The effects of dissolved organic matter on the decomposition of di-*n*-butyl phthalate by ozone/hydrogen peroxide process

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Abstract The effects of the dissolved organic matter (DOM) on the ozone decay and the di-*n*-butyl phthalate (DBP) decomposition during ozone/hydrogen peroxide (O_3/H_2O_2) process were investigated (DBP-d_4 was used instead of DBP). Four surface waters, two secondary municipal sewage effluents (SMSEfs) and Suwannee river natural organic matter were used as DOM. The ozone decompositions in the DOM solutions were separated by instantaneous ozone consumption and slower ozone decay. The effect of H_2O_2 addition on the ozone decay was clearly observed at slower ozone decay. Ozone decomposition rate at slower ozone decay increased linearly with H_2O_2 dose. DBP-d_4 was exponentially decreased with ozone consumption. Ozone consumption required to decompose 90% of DBP-d_4 (($\Delta O_3)_{90\%}$) in SMSEFs was higher than those in surface waters. The ($\Delta O_3)_{90\%}$ per DOC of DOM values were from 22 to 23 μmole/mgC for SMSEFs and from 10 to 17 μmole/mgC for surface waters. The ($\Delta O_3)_{90\%}$ values were correlated to specific ultraviolet absorbance at 254 nm ($SUVA_{254}$) for surface waters.

Keywords Di-*n*-butyl phthalate; dissolved organic matter; hydroxyl radical; ozone; ozone/hydrogen peroxide process; specific ultraviolet absorbance

Introduction

The hydroxyl radical (HO•) is a highly reactive oxidant (Hoigné, 1998) and reacts with many organic compounds at nearly diffusion control rates in water (Buxton *et al*., 1988). The water treatment technologies using HO• as a main oxidant are referred to as advanced oxidation processes (AOPs) (Hoigné, 1998) and are applied for drinking water and wastewater treatments. Recently, a number of the reproductive effects on human and wildlife have been reported and such phenomena are suspected to be caused by the exogenous compounds (e.g. organochlorine compounds and pesticides) known as endocrine disrupting chemicals (EDCs) (Colborn *et al*., 1993). AOPs are effective technologies for the decompositions of EDCs; ozone based AOPs (e.g. ozone/hydrogen peroxide (O_3/H_2O_2) process) are especially promising because some EDCs were extremely highly reactive with ozone (Kosaka, 2002).

In environmental water, EDCs always co-exist with dissolved organic matter (DOM) such as natural organic matter (NOM) and effluent organic matter (EfOM) represented by dissolved organic carbon (DOC) or chemical oxygen demand (COD). Competitive reactions between EDCs and DOM toward oxidants (i.e. ozone and HO•) occur in ozone using processes. Several groups of EDCs (e.g. phenolic compounds) are highly reactive with ozone (Kosaka, 2002), and their controls are possible regardless of the DOM co-existence because the control of ozone during the processes is possible. On the other hand, the controls of other EDCs not reactive with ozone (e.g. PCBs and phthalate esters) are difficult

because the control of HO• during the processes is not possible. For the controls of such EDCs, it is necessary to understand the effects of DOM during the processes.

The effects of DOM and DOM types on the decomposition of the EDC decomposed only by HO• during an O_3/H_2O_2 process were investigated in this research. We especially examined the ozone decay and the relationship between ozone consumptions and target compound decompositions. Di-*n*-butyl phthalate (DBP), a kind of common phthalate ester and suspected EDC, was used as a model compound.

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Methods

Reagents and solutions

Ozone solution was made by introducing ozone gas produced from an ozone generator (OS-1N, Mitsubishi) into ultrapure water. Instead of DBP, DBP-d_4 (Wako) was used because DBP is frequently detected from air and water and it is very time-consuming to measure the DBP of many samples precisely without DBP contamination. DBP-d_4 is decomposed only by HO•, because the reaction rate constant of DBP with ozone and that of DBP-d_4 with HO• are <0.2 and 5.3×10^9 1/(M•s), respectively (Kosaka, 2002). Ultrapure water purified with an ultrapure water system (Easypure RF, Barnstead) was used for the preparation of the solutions. Four surface waters, two secondary municipal sewage effluents (SMSEfs) and a commercially available natural organic matter (Suwannee river natural organic matter (SRNOM)) were used as DOM. Their water qualities are listed in Table 1. In Table 1, SUVA$_{254}$, ultraviolet absorbance at 254 nm per 1 mg of DOM as DOC, is an index for DOM property and is considered to correlate with aromatic content per 1 mg of DOM as DOC (Westerhoff *et al*., 1999). To compare with the effect of the DOM types, pH, DOC and the ratio of IC to DOC (IC/DOC) of the DOM solutions were regulated at 7.0, 1.4 mgC/L and in the range 3.3–4.7, respectively. Phosphate buffer solution (4.5 mM), ultrapure water and NaHCO$_3$ solution were added for the adjustments of pH, DOC and IC/DOC, respectively. Since IC values of the DOM solutions used in this study were low, the effect of carbonate (i.e. HCO$_3^-$) as a radical scavenger is assumed to be minor. The sample solutions were prepared by adding the small amounts of DBP-d_4 and H$_2$O$_2$ solutions into DOM solutions.

Experimental procedure

The experiment was conducted with a continuous flow reactor. Ozone and sample solutions were introduced into a mixing connector separately by the dual plunger pumps. The flow rate of ozone solution was 4.5 mL/min and that of sample solution was 13.5 mL/min. After mixing, the combined solution passed in a Teflon tube reactor (*i.d.* 1.6 mm). Reaction times were from 2.3 to 26.8 s and were changed by changing the length of the tube. At the outlet of the tube, the combined solution was mixed with indigo solution for ozone analysis and with sodium thiosulfate solution for DBP-d_4 analysis. The temperatures of the combined solutions were 21 ± 2°C.

Table 1 Water qualities of environmental waters and a commercially available DOM

	pH	DOC (mg/L)	IC (mg/L)	SUVA$_{254}$ (L/(mgC•cm))
Lake Biwa (Feb.)	7.2	1.9	9.0	0.010
Lake Biwa (May)	7.2	1.9	9.0	0.010
Seta river	7.3	2.0	8.3	0.015
Soma river	7.6	2.1	8.6	0.021
SRNOM	–	–	–	0.043
SMSEf A	7.2	5.4	17.8	0.016
SMSEf B	6.3	4.9	7.2	0.019

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Analytical methods

Ozone concentration in water was measured by the indigo method. DBP-d_4 was analyzed by a GC/MS (QP-5000, Shimadzu) equipped with a DB-5 column (J&W). Hydrogen peroxide in the sample solutions was determined spectrophotometrically using *N,N*-dimethyl-*p*-phenylenediamine (Wako) or 2,9-dimethyl-1,10-phenanthroline (Shigma). DOC and IC were measured by a TOC analyzer (TOC-5000A, Shimadzu). Before DOC measurement, the sample solutions were acidified with HCl solution (pH2–3) and purged by nitrogen gas to remove IC in the solutions.

Results and discussion

Ozone decay kinetics

Figure 1 shows the profiles of the residual ratios of ozone in the DOM solutions during ozonation when the initial ozone concentrations were around 30 μM. The order of the faster ozone decomposition was SRNOM, SMSEfs, the Soma river, the Seta river, Lake Biwa (Feb.) and Lake Biwa (May). The difference of the profiles among the DOM solutions was due to the difference of the DOM types because the DOC concentrations of all DOM solutions were the same. As described by earlier researchers (Westerhoff *et al.*, 1999), in this research the ozone decay was modelled in two phases, that is, instantaneous ozone consumption and slower ozone decay phase were represented by a first-order reaction. In the research, the two phases were separated after several tens of seconds, but it was shown that the first phase was finished in less than several seconds. The two phases were practically separated at the first measuring time.

DOM is a mixture of heterogeneous organic compounds and has many reaction sites with ozone and HO•. It is known that there are some reaction types in the reactions of DOM with ozone and HO• (Staehelin and Hoigné, 1985).

$$DOM_d + O_3 \rightarrow products \tag{1}$$

$$DOM_i + O_3 \rightarrow products \tag{2}$$

$$DOM_s + HO\cdot \rightarrow products \tag{3}$$

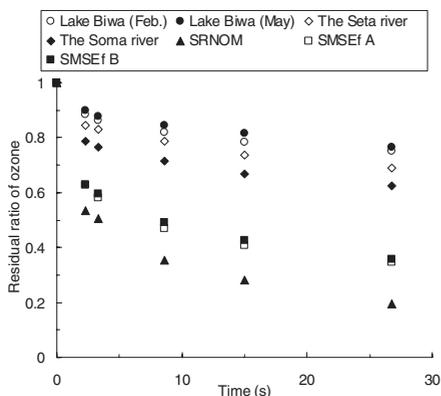$$DOM_p + HO\cdot \rightarrow products + O_2^- \tag{4}$$

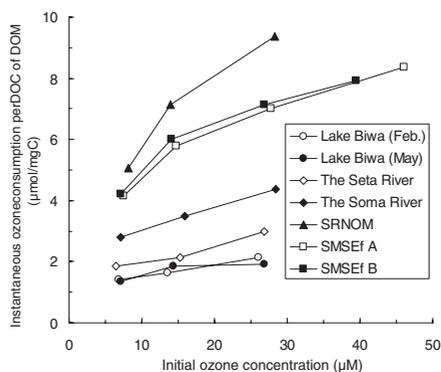**Figure 1** Profiles of the residual ratios of ozone in the DOM solutions during ozonation

Figure 2 The effects of initial ozone concentrations on the instantaneous ozone consumptions per DOC of DOM

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where DOM_d, DOM_i, DOM_s and DOM_p are reaction sites of DOM for direct reaction, initiation, inhibition and promotion, respectively, and O_2^- is the superoxide anion. O_2^- rapidly reacts with ozone ($k = 1.6 \times 10^9$ 1/(M•s), (Buxton *et al.*, 1988), and ozone consumption increases with O_2^- generations. Thus, it can be said that ozone was consumed by O_2^- as well as DOM in Figure 1.

Figure 2 shows the effects of initial ozone concentrations on the instantaneous ozone consumptions per DOC of DOM when the initial ozone concentrations were from around 5 to 30 μM for surface waters and from around 5 to 50 μM for SMSEfs. In the case of Lake Biwa (Feb.) and (May) waters, the instantaneous ozone consumptions were not so affected by the initial ozone concentrations and were around 2 μmol/mgC. On the other hand, in the case of the other five solutions, the instantaneous ozone consumptions increased with the initial ozone concentrations. And, the instantaneous ozone consumption at the same ozone concentration was larger in order of SRNOM, SMSEfs, the Soma river and the Seta river. Considering the profiles of the ozone residual ratios at the initial and secondary phases, the difference in the two phases is due to the difference of the component of consuming ozone. Thus, instantaneous ozone consumptions of all DOM solutions were assumed to be independent of the initial ozone concentration if they were high enough for the amount of reaction sites of DOM reacting rapidly with ozone.

The profiles of the residual ratios of ozone for Lake Biwa (Feb.) during ozonation and O_3/H_2O_2 process are shown in Figure 3 (H_2O_2 dose: around 50 μM). Although ozone decay was always faster during O_3/H_2O_2 process than during ozonation, the difference of the ozone decay of the two processes was observed more clearly at the secondary phase. This tendency was shown for other DOM solutions. This means that ozone reacted mainly not with H_2O_2 but with DOM or activated oxygen at the first phase. In this research, the ratio of H_2O_2 dose to DOC of DOM was less than 36 μmol/mgC. Therefore, it was found that under these experimental conditions the effect of H_2O_2 addition on the ozone decay is shown after instantaneous ozone consumption.

The effects of H_2O_2 dose on the first-order rates of ozone decomposition rate of the Seta river, the Soma river, SRNOM and SMSEf A at the secondary phase are shown in Figure 4. The data at the highest initial ozone concentration were used to minimize the effects of instantaneous ozone consumption on the secondary phase. Initial ozone concentrations were around 50 μM for SMSE A and were around 30 μM for other waters. The rate constants of the ozone decomposition always increased linearly with H_2O_2 dose. When HO• is mainly scavenged by DOM, the ozone decay is represented by Eq. (5) (Staehelin and Hoigné, 1985)

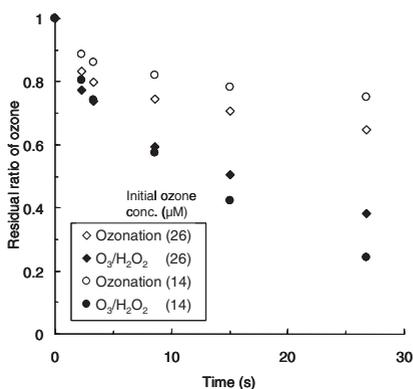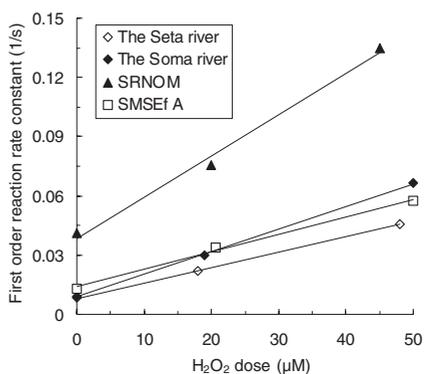**Figure 3** Profiles of the residual ratios of ozone during ozonation and O_3/H_2O_2 process

Figure 4 The effects of H_2O_2 doses on ozone decompositions at slower ozone decay

$$-\frac{d[O_3]}{dt} = k_d[DOM_d][O_3] + (k_i[DOM_i] + k_{H2O2}[H_2O_2])(1 + \frac{k_p[DOM_p]}{k_s[DOM_s]})[O_3] \qquad (5)$$

where k_d, k_i, k_s and k_p are reaction rate constants of DOM_d, DOM_i, DOM_s and DOM_p with ozone, respectively, and k_{H2O2} is an apparent reaction rate constant of H_2O_2 with ozone. In this experiment, H_2O_2 residuals were not so changed. Therefore, it was shown that the linearity relationship in Figure 4 was explained with Eq. (5) when the change of each type of DOM was considered to be constant at the secondary phase.

DBP-d_4 decomposition in the DOM solutions by O_3/H_2O_2 process

Figure 5 shows the relationships between ozone consumption per DOC of DOM and the residual ratios of DBP-d_4. Initial concentrations of DBP-d_4 were from 0.04 to 0.19 μM, initial ozone concentrations were from around 5 to 30 μM for surface waters and from around 5 to 50 μM for SMSEfs, and H_2O_2 dose was around 20 and 50 μM. The residual ratios of DBP-d_4 were not so affected under these experimental conditions at the same ozone consumption and decreased exponentially with ozone consumption. Thus, it was indicated that the removal efficiency of DBP-d_4 could be evaluated with ozone consumption even though the DBP-d_4 decomposition rate was dependent upon treatment conditions (e.g. ozone and H_2O_2 doses). Also, it was thought that the results of Figure 5 were obtained because DBP-d_4 decomposition obeyed Eq. (6) (Hoigné *et al.*, 1989)

$$-\ln([DBP-d_4]/[DBP-d_4]_0) = \eta(\Delta O_3)k_{DBP-d4} / \sum k_i[S_i] \qquad (6)$$

where η is a stoichiometric factor of HO• generation per ozone consumption, (ΔO_3) (M) is the ozone consumption, k_{DBP-d4} (1/(M•s)) is a reaction rate constant of DBP-d_4 with HO•, $[S_i]$ (M) is the concentration of solute i and k_i (1/(M•s)) is a reaction rate constant of S_i with HO•. When DOM is a main HO• scavenger, $\Sigma k_i[S_i]$ is assumed to be the rate constant of DOM with HO• in Eq. (6). The HO• scavenging effects of DOM in SMSEfs were higher than those in surface waters. Ozone consumptions required to decompose 90% of DBP-d_4 $((\Delta O_3)_{90\%})$ per DOC of DOM were from 22 to 23 μmol/mgC for SMSEfs and from 10 to 17 μmol/mgC for surface waters. The value of $(\Delta O_3)_{90\%}$ is based on the competitive reaction between DBP-d_4 and DOM toward HO•.

In the case of SMSEfs, DBP-d_4 decomposition per ozone consumption was changed at around 7 μmol/mgC of ozone consumption. This is due to the great change of η and/or $\Sigma k_i[S_i]$ at the ozone consumption by the progression of the DOM oxidation. It was assumed that $\Sigma k_i[S_i]$ is not changed so dramatically because the HO• reaction is relatively
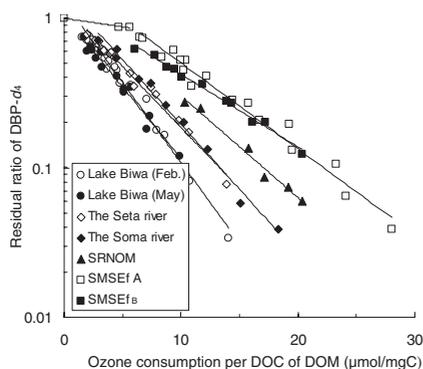

Figure 5 Relationship between the ozone consumption per DOC of DOM and the residual ratio of DBP-d_4
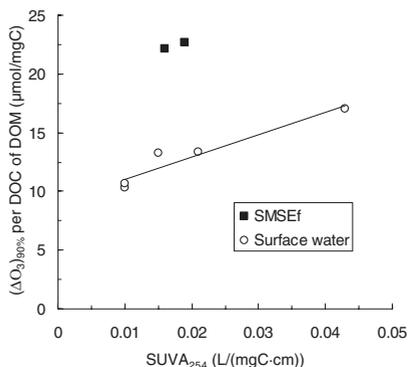

Figure 6 Relationship between SUVA$_{254}$ and $(\Delta O_3)_{90\%}$ per DOC of DOM

non-selective. Thus, the results described above were due to the great change of the η value. Such tendency was not clearly observed for SRNOM although the amount of instantaneous ozone consumption was the highest. Therefore, it was suggested that the change of η is not related to the amount of instantaneous ozone consumption and there were some components whose η is extremely different in SMSEFs.

Figure 6 shows the relationship between $SUVA_{254}$ of the DOM solutions and $(\Delta O_3)_{90\%}/[DOC]$. The $SUVA_{254}$ values for surface waters were correlated with the $(\Delta O_3)_{90\%}/[DOC]$ values. Thus, it was shown that $(\Delta O_3)_{90\%}$ is able to be used as an index for DOM when the DOM origins are similar.

Conclusions

The following conclusions were obtained from this research. First, ozone decompositions were different among the DOM solutions and were faster in order of SRNOM, SMSEfs, the Soma river, the Seta river, Lake Biwa (Feb.) and Lake Biwa (May). Secondly, ozone decompositions were represented by two phases, that is, instantaneous ozone consumption and slower ozone decay. The effect of H_2O_2 addition on the ozone decay was clearly observed after instantaneous ozone consumption when the ratio H_2O_2 dose to DOM was less than 36 µmol/mgC. Thirdly; the rate constant of ozone decomposition at the secondary phase increased with H_2O_2 dose when the ozone decomposition rate was determined as first-order reaction. Fourthly, the residual ratios of DBP-d_4 decreased exponentially with ozone consumption. The values of $(\Delta O_3)_{90\%}/[DOC]$ were from 22 to 23 µmol/mgC for SMSEFs and 10 to 17 µmol/mgC for surface waters. Finally, the values of $SUVA_{254}$ for surface waters were correlated with $(\Delta O_3)_{90\%}/[DOC]$.

Acknowledgement

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