Environmental Pollution xxx (2016) 1–7

Contents lists available at ScienceDirect

Environmental Pollution

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

Source-water odor during winter in the Yellow River area of China: Occurrence and diagnosis☆

Xia Li [a], Jianwei Yu [a, *], Qingyuan Guo [a], Ming Su [b], Tingting Liu [a], Min Yang [b], Yu Zhao [c]

[a] Key Laboratory of Drinking Water Science and Technology, Research Center for Eco-Environmental Sciences, Chinese Academy of Sciences, Beijing, 100085, China

[b] State Key Laboratory of Environmental Aquatic Chemistry, Research Center for Eco-Environmental Sciences, Chinese Academy of Sciences, Beijing, 100085, China

[c] Food and Drug Anti-doping Laboratory, China Anti-Doping Agency, Beijing 100029, China

ARTICLE INFO

Article history:
Received 25 February 2016
Received in revised form
29 June 2016
Accepted 29 June 2016
Available online xxx

Keywords:
Taste and odor
Fishy odor
Drinking water
GC×GC-TOFMS
Yellow River

ABSTRACT

Yellow River source water has long suffered from odor problems in winter. In this study, odor characteristics, potential odorants, and algae in the source water of six cities (Lanzhou, Yinchuan, Hohhot, Zhengzhou, Jinan and Dongying) along the Yellow River were determined in winter (February to March 2014). According to flavor profile analysis (FPA), moderate to strong fishy odors occurred in all cities, except for Lanzhou. At the same time, mild earthy/musty odors and septic/swampy odors were also detected. The strong fishy odor (FPA intensity, 8.5) in Yinchuan was attributed to the abnormal growth of *Dinobryon* (cell density, 5.7×10^4 cells/mL), while the fishy odors in Hohhot, Zhengzhou, Jinan, and Dongying might be caused by *Melosira* and *Cyclotella, Cryptomonas, Dinobryon*, and *Synedra,* respectively. Unsaturated aldehydes, which have been reported to cause fishy odors, were not detected in all samples. However, some saturated aldehydes, including hexanal, heptanal, nonanal, decanal, and benzaldehyde, were detected with a total concentration range of 690 ng/L to 2166 ng/L, and might have partly contributed to the fishy odors. In addition, 2-MIB (5.77–21.12 ng/L) and geosmin (2.26–9.73 ng/L) were responsible for the earthy/musty odors in the Yellow River source waters, and dimethyl disulfide (648.2 ng/L) was responsible for the rancid/swampy odor (FPA intensity, 8.0) episode in Yinchuan. This is a comprehensive study reporting on the occurrence and possible reasons for the odor issues in the Yellow River source water during winter.

1. Introduction

Taste and odor (T/O) episodes in drinking water have been a recurring problem in many countries (Hayes and Burch, 1989; Izaguirre et al., 1999; Sun et al., 2013). The origins of T/O problems in drinking water are often found in source waters (Izaguirre et al., 1999). The occurrence of T/O episodes is often associated with eutrophic waters during summer or early autumn (Watson, 2003; Li et al., 2010; Ma et al., 2013), such as the well documented earthy/musty odor caused by two algal-derived terpenoids (2-MIB and geosmin) that originate from typical Cyanobacteria (Watson et al., 2000; Lin et al., 2002; Li et al., 2010; Sun et al., 2013) or Actinomycetes (Lanciotti et al., 2003). However, fishy/rancid/oily odors have been increasingly reported in some meso-oligotrophic systems during early spring and winter, even with ice-cover present (Burlingame et al., 1992; Naumenko, 1992; Watson et al., 2001). In these cases, T/O episodes are commonly associated with the growth of diatoms (Wendel and Juttner, 1996), Chrysophyta (Wee et al., 1994; Watson et al., 2001; Watson and Satchwill, 2003), Cryptophyta and dinoflagellates (Watson et al., 2001). Some unsaturated fatty acid derivatives, such as 2,4-heptadienal, 2,4-decadienal, 2,4,7-decatrienal, and 2,6-nonadienal, have been speculated as responsible for such odors (Wee et al., 1994; Khiari et al., 1995; Wendel and Juttner, 1996). Compared with earthy/musty odors, fishy odor problems are not well understood, and related information and research is still very limited.

The Yellow River is one of the most important water sources in China, especially for those cities along its banks and within its watershed. To cope with the high turbidity of the river water, sand settling reservoirs have been constructed in many cities, which

☆ This paper has been recommended for acceptance by Dr. Chen Da.

* Corresponding author.
E-mail address: jwyu@rcees.ac.cn (J. Yu).

http://dx.doi.org/10.1016/j.envpol.2016.06.069
0269-7491/

have created ideal conditions for algal growth and increased the occurrence of fishy odors during winter. Except for one case study that reported on the abnormal growth of *Dinobryon* as possibly being responsible for such odor issues (Zhao et al., 2013), information regarding the odor characteristics, potential odorants, and related algae is still unavailable.

In this study, the occurrences of odors and algae in source waters of six cities (Lanzhou, Yinchuan, Hohhot, Zhengzhou, Jinan, and Dongying) along the Yellow River in China were determined during winter (February to March 2014). Flavor profile analysis (FPA) was used to characterize the odor profiles of source water, and two-dimensional (2D) gas chromatography with time-of-flight mass spectrometry (GC×GC-TOFMS), an analytical instrument with high resolution, sensitivity, and separation capacity (Chin et al., 2011; da Silva et al., 2014), was used to simultaneously determine 16 specific odorants. The results of this study will provide useful knowledge for the better control of odor problems in the Yellow River source waters.

2. Methods and materials

2.1. Study sites and sampling

This study was conducted from February to March 2014. Six cities along the Yellow River, including Lanzhou, Yinchuan, Hohhot, Zhengzhou, Jinan, and Dongying, were selected for study, as shown in Fig. 1. Except for Lanzhou, each city has a sand settling reservoir to reduce the high turbidity of the river water. Raw water samples were taken from the reservoirs at 0–0.5 m under the water surface. The samples from Lanzhou were directly taken from the river. Triplicate samples were collected in 500 mL amber bottles, with 5 mL Lugol's solution added in one bottle for algal fixation and 5 mL $HgCl_2$ solution added in the other two bottles for FPA evaluation and odorant quantification. All samples were stored in thermotanks with ice bags and delivered to the laboratory as soon as possible. Typical water quality parameters are shown in Table 1.

2.2. Chemicals and reagents

Sixteen odor reference standards (purity > 95%), including two terpenoids (2-MIB, geosmin), four sulfides (dimethyl sulfide, dimethyl disulfide, dimethyl trisulfide, and diethyl disulfide) and ten aldehydes (hexanal, heptanal, nonanal, decanal, and benzaldehyde, 2-octenal, β-cyclocitral, 2,4-heptadienal, 2,6-nonadienal, and 2,4-decadienal), were purchased from Sigma-Aldrich (USA), with stock solutions of 100 mg/L stored in methanol. Detailed information on the 16 odorous compounds is shown in Table 2. Analytical grade NaCl, KI, $HgCl_2$, and Na_2SO_4 were obtained from Beijing Chemicals Ltd., China. Both NaCl and Na_2SO_4 were heated at 450 °C for 2 h before use. Ultrapure water (18.2 MΩ cm) was produced with a Milli-Q purification system.

2.3. Sample pre-concentration

Sample pre-concentration was performed using liquid-liquid extraction as follows: 500 mL water samples were filtered through 1.2 μm glass fiber filters prior to liquid-liquid extraction, and extracted twice using dichloromethane as the extracting solvent with a volume of 50 mL and 25 mL, respectively. Dehydration was then carried out with Na_2SO_4. Samples were concentrated to a final volume of 100 μL by rotary evaporation and under a gentle stream of nitrogen. The overall concentration factor was 5000. All pre-concentrated samples were stored at −20 °C prior to analysis.

2.4. Odor evaluation

The odor characteristics of water samples were evaluated by FPA. A detailed description of the training and application procedures can be found in the Standard Methods for Water and Wastewater (APHA, 2005). Namely, four non-smokers with normal olfactory function and no known anosmia were selected as the panelists in this study. Seven-point scales of 1–12 were used to describe the intensity of samples (1: odor threshold, 2–4: weak odor intensity, 6–8: moderate odor intensity, 10–12: strong odor intensity). The evaluation was conducted immediately on the day samples were received. Each panelist gave the evaluation of odor characteristics and intensity, respectively, which were then averaged and used as the final evaluation result.

2.5. GC×GC-TOFMS analysis

A 2D gas chromatograph with time-of-flight mass spectrometer (LECO, USA), equipped with a multipurpose sampler (Gerstel, Germany), was used for odorant analysis. The GC was equipped with an Rxi-5silv column (30 m × 0.25 mm i.d. × 0.25 μm film thickness, Restek, USA) and a secondary Rxi-17 column (1.79 m × 0.1 mm i.d. × 0.1 μm film thickness, Restek, USA). Sample extracts (1 μL) were injected into the GC×GC-TOFMS in splitless mode with an inlet temperature of 250 °C. The carrier gas was ultrapure helium at 1.0 mL/min. The temperature program of the first column was: 40 °C for 0.2 min, then raised by 4°C/min to 280 °C, and finally maintained at 280 °C for 5 min. The temperature of the second oven was programmed at 45 °C for 0.2 min, then raised by 5°C/min to 285 °C, and maintained at 285 °C for 5 min. The separation time of the second dimension was 5.0 s, including 1.5 s for a cold pulse time and 1.0 s for a hot pulse time. The transfer line linking the secondary oven with the mass spectrometer was maintained at 250 °C. The MS detector was operated in full-scan mode (m/z 50–500), with a data acquisition rate of 100 spectra/s. The odorant concentrations were determined by external standard methods. Every water sample batch was analyzed in duplicate, and the odorant concentrations were the average values of the parallel analyses. In this study, 16 typical odorants were selected for quantification. The methodology used was developed in our previous study (Guo et al., 2015), the accuracy and precision of which was satisfactory.

2.6. Algal enumeration

Algal taxa and cell counts were performed with a 1 mL phytoplankton counter chamber using a microscope (BX 51 Olympus, Japan) under a 20× objective lens. For the samples with high cell density, cell numbers were counted without concentration. For other samples, cell numbers were counted after 10× preconcentration (from 100 mL to 10 mL) by settling in Lugol's solution, and triplicate 1 mL concentrated samples were collected separately and counted. Algae were identified to genera or to species based on morphological observation, as Su et al. (2014) indicated.

3. Results and discussion

3.1. Odor characteristics

The odor characteristics of the water samples were evaluated by FPA, as shown in Table 3. The source water from Yinchuan exhibited strong fishy and rancid/swampy odors, while samples from Hohhot, Zhengzhou, Jinan, and Dongying were described as having moderately fishy or related odors. No fishy odor was perceived in

Please cite this article in press as: Li, X., et al., Source-water odor during winter in the Yellow River area of China: Occurrence and diagnosis, Environmental Pollution (2016), http://dx.doi.org/10.1016/j.envpol.2016.06.069