Max | Mean | Min | Max | Mean | Min | Max | Mean |
| n-Butylbenzene             | 1.17E-00 | 1.17E-00 | 1.17E-00 | 1.17E-00 | 1.17E-00 | 1.17E-00 | 1.17E-00 | 1.17E-00 | 1.17E-00 | 1.17E-00 | 1.17E-00 | 1.17E-00 | 1.17E-00 | 1.17E-00 | 1.17E-00 |
| Hexachlorobutadiene        | 7.75E-00 | 7.75E-00 | 7.75E-00 | 3.50E-00 | 1.03E-00 | 1.03E-00 | 6.33E-00 | 5.33E-00 | 5.33E-00 | 3.50E-00 | 1.03E-00 | 1.03E-00 | 6.33E-00 | 5.33E-00 | 5.33E-00 |
| Crotonaldehyde             | 8.78E-00 | 6.19E-00 | 8.78E-00 | 4.83E-00 | 2.23E-00 | 2.23E-00 | 4.83E-00 | 2.23E-00 | 2.23E-00 | 4.83E-00 | 2.23E-00 | 2.23E-00 | 4.83E-00 | 2.23E-00 | 2.23E-00 |
| Heptanal                   | 1.58E-00 | 1.07E-00 | 1.58E-00 | 1.07E-00 | 1.07E-00 | 1.07E-00 | 1.07E-00 | 1.07E-00 | 1.07E-00 | 1.07E-00 | 1.07E-00 | 1.07E-00 | 1.07E-00 | 1.07E-00 | 1.07E-00 |
| Benzaldehyde               | 1.06E-00 | 1.06E-00 | 1.06E-00 | 1.06E-00 | 1.06E-00 | 1.06E-00 | 1.06E-00 | 1.06E-00 | 1.06E-00 | 1.06E-00 | 1.06E-00 | 1.06E-00 | 1.06E-00 | 1.06E-00 | 1.06E-00 |
| Nonanal                    | 2.14E-00 | 2.21E-00 | 2.14E-00 | 2.18E-00 | 1.46E-00 | 1.46E-00 | 3.07E-00 | 2.62E-00 | 2.62E-00 | 3.07E-00 | 2.62E-00 | 2.62E-00 | 3.07E-00 | 2.62E-00 | 2.62E-00 |
| trans,cis-2,4-Heptadienal  | 2.14E-00 | 6.94E-00 | 2.14E-00 | 4.30E-00 | 2.62E-00 | 2.62E-00 | 4.30E-00 | 2.62E-00 | 2.62E-00 | 4.30E-00 | 2.62E-00 | 2.62E-00 | 4.30E-00 | 2.62E-00 | 2.62E-00 |
| trans-2-Decenal            | 2.14E-00 | 1.96E-00 | 2.14E-00 | 1.27E-00 | 8.88E-00 | 8.88E-00 | 1.27E-00 | 8.88E-00 | 8.88E-00 | 1.27E-00 | 8.88E-00 | 8.88E-00 | 1.27E-00 | 8.88E-00 | 8.88E-00 |

Only the values that were >1 are showed here; the RQtotal was the sum of all of the chemicals, not just the chemicals with the RQ above 1.

Acetaldehyde here is a good example. Considering the integrated ecological risk, the minimum RQtotal were all higher than one in every basin. The result indicates that combative effects of pollutants may pose potential risk to fish. The mean of RQtotal was the highest in Yellow River basin, followed by Yangtze River basin, Huaihe River basin, Haihe River basin, and Liaohe River basin.

#### 3.3. Human health risk assessment

There were 37, 50, 73, 37 and 69 VOCs detected in Yangtze River basin, Huaihe River basin, Yellow River basin, Haihe River basin, and Liaohe River basin, respectively. Because of the lack of toxicity data for some pollutants, the human health risks were only undertaken for pollutants, which could obtain efficient toxicity data. Non-carcinogenic risk was expressed as HI, while carcinogenic risk as R (detailed description shown in Supporting information).

In general, if HI value is greater than one, it indicates potential adverse health effects and needs further study (Wu et al., 2010). In this study, for both ingestion and dermal adsorption pathways, the maximum HI were all less than one in every basin (data are not shown). This result indicates that measured pollutants with available toxicity data may pose little or no non-carcinogenic health risks for consumers when drinking or bathing.

Carcinogenic risk values greater than 10^{-3} are generally considered unacceptable. Risks of almost all compounds calculated were at or below the level of 10^{-6} for ingestion pathway except crotonaldehyde. For dermal adsorption pathway, risks were all at or below the level of 10^{-6}. However, this acceptable level may change based on national standards and environmental policies and may be as high as 10^{-4} (Gao et al., 2012). Considering 10^{-4} as the limit, the mean of RQtotal for ingestion pathway still exceeded the acceptable level in all 5 basins mainly due to the contribution of crotonaldehyde (shown in Table 4). This compound also posed ecological risk in all 5 basins as discussed before. Therefore, the source water may pose potential carcinogenic risk because of the crotonaldehyde existence if using for drinking.

#### 3.4. Olfactory assessment

As is known, odor is caused by one or more volatileized chemical compounds, generally at the concentration higher than their OTCs. Similarly, an odor hazard index (OHI) value was defined. If OHI is lower than 1, it indicates the odor level is acceptable in the environment. Otherwise, exposing individuals to odors may cause risk of human discomfort and unwanted syndromes. Since the OTCs of different compounds are quite different (Table S4), taste and odor events are often blamed for those with low OTCs. The OHI above one are shown in Table 5 for the compounds detected with OTCs obtained. Results showed that OHI values of common VOCs (data are not shown) except naphthalene in the Yellow River basin and the Liaohe River basin were far below 1, so common VOCs rarely obtained. Results showed that OHI values of common VOCs (data are not shown) except naphthalene in the Yellow River basin and the Liaohe River basin were far below 1, so common VOCs rarely cause taste and odor problems. Naphthalene have not only been classified as a potential human carcinogen (Preuss et al., 2003), but also as an odor of mothballs (Young et al., 1996). Aldehydes were often reported to be associated with fishy odor episode (Suffet et al., 2004; Watson et al., 2001; Zhao et al., 2013). In our investigation, the concentrations of aldehydes, such as hexanal, heptanal, octanal, benzaldehyde, nonanal, and trans,cis-2,6-nonadienal exceeded their OTCs. Surprisingly, the OHI values of benzaldehyde and nonanal showed that the concentrations of these two compounds were over 100 or even 1000 times higher than their OTCs. However, it should be noted that their OTCs might have great uncertainties. Haese et al. (2014) reviewed that the OTC of benzaldehyde was a range of 0.01–4600 µg L^{-1}. Therefore, it is extremely possible that we overestimated its OHI value due to using the conservative OTC of...
Table 4
Carcinogenic risk through ingestion (Rin) of based on the minimum concentrations and maximum concentrations detected in typical drinking water sources from 5 major river basins, China.

| Compounds      | Yangtze River | Huaire River | Yellow River | Haihe River | Liaohe River |
|----------------|---------------|--------------|--------------|-------------|--------------|
|                | Min           | Max          | Mean         | Min          | Max          | Mean         | Min          | Max          | Mean         | Min          | Max          | Mean         |
| Crotonaldehyde | 3.28E-04      | 1.83E-04     | 2.56E-04     | 1.18E-04     | 4.24E-04     | 2.20E-04     | 2.27E-04     | 1.44E-04     | 9.99E-05    | 1.82E-04     | 9.99E-05    |
| Total          | 3.28E-04      | 1.83E-04     | 2.56E-04     | 1.22E-04     | 4.24E-04     | 2.42E-04     | 2.27E-04     | 1.26E-04     | 1.84E-04    | 1.10E-04     | 1.10E-04    |

Only the values that were >10^-4 are showed here; the Rtotal was the sum of all of the chemicals, not just the chemicals with the R above 10^-4.

Table 5
Odor hazard index (OHI) based on the minimum concentrations and maximum concentrations detected in typical drinking water sources from 5 major river basins, China.

| Compounds                  | Yangtze River | Huaire River | Yellow River | Haihe River | Liaohe River |
|----------------------------|---------------|--------------|--------------|-------------|--------------|
|                            | Min           | Max          | Mean         | Min          | Max          | Mean         | Min          | Max          | Mean         | Min          | Max          |
| Naphthalene                | 1.38E+00      | 1.02E+00     | 1.72E+00     | 3.43E+00     | 1.16E+00     | 1.24E+00     | 1.20E+00     | 1.16E+00     | 1.24E+00     | 1.20E+00     |
| Hexanal                    | 1.09E+00      | 1.02E+00     | 2.21E+00     | 3.43E+00     | 1.16E+00     | 1.24E+00     | 1.20E+00     | 1.16E+00     | 1.24E+00     | 1.20E+00     |
| Octanal                    | 4.80E+00      | 4.89E+00     | 5.26E+00     | 8.10E+00     | 6.80E+00     | 7.70E+00     | 5.80E+00     | 6.50E+00     | 7.60E+00     | 5.80E+00     |
| Benzaldehyde               | 3.34E+02      | 3.62E+02     | 3.96E+02     | 5.26E+02     | 6.80E+02     | 7.70E+02     | 5.80E+02     | 6.50E+02     | 7.60E+02     | 5.80E+02     |
| Nonanal                    | 3.42E+02      | 3.53E+02     | 3.50E+01     | 3.48E+02     | 3.50E+01     | 3.48E+02     | 3.50E+01     | 3.48E+02     | 3.50E+01     | 3.48E+02     |
| IPMP                       | 1.94E+00      | 1.20E+00     | 2.69E+00     | 3.78E+00     | 4.50E+00     | 5.20E+00     | 4.10E+00     | 4.70E+00     | 5.30E+00     | 4.70E+00     |
| IBMP                       | 7.95E+00      | 3.87E+00     | 1.34E+00     | 1.34E+00     | 1.34E+00     | 1.34E+00     | 1.34E+00     | 1.34E+00     | 1.34E+00     | 1.34E+00     |
| trans,cis-2,6-Nonadienal   | 2.72E+00      | 2.72E+00     | 2.72E+00     | 2.72E+00     | 2.72E+00     | 2.72E+00     | 2.72E+00     | 2.72E+00     | 2.72E+00     | 2.72E+00     |
| MIB                        | 1.92E+00      | 1.92E+00     | 1.92E+00     | 1.92E+00     | 1.92E+00     | 1.92E+00     | 1.92E+00     | 1.92E+00     | 1.92E+00     | 1.92E+00     |
| TCA                        | 1.29E+00      | 9.46E+00     | 2.50E+00     | 2.50E+00     | 2.50E+00     | 2.50E+00     | 2.50E+00     | 2.50E+00     | 2.50E+00     | 2.50E+00     |
| Geosmin                    | 3.17E+00      | 2.77E+00     | 2.77E+00     | 2.77E+00     | 2.77E+00     | 2.77E+00     | 2.77E+00     | 2.77E+00     | 2.77E+00     | 2.77E+00     |

Only the values that were >1 are showed here.
trans,trans-IPMP, waters. Additionally, odor problems occurred extensively in source that crotonaldehyde did a little carcinogenic risk if the water was risk at every basin. However, no human health risk existed except decenal in source water posed a potential ecological risk in some chlorobutadiene, hexanal, and MIB in the Yellow River basin; paid attention to in the Yangtze River basin; hexachlorobutadiene, trans-trans,hexanal, heptanal, octanal, benzaldehyde, nonanal, decanal, n showed that xylenes, evaluated for ecological, human health, and olfactory risks. Results 2006 or GB3838-2002), most of which were much lower than the and the Ministry of Water Resources’ Special Funds for Scientific Research on Public Causes (Grant No. 201201032).

Appendix A. Supplementary data
Supplementary data related to this article can be found at http://dx.doi.org/10.1016/j.envpol.2015.06.027.

References
Bao, M.L., Barbieri, K., Burrini, D., Griffin, O., Pantani, F., 1997. Determination of trace levels of taste and odor compounds in water by microextraction and gas chromatography-ion-trap detection-mass spectrometry. Water Res. 31, 1719–1727.
Burgos, L., Lehmann, M., de Andrade, H.H.R., de Abreu, B.R.R., de Souza, A.P., Juliano, V.B., Dihl, R.R., 2014. In vivo and in vitro genotoxicity assessment of 2-methylisoborneol, causal agent of earthy-musty taste and odor in water. Eco- toxicol. Environ. Saf. 100, 282–286.
Carter, J.M., Lapham, W.W., Zorgolis, J.S., 2008. Occurrence of volatile organic compounds in aquifers of the United States. J. Am. Water Resour. Assoc. 44, 399–416.
Chary, N.S., Fernandez-Alba, A.R., 2012. Determination of volatile organic compounds in drinking and environmental waters. Trends Anal. Chem. 32, 60–75.
Chen, J., Xie, P., Ma, Z.M., Niu, Y., Tao, M., Deng, X.W., Wang, Q., 2010. A systematic study on spatial and seasonal patterns of eight taste and odor compounds with relation to various biotic and abiotic parameters in Gonghu Bay of Lake Taihu. China. Sci. Total Environ. 409, 314–325.
Chen, X.C., Luo, Q., Chen, H., Wei, Z., Wang, Z., Xu, K., 2013a. Occurrence and distribution of volatile organic compounds in conventional and advanced drinking water treatment process. Environ. Sci. China 12, 4642–4648.
Chen, X.C., Luo, Q., Yuan, S.G., Wei, Z., Song, H.W., Wang, D.H., Wang, Z.J., 2013b. Simultaneous determination of ten taste and odor compounds in drinking water by solid-phase microextraction combined with gas chromatography-mass spectrometry. J. Environ. Sci. 25, 2313–2323.
Cho, E., Kim, J., Chung, S., Seo, D., Son, Y., 2014. Occurrence of micropollutants in four major rivers in Korea. Sci. Total Environ. 491–492, 138–147.
Dabrowska, A., 2013. Possible reasons for elevated aldehyde levels in surface waters. Ochr. Sr. 35, 13–16.
Dabrowska, A., Nawrocka, J., 2013. Aldehyde concentrations in wet deposition and river waters. Sci. Total Environ. 452–453, 1–9.
Du, X., Li, X.H., Luo, T.L., Matsuur, N., Kadokami, K., Chen, J.W., 2013. Occurrence and aquatic ecological risk assessment of typical organic pollutants in water of Yangtze River estuary. Procedia Environ. Sci. 18, 882–889.
Fink, P., 2007. Ecological functions of volatile organic compounds in aquatic sys- tems. Mar. Freshw. Behav. Phys. 40, 155–168.
Gao, J.J., Liu, L.H., Liu, X.R., Lu, J., Hao, H., Yuan, H., Zhou, H.D., 2012. The organic contamination survey and health risk assessment of 16 source water reservoirs in Haihe River basin. Water Sci. Technol. 65, 998–1006.
Green, T., Lee, R., Farrar, D., Hill, J., 2003. Assessing the health risks following environmental exposure to hexachlorobutadiene. Toxicol. Lett. 138, 63–73.
Guo, L., Wu, F.C., He, H.P., Zhang, R.Q., Li, H.X., Feng, C.L., 2012. Distribution characteristics and ecological risk assessment of PAHs in surface waters of China. Sci. Earth Sci. 55, 914–925.
Guo, L., 2007. Doing battle with the green monster of Taihu Lake. Science 317, 1166.
Hoffman, A., 2001. Determination of trace amounts of off- flavor compounds in water by stir bar sorptive extraction and thermal desorption GC-MS. Rapid Commun. Mass Spectrom. 27, 847–850.
Huang, D.N., Wang, X.Y., Deng, C.H., 2013. Enrichment and determination of crotonaldehyde using magnetic multiwalled carbon nanotubes as an adsorbent and a matrix for matrix-assisted laser desorption/ionization time-of-flight mass spectrometry. Rapid Commun. Mass Spectrom. 27, 847–850.
Liu, L.H., Zhou, H.D., 2011. Investigation and assessment of volatile organic com- pounds in water sources in China. Environ. Monit. Assess. 173, 825–836.
Ma, H.L., Zhang, H.J., Wang, L.X., Wang, J.C., Chen, J.P., 2014. Comprehensive screening and priority ranking of volatile organic compounds in Daliao River, China. Environ. Monit. Assess. 186, 2813–2827.
Morgan, M.J., Lapham, W.W., Rowe, R.L., Zogorski, J.S., 2004. Volatile organic compounds in ground water from rural private wells, 1986 to 1999. J. Am. Water Resour. Assoc. 40, 1141–1157.
Nga, T.K., Hursthouse, A.S., Enfield, S., Stirling, D., Adams, C.J., 2015. Assessment of the health risk, aesthetic and agricultural quality of rainwater, surface water and groundwater in the Shale Bedrock Areas, Southeastern Nigeria. Water Qual. Expo. Health 7, 153–178.
Nikolou, A.D., Goulasopoulos, S.K., Kostopoulou, M.N., Kolokythas, G.A., Lekkas, T.D., 2002. Determination of volatile organic compounds in surface waters and treated wastewater in Greece. Water Res. 36, 2883–2890.
Niri, V.H., Bragg, L., Pawliszyn, J., 2008. Fast analysis of volatile organic compounds and disinfection by-products in drinking water using solid-phase micro-extraction–gas chromatography/time-of-flight mass spectrometry. J. Chromatogr. A 1201, 222–227.
Ochiai, N., Sasamoto, K., Takino, M., Yamashita, S., Daishima, S., Katsuda, K., 1997. Determination of trace levels of taste and odor compounds in water by microextraction and gas chromatography-ion-trap detection-mass spectrometry. Water Res. 31, 1719–1727.
Ochiai, N., Sasamoto, K., Takino, M., Yamashita, S., Daishima, S., Heiden, A., Hoffman, A., 2001. Determination of trace amounts of off-flavor compounds in drinking water by stir bar sorptive extraction and thermal desorption GC-MS. Analyst 126, 1652–1657.
Papageorgiou, A., Voutsis, D., Papadakis, N., 2014. Occurrence and fate of ozonation by-products at a full-scale drinking water treatment plant. Sci. Total Environ.
481, 392–400.
Peng, S.F., Ding, Z., Zhao, L., Fei, J., Xuan, Z.B., Huang, C.X., Chen, X.D., 2014. Determination of seven odorants in purified water among worldwide brands by HS-SPME coupled to GC-MS. Chromatographia 77, 729–735.
Peter, A., 2008. Taste and Odor in Drinking Water: Sources and Mitigation Strategies (Ph.D. thesis). Swiss Federal Institute of Technology Zurich, Zurich, Switzerland.
Peter, A., Köster, O., Schildknecht, A., von Gunten, U., 2009. Occurrence of dissolved and particle-bound taste and odor compounds in Swiss lake waters. Water Res. 43, 2191–2200.
Preuss, R., Angerer, J., Drexler, H., 2003. Naphthalene—an environmental and occupational toxicant. Int. Arch. Occup. Environ. Health 76, 556–576.
Robertson, R.F., Hammond, A., Jauncey, K., Beveridge, M.C.M., Lawton, L.A., 2006. An investigation into the occurrence of geosmin responsible for earthy-musty taints in UK farmed rainbow trout, Onchorhynchus mykiss. Aquaculture 259, 153–163.
Rowe, B.L., Toccalino, P.L., Moran, M.J., Zogorski, J.S., Price, C.V., 2007. Occurrence and potential human-health relevance of volatile organic compounds in drinking water from domestic wells in the United States. Environ. Health Perspect. 115, 1539–1546.
Serrano, M., Silva, M., Gallego, M., 2013. Development of an environment-friendly microextraction method for the determination of aliphatic and aromatic aldehydes in water. Anal. Chim. Acta 784, 77–84.
Srinivasan, R., Sorial, G.A., 2011. Treatment of taste and odor causing compounds 2-methyl isoborneol and geosmin in drinking water: a critical review. J. Environ. Sci. 23, 1–13.
Suffet, I.H.M., Schweitze, L., Khiari, D., 2004. Olfactory and chemical analysis of taste and odor episodes in drinking water supplies. Rev. Environ. Sci. Biotechnol. 3, 3–13.
Sun, D.L., Yu, J.W., Yang, M., Lin, T.F., Guo, Z.H., Gu, J.N., Li, S., Han, W., 2009. Occurrence of odor-causing compounds in surface water from the Three Gorges Reservoir, China. Hum. Ecol. Risk Assess. 15, 1593–1607.
Yang, Y.Y., Yun, X.Y., Liu, M.X., Jiang, Y., Li, Q.X., Wang, J., 2014. Concentrations, distributions, sources, and risk assessment of organochlorine pesticides in surface water of the East Lake, China. Environ. Sci. Pollut. Res. 21, 3041–3050.
Young, W.F., Horth, H., Crane, R., Ogden, T., Arnott, M., 1996. Taste and odor threshold concentrations of potential potable water contaminants. Water Res. 30, 331–340.
Yu, J.W., Zhao, Y.M., Yang, M., Lin, T.F., Guo, Z.H., Gu, J.N., Li, S., Han, W., 2009. Occurrence of odour-causing compounds in different source waters of China. J. Water Supply Res. Technol. Aqua 58, 387–394.
Zhu, Y., Yang, Y., Liu, M., Zhang, M., Wang, J., 2015. Concentration, distribution, source, and risk assessment of PAHs and heavy metals in surface water from the Three Gorges Reservoir, China. Hum. Ecol. Risk Assess. 21, 1593–1607.

X. Chen et al. / Environmental Pollution 206 (2015) 64–72