

Formation of aldehyde during ozonation of taste and odour compounds in water

Fei Qi, Bingbing Xu, Li Feng, Zhonglin Chen, Liqiu Zhang and Dezhi Sun

ABSTRACT

This study was conducted to investigate ketoaldehydes as another form of taste and odour (T&O) compound generated during the ozonation of commonly known T&O compounds, such as 2-methylisoborneol (MIB) and 2,4,6-trichloroanisole (TCA), which are typical T&O compounds. The ketoaldehydes generated during the ozonation process of T&O were studied. Results revealed that the main aldehydes produced during ozonation of MIB and TCA were formaldehyde, acetaldehyde, propionic aldehyde, *n*-butyl aldehyde, glyoxal and methyl glyoxal. The production of aldehydes during ozonation of T&O depended on several variables, including ozone dosage, temperature, water pH and the concentration of the matrix. According to results, ozonation is not an effective method for removal of MIB and decreasing the yield of aldehydes. Conversely, increasing ozone dosage or hydroxyl radicals resulted in a lower yield of aldehydes and higher removal efficiency of TCA.

Key words | 2-methylisoborneol, 2,4,6-trichloroanisole, aldehyde, ozonation, taste and odour

Fei Qi (corresponding author)

Li Feng

Liqiu Zhang

Dezhi Sun

Beijing Key Lab for Source Control Technology of Water Pollution, College of Environmental Science and Engineering, Beijing Forestry University, Beijing, China

E-mail: qifei_hit@yahoo.com.cn; qifei@bjfu.edu.cn

Bingbing Xu

State Key Laboratory of Environmental Criteria and Risk Assessment, Chinese Research Academy of Environmental Sciences, Beijing, China

Fei Qi

Zhonglin Chen

State Key Laboratory of Urban Water Resource and Environment, Harbin Institute of Technology, Harbin, China

INTRODUCTION

Taste and odour (T&O) is one of the basic criterion of safe drinking water (Parinet *et al.* 2010). However, T&O problems are increasing in source water, especially lakes or reservoirs that have been subject to eutrophication and blue-green algae blooms (Cortada *et al.* 2011). In recent years, T&O in drinking water has become a persistent problem for water supply entities worldwide; this is a source of concern for the drinking water industry because consumers associate off-flavours with poor drinking water quality (Laaks *et al.* 2010). Several types of chemicals that are secondary metabolic products of cyanobacteria and actinomycetes present in water sources have been reported to cause problems with T&O (Dixon *et al.* 2011). The main compounds responsible for T&O are 2-methylisoborneol (MIB) and 2,4,6-trichloroanisole (TCA), which cause a significant earthy musty taste in drinking water. However, the conventional treatment processes (pre-chlorination, coagulation, sediment, sand filtration and disinfection) cannot remove these T&O compounds efficiently (Lalezary

et al. 1986). Accordingly, several pre-treatment and advanced treatment technologies have been introduced to remove T&O, including activated carbon adsorption (McGuire 1999; Liang *et al.* 2006; Matsui *et al.* 2010; Park *et al.* 2010) and peroxidation via chlorination (Cl₂), chlorine dioxide (ClO₂) and potassium permanganate (Lalezary *et al.* 1986; Liang *et al.* 2006).

Ozone (O₃) is an effective oxidant for the removal of micro-pollutants during drinking water or wastewater treatment. Due to its high oxidation–reduction potential, ozone can remove T&O effectively. Indeed, it has been shown that reaction between hydroxyl radicals (·OH) and T&O dominates the ozonation process, which was confirmed by the effects of water pH on the kinetic constants of ozonation of MIB (Westerhoff *et al.* 2006; Liang *et al.* 2007). Moreover, the degradation pathways of MIB by ozonation have been investigated (Qi *et al.* 2009).

However, there are some drawbacks to the application of ozonation in removing T&O from drinking water. For

example, water quality affected the removal efficiency of T&O by ozonation (Von Gunten 2003). The critical water quality parameters were found to be natural organic matter (NOM), water pH, alkalinity and micro-pollutants. NOM in water can significantly inhibit the removal efficiency of T&O, as can water pH and alkalinity (Morioka *et al.* 1993). Micro-pollutants in water can also compete for ozone or $\cdot\text{OH}$ with T&O compounds, resulting in inhibited removal efficiency. Additionally, by-products such as bromate, ketoaldehyde and ketone acid can be generated during ozonation. Bromate is a potential carcinogen to humans (Griffini *et al.* 1999), and formaldehyde (FA) and acetaldehyde (AcA) have been shown to produce respiratory tumours, while glyoxal (Gly) has been found to promote stomach tumours (Can & Gurol 2003). The presence of ketoaldehydes and ketone acids can result in high levels of biologically degradable organic carbon (BDOC) or assailable organic carbon that can increase the microbiological risk to humans and be generated in the distribution system (Carlson & Amy 1998).

Ketoaldehydes also can lead to flavour problems, such as strong fragrant odours in water (Froese *et al.* 1999). In our previous study (Qi *et al.* 2009), some ketoaldehydes such as d-camphor, FA, AcA, propionic aldehyde (ProA), *n*-butyl aldehyde (ButA), Gly and methyl glyoxal (MeGly) were found to be generated during ozonation of MIB. Although ozonation can remove T&O effectively, the generation of ketoaldehydes may lead to a significant fragrant odour in water. Overall, these findings indicate that T&O problems in drinking water cannot be resolved by ozonation alone. Therefore, it is important to elucidate the producing fields of aldehydes and the mechanisms by which they are produced during ozonation treatment of T&O.

This study was conducted to discuss the problems associated with ketoaldehydes as another type of T&O generated during ozonation of T&O compounds. Typical T&O compounds, MIB and TCA, were selected as model compounds, and the fields and conditions in which ketoaldehydes were generated from these compounds during ozonation were studied. Moreover, the effects of several variables including ozone dosage, water pH and the concentration of the matrix were investigated.

MATERIALS AND METHODS

Chemicals

MIB was synthesized using the method described by Wood & Snoevink (1977). The purity of the synthesized MIB was confirmed to be greater than 95.0% by gas chromatography–mass spectrometry (GC–MS). TCA was obtained from Tokyo Kasei Kogyo Co. Ltd (Tokyo, Japan). A standard mixture containing six different ketoaldehydes each at a concentration of 1 mg mL^{-1} was purchased from Aldrich (USA). The derivatization reagent, (*O*-(2,3,4,5,6-pentafluorobenzyl) hydroxylamine (PFBHA) hydrochloride), was supplied by Sigma-Aldrich (USA). All other reagents used were of analytical purity or higher grade. A stock solution of MIB and TCA was prepared with purified water ($\geq 18.0\text{ m}\Omega\text{ cm}$) produced using a Millipore Milli-Q system.

Experimental procedures

The ozonation of T&O compounds was performed in a cylindrical glass reactor (volume 1,000 mL). Ozone was produced by a laboratory ozone generator (DHX-SS-1G, Harbin Jiu Jiu Electrochemistry Engineering Ltd, China), with a maximum ozone production of 9 g h^{-1} , using pure oxygen as the feed gas. After the generator reached a steady state, ozone gas was bubbled into ultra-pure water in the reactor with a silica dispenser until the desired dissolved ozone concentration was attained, after which the ozone flow was stopped. In the reaction process, ozone was introduced only once. Stock solution (1 mL) of MIB or TCA was then immediately introduced into the reactor and the magnetic stirrer was turned on. In this study, the dissolved ozone concentration of the reactor was controlled by varying the oxygen flux, the voltage of the ozone production and the time at which ozone was introduced into the reactor. Because ozone was added into the reaction system only once, the concentration of dissolved ozone and MIB (or TCA) was attenuated during the reaction. The ozonation reaction lasted 30 min in which time the dissolved ozone was almost consumed. Accordingly, the volatilization of ozone, MIB (or TCA) and aldehydes was ignored because of the use of this experimental method and the sealed

reactor. Samples were collected at the specified times and instantly quenched by the addition of an aliquot of $1.0 \text{ mol L}^{-1} \text{ Na}_2\text{S}_2\text{O}_3$ solution (1 mL). When ozone was introduced, the oxygen flux, purging time and voltage for ozone production were varied to adjust the concentration of the dissolved ozone. The maximum ozone concentration obtained in the water was $312.5 \text{ } \mu\text{mol L}^{-1}$. Phosphate buffer (1.0 mmol L^{-1}) was used to buffer the reaction solution at the beginning of the reaction to maintain the water pH at 7.0. To obtain valid data, all experiments were repeated three times, and the data were averaged.

Analytical methods

Gas ozone yield and dissolved ozone analysis

The gas ozone yield was analysed by the iodometry method (American Public Health Association 1998). The dissolved ozone was measured by the indigo method (Bader & Hoigné 1981).

Analysis of MIB and TCA concentration

Samples of aqueous MIB or TCA were extracted by *n*-pentane, in which a 25 mL sample and 1 mL *n*-pentane were used. For the extraction, the water sample (25 mL) was placed in a 25 mL separatory funnel and 2.0 g KH_2PO_4 and 3.0 g NaCl were subsequently added, after which the solution was extracted with 1.0 mL *n*-pentane by mechanical shaking for 5 min. The organic phase was then dried with anhydrous sodium sulphate and transferred to an auto-sampling vial. At appropriate times, a $1 \text{ } \mu\text{L}$ sample of the solution was injected into the GC–MS system. The samples were then analysed by GC–MS (GC6890-MS5973N, Agilent, USA) in SIM (selected ions monitor) mode as described by Shin & Ahn (2004). All mass spectra were obtained with an Agilent GC6890-MS5973N instrument. The ion source was operated in the electron-impact mode (electron energy 70 eV, $230 \text{ }^\circ\text{C}$) and the full-scan mass spectra were recorded for identification of analytes at high concentration. Confirmation of trace chemicals was conducted based on characteristic MS ions and comparison with the known GC retention times for each T&O compound. The ions selected in this investigation were m/z 95

(for quantitative analysis) and m/z 168 (for qualitative analysis) for MIB, and m/z 195 (for qualitative analysis) and m/z 196 (for quantitative analysis) for TCA. The detection limits were 0.2 and $0.4 \text{ } \mu\text{g L}^{-1}$ for MIB and TCA, respectively, and the RSD of both MIB and TCA was less than 5.3%. Experiments were carried out in triplicate, and the average values were reported.

Aldehyde analysis using a gas chromatography-electron capture detector (GC-ECD)

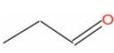
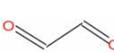
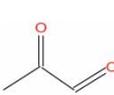
PFBHA derivation and GC-ECD analysis were employed to measure the aldehydes generated during ozonation of MIB or TCA. Quenched samples (20 mL) were derivatized with PFBHA, after which the PFBHA-derivatized polyfunctional compounds were extracted with *n*-hexane. The derivatization process was conducted according to the US Environmental Protection Agency (EPA) Method 556 (Munch *et al.* 1998). After the derivatization procedure, aldehydes were identified and quantified by GC-ECD (GC 6890N, Agilent, USA) analysis using an HP-5 column ($30 \text{ m} \times 0.25 \text{ mm} \times 0.25 \text{ } \mu\text{m}$, Agilent, USA). The detailed quality control results are shown in Table 1. As reported by Nawrocki *et al.* (1996), pure reagent water without aldehydes in the laboratory was difficult to find. In this study, FA, AcA and Gly were also detected in super pure water obtained from a Milli-Q system (Table 1). The average values of the three analyses are shown in the tables and figures of this study.

RESULTS AND DISCUSSION

Yields of aldehyde produced during ozonation of MIB or TCA

The effective removal of MIB and TCA were 31.0 and 49.0%, respectively, when the initial concentration of each compound was $1.0 \text{ } \mu\text{mol L}^{-1}$ and the ozone dosage was 2.2 mg L^{-1} (Table 2). As shown in Figure 1, some aldehyde by-products were produced under these conditions. The total aldehyde yield was 17.24 and $8.08 \text{ } \mu\text{g L}^{-1}$ after ozonation of MIB and TCA, respectively. The aldehyde yield of MIB was higher than that of TCA. In detail, the main aldehyde by-products produced during ozonation of MIB were

Table 1 | Information on low molecular weight aldehyde by-products

Name	Abbreviation	Molecular formula	Molecular weight	CAS No.	Retention time (min)	Method detection limit ($\mu\text{g L}^{-1}$)
Formaldehyde ^a	FA		30.03	50-00-0	7.20	0.1
Acetaldehyde ^b	AcA		44.05	75-07-0	8.28 (E-CH ₃ CH-PFBO); 8.41 (Z-CH ₃ CH-PFBO)	0.1
Propionic aldehyde	ProA		58.08	123-38-6	9.54 (E-C ₂ H ₅ CH-PFBO); 9.64 (Z-C ₂ H ₅ CH-PFBO)	0.05
Butyl aldehyde	ButA		72.11	123-72-8	12.25 (E-C ₃ H ₇ CH-PFBO); 12.41 (Z-C ₃ H ₇ CH-PFBO)	0.05
Glyoxal aldehyde ^c	Gly		58.04	107-22-2	25.84 (E-PFBO-HCCH-PFBO); 26.31 (Z-PFBO-HCCH-PFBO)	0.03
Methyl glyoxal aldehyde	MeGly		72.00	78-98-8	27.30 (E-PFBO-HCCH ₃ CH-PFBO); 27.88 (Z-PFBO-HCCH ₃ CH-PFBO)	0.03

^aIn our laboratory, FA was detected at $1.3 \mu\text{g L}^{-1}$ in super purity water from Milli-Q system.

^bIn our laboratory, AcA was detected at $1.0 \mu\text{g L}^{-1}$ in super purity water from Milli-Q system.

^cIn our laboratory, Gly was detected at $0.4 \mu\text{g L}^{-1}$ in super purity water from Milli-Q system. The data shown in this study were detection values in super purity water from Milli-Q system.

Table 2 | Taste and odour pollutants removed by ozonation alone^a

T&O pollutants	Residual concentration ($\mu\text{mol L}^{-1}$)	Removal efficiency (%)
MIB	0.69	31.0
TCA	0.51	49.0

^a $[\text{O}_3]_0 = 2.2 \text{ mg L}^{-1}$, $\text{pH} = 7.0$, $[\text{MIB}]_0 = 1.0 \mu\text{mol L}^{-1}$, $[\text{TCA}]_0 = 1.0 \mu\text{mol L}^{-1}$, reaction time was 30 min.

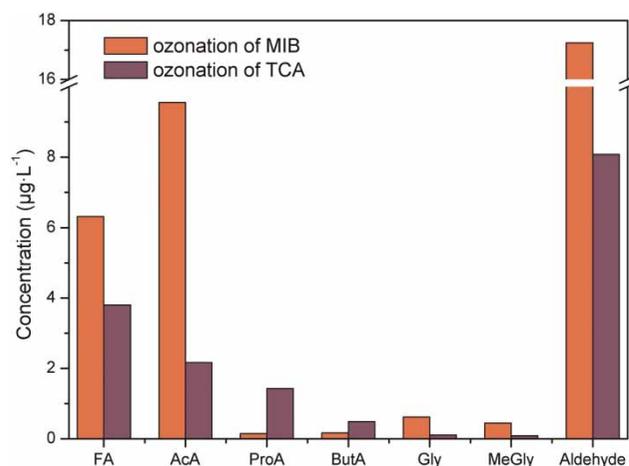


Figure 1 | Yields of aldehydes generated during ozonation of T&O compounds. Experimental conditions: $[\text{O}_3]_0 = 2.23 \text{ mg L}^{-1}$, $[\text{MIB}]_0 = [\text{TCA}]_0 = 1.0 \mu\text{mol L}^{-1}$, reaction temperature = 25°C , reaction time = 30 min, solution $\text{pH} = 7.0$.

FA and AcA at 6.31 and $9.55 \mu\text{g L}^{-1}$, respectively. The main aldehyde by-products produced during ozonation of TCA were FA, AcA and ProA at 3.8 , 2.17 and $1.43 \mu\text{g L}^{-1}$, respectively. In addition, ButA, Gly and MeGly were produced in much lower yields. These findings confirmed that the yields of each type of aldehyde in response to ozonation of MIB and TCA differed significantly.

Figure 2 shows the variation of total aldehyde yields during the ozonation process. The production of aldehydes during ozonation of MIB and TCA increased during the initial reaction step and then decreased. The maximum peak of TCA was at 20 min and that of MIB was at 10 min. These findings indicated that the aldehydes generated from the model compounds were degraded by ozone or $\cdot\text{OH}$, resulting in decreasing total aldehyde yields. According to previous studies, the reaction rate constants of MIB and ozone were higher than those of TCA. However, the maximum yields of total aldehydes of TCA were higher than those of MIB.

Generation of aldehydes during ozonation of MIB

Figure 3 shows the generation of all types of aldehydes during ozonation of MIB. The curves of FA and ProA

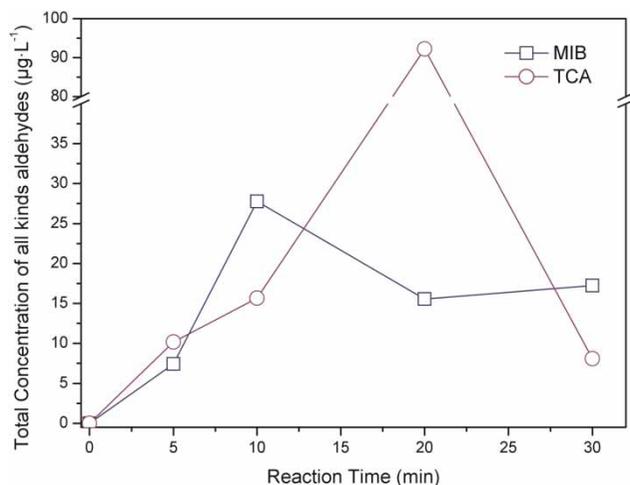


Figure 2 | Variations in yields of total aldehydes generated during ozonation of T&O compounds with reaction time. Experimental conditions: $[O_3]_0 = 2.23 \text{ mg L}^{-1}$, $[MIB]_0 = [TCA]_0 = 1.0 \text{ } \mu\text{mol L}^{-1}$, reaction temperature = $25 \text{ } ^\circ\text{C}$, reaction time = 30 min, solution pH = 7.0.

showed an inflexion at the same reaction times. Specifically, the yields of FA and ProA increased during the initial reaction step (before 10 min) and then decreased. However, no inflexions were observed in the curves of AcA, ButA, Gly and MeGly. For these types of aldehydes, generation yields increased as the reaction time followed. This lack of inflexion points was likely due to the low levels of these compounds, which ranged from 0.1 to $0.7 \text{ } \mu\text{g L}^{-1}$.

Generation of aldehydes during ozonation of TCA

As shown in Figure 4, the generation of aldehydes during ozonation of TCA differed remarkably from the generation during MIB ozonation. Specifically, the curves of all six aldehydes showed inflexions during ozonation of TCA. For FA, Ac, ProA and Gly, the inflexion emerged at a reaction time of 20 min, while it occurred at 10 min for ButA and MeGly. Similar to the ozonation of MIB, AcA was the aldehyde produced at the greatest levels during ozonation of TCA.

Effect of ozone dosage on yields of aldehydes

Ozone dosage had a remarkable effect on the removal of model compounds, resulting in different yields of by-products (Figure 5). For MIB, there was a remarkable difference in total aldehyde concentration, which varied

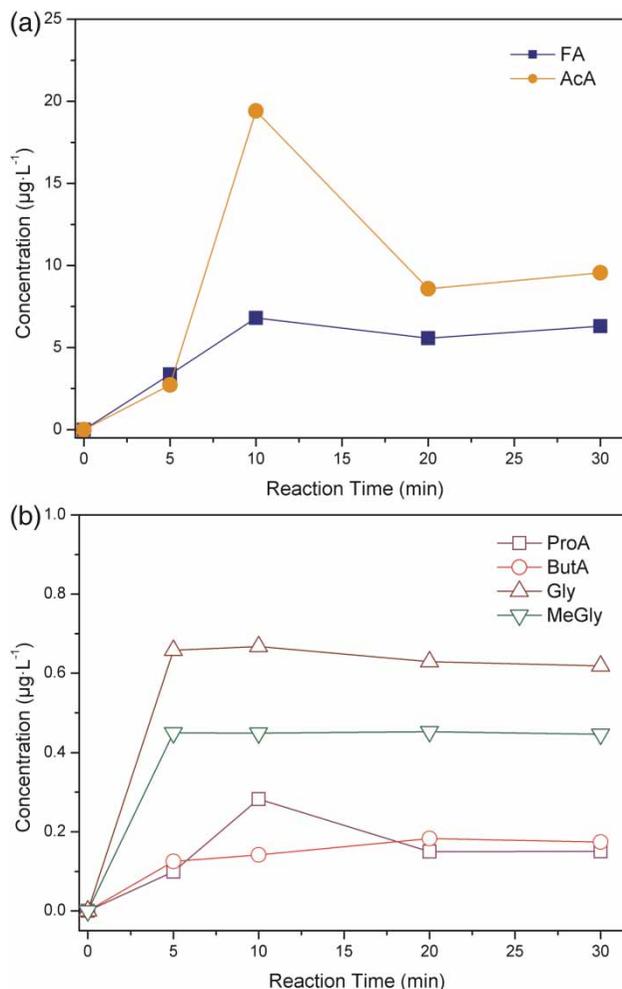


Figure 3 | Variations in yields of six aldehydes generated during ozonation of MIB compounds with reaction time. Experimental conditions: $[O_3]_0 = 2.23 \text{ mg L}^{-1}$, $[MIB]_0 = [TCA]_0 = 1.0 \text{ } \mu\text{mol L}^{-1}$, reaction temperature = $25 \text{ } ^\circ\text{C}$, reaction time = 30 min, solution pH = 7.0.

from 6.78 to $17.33 \text{ } \mu\text{g L}^{-1}$. Regardless of the ozone dosage, the main aldehyde by-products were FA and AcA. In addition, the effect of ozone dosage on the yield of FA was consistent with the total yields. The lowest yield was observed on 1.5 mg L^{-1} ozone dosage. Less than or greater than this dosage, the yields increased at different scales. This variation phenomenon was also observed for ProA, but the yield for this aldehyde was much lower than $0.7 \text{ } \mu\text{g L}^{-1}$. Lower levels of ozone dosage (0.5 and 1.5 mg L^{-1}) affected the yields of AcA insignificantly, but a higher ozone dosage (2.0 mg L^{-1}) resulted in higher yields of the concentration of AcA. As the ozone dosage increased, the yield of ButA, Gly and MeGly increased. Therefore, increasing ozone dosage

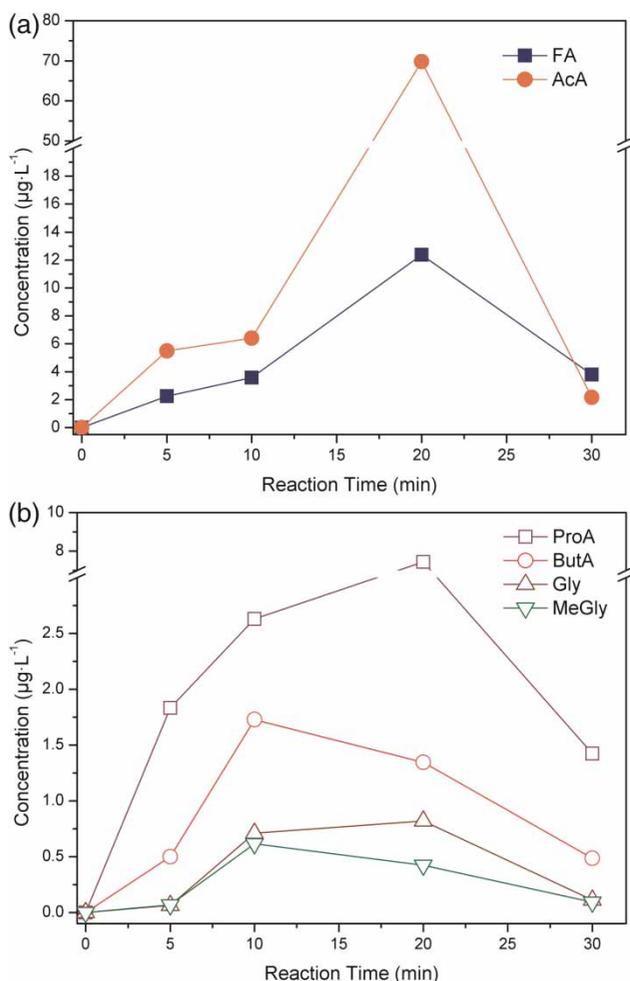


Figure 4 | Variations in yields of six aldehydes generated during ozonation of TCA compounds with reaction time. Experimental conditions: $[O_3]_0 = 2.23 \text{ mg L}^{-1}$, $[MIB]_0 = [TCA]_0 = 1.0 \text{ } \mu\text{mol L}^{-1}$, reaction temperature = $25 \text{ } ^\circ\text{C}$, reaction time = 30 min, solution pH = 7.0.

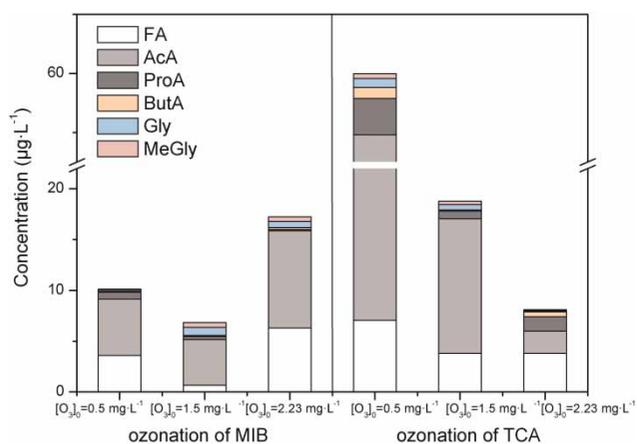


Figure 5 | Effects of ozone dosage on the formation of aldehydes during ozonation. Experimental conditions: $[MIB]_0 = [TCA]_0 = 1.0 \text{ } \mu\text{mol L}^{-1}$, reaction temperature = $25 \text{ } ^\circ\text{C}$, reaction time = 30 min, solution pH = 7.0.

was not an effective method for removing MIB and reducing the generation of aldehyde synchronously.

For TCA, there was a remarkable relationship between the yields of aldehyde produced and the ozone dosage. Specifically, as the ozone dosage increased, the formation of total aldehyde decreased significantly from 59.95 to $8.14 \text{ } \mu\text{g L}^{-1}$. Accordingly, the removal of T&O compounds and control of the generation of aldehydes synchronously could be achieved by ozonation. The chemical structure of TCA was likely attributable to the high capacity for removal efficiency and control of aldehyde generation. TCA is an aromatic compound, which resulted in there being a higher reaction rate constant with ozone ($0.06 \pm 0.01 \text{ L mol}^{-1} \text{ s}^{-1}$) and $\cdot\text{OH}$ ($5.1 \pm 0.11 \times 10^9 \text{ L mol}^{-1} \text{ s}^{-1}$) (Andreas & Von Gunten 2007). FA and AcA were the main aldehyde by-products during ozonation of TCA. The yield of ProA was also much higher than that of ButA, Gly and MeGly, but this level was much lower than that for FA and AcA. The formation amount of FA and AcA decreased as the ozone dosage increased; however, the amount of ProA did not vary greatly in response to differences in ozone. Finally, the concentration of Gly decreased as the ozone dosage increased, which was likely a result of the oxidation of TCA.

During ozonation, the ozone dosage and the matrix had significant effects on the yield of aldehydes. In a previous study (Dabrowska *et al.* 2005), the total yield of aldehydes increased as ozone dosage increased (0.1 – 0.8 mg L^{-1}), even in different water matrices. However, when the ozone dosage was between 1.0 and 2.0 mg L^{-1} , the effect of the water matrix was greater. In the present study, the effects of ozone dosage on MIB and TCA differed, indicating that the chemical structure was responsible for this phenomenon.

Effect of initial concentration of model compounds on yields of aldehydes

For MIB, the initial concentration exhibited a significant effect on the formation of aldehydes (shown in Figure 6). As the initial concentration increased, the total aldehydes first decreased, then increased. This effect was consistent with that of the ozone dosage. Whatever the initial concentration, the main aldehyde by-products were still FA and AcA. The concentration of FA first decreased, then increased, while the opposite was true for AcA. When

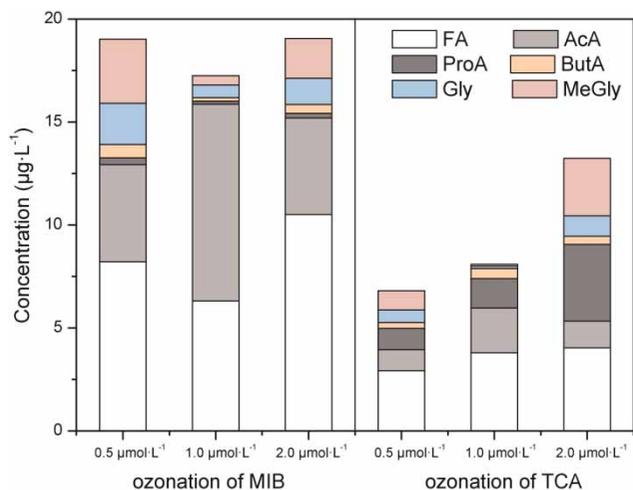


Figure 6 | Effects of initial concentrations of MIB and TCA on the formation of aldehydes during ozonation. Experimental conditions: $[O_3]_0 = 2.23 \text{ mg L}^{-1}$, reaction temperature = 25°C , reaction time = 30 min, solution pH = 7.0.

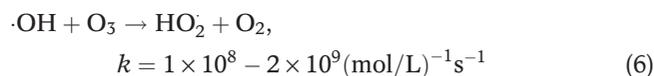
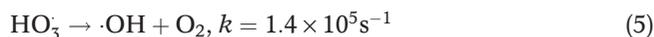
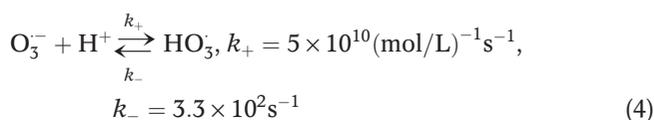
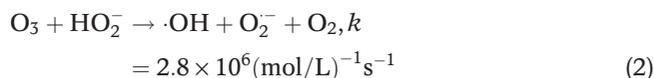
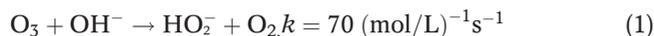
compared to FA and AcA, the levels of ButA, Gly and MeGly were small. The variations of ProA, ButA, Gly and MeGly decreased first, then increased.

Conversely, the initial concentration had a positive effect on the formation of aldehydes. As the initial concentration of TCA increased, the total yield of aldehydes increased. In experimental conditions, the yields of total aldehydes were from 6.87 to $13.26 \text{ } \mu\text{g L}^{-1}$. FA, AcA and ProA were the main aldehyde by-products. The amount FA and ProA produced increased significantly as the concentration of TCA increased. The concentration of AcA and ButA increased initially with the increasing of the initial concentration, and then decreased. For Gly and MeGly, the variation was the opposite to that of AcA and ButA.

Effect of water pH on yields of aldehyde

In distilled water, the ozone decomposition rate and oxidation capacity for the removal of organic pollutants is dependent on the pH of the water (Von Gunten 2003). Equations (1)–(6) show the mechanism of ozone decomposition in pure water (Von Gunten 2003). In this process, hydroxide ion (OH^-) is the initiator of the chain reaction of ozone decomposition. As the water pH increases, the decomposition of ozone is accelerated and $\cdot\text{OH}$ may be formed. According to the above reactions, the oxidation capacity of ozonation was enhanced by the increasing

water pH.



The effects of water pH on the yield of aldehydes during ozonation of MIB and TCA are shown in Figure 7. The variations in total aldehyde were consistent with the effects of ozone dosage and the initial concentration. For FA, ProA, Gly and MeGly, the yield first decreased as the water pH increased, and then decreased. For AcA, the yield observed

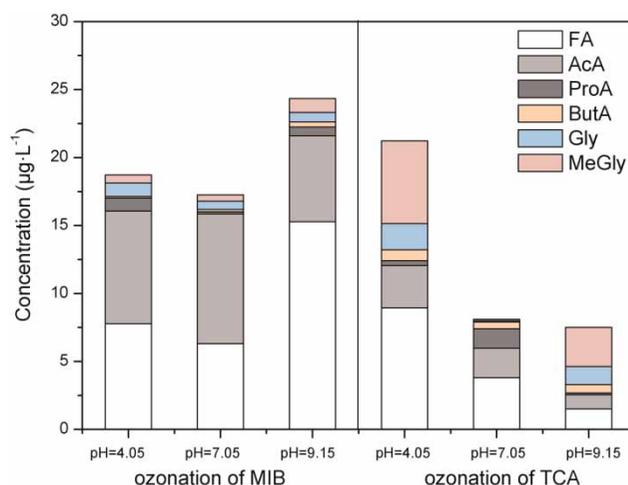


Figure 7 | Effects of solution pH on the formation of aldehydes during ozonation. Experimental conditions: $[O_3]_0 = 2.23 \text{ mg L}^{-1}$, $[\text{MIB}]_0 = [\text{TCA}]_0 = 1.0 \text{ } \mu\text{mol L}^{-1}$, reaction time = 30 min.

was the opposite. The yield of ButA increased as water pH increased. Therefore, the generation of aldehydes and the effects of various factors on the degradation of MIB was not limited to ozone or ·OH and the chemical structure was the key influencing factor. The neutral water pH was favoured for the lowest yield of aldehydes during ozonation of MIB.

As water pH increased, the formation of total aldehydes decreased. Increasing water pH can result in enhanced capacity for oxidation or mineralization, leading to the degradation of TCA and the control of aldehyde levels synchronously. The yields of FA, AcA and ButA decreased as water pH increased. The formation of ·OH was the key factor in this decrease. The yield of ProA initially increased as water pH increased, and then decreased. This was opposite to the yields of Gly and MeGly. Because the yields of ProA, Gly and MeGly were much lower than those of FA and AcA, the formation of total aldehydes was influenced mainly by FA and AcA. According to the results of ozone dosage, initial concentration and water pH, the increasing ozone dosage or ·OH could lead to a lower yield of aldehydes and higher removal efficiency of TCA.

CONCLUSIONS

Based on the above experimental results, the following conclusions can be drawn:

1. During removal of T&O pollutants (MIB and TCA) by ozonation, the formation of aldehydes was a remarkable drawback. FA, AcA, ProA, ButA, Gly and MeGly aldehyde were the main aldehyde by-products produced during ozonation of MIB or TCA.
2. Ozonation is not an effective method to remove MIB and decrease the yield of aldehydes. However, for TCA, increasing ozone dosage or hydroxyl radicals could result in a lower yield of aldehydes and a higher removal efficiency of TCA.

ACKNOWLEDGEMENTS

This work was conducted with the financial support of the National Natural Science Foundation of China

(No. 51108030, 40903038 and 41273137), the Beijing Natural Science Foundation (No. 8132033), the Specialized Research Fund for the Doctoral Program of Higher Education (No. 20100014120001), and the China Post Doctoral Science Foundation (No. 201104060 and 2012M520006).

REFERENCES

- Andreas, P. & Von Gunten, U. 2007 Oxidation kinetics of selected taste and odor compounds during ozonation of drinking water. *Environ. Sci. Technol.* **41** (2), 626–631.
- Bader, H. & Hoigné, J. 1981 Determination of ozone in water by the indigo method. *Water Res.* **15** (4), 449–456.
- Can, Z. & Gurol, M. 2003 Formaldehyde formation during ozonation of drinking water. *Ozone Sci. Eng.* **25**, 41–51.
- Carlson, K. H. & Amy, G. L. 1998 BOM removal during biofiltration. *J. Am. Water Works Assoc.* **90** (12), 42–52.
- Cortada, C., Vidal, L. & Canals, A. 2011 Determination of geosmin and 2-methylisoborneol in water and wine samples by ultrasound-assisted dispersive liquid–liquid microextraction coupled to gas chromatography-mass spectrometry. *J. Chromatogr.* **1218** (1), 17–22.
- Dabrowska, A., Kasprzyk-Hordern, B. & Nawrocki, J. 2005 Aldehydes formation during water disinfection by ozonation and chlorination process. *Glob. NEST J.* **7** (1), 61–67.
- Dixon, M. B., Falconet, C., Ho, L., Chow, C. W. K., O'Neill, B. K. & Newcombe, G. 2011 Removal of cyanobacterial metabolites by nanofiltration from two treated waters. *J. Hazard. Mater.* **188** (1–3), 288–295.
- Froese, K. L., Wolanski, A. & Hrudey, S. E. 1999 Factors governing odorous aldehyde formation as disinfection byproducts in drinking water. *Water Res.* **33** (6), 1355–1364.
- Griffini, O., Bao, M. L., Barbieri, K., Burrini, D., Santianni, D. & Pantani, F. 1999 Formation and removal of biodegradable ozonation by-products during ozonation-biofiltration treatment: Pilot scale evaluation. *Ozone Sci. Eng.* **21** (1), 79–98.
- Laaks, J., Jochmann, M. A., Schilling, B. & Schmidt, T. C. 2010 In-tube extraction of volatile organic compounds from aqueous samples: an economical alternative to purge and trap enrichment. *Analytical Chem.* **82** (18), 7641–7648.
- Lalezary, S., Pirbazari, M. & McGuire, M. J. 1986 Oxidation of five earthy-musty taste and odour compounds. *J. Am. Water Works Assoc.* **78** (3), 62–69.
- Liang, C., Wang, D., Chen, J., Zhu, L. & Yang, M. 2007 Kinetics analysis on the ozonation of MIB and geosmin. *Ozone Sci. Eng.* **29** (3), 185–189.
- Liang, C. Z., Wang, D. S., Ge, X. P., Yang, M. & Sun, W. 2006 Comparative study on the removal technologies of 2-methylisoborneol (MIB) in drinking water. *J. Environ. Sci.* **18** (1), 47–51.
- Matsui, Y., Nakano, Y., Hiroshi, H., Ando, N., Matsushita, T. & Ohno, K. 2010 Geosmin and 2-methylisoborneol adsorption

- on super-powdered activated carbon in the presence of natural organic matter. *Water Sci. Technol.* **62** (11), 2664–2668.
- McGuire, M. J. 1999 Advances in treatment processes to solve off-flavor problems in drinking water. *Water Sci. Technol.* **40** (6), 153–164.
- Ministry of Construction & Ministry of Public Health of China 2006 Sanitary standard for drinking water (GB5749-2006), Beijing.
- Morioka, T., Motoyama, N., Hoshikawa, H., Murakami, A., Okada, M. & Moniwa, T. 1993 Kinetic analysis on the effects of dissolved inorganic and organic substances in raw water on the ozonation of geosmin and 2-MIB. *Ozone Sci. Eng.* **15** (1), 1–18.
- Munch, J. W., Munch, D. J., Winslow, S. D., Wendelken, S. C. & Pepich, B. V. 1998 Determination of carbonyl compounds in drinking water by pentafluorobenzylhydroxylamine derivatization and capillary gas chromatography with electron capture detection. *EPA Method 556*, S. 556-1–556-37.
- Nawrocki, J., Kalkowska, I. & Dabrowska, A. 1996 Optimization of solid-phase extraction method for analysis of low-ppb amounts of aldehydes-ozonation by products. *J. Chromatogr.* **749**, 157–163.
- Parinet, J., Rodriguez, M. J. & Sérodes, J. 2010 Influence of water quality on the presence of off-flavour compounds (geosmin and 2-methylisoborneol). *Water Res.* **44** (20), 5847–5856.
- Park, S., Heo, T., Park, N., Na, K., Jun, H. & Jung, J. 2010 Application of air stripping to powdered activated carbon adsorption of geosmin and 2-methylisoborneol. *J. Water Supply: Res. Technol. – AQUA* **59** (8), 492–500.
- Qi, F., Xu, B., Chen, Z., Ma, J., Sun, D. & Zhang, L. 2009 Efficiency and products investigations on the ozonation of 2-methylisoborneol in drinking water. *Water Environ. Res.* **81** (12), 2411–2419.
- Shin, H. S. & Ahn, H. S. 2004 Simple, rapid, and sensitive determination of odorous compounds in water by GC–MS. *Chromatographia* **59** (1–2), 107–113.
- Standard Methods for the Examination of Water and Wastewater* 1998 20th edition, American Public Health Association/American Water Works Association/Water Environment Federation, Washington, DC.
- Von Gunten, U. 2003 Ozonation of drinking water: Part I. Oxidation kinetics and product formation. *Water Res.* **37** (7), 1443–1467.
- Westerhoff, P., Nalinakumari, B. & Pei, P. 2006 Kinetics of MIB and geosmin oxidation during oxidation. *Ozone Sci. Eng.* **28** (5), 277–286.
- Wood, N. F. & Snoevink, V. L. 1977 2-Methylisoborneol, improved synthesis and a quantitative gas chromatographic method for trace concentrations producing odor in water. *Chromatographia* **132** (3), 405–420.

First received 25 March 2012; accepted in revised form 25 December 2012