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Diagnosing complex odor problems occurring in micro-polluted source water: Primary approach and application☆

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ABSTRACT

The odor problems in river-type micro-polluted water matrixes are complicated compared to those in lakes and reservoirs. For example, the TY River in Jiangsu Province has been associated with complex odors, whereas the specific odor compounds were not clear. In this paper, a comprehensive study on characterizing the odors and odorants in source water from the TY River was conducted. Six odor types, including earthy, marshy, fishy, woody, medicinal, and chemical odors, were detected for the first time; correspondingly, thirty-three odor-causing compounds were identified. By means of evaluating odor activity values and reconstituting the identified odorants, 95, 93, 92, 90, 89 and 88% of the earthy, marshy, fishy, woody, medicinal and chemical odors in the source waters could be clarified. Geosmin and 2-methylisoborneol were associated with earthy odor, while amyl sulfide, dibutyl sulfide, propyl sulfide, dimethyl disulfide, dimethyl trisulfide and indole were related to marshy odor. The major woody and fishy odor compounds were vanillin, geraniol, β-cyclocitral and 2,4-decadienal, 2-octenal, respectively. Medicinal and chemical odors were mainly caused by 2-chlorophenol, 4-bromophenol, 2,6-dichlorophenol and naphthalene, and 1,4-dichlorobenzene, respectively. This is the first study in which six odor types and thirty-three odorants were identified simultaneously in a river-type micro-polluted water source, which can offer a reference for odor management in drinking water treatment plants.

1. Introduction

Odors & tastes in source waters have been important issues of concern for drinking water supplies in recent years (Suffet et al., 1999; Watson, 2004; Yang et al., 2008; Wang et al., 2019a, 2020). To remove odors/odorants effectively, the target compounds responsible for the odors should be clear, because there are different treatment technologies and methods for various classes of odor-causing compounds. However, odor incidents occurring in water matrixes might involve microbial metabolites or contamination by domestic and industrial sewage (Suffet et al., 2004; Watson 2004; Ma et al., 2016; Wang et al., 2019b). Besides musty or earthy odors caused by 2-methylisoborneol (2-MIB) and geosmin (Li et al., 2012), marshy, chemical, medicinal odors, etc. are deemed as irritating, disgusting and solvent flavors, which people connect with toxicity, anthropogenic pollution, spillage of chemical substances or drugs (Guo et al., 2016a, 2020; Wang et al., 2019b). These problems require rapid management of the drinking water treatment plant to determine what target compounds are responsible for the odors, and how to deal with the presenting odor problems. Additionally, the odors emerging in water matrixes are becoming more numerous, serious and complex (Li et al., 2019; Wang et al., 2019a; Zhang et al., 2020). The characterization of odors and the corresponding odorants in complicated water matrixes, especially river-type water sources, is always a difficult problem.

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Usually, identification of the odorants in a water matrix has been accomplished by gas chromatography coupled with mass spectrometry (GC/MS), GC/MS equipped with an olfactory port (GC/O) or GC/MS with solid-phase micro-extraction (SPME) (Lin et al., 2002; Yu et al., 2009). In particular, SPME-GC/MS has received wide acceptance for environmental odor characterization because of its simplicity and sensitivity; odor-causing compounds, including 2-MIB, 1-octen-3-ol, 1-octen-3-one, 3-octanone and several alkyl-methoxypyrazines, have been identified successfully in water matrixes using this method (Callejon et al., 2016; Godayol et al., 2011). In recent years, with the rapid development of analytical technologies, more powerful chromatography systems and detectors, including comprehensive two-dimensional gas chromatography (GC/GC) with greater separating power, time-of-flight mass spectrometry with improved mass accuracy and resolution, and triple quadrupole tandem mass spectrometry with higher sensitivity, have been used for identifying and determining indistinguishable odor-causing compounds in complex odor matrixes (Adahchour et al., 2008; Shi et al., 2014; Guo et al., 2015; Wang et al., 2019a). In particular, the combination of the above technologies has been a useful and practical way for complex odorant identification; GC/GC had been used for identifying indistinguishable odorants corresponding to olfactometry peaks evaluated by GC/O (Guo et al., 2019b). To confirm the odor contribution of the identified compounds, the use of odor activity values (OAVs) and reconstitution tests has been adopted (Benkwitz et al., 2012; Guo et al., 2019a). By means of the above approaches, odorants in food industries including coffee, wine, fruit and water matrixes were identified and confirmed successfully (Chin et al., 2011; Benkwitz et al., 2012; Guo et al., 2016a).

The TY River is an important water source for domestic and industrial water needs in Jiangsu Province, which serves complex functions as a source of drinking water and irrigation water, as well as being used for navigation and flood drainage (Wang et al., 2010; 2019c). In recent years, the rapid development of urbanization, industry and agriculture along the TY River has resulted in the decline of water quality, presenting micro-polluted characteristics and suffering from complex odor problems (Wang et al., 2010; Gao et al., 2019). Usually, the existence of complex odors means that more than one odor type exists in the water with moderate or strong intensities (Guo et al., 2016a; Watson, 2004). When various pollutants with relatively low concentrations coexist in source water, it is usually called micro-polluted water, which has limited biodegradability and is hard to further purify; the treatment process needs to be specially designed for such micro-polluted water (Gan et al., 2020; Yu et al., 2019; Zhou et al., 2016). It is worth noting that the target odor-causing compounds in the TY River are unclear, which makes it difficult to adopt efficient approaches to remove the odors effectively in local drinking water treatment plants.

In this study, odor characteristics were evaluated comprehensively, and the corresponding odorants were identified and confirmed systematically to clarify the odor problems in source water from the TY River. Specifically, the odor characteristics in source water of TY River were evaluated via flavor profile analysis (FPA), and odor-causing compounds were first identified by a combination of GC/O and GC/GC, and then quantified through gas chromatography with triple quadrupole tandem mass spectrometry (GC/MS/MS). Then the identified odorants were confirmed by evaluation of OAVs and reconstitution tests. This is the first time that odor compounds in a river-type micro-polluted water source with such highly complex odors have been clarified. The results will offer sufficient understanding and a data base for odor management in water works with complicated odor problems.

2. Materials and methods

2.1. Standard substances and reagents

Altogether thirty-three standard substances including dimethyl disulfide (DMDS), hexanal, propyl sulfide, ethylbenzene, heptanal, p-xylene, 2,4-heptadienal, isopropylbenzene, 2-chlorophenol, dimethyl trisulfide (DMTS), 4-chlorotoluene, 3-methylstyrene, 2-octenal, 3-methylphenol, 2,4-octadienal, 1,4-dichlorobenzene, dibutyl sulfide, linalool, 2,6-dimethylphenol, 2-methylisoborneol (2-MIB), indole, β-cyclocitral, 2,4-decadienal, 4-bromophenol, geraniol, nerol, naphthalene, 2,6-dichlorophenol, 3-methylindole, amyl sulfide, 2-nitrophenol, geosmin and vanillin at chromatographic purity were purchased from Sigma-Aldrich (USA) for verification of potential odorants. Reagents including dichloromethane, methanol, alkanes (C7–C30) of HPLC grade were obtained from Supelco Co. (USA). 500 mg/L solutions of standard substances were diluted using methanol.

2.2. Sampling and pretreatment

Water samples used for odor evaluation and analysis were taken from the inlet of a drinking water treatment plant (DWTP) from January to December 2019. This DWTP is located at Yancheng City, Jiangsu Province and uses the TY River as a raw water source. Every month 2 L of source water were collected in an amber glass bottle with no head space, and then transported to the laboratory immediately in an insulated box with ice bags to maintain the temperature below 4 °C. After receiving the samples, sensory evaluation and pre-concentration of water samples were accomplished by FPA and liquid-liquid extraction (LLE) at once (Guo et al., 2016b). Instrumental analyses of odorants, including GC/MS/MS, GC/O, and GC/GC, were accomplished within two days. Each batch of water samples was analyzed in parallel, and concentrations of identified odorants were averaged in the duplicate analyses.

2.3. Sensory analysis

Odor characteristics of water samples were evaluated by FPA (APHA, 2005). In this study, FPA utilized a seven-point scale from 1 to 12, such as 1: threshold value, 2: very weak odor intensity, 4: weak odor intensity, 6&8: moderate odor intensity, 10&12: strong odor intensity, were adopted to describe the odor intensities of water samples. The panelists consisted of 5–6 non-smokers with normal olfactory function, with ages between 24 and 45 years. The 3-alternative forced choice (3-AFC) method was used for determining the odor threshold concentration (OTC) of related odor-causing compounds (ASTM, 1997); the specific procedures are described in the supporting information. It's worth noting that OTC is a range of concentrations in reality, and is not a single value as shown in Table S1, suggesting an OAV will have intervals around the average value.

2.4. Odorant identification

Odorant identification in source water of the TY River was achieved with the help of GC/O and GC/GC (Guo et al., 2016a), while quantification of odorants was accomplished using GC/MS/MS (Wang et al., 2019a). During the GC/O analysis, an odor panelist sits at the olfactory port of the GC and tries to identify GC peaks that match certain odor types. Then a panel of trained assessors have to smell purchased standards representing the GC peaks to confirm that the chemicals actually give off the odor types previously described by olfactory port sniffing. An olfactory detector (Gerstel, Germany) was adopted to acquire olfactometry peaks, while quadrupole mass spectrometry (Agilent 5975, Agilent technologies, USA) was used for obtaining chromatography peaks. The odor characteristics of olfactometry peaks were described and recorded while the peaks were eluted during the mass spectrometry runs, and the odor intensities varied in the range from 1 to 4 (1 = low; 2 = medium; 3 = high; 4 = very high). At least 4 h separation between GC/O analyses was provided for each analyst to avoid fatigue and contamination. A 1 μL sample extract was injected into the gas chromatograph in splitless mode and 250 °C inlet temperature; a low polarity capillary column (Rxi-5silv, 30 m × 0.25 mm × 0.25 μm, Restek Co., USA) was adopted. The temperature program of the GC oven was as follows: 40 °C (0.2 min) → 280 °C (at 5 °C/min) → 280 °C (hold 5 min). The flow velocity of helium as carrier gas was 1.35 mL/min. The outlet of the column in the GC oven was split to mass spectrometer and olfactometry detection ports with a flow ratio of 1–2 (0.45 and 0.9 mL/min, respectively) simultaneously. The temperatures of the transfer line, mixing chamber, MS source, MS quadrupole and auxiliary column were 150 °C, 200 °C, 230 °C, 150 °C and 180 °C, respectively. The MS was operated in full-scan mode and the solvent delay time was set at 4.5 min. The methods of GC/GC and GC/MS/MS are described in the supporting information.

2.5. Odorant confirmation

To evaluate and confirm identified odorants' contributions to the whole odor profile, odor activity value (OAV) evaluation and reconstitution tests were adopted. The OAV was calculated by dividing the odorant's concentration by the corresponding average OTC; an odorant with an OAV more than one is considered to be responsible for odor, and a greater OAV means more contribution to the whole odor profile (Benkwitz et al., 2012). Reconstitution tests were completed to evaluate the whole odor types and intensities by reconstituting all identified odorants in their actual concentrations in source water from the TY River, then the odor characteristics of the reconstituted and practical samples were evaluated and compared by spider web diagrams (Benkwitz et al., 2012; Guo et al., 2019a). The odor contribution ratios of the reconstituted samples to the odor characteristics of practical source water from the TY River were calculated by dividing the odor intensity of the reconstituted sample by that of the practical source water (Guo et al., 2019a). Considering the influence of water factors on odor type and intensity, finished water without odor from the water purification plant adopting the TY River as raw water was employed as the water matrix for the reconstitution test. Table S1 indicates the odor characteristics of identified odorants in the TY River.

3. Results and discussion

3.1. Odor characteristics of TY river

The odor types and intensities of source waters in the TY River are shown in Fig. 1. Six odor classes were detected, including earthy, marshy, fishy, woody, medicinal and chemical odors with intensities of 3.3–6.6, 5.7–6.8, 2.6–5.3, 4.2–5, 4.2–4.5 and 4.6–5, respectively, indicating that the odor characteristics were complicated. The earthy and fishy odors showed obvious seasonal change tendencies since high odor intensities occurred in summer and autumn, while the variations of woody, marshy, medicinal and chemical odor intensities were not obvious, which was similar to findings in previous studies on odors and odorants (Wang et al., 2019b; Guo et al., 2020). Usually, earthy and fishy odors are associated with microbial metabolism and bacterial activity, and the

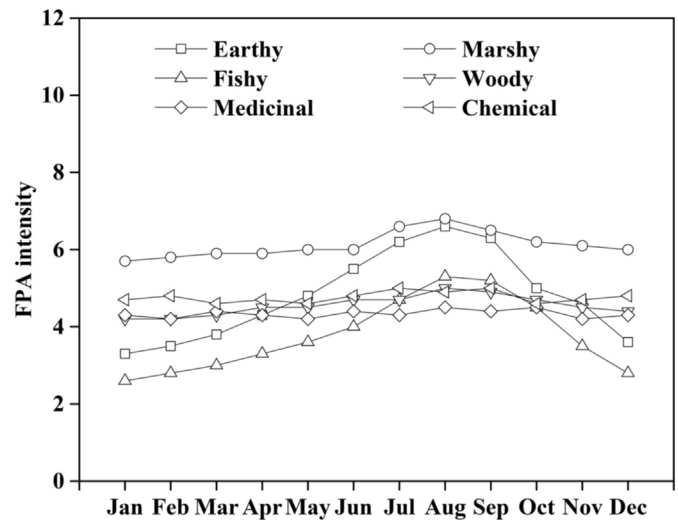

Fig. 1. Odor characteristics of TY River from January to December 2019.

high temperature and abundant sunlight in summer and autumn seasons are beneficial for microbial activities (Sun et al., 2013). Medicinal, chemical, marshy and woody odors are mainly related to exogenous pollution, which is not much influenced by seasonal changes (Agus et al., 2012; Guo et al., 2020). This will be further elucidated in the next section.

3.2. Odorants identified in TY river

The sensory evaluation results for source water in the TY River displayed that earthy, marshy, fishy, woody, chemical and medicinal odors with intensities of 6.6, 6.8, 5.3, 5, 4.9, 4.5, respectively, were associated with the water sample of August. It is worth emphasizing that additional odor peaks were detected by GC/O. As Table 1 and Fig. 2 show, thirty olfactory odor peaks, including six marshy peaks, two earthy peaks, five fishy peaks, five woody peaks, six medicinal peaks and six chemical peaks, were detected. By using GC/GC to search for the odor-causing compounds corresponding to olfactory peaks detected by GC/O, (Fig. S1), thirty-three odor compounds in the TY River were screened and identified by comparison with standard substances (Table 1), which corresponded to the thirty olfactory odor peaks. Furthermore, the olfactory odor peaks were also discovered in source water samples from the other tested months, as shown in Table S2.

As shown in Table 1, relevant odorants for the marshy peaks 1, 3, 10, 16 and 20 were identified as DMDS, propyl sulfide, DMTS, dibutyl sulfide and indole, and marshy peak 27 was related to 3-methylindole and amyl sulfide. A total of seven compounds with marshy odors were identified in source waters of the TY River. Usually these compounds have been associated with marshy/rancid/swampy odors in water matrixes (Wang et al., 2019b). DMDS, propyl sulfide, DMTS, dibutyl sulfide, 3-methylindole and amyl sulfide had been discovered in previous odor studies across China (Guo et al., 2015), especially DMTS, which was found to be an important compound with septic odor in the Wuxi odor event (Yu et al., 2009). The detected marshy odor compounds were related to domestic or industrial sewage, agricultural operations, etc. (Schiffman et al., 2001; Watson, 2004; Liu et al., 2012; Lu et al., 2013), indicating that the source waters in the TY River were easily contaminated.

The chemical odors for olfactory peaks No. 4, 6, 8, 15, 25 were identified as ethylbenzene, p-xylene, isopropylbenzene, 1,4-dichlorobenzene, and naphthalene, while No. 11 was recognized

Table 1
Summary of characteristic olfactometry peaks and identified odorants in source waters of TY River.

Peak No.	Olfactometry peaks	Compounds	RT (min)	RI	Odor description
1	Marshy	DMDS	4.06–4.12	722	Marshy, swampy
2	Woody	Hexanal	4.62–4.69	806	Grassy, almond
3	Marshy	Propyl sulfide	6.45–6.52	868	Marshy, swampy
4	Chemical	Ethylbenzene	6.88–6.96	893	Chemical, plastic
5	Fishy	Heptanal	7.26–7.32	905	Fishy, oily
6	Chemical	p-Xylene	7.56–7.63	907	Chemical, solvent
7	Fishy	2,4-Heptadienal	8.00–8.08	921	Fishy, oily
8	Chemical	Isopropylbenzene	8.28–8.33	928	Chemical, plastic
9	Medicinal	2-Chlorophenol	8.68–8.73	960	Medicinal
10	Marshy	DMTS	9.06–9.12	972	Marshy, swampy
11	Chemical	4-Chlorotoluene	9.50–9.56	974	Chemical, solvent
		3-Methylstyrene	9.68–9.73	993	Chemical, medicinal
12	Fishy	2-Octenal	10.16–10.22	1013	Fishy, oily
13	Medicinal	3-Methylphenol	10.50–10.58	1014	Medicinal
14	Fishy	2,4-Octadienal	10.80–10.86	1021	Fishy, oily
15	Chemical	1,4-Dichlorobenzene	11.32–11.38	1040	Chemical, solvent
16	Marshy	Dibutyl sulfide	12.06–12.12	1067	Marshy, swampy
17	Woody	Linalool	12.48–12.56	1082	Fragrant, orange
18	Medicinal	2,6-Dimethylphenol	13.69–13.73	1127	Medicinal
19	Earthy	2-MIB	14.59–14.66	1161	Musty
20	Marshy	Indole	14.92–14.99	1174	Stinky, foul smell
21	Woody	β-Cyclocitral	15.28–15.33	1204	Fragrant, orange
22	Fishy	2,4-Decadienal	15.60–15.66	1220	Fishy, oily
23	Medicinal	4-Bromophenol	16.00–16.09	1221	Medicinal
24	Woody	Geraniol	16.32–16.37	1225	Fragrant, mushroom
		Nerol	16.33–16.39	1226	Fragrant, woody
25	Chemical	Naphthalene	16.60–16.68	1231	Chemical, solvent
26	Medicinal	2,6-Dichlorophenol	16.90–16.98	1261	Medicinal
27	Marshy	3-Methylindole	17.13–17.19	1264	Stinky, foul smell
		Amyl sulfide	17.28–17.33	1266	Marshy, swampy
28	Medicinal	2-Nitrophenol	18.05–18.11	1297	Medicinal
29	Earthy	Geosmin	20.22–20.29	1386	Earthy
30	Woody	Vanillin	20.90–20.98	1392	Fragrant, orange

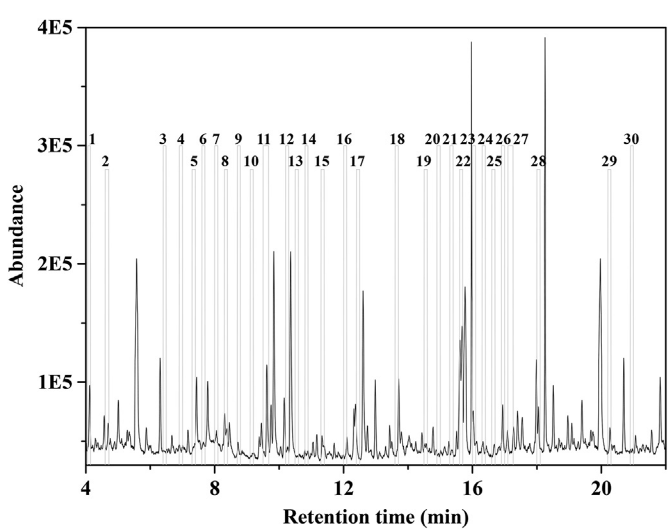

Fig. 2. Olfactogram overlaid on a GC/O chromatogram for source water of August in full-scan mode, pre-concentration method: LLE, pre-concentration factor: 1000, histogram: olfactory peaks, a total of thirty olfactory peaks were detected.

as 4-chlorotoluene and 3-methylstyrene. Usually benzenes are deemed as important chemical products, and mainly come from coking, gasoline and petroleum industries (Botalova et al., 2009).

Woody olfactory peaks No. 2, 17, 21, 24, 30 were screened as hexanal, linalool, β-cyclocitral, geraniol, nerol, and vanillin, respectively. These compounds were mainly associated with industrial solvents or additives for perfumes or industrial wastewater discharge (Elsharif and Buettner, 2018).

Olfactory peaks No. 9, 13, 18, 23, 26 and 28 with medicinal odors were identified as 2-chlorophenol, 3-methylphenol, 2,6-dimethylphenol, 4-bromophenol, 2,6-dichlorophenol and 2-nitrophenol. Phenolic odorants with medicinal odors, which are associated with agriculture and industrial businesses, have been previously detected in sources for drinking water supplies and wastewater (Davi and Gnudi, 1999; Agus et al., 2012).

The detection of so many compounds, such as sulfides, indoles, phenols, benzenes, etc., suggested that the micro-polluted water matrix of the TY River suffered from exogenous pollution. This river is located in a highly developed agricultural, urbanized and industrialized area in eastern Jiangsu Province of China. Besides providing the source water for drinking water, the river also is used for navigation, irrigation and flood drainage. Therefore, it is easily contaminated by industrial and man-made pollution, and suspension of the water supply has occurred due to discharge of wastewater and waste slag containing volatile organic compounds in the past several years (Wang et al., 2010, 2019c; Gao et al., 2019). The marshy, chemical, medicinal and woody odor occurrence might be related to exogenous contamination, indicating that further protection should be required in the future.

The olfactory peaks No. 19 and 29 with earthy odors were identified as 2-MIB and geosmin. These two compounds are the most commonly occurring musty/earthy odorants in water worldwide (Lin et al., 2002; Watson, 2004; Li et al., 2019), and are usually correlated with the proliferation of cyanobacteria and actinomycetes (Li et al., 2012; Sun et al., 2013).

Other olfactory peaks No. 5, 7, 12, 14, 22 with fishy odors were identified as heptanal, 2,4-heptadienal, 2-octenal, 2,4-octadienal, 2,4-decadienal, respectively, which have been reported to be associated with fishy odor events (Li et al., 2016; Liu et al., 2019). These aldehyde compounds are mainly associated with algal metabolites (Watson, 2004; Zhang et al., 2013). Occurrences of the above compounds might correlate with the microalgae blooms that occur every year, especially in summer and autumn seasons (Wang et al., 2010). The various odorants associated with exogenous pollution and microbial metabolism suggested the complexity of river-type source waters, which need more attention and protection in the future.

3.3. Evaluation of identified odorants' contributions

Table S2 lists the identified odorants in source waters of the TY River from January to December 2019. The detection ratios of earthy, marshy, fishy, woody, medicinal, chemical odor peaks and corresponding compounds were 100% during all of 2019, suggesting the existence of serious odor problems in the TY River. To evaluate identified odorants' contributions to odors in the TY River, a total of thirty-three identified compounds were analyzed quantitatively, and their OAVs were evaluated. As shown in Fig. 3, the identified compounds were sorted into earthy/musty odorants (2-MIB, geosmin), marshy odorants (DMDS, propyl sulfide, DMTS, dibutyl sulfide, indole, 3-methylindole, amyl sulfide), fishy odorants (heptanal, 2,4-heptadienal, 2-octenal, 2,4-octadienal, 2,4-decadienal), woody odorants (hexanal, linalool, β-cyclocitral, geraniol, nerol, vanillin), medicinal odorants (2-chlorophenol, 3-methylphenol, 2,6-dimethylphenol, 4-bromophenol, 2,6-dichlorophenol, 2-nitrophenol) and chemical odorants (ethylbenzene, p-xylene, isopropylbenzene, 1,4-dichlorobenzene, naphthalene, 4-chlorotoluene, 3-methylstyrene) based on their smell features and material structures. Among odorants identified in TY River, the concentrations of 2-MIB and geosmin with typical earthy odor were 28–39 ng/L and 8–17 ng/L, respectively. However, the average OTC of 2-MIB and geosmin are 10 and 4 ng/L (Watson,

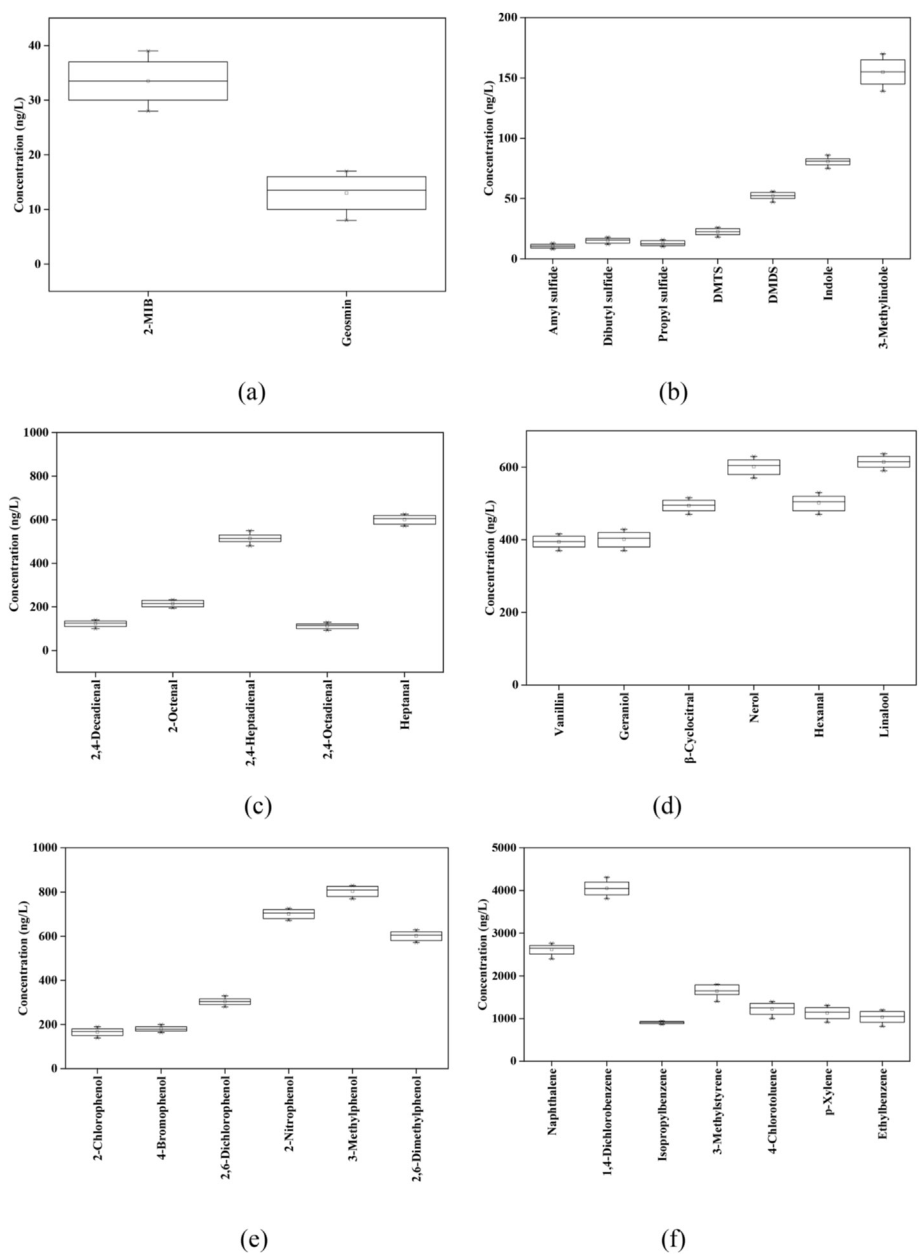

Fig. 3. Concentrations of detected odorants in source waters of TY River, (a) earthy odorants, (b) marshy odorants, (c) fishy odorants, (d) woody odorants, (e) medicinal odorants, (f) chemical odorants.

2004), so that the concentrations of the above two compounds clearly exceeded the corresponding OTCs. The concentrations of marshy odorants, including DMDS, propyl sulfide, DMTS, dibutyl sulfide, indole, 3-methylindole and amyl sulfide, were 47–56, 10–16, 18–26, 12–18, 75–86, 139–170 and 8–13 ng/L, respectively. The compounds with OAVs greater than one are considered to be important in the corresponding odor profiles on the basis of their OAV rank (Benkwitz et al., 2012; Guo et al., 2016b). Therefore 2-MIB and geosmin should be the key earthy odorants as shown in Fig. 4, while the important marshy odorants would be amyl sulfide, dibutyl sulfide, propyl sulfide, DMTS, DMDS and indole. The results appear reasonable since these compounds have been detected in odor incidents involving earthy, musty, swampy, rancid and septic odors (Suffet et al., 2004; Watson, 2004; Wang et al., 2019b). It is worth noting that the OTCs of some odorants were not consistent with values described in previous literature (Gemert, 2011). For consistency, the OTCs used for calculating OAVs in this study were practically determined according to the 3-AFC method (ASTM, 1997), which avoided deviations due to differences in testing methods. Concentrations of fishy odorants, including heptanal, 2,4-heptadienal, 2-octenal, 2,4-octadienal, 2,4-decadienal, were 571–626, 480–550, 195–233, 92–130, 100–140 ng/L; 2,4-decadienal and 2-octenal, with OAVs higher than one, should be the major fishy odor-causing compounds.

Hexanal, linalool, β-cyclocitral, geraniol, nerol, and vanillin with woody odor were detected with concentrations of 470–530, 590–637, 470–516, 370–429, 570–630 and 370–416 ng/L, respectively. Vanillin, geraniol, and β-cyclocitral with OAVs greater than one should be the important woody odorants.

Concentrations of 2-chlorophenol, 3-methylphenol, 2,6-dimethylphenol, 4-bromophenol, 2,6-dichlorophenol and 2-nitrophenol with medicinal odor were 139–190, 769–830, 571–629, 163–200, 280–330, 672–726 ng/L, while concentrations of chemical odor compounds, including ethylbenzene, p-xylene, isopropylbenzene, 1,4-dichlorobenzene, naphthalene, 4-chlorotoluene and 3-methylstyrene, were 816–1200, 912–1311, 860–939, 3811–4311, 2399–2766, 999–1399 and 1400–1800 ng/L. According to the calculation and ranking of OAVs, 2-chlorophenol, 4-bromophenol, 2,6-dichlorophenol and naphthalene, 1,4-dichlorobenzene should be the major medicinal and chemical odor compounds, respectively. However, because synergistic effects of odors could exist among odorants, and the odor types and intensities of odorant mixtures might be influenced (Watson, 2004; Guo et al., 2019a), it is necessary to verify the identified odorants by reconstitution tests.

3.4. Confirmation of identified odorants in TY river

As Fig. 5 shows, the odor types and intensities of source water and reconstituted water samples were compared. The odor intensities of earthy, marshy, fishy, woody, medicinal and chemical odors in the reconstituted water sample could explain 95, 93, 92, 90, 89 and 88% of the corresponding odor characteristics in source water of the TY River. Thus, there is no doubt that almost all the odorants in TY River were screened and identified in this study. Specifically, earthy odor is mainly related to geosmin and 2-MIB, marshy odor is caused by sulfides, and fishy odor is caused by aldehydes. On the one hand, the finding of 89% and 88% of the medicinal and chemical odors' contributions in the reconstituted sample indicated that the primary compounds with medicinal and chemical odors were identified and verified. On the other hand, it suggested the importance of the identified medicinal and chemical odorants, especially compounds with OAVs higher than one, which was also consistent with the evaluation of OAVs (Fig. 4). However, it is worth highlighting that even though the thirty-three identified compounds were all included in the reconstituted water samples, the odor intensities of source waters could not be 100% explained, suggesting that the odors in the TY River were very complicated and might be affected by other materials. Undetected odor-causing compounds with concentrations under limit of detection might have existed, and other organic matters have been reported to influence odors and odorants (Whelton and Dietrich, 2004; Li et al., 2020).

In this study, a large number of compounds, including amyl sulfide, dibutyl sulfide, propyl sulfide, dimethyl disulfide, dimethyl trisulfide, indole, 2-chlorophenol, 4-bromophenol, 2,6-dichlorophenol, naphthalene, 1,4-dichlorobenzene, etc., were identified in the TY River. Although their odor characteristics were the main focus here, it should be noted that toxicity was not discussed in this study. Even though the concentrations of the investigated compounds were lower than the reported toxic levels (Ayanda et al., 2016; Ben-Youssef et al., 2009; Du et al., 2018; Jin

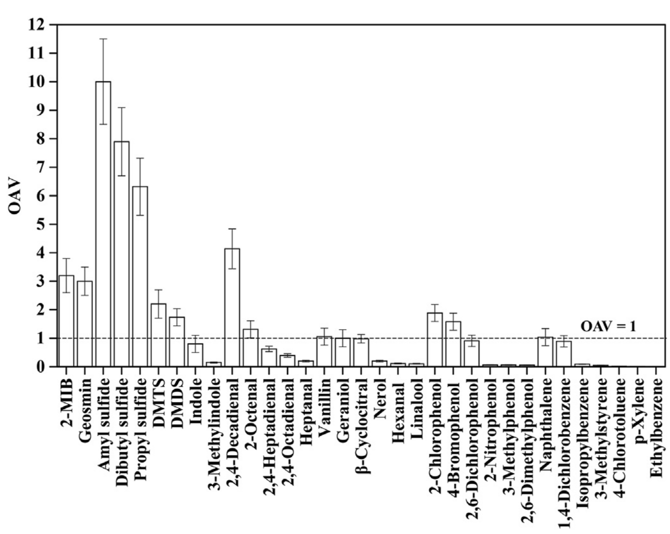

Fig. 4. OAVs rank of identified odorants in source waters of TY River.

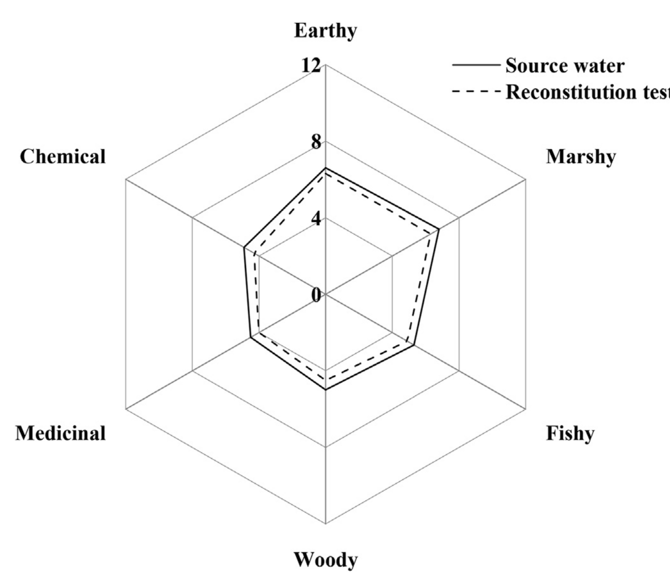

Fig. 5. Odor characteristics of source water taken at August 2019 and corresponding reconstituted sample in odorless water.

et al., 2020), combined toxicity effects should not be ignored and need to be further explored in future study.

4. Conclusions

In this paper, the odors and odor-causing compounds in micro-polluted source water from the TY River were studied comprehensively. Earthy, marshy, fishy, woody, medicinal and chemical odors were detected. Thirty olfactory odor peaks were identified by GC/O, and correspondingly thirty-three odorants were identified successfully with the help of GC/GC. By means of OAV evaluation and reconstitution of the identified odorants, 95, 93, 92, 90, 89 and 88% of earthy, marshy, fishy, woody, medicinal and chemical odor characteristics in source waters could be explained. 2-MIB and geosmin were associated with earthy odor, while amyl sulfide, dibutyl sulfide, propyl sulfide, DMTS, DMDS and indole were involved with marshy odor. The remarkable fishy and woody odor compounds were 2,4-decadienal, 2-octenal and vanillin, and geraniol, β-cyclocitral, respectively. Medicinal and chemical odors were mainly caused by 2-chlorophenol, 4-bromophenol, 2,6-dichlorophenol and naphthalene, and 1,4-dichlorobenzene, respectively. This is the first study to systematically evaluate complex odors and identify the responsible compounds in a river-type micro-polluted water source, which could offer sufficient understanding and data base for odor management in water enterprises with complicated odor problems.

Credit author statement

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Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.envpol.2020.116373.

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