

Odorant screening and possible origin analysis of odor episodes in one reservoir in northern China

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ABSTRACT

Odorous drinking water problem occurred repeatedly in one city in northern China in recent years. The uniqueness of this odor episode lay in two aspects: (1) the odorous chemicals were quite different from common odorants, such as geosmin and 2-MIB; and (2) it occurred repeatedly in different seasons during a time span of more than 2 years. The screening of odorants was the first and one of the most important steps to address this problem. The field study eliminated the possibility of external pollution and targeted on odorous algal excretion. Odorous water samples were taken at different locations. Headspace solid phase microextraction combined with gas chromatography/mass spectrometry (GC/MS) was employed to identify possible odorants. Algal species were observed under a microscope. The GC/MS results indicated that pyrazines and aldehydes, rather than geosmin and 2-MIB, were the most possible peace breakers. Other odorants, such as ketones and thiols, were also detected at trace level. The planktonic algae were detected in high populations in the reservoir. Diatom was regarded as the most possible source of the odor. Guidelines for odorants removal in water treatment process were made to help the local water company address future odor problem.

Key words | algae, drinking water, odor, screening

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INTRODUCTION

Odor problem is a common nuisance for the water industry, especially for those depending on lakes, reservoirs, or other kinds of impoundments as water source (Young *et al.* 1999; Watson *et al.* 2009; Peter *et al.* 2009). Odorous compounds have very low threshold concentrations of perception ($\mu\text{g/L}$ or even ng/L level). These trace contaminants are recalcitrant to conventional treatment processes. Hence, if not addressed successfully, they will cause complaints and distrust of drinking water quality by the public.

The majority of odorous compounds are microorganism-related (Suffet *et al.* 1996; Ginzburg *et al.* 1998; Watson 2003; Yang *et al.* 2008; Deng *et al.* 2012). In recent years, odor problems have also been haunting China (Zhang *et al.* 2010, 2011b). In May 2007, a severe drinking water pollution incident happened in Lake Taihu, China. The extraordinary strong septic odor was caused by the decay of a heavy algae mat around the water intake, which got into the tap water and

destroyed the well-being of two million residents in Wuxi City, which in turn sparked serious social consequences (Qin *et al.* 2010; Zhang *et al.* 2011a). The odorants were quickly screened and identified as volatile sulfur chemicals, including dimethyl sulfur, dimethyl disulfur, dimethyl trisulfur, etc. This information prompted the development of emergency drinking water treatment technology greatly. During June and July of 2007, another city named Qinhuangdao in North China, which used reservoirs as its water source, suffered from a severe algae bloom and odor incident (Zhang *et al.* 2009). By the end of June, the algae amount in raw water had climbed to over 20 million/L with the dominant genus being *Anabaena* spp. The concentration of geosmin in source water remained at over 1,000 ng/L . The finished water exhibited a strong earthy and musty off-flavor, which rendered the water unusable. According to the profile and concentration of odorant, a total dosage of 80 mg/L of powdered activated carbon

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(PAC) was fed at the water intake and was mixed well to adsorb the odorants. Therefore, when odorous issues occur, it is very important to quickly identify the odorants, find the origins, and develop treatment measures to solve the problem.

Reservoir E is an important water source for H city in northern China. Since this reservoir came into service in the early spring of 2009, odorous source water problems have been recurrent. Odor complaints first appeared in March 2009 with an attendant algae bloom. The situation ceased after a month when the total algae population in raw water declined to below 1.4 million/L. In February 2010, a strong off-flavor was sensed when the total algae population in raw water rose to 25.7 million/L. This odor episode lasted for more than 2 months and ceased at the end of April. However, algae bloomed again in the summer of 2010 and the smell in the finished water lasted for the whole of August. These odor episodes affected hundreds of thousands of residents, especially during the Chinese Lunar New Year holiday in winter. It drew extensive consumer complaints and put great pressure on the local water treatment plant (WTP) that used Reservoir E as its water source, i.e. JH WTP.

The objectives of this study included: (1) to identify the odor compounds in source water that triggered the odor episodes; (2) to screen possible odorants-releasing algae; and (3) to give suggestions of water treatment process optimization in dealing with the odorous events.

MATERIALS AND METHODS

Field sampling

In the preliminary field study, the flavor profile analysis (FPA) was employed to determine the odor group and

intensity of the raw water *in situ*. Samples from five sites, i.e. inlet, main body, outlet of the reservoir, influent, and effluent of the treatment plant, were collected for FPA analysis and odorants identification. Meanwhile, samples collected at the main body of the reservoir were used for algae count. The sampling was performed at a depth of 0.5 m below the surface using 200 mL amber glass vials and sealed with polytetrafluoroethylene (PTFE) septum caps, leaving no headspace to avoid volatilization (*Standard Methods for the Examination of Water and Wastewater 1995*; *Standard Examination Methods for Drinking Water – Collection and Preservation of Water Samples 2006*). The sampling period lasted for about 2 months to study the variation of algae amount and specific sampling dates are shown later in [Figure 2](#).

FPA analysis

The FPA analysis of the samples was conducted according to the standard method (*Standard Methods for the Examination of Water and Wastewater 1995*). All samples were analyzed in a 45 °C water bath using 500 mL Erlenmeyer flasks. Impressions of odor attributes and their intensities were recorded by each panelist. It should be noted that, instead of at least four panel members, we only had two panelists available to perform the analysis at that time. Thus, the method used herein was a simplified FPA. Accordingly, the flavor profile achieved by this panel was an indicator of an FPA result ([Table 1](#)).

Odorants analysis

Reagent water was obtained from a Milli-Q water purification system (Millipore, Molsheim, France). Sodium

Table 1 | Results of flavor profile analysis of water samples

Panelist	Reservoir E			JH WTP	
	Inlet	Main body	Outlet	Influent	Effluent
Odor description indicator	Earthy	Fishy, earthy	Fishy, earthy	Fishy	Chlorinous
FPA intensity indicator					
Panelist A	2	4	2	6	6
Panelist B	4	2	4	6	6
Geometric mean	2.7	2.7	2.7	6	6

chloride (NaCl) was purchased from Sigma–Aldrich and heated at 450 °C for 4 hours before use.

The headspace solid-phase microextraction (SPME) process was carried out on a divinylbenzene/carboxenTM/polydimethylsiloxane stableflexTM (DVB/CAR/PDMS) SPME fiber, which was conditioned at 270 °C for 2 hours in accordance with manufacturer instructions. Two grams of NaCl was added to a 20 mL vial containing a 10 mL sample. The vial was sealed with a silicone-PTFE septum cap and placed in a water bath. The sample was first heated to 65 °C and shaken for 10 min, followed by 25 min headspace extraction at 65 °C. The SPME fiber was desorbed in a Split/Splitless Injector at 280 °C for 3 min.

A Shimadzu GC/MS-QP 2010 Plus system (Shimadzu, Tokyo, Japan) with a 30 m × 0.25 mm i.d. (0.25 μm film thickness) Inert Cap 5 MS/Sil column was applied to analyze possible odorants. The oven temperature was held at 60 °C for 1 min, raised to 250 °C at 15 °C/min, kept at 250 °C for 5 min then raised to 300 °C at 20 °C/min, and kept at 300 °C for 2 min. The carrier gas was helium and kept at 39.7 cm/sec constant flow. The Split/Splitless Injector was held at 280 °C in splitless mode. The transfer-line temperature was 300 °C and the ion trap temperature was 200 °C. Full-scan mass spectra (*m/z* 50–300) were recorded for the identification of analytes.

Algae enumeration

We used an OLYMPUS BX53 Optical Microscope (Olympus, Tokyo, Japan), an HL-JS Plankton Counting Chamber (Wuhan Hengling Technology Ltd, Wuhan, China), and a 1,000 mL funnel (Zhengzhou Xinghua Glasswork, Zhengzhou, China) for the purpose of algae cell counting.

Fifteen mL of Lugol's solution was added to the 1,000 mL sample, which was later transferred into the funnel for 24-hour sedimentation. After discarding the supernate, 30 mL remains were left for counting. We then added 0.1 mL of the remaining sample into the counting chamber. Having settled for several minutes, the cells were counted in keeping with the standard methods (*Standard Methods for the Examination of Water and Wastewater* 1995; Zhou 2011). Pictures of algae were taken by software connected to the microscope.

RESULTS AND DISCUSSION

FPA analysis

The odors commonly observed in drinking water can be categorized into eight groups, as described in the drinking water taste and odor wheel (Suffet *et al.* 1999). FPA was applied to classify odor profile and evaluate odor strength. Samples of different locations were examined and the results are listed in Table 1.

The major odors perceived were fishy and earthy, which coincided with consumers' complaints. As elucidated in the table, three samples of the reservoir had a mean odor intensity of FPA 2.7. It is worth noting that the sample of reservoir inlet was sensed as earthy while the sample of main body and outlet gave off a mixed odor of earthy and fishy, which indicated a contribution of algae activity in the reservoir in the emergence of the fishy odor. The influent of the WTP had a clear fishy smell of FPA 6. This was mainly due to the release of the intracellular odor compounds, which was the consequence of the rupture of algae cells caused by feeding potassium permanganate as a pre-oxidation process. Chlorinous effluent was the result of chlorine disinfection, with WTP effluent free chlorine residual being 0.5 mg/L.

The FPA study revealed important information about the raw water, and evidence pointed to algae metabolite as the highly suspicious cause of the off-flavor.

Identification of odorants in the reservoir

Figure 1 shows the chromatograms of the head space SPME-gas chromatography/mass spectrometry (GC/MS) analysis of different locations of the reservoir.

We detected significantly more odorants in the sample taken from the main body of the reservoir than that from the reservoir inlet, which implied a dominant role of algae activities in the production and accumulation of odorants. An in-depth analysis into the mass spectrum revealed possible compounds in the raw water, as shown in Tables 2–6.

Many possible odorants, i.e. pyrazines, β-ionone, β-cyclocitral, thiols, and aldehydes showed up in the analysis.

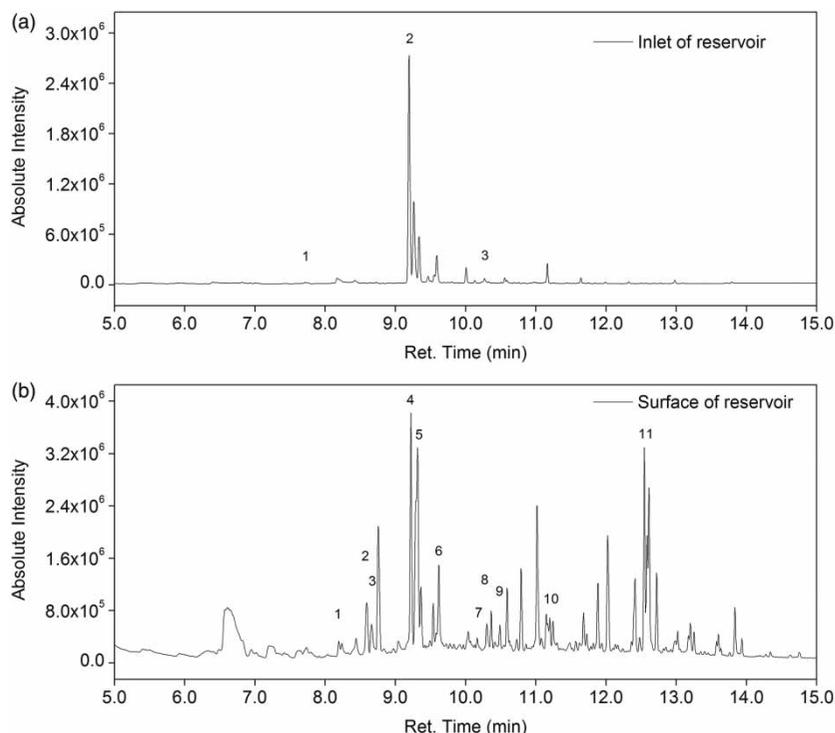


Figure 1 | Gas chromatography/mass spectrometry (GC/MS) chromatograms of the non-filtered water samples. (a) 0.5 m below the surface of the inlet of Reservoir E (1: 1-propene-1-thiol; 2: 3-tert-butyl-4-hydroxyanisole; 3: decanal). (b) 0.5 m below the surface of the main body of Reservoir E (1: hexanal; 2: cis-4-heptenal; 3: heptanal; 4: 3-*t*-butyl-4-hydroxyanisole; 5: 3-(4-morpholino)propionitrile; 6: trans,trans-2,4-heptadienal; 7: IPMP; 8: decanal; 9: IBMP; 10: trans,trans-2,4-decadienal; 11: 4-(2-aminoethyl)morpholine).

Table 2 | Possible compounds in the non-filtered water sample at 0.5 m below the surface of the inlet of Reservoir E

Compound name	Molecular formula	CAS number	Odor	Odor threshold
1 Decanal	C ₁₀ H ₂₀ O	112-31-2	Green wood ^a	2 µg/L ^b
2 3-pentanone, 2,2,4,4-tetramethyl-	C ₉ H ₁₈ O	815-24-7		
3 1-propene-1-thiol	C ₃ H ₆ S	925-89-3	Rotten, durian ^c	
4 2,2,4-trimethyl-1,3-pentanediol diisobutyrate	C ₁₆ H ₃₀ O ₄	6846-50-0		0.13 µg/L ^d
5 trans-2-dodecen-1-ol	C ₁₂ H ₂₄ O	69064-37-5		
6 3-tert-butyl-4-hydroxyanisole	C ₁₁ H ₁₆ O ₂	121-00-6		
7 hexanedioic acid, bis(2-methylpropyl) ester	C ₁₄ H ₂₆ O ₄	141-04-8		
8 3,5-di-tert-butyl-4-hydroxybenzaldehyde	C ₁₅ H ₂₂ O ₂	1620-98-0		
9 dibutyl phthalate	C ₁₆ H ₂₂ O ₄	84-74-2		

^aKotseridis & Baumes (2000); ^bButtery *et al.* (1988); ^cLi *et al.* (2012); ^dCain *et al.* (2005).

Nonetheless, two commonly found earthy/musty compounds, geosmin and 2-MIB, were not detectable in this case. Among the species of off-flavor compounds observed, 2-isopropyl-3-methoxypyrazine (IPMP), 2-isobutyl-3-methoxypyrazine (IBMP), and aldehydes seemed to be the most possible contaminants for this odor episode according to their odor

property and low odor threshold concentrations. However, other chemicals, such as 6-methyl-5-hepten-2-one and β -ionone, as well as thiols and indole, were also highly suspicious.

These chemicals were also detected in other lakes and reservoirs and were identified as algal-related odorants.

Table 3 | Possible compounds in the non-filtered water sample at 0.5 m below the surface of Reservoir E

	Compound name	Molecular formula	CAS number	Odor	Odor threshold
1	dimethyl disulfide	C ₂ H ₆ S ₂	624-92-0	Decaying vegetation ^a	<4 µg/L ^b
2	dimethyl trisulfide	C ₂ H ₆ S ₃	3658-80-8	Swampy ^a	10 ng/L ^b
3	cis-3-hexenyl acetate	C ₈ H ₁₄ O ₂	3681-71-8	Grassy ^c	1.5 µg/L ^d
4	trans,trans-2,4-heptadienal	C ₇ H ₁₀ O	4313-03-5	Fishy, rancid ^e	2.5–5 µg/L ^c
5	cis-4-heptenal	C ₇ H ₁₂ O	6728-31-0	Oily, slight citrus ^f	0.8 µg/L ^g
6	heptanal	C ₇ H ₁₄ O	111-71-7	Rancid oil, fruity ^h	3 µg/L ^b
7	2,3-benzopyrrole (indole)	C ₈ H ₇ N	120-72-9	Septic ⁱ	300 µg/L ^j
8	2-isopropyl-3-methoxypyrazine	C ₈ H ₁₂ N ₂ O	25773-40-4	Earthy, musty, potato bin ^k	2 ng/L ^k
9	6-methyl-5-hepten-2-one	C ₈ H ₁₄ O	110-93-0	Woody ^l	50 µg/L ^g
10	hexanal	C ₆ H ₁₂ O	66-25-1	Fishy, earthy, fruity ^h	4.5 µg/L ^b
11	trans-2, cis-6-nonadienal	C ₉ H ₁₄ O	557-48-2	Cucumber ^m	4 ng/L ⁿ
12	2-isobutyl-3-methoxypyrazine	C ₉ H ₁₄ N ₂ O	24683-00-9	Earthy, musty, bell pepper ^k	2 ng/L ^j
13	β-cyclocitral	C ₁₀ H ₁₆ O	432-25-7	Wooden ^o	3 µg/L ⁿ
14	trans, trans-2,4-decadienal	C ₁₀ H ₁₆ O	25152-84-5	Fishy ^e	70 ng/L ^p
15	3- <i>t</i> -butyl-4-hydroxyanisole	C ₁₁ H ₁₆ O ₂	121-00-6		
16	β-ionone	C ₁₃ H ₂₀ O	79-77-6	Flowery, violet ^b	7 ng/L ^b
17	methyl laurate	C ₁₃ H ₂₆ O ₂	111-82-0		
18	4-methyldodecane	C ₁₃ H ₂₈	6117-97-1		
19	2,4-di- <i>tert</i> -butylphenol	C ₁₄ H ₂₂ O	96-76-4		
20	2,6-di- <i>tert</i> -butylphenol	C ₁₄ H ₂₂ O	128-39-2		
21	3,5-di- <i>tert</i> -butylphenol	C ₁₄ H ₂₂ O	1138-52-9		
22	diisobutyl phthalate	C ₁₆ H ₂₂ O ₄	84-69-5		

^aSuffet *et al.* (1999); ^bCotsaris *et al.* (1995); ^cYoung & Suffet (1999); ^dKhiari *et al.* (1995); ^eWatson *et al.* (2001); ^fRashash *et al.* (1997); ^gLeffingwell & Leffingwell (1991); ^hFabrellas *et al.* (2004); ⁱKhiari *et al.* (1997); ^jVan Gemert (2006); ^kMallevalle & Suffet (1987); ^lSympoura *et al.* (2009); ^mDevos (1990); ⁿRashash *et al.* (1996); ^oZhang *et al.* (2011a); ^pButtery *et al.* (1971).

Table 4 | Possible compounds in the non-filtered water sample at 0.5 m below the surface of the outlet of Reservoir E

	Compound name	Molecular formula	CAS number	Odor	Odor threshold
1	decanal	C ₁₀ H ₂₀ O	112-31-2	Green wood ^a	2 µg/L ^b
2	3,5-dimethyl-4-heptanone	C ₉ H ₁₈ O	19549-84-9		
3	1-dodecen-3-ol	C ₁₂ H ₂₄ O	4048-42-4		
4	2-isobutyl-3-methoxypyrazine	C ₉ H ₁₄ N ₂ O	24683-00-9	Earthy, musty, bell pepper ^c	2 ng/L ^d
5	1-12 aldehyde	C ₁₂ H ₂₄ O	112-54-9		
6	trans-2-dodecen-1-ol	C ₁₂ H ₂₄ O	69064-37-5		
7	dimethyl disulfide	C ₂ H ₆ S ₂	624-92-0	Decaying vegetation ^e	<4 µg/L ^f
8	trans, trans-2,4-decadienal	C ₁₀ H ₁₆ O	25152-84-5	Fishy ^g	70 ng/L ^h
9	3- <i>t</i> -butyl-4-hydroxyanisole	C ₁₁ H ₁₆ O ₂	121-00-6		
10	heptanal	C ₇ H ₁₄ O	111-71-7	Rancid oil, fruity ⁱ	3 µg/L ^f
11	1-tridecene	C ₁₃ H ₂₆ O	2437-56-1		

^aKotseridis & Baumes (2000); ^bButtery *et al.* (1988); ^cMallevalle & Suffet (1987); ^dVan Gemert (2006); ^eSuffet *et al.* (1999); ^fCotsaris *et al.* (1995); ^gWatson *et al.* (2001); ^hButtery *et al.* (1971); ⁱFabrellas *et al.* (2004).

Table 5 | Possible compounds in the non-filtered water sample of the influent of JH water treatment plant

	Compound name	Molecular formula	CAS number	Odor	Odor threshold
1	trans,trans-2,4-heptadienal	C ₇ H ₁₀ O	4313-03-5	Fishy, rancid ^a	2.5–5 µg/L ^b
2	2-isopropyl-3-methoxypyrazine	C ₈ H ₁₂ N ₂ O	25773-40-4	Earthy, musty, potato bin ^c	2 ng/L ^c
3	2-isobutyl-3-methoxypyrazine	C ₉ H ₁₄ N ₂ O	24683-00-9	Earthy, musty, bell pepper ^c	2 ng/L ^d
4	3-t-butyl-4-hydroxyanisole	C ₁₁ H ₁₆ O ₂	121-00-6		
5	6-methyl-5-hepten-2-one	C ₈ H ₁₄ O	110-93-0	Woody ^e	50 µg/L ^f
6	trans, trans-2,4-decadienal	C ₁₀ H ₁₆ O	25152-84-5	Fishy ^a	70 ng/L ^g
7	heptanal	C ₇ H ₁₄ O	111-71-7	Rancid oil, fruity ^h	3 µg/L ⁱ
8	1-tridecene	C ₁₃ H ₂₆ O	2437-56-1		
9	methyl laurate	C ₁₃ H ₂₆ O ₂	111-82-0		

^aWatson *et al.* (2001); ^bYoung & Suffet (1999); ^cMallevalle & Suffet (1987); ^dVan Gemert (2006); ^eSympoura *et al.* (2009); ^fLeffingwell & Leffingwell (1991); ^gButtery *et al.* (1971); ^hFabrellas *et al.* (2004); ⁱCotsaris *et al.* (1995).

Table 6 | Possible compounds in the non-filtered water sample of the effluent of JH water treatment plant

	Compound name	Molecular formula	CAS number	Odor	Odor threshold
1	trans,trans-2,4-heptadienal	C ₇ H ₁₀ O	4313-03-5	Fishy, rancid ^a	2.5–5 µg/L ^b
2	2-isopropyl-3-methoxypyrazine	C ₈ H ₁₂ N ₂ O	25773-40-4	Earthy, musty, potato bin ^c	2 ng/L ^c
3	2-isobutyl-3-methoxypyrazine	C ₉ H ₁₄ N ₂ O	24683-00-9	Earthy, musty, bell pepper ^c	2 ng/L ^d
4	3-t-butyl-4-hydroxyanisole	C ₁₁ H ₁₆ O ₂	121-00-6		
5	6-methyl-5-hepten-2-one	C ₈ H ₁₄ O	110-93-0	Woody ^e	50 µg/L ^f
6	trans, trans-2,4-decadienal	C ₁₀ H ₁₆ O	25152-84-5	Fishy ^a	70 ng/L ^g
7	heptanal	C ₇ H ₁₄ O	111-71-7	Rancid oil, fruity ^h	3 µg/L ⁱ
8	4-methyldodecane	C ₁₃ H ₂₈	6117-97-1		
9	methyl laurate	C ₁₃ H ₂₆ O ₂	111-82-0		

^aWatson *et al.* (2001); ^bYoung & Suffet (1999); ^cMallevalle & Suffet (1987); ^dVan Gemert (2006); ^eSympoura *et al.* (2009); ^fLeffingwell & Leffingwell (1991); ^gButtery *et al.* (1971); ^hFabrellas *et al.* (2004); ⁱCotsaris *et al.* (1995).

Peter *et al.* (2009) reported the existence of IPMP, IBMP, β-ionone, and β-cyclocitral in Lake Zurich, Lake Greifensee, and Lake Lucerne. Hexanal, decanal, β-cyclocitral, and β-ionone were detected in a eutrophic shallow lake (Jüttner 1984). Yano *et al.* (1988) found that trans,trans-2,4-heptadienal and trans,cis-2,4-heptadienal were the reigning off-flavor compounds in a water bloom episode. Trans,trans-2,4-decadienal was also a potent odorant excreted by algae during their metabolic activities (Watson & Satchwill 2003). Cotsaris *et al.* (1995) summarized that alkenes, saturated and unsaturated aliphatic alcohols, aldehydes, ketones, sulfides, and pyrazines were the main odorants produced by algae.

However, the conformation of odorants screening still needs more evidence from the next odor episode since the

odorants vary greatly with season and location. In this research, we collected the samples in early autumn. In general, microorganism activity reaches a climax in summer and early autumn and ceases gradually when the temperature decreases. Yet, as mentioned in the introduction section, two out of the three odor episodes happened in winter. The literature suggested that certain algae species could survive the ice-covered lake and render the water body odorous (Wiedner & Nixdorf 1998; Watson *et al.* 2001). We are still waiting for the next odor episode in winter to testify our results.

Odorant treatment measures for local WTP

Comprehensive measures were established according to lab test and literature review. For the off-flavor compounds

detected, pyrazines have been reported to be effectively adsorbed by activated carbon (Liang *et al.* 2005; An *et al.* 2012). On the other hand, oxidation is a feasible way for the elimination of the odorants of interest. Strong oxidants, such as chlorine, were able to oxidize heptanal and trans-2,cis-6-nonadienal (Zhang *et al.* 2012) while ultraviolet/H₂O₂ could mitigate off-flavors caused by trans,trans-2,4-heptadienal, trans,trans-2,4-decadienal and trans-2,cis-6-nonadienal (Jo 2008).

Thus, a comprehensive treatment measure was developed for the local water company. Potassium permanganate of 0.5–1 mg/L was applied in the water intake to remove the reductive odorous chemicals, including volatile sulfur compounds, aldehydes, and ketones. More importantly, the pre-oxidation will destabilize the algae and natural organic matter and enhance coagulation. PAC of 5–20 mg/L was fed at the influent of the WTP to adsorb residual odorants, such as pyrazines. The PAC also acts as a quenching reagent for excessive potassium permanganate to guarantee the water quality. The comprehensive measure was efficient, as the finished water was odorless after treatment.

Screening of odor-rendering algae species

Figure 2 shows the variation of total algae amount and composing genera in the studied period.

As shown in Figure 2, the total algae amount almost remained above 8×10^6 /L during the whole sampling period and green algae was the major genus in the community.

Microscopic analysis revealed more details about the algae species in the raw water. Figure 3 shows specific algae

species detected. The dominant species of respective genus are *Chlorella* and *Westella* of green algae, and *Cyclotella* of diatom. *Microcystis* and *Merismopedia* of Cyanophyta were also observed in small amounts.

The algae species above have been reported to be related with odorants production in a water body. Unsaturated aldehydes, such as trans,trans-2,4-heptadienal, trans-2,cis-6-nonadienal, and trans,trans-2,4-decadienal, were reported to derive from polyunsaturated fatty acids (Wendel & Jüttner 1996; Qiang *et al.* 1997; Miralto *et al.* 1999; Müller-Navarra *et al.* 2000). Miralto and his colleagues found that diatom was able to synthesize trans,trans-2,4-decadienal in the aim of interrupting the proliferative activities of the grazers (Miralto *et al.* 1999). *Microcystis* proved to be a major source of 6-methyl-5-hepten-2-one (Jones & Korth 1995). A correlation between β -cyclocitral, β -ionone, and *Microcystis* was also found (Jüttner *et al.* 1986; Jones & Korth 1995; Li *et al.* 2005; Chen *et al.* 2010). Hexanal and decanal were associated with diatom and green algae in an early study (Jalliffier-Merlon *et al.* 1991).

The dominant perceptible odors in the episodes were described as fishy and earthy, and the major odorants responsible for the off-flavor were aldehydes and pyrazines. A substantial amount of literature reports diatom's production of aldehydes (Pohnert *et al.* 2002; Ianora *et al.* 2003; Caldwell *et al.* 2004; Casotti *et al.* 2005). Among the detected aldehydes, trans,trans-2,4-decadienal and trans,trans-2,4-heptadienal were confirmed to be important chemicals in grazer inhibition activity of diatom (D'Ippolito *et al.* 2002; Adolph *et al.* 2003; Ceballos & Ianora 2003; Taylor *et al.* 2007). Meanwhile, evidence shows that diatom has advantages over other algae under low-temperature conditions (Wiedner & Nixdorf 1998), which probably explains the repeated odor episodes in winter. Hence, diatom was regarded to be the most possible source of this off-flavor episode. However, algae species that could produce pyrazines were not detected in the study.

It should be noted that benthic algae were not investigated due to sampling limitations. It was well known that benthic algae were capable of producing off-flavor compounds (Berglind *et al.* 1983; Watson & Ridal 2004; Izaguirre *et al.* 2007), even in oligotrophic water bodies (Jähnichen *et al.* 2011). Among the benthic algae, *Oscillatoriales* (Berglind *et al.* 1983) and *Phormidium* (Izaguirre 1992)

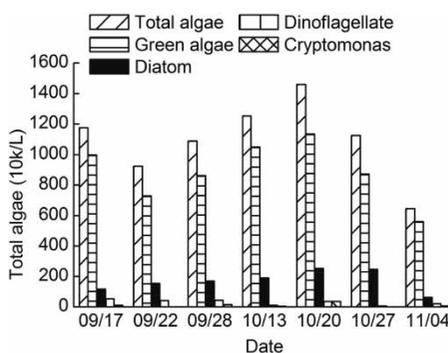


Figure 2 | Variation of algae amount in the studied period in 2011.



Figure 3 | Photomicrographs of algae in the tested water samples (1. *Chlorella*; 2. *Westella*; 3. *Pediastrum*; 4. *S. quadricauda*; 5. *Cosmarium*; 6. *Cyclotella*; 7. *Merismopedia*; 8. *Microcystis*; 9. *Pinnularia*).

were reported to be specific sources of geosmin and 2-MIB. Thus the contribution of benthic microorganism should be investigated in the future.

CONCLUSIONS

Through the investigation by FPA method, algae enumeration, and GC/MS analysis, the following conclusions about the off-flavor episodes could be made:

- (1) Among all the observed odorants, IBMP, IPMP, 1-hexanal, trans,trans-2,4-heptadienal, cis-4-heptenal, heptanal, and trans,trans-2,4-decadienal were regarded as major contributors to the odor incidents for their fishy and earthy odor that matched the profile of the odor problem in field study and previous reports.
- (2) Diatom was considered as the main source of odorous chemicals according to the microscopic observation and their properties of excreting fishy odorants.

- (3) The sequential feeding of potassium permanganate and PAC was developed to address diverse odorants in the next odor episode.

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