Characterization of organic matter in ozonation and biological treatment

Fahmi, Wataru Nishijima and Mitsumasa Okada

ABSTRACT

The multi-stage ozonation-biological treatment process was evaluated to compare the performance of dissolved organic carbon (DOC) removal from two water sources between the conventional single-stage and the multi-stage ozonation-biological treatment process. Characteristic changes in DOC during these treatment processes were also evaluated by biodegradability and hydrophilicity. Water sources used in this study of DOC removal were Minaga reservoir water and secondary effluent from a domestic wastewater treatment plant. DOC was fractionated into three fractions as follows: hydrophilic, hydrophobic acid and hydrophobic base/neutral. In the multi-stage ozonation-biological treatment process, more biodegradable dissolved organic carbon (BDOC) was produced in comparison with the single-stage ozonation-biological treatment process, by the removal of BDOC produced by ozonation, and consequently more DOC was removed from the raw water. The improvement in DOC removal in the multi-stage ozonation-biological treatment process was mainly attributed to the decrease in hydrophobic acid fraction in raw water. Higher DOC removal was obtained in reservoir water than the secondary effluent, both in the single-stage and the multi-stage ozonation-biological treatment process, because DOC in the secondary effluent was less susceptible to ozone.

Key words | biodegradable dissolved organic carbon (BDOC), dissolved organic carbon (DOC), hydrophilic, hydrophobic, multi-stage ozonation-biological treatment process

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INTRODUCTION

Dissolved organic matter (DOM) remaining in drinking water is known to be responsible for the production of undesirable disinfection by-products such as trihalomethanes, haloacetic acids and haloaldehydes during the chlorination process (MacCarthy *et al.*, 1989). It may also enhance bacterial regrowth in the water distribution system (Owen *et al.*, 1995).

The combination of ozonation and biological treatment is an effective process to remove DOM in raw water for drinking water (Servais *et al.*, 1992; Prevost *et al.*, 1992). Ozone reacts with DOM and increases biodegradability (Rittmann & Huck, 1989). The increase in biodegradability by ozonation seems to be induced by the breakdown of larger molecules into smaller ones (Amy *et al.*, 1988), increase in polarity and hydrophilicity of DOM by formation of hydroxyl, carbonyl and carboxyl groups, and decrease in double bonds and aromaticity (Urfer *et al.*, 1997). Biological treatment does not necessarily change the nature of DOM. However, the biodegradable fraction that is produced during ozonation is selectively removed and mineralized in the biological treatment (Koechling *et al.*, 1996). Therefore, the production of BDOC is considered to be the essential factor that determines the performance of the ozonation and biological treatment process (Nishijima *et al.*, 1997).

It is known that the production of BDOC by ozonation is limited. Siddiqui *et al.* (1997) reported that increasing the ozone dose beyond an O_3:DOC ratio of 1:1 did not further improve BDOC production. The maximum BDOC produced was 40–50%. They suggested that the

remaining organic compounds required much more ozone to be converted to biodegradable forms. Roche *et al.* (1994) also showed that BDOC increased with the increase in ozone dose up to 0.5 mg O_3 per mg DOC^{-1}. However, further ozonation did not have a significant effect on the production of BDOC. One attempt to improve BDOC production in the ozonation and biological treatment process has been through repeated ozonation of biodegraded water. Yasui & Miyaji (1992) reported that repeated ozonation followed by biological treatment improved DOM removal compared with single ozonation followed by biological treatment. However, the DOM used by Yasui & Miyaji (1992), which was diluted filtrate of biologically treated night soil, seems to be more sensitive to ozone than DOM in drinking water sources. More than 70% of the DOM was removed by single ozonation for 64 min followed by biological treatment. Improvement of DOM removal by repeated ozonation followed by biological treatment (multi-stage ozonation-biological treatment process) should be evaluated for DOM in various drinking water sources. Characteristic changes of DOM during both conventional single-stage ozonation-biological treatment and multi-stage ozonation-biological treatment processes should also be evaluated to help understand what is occurring in ozonation and biological treatment.

The objective of this study is to compare the performances of DOC removal for two water sources in the conventional single-stage and the multi-stage ozonation-biological treatment processes. Characteristic changes in DOC during ozonation and biological treatment were also evaluated by biodegradability and hydrophilicity.

MATERIALS AND METHODS

Water sources

Water samples were collected from two water sources in Higashi-Hiroshima, Japan, i.e. Minaga reservoir water and secondary effluent from a domestic wastewater treatment plant. The collected waters were filtered through Whatman GF/C glass fibre filters (pore size = 1.2 μm) and concentrated to produce about 10 mg DOC l^{-1} by vacuum evaporator (Rotavapor, BUCHI) at 40°C.

Ozonation and biological treatment

All the ozonation experiments were conducted in semi-batch mode with continuous ozonation in a 5-l cylindrical reactor. Ozone was generated from an ozone generator (Fuji Electric PO-05) using dried air, and was introduced into the reactor through a porous glass diffuser. The ozone dose was 4.4 mg O_3 l^{-1} min^{-1}. Ozone was supplied continuously for 20 min in the single-stage ozonation-biological treatment process, and was supplied for 5 min in each stage of the multi-stage ozonation-biological treatment process. Ozonation and biological treatment were repeated four times in the multi-stage ozonation-biological treatment process.

The separated hydrophobic acid and hydrophilic fractions from the Minaga reservoir water were also passed through the multi-stage ozonation-biological treatment process to clarify the role of each fraction in BDOC production. Concentrated Minaga reservoir water with *ca* 10 mg DOC l^{-1} was fractionated by DAX-8 resin as described in the following section on analytical procedure. Hydrophobic acid and hydrophilic fractions were ozonated at an ozone dose of 4.4 mg O_3 l^{-1} min^{-1} for 5 min followed by biological treatment. The procedure was repeated twice.

Biological treatment was performed according to the bioassay procedure developed by Kim *et al.* (1996). The water sample was sterilized by filtration through a 0.2 μm polycarbonate filter (Nuclepore membrane filter, Whatman). One millilitre of river water filtered through a 2 μm polycarbonate filter was added to 100 ml of the sterilized sample as an inoculum. The sample was incubated at 20°C in the dark for 4 days, because maximum DOC removal in the sampled water would be obtained within this incubation time, and further incubation would not give additional DOC removal as shown by Kim *et al.* (1996). BDOC was defined as the difference between initial DOC and DOC after incubation.

Analytical procedure

DOC was used as an indicator of DOM in the source water for drinking water. DOC fractionation for water samples was carried out based on the modified method of Leenheer (1981). The original fractionation method of Leenheer (1981) produced six fractions; hydrophilic acid, base and neutral fractions, and hydrophobic acid, base and neutral fractions. In this study, however, DOC was fractionated into three: hydrophilic, hydrophobic acid and hydrophobic base/neutral fractions. The Supelite DAX-8 resin, a macroporous methyl metacrylate copolymer (Supelco, Bellefonte, PA), was used in this study instead of the XAD-8 used by Leenheer (1981), because the manufacture of the XAD-8 resin has recently ceased. Farnworth (1995) reported that XAD-8 could be substituted by Supelite DAX-8. The water sample was filtered through a 0.45 μm polycarbonate filter (Nuclepore membrane filter, Whatman) and acidified to pH 2 by concentrated HCl. The sample was passed through a glass column (30 cm long, 2.5 cm diameter) packed with DAX-8 resin, at a flow rate of 3 ml min^{-1}. Then 0.5 bed volume of 0.1 N NaOH solution was passed through the column, followed by 1.5 bed volumes of distilled water. The DAX-8 was washed with methanol followed by distilled water before reuse for the next analysis.

The hydrophobic substances would be adsorbed onto the DAX-8 resin at pH 2. Therefore, the non-adsorbed fraction of DOC which passed through the DAX-8, was defined as the hydrophilic fraction. The adsorbed fraction that was desorbed by the 0.1 N NaOH was defined as the hydrophobic acid fraction. The remaining DOC fraction on the resin after 0.1 N NaOH extraction was defined as the hydrophobic base/neutral fraction. This fraction was determined by deducting the hydrophilic and hydrophobic acid fractions from the initial DOC. Ozone concentration was determined by the iodometric method (APHA-AWWA-WPCF, 1985).

RESULTS AND DISCUSSION

BDOC production

Figure 1 shows the removal of DOC by the single- and multi-stage ozonation-biological treatment processes for the Minaga reservoir water. BDOC in the raw water was about 10% of total DOC. In the single-stage treatment, ozonation for 5 min mineralized approximately 6% of DOC and increased BDOC up to 34% of the initial DOC. Another 5 min of ozonation produced a little more BDOC and increased DOC removal. However, the increase in the ozonation time from 10 to 20 min did not improve DOC removal or BDOC production. Total DOC removal after the biological treatment was not significantly different from 10 min ozonation (48%) and 20 min ozonation (52%). This is in agreement with the results reported by Siddiqui *et al.* (1997) and Roche *et al.* (1994). BDOC

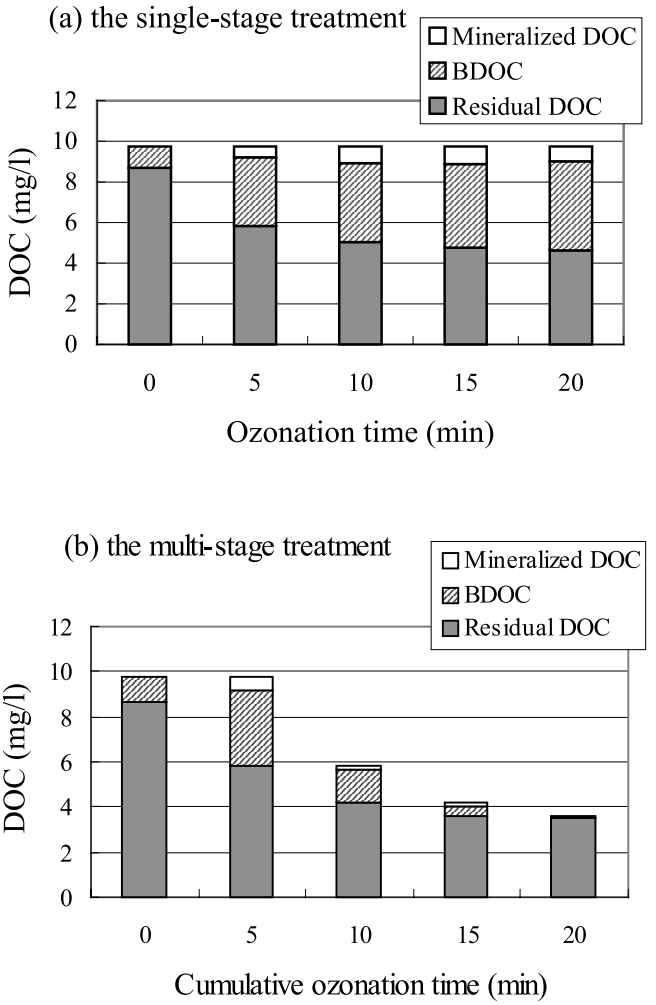

Figure 1 | The removal of DOC in the single- and multi-stage ozonation-biological treatment processes for the Minaga reservoir water.

production by ozonation levelled off even if the ozone dose or reaction time was increased in their studies.

On the other hand, additional BDOC was produced in the 2nd and 3rd stages of ozonation in the multi-stage treatment process, yielding 18% and 5% of BDOC, respectively. The total BDOC production in the four stages of the multi-stage treatment process reached 52%, and total DOC removal was 64%, whereas the single-stage ozonation produced 34% BDOC, and total DOC removal after biological treatment was 52% for the same total ozonation time. The difference in BDOC production between the single-stage and the multi-stage ozonation-biological treatment processes indicates that BDOC could be produced by ozonation if the BDOC was removed by biological treatment.

Figure 2 shows the production of BDOC by the single- and multi-stage ozonation-biological treatment processes for the secondary effluent. The results were significantly different from those for the Minaga reservoir water. Although a small amount of BDOC was produced in the first 5 min of ozonation, further production of BDOC was not noted by subsequent ozonation or by repeated ozonation after biological treatment in the single- and multi-stage ozonation-biological treatment processes, respectively. Moreover, the total BDOC production both in the single- and multi-stage processes was less than that for the Minaga reservoir water. It is most likely that DOC in the secondary effluent is less susceptible to ozone.

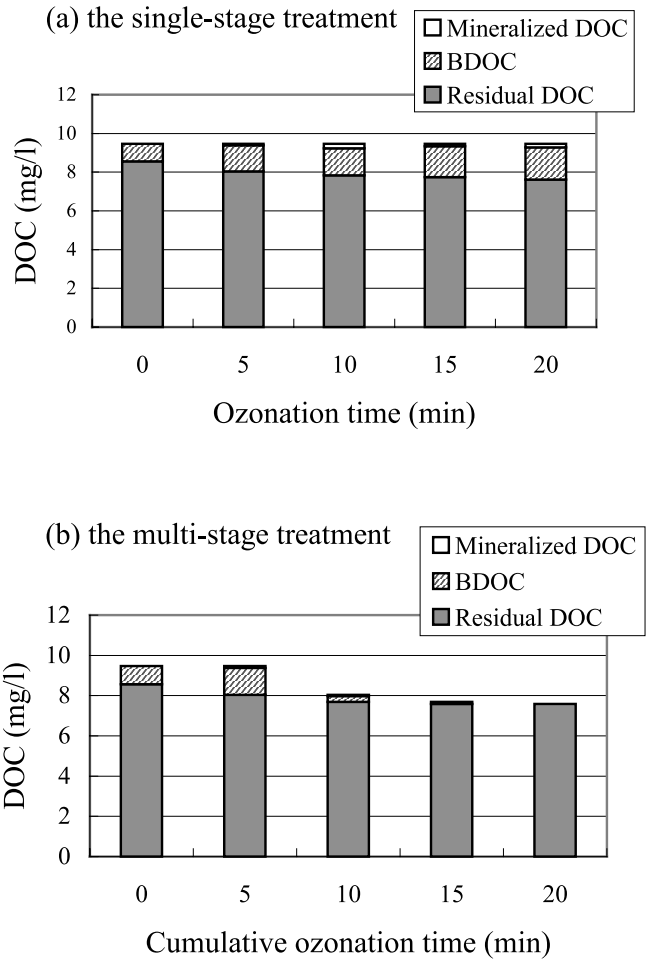

Figure 2 | The removal of DOC in the single- and multi-stage ozonation-biological treatment processes for the secondary effluent.

Hydrophilic and hydrophobic fractions of DOC

DOC fractions of Minaga reservoir water in the single-stage and the multi-stage ozonation-biological treatment processes are shown in Figure 3. Hydrophilic, hydrophobic acid and hydrophobic base/neutral fractions in Minaga reservoir water were 46%, 41% and 13% respectively. The composition of organic fractions changed significantly after ozonation. In the single-stage ozonation-biological treatment process, hydrophobic acid decreased after 5 min of ozonation, and continued to gradually decrease with further ozonation. In contrast, the hydrophilic fraction increased with the decrease in the hydrophobic acid fraction. Based on the initial DOC concentration, the hydrophilic fraction increased from 46% to 61%, the hydrophobic acid fraction decreased from 41% to 23%, the hydrophobic base/neutral fraction decreased from 13% to 8%, and about 8% was completely mineralized in 20 min ozonation.

The results indicate that the DOM changed from hydrophobic to hydrophilic with ozonation. This is in accordance with the previous studies reported by Bose *et al.* (1994), and Takahashi *et al.* (1995). It is likely that the increase in hydrophilicity with ozonation was due to the large increase in carboxyl content, as well as increases in other polar functional groups such as ketone and aldehyde (Bose *et al.*, 1994). However, further ozonation did not

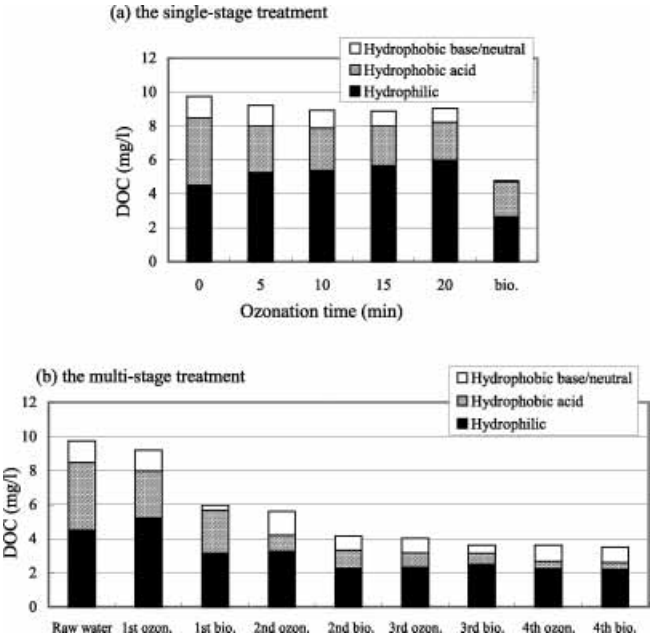

Figure 3 | Fractionation of DOC in the single- and multi-stage ozonation-biological treatment processes for the Minaga reservoir water (ozon.=ozonation, bio.=biological treatment).

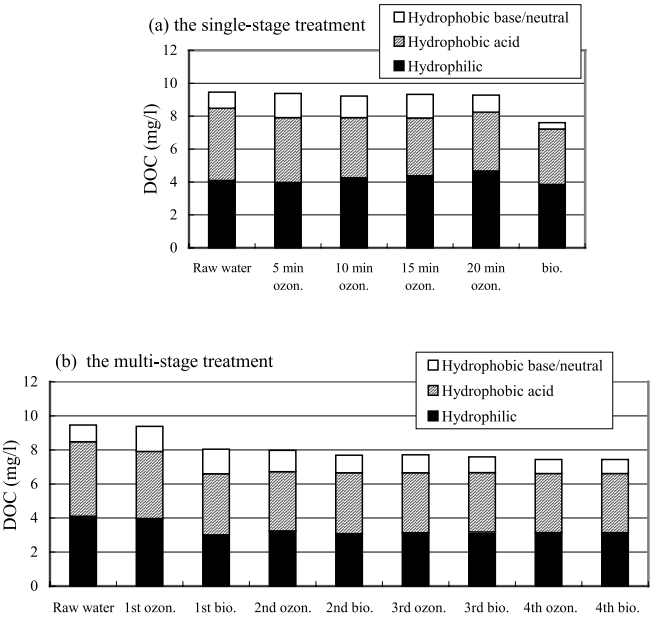

Figure 4 | Fractionation of DOC in the single- and multi-stage ozonation-biological treatment processes for the secondary effluent (ozon.=ozonation, bio.=biological treatment).

decrease both hydrophobic and hydrophilic fractions significantly, i.e. longer ozonation could not decrease DOC. Biological treatment of the ozonated sample resulted in a significant decrease both in hydrophilic and hydrophobic base/neutral fractions (Figure 3a), suggesting that these fractions might be responsible for the increase in BDOC in Figure 1a. However, hydrophobic acid did not change significantly during biological treatment. These substances are generally known to be refractory (Barber, 1968). In the multi-stage ozonation-biological treatment process, the 1st stage ozonation changed hydrophobic acid to hydrophilic. The following biological treatment removed both hydrophilic and hydrophobic base/neutral fractions. The 2nd stage ozonation changed the remaining hydrophobic acid to hydrophilic and hydrophobic base/neutral, and these fractions were removed by the following biological treatment. The decrease in hydrophobic acid fraction from 5 to 10 min in the single-stage ozonation was relatively small (from 28.2% to 25.6%), whereas a significant decrease (from 26% to 9.5%) was observed in the 2nd stage of ozonation in the multi-stage ozonation-biological treatment process. Therefore, significant production of BDOC in the 2nd stage ozonation in the multi-stage ozonation-biological treatment process (Figure 1b), was due to the significant decrease in non-biodegradable hydrophobic acid, which transformed to hydrophilic acid and hydrophobic base/neutral (Figure 3b).

Figure 4 shows DOC fractions of the secondary effluent in the single-stage and the multi-stage ozonation-biological treatment processes. The secondary effluent had almost the same composition as Minaga reservoir water, in which raw water consisted of 44% hydrophilic, 46% hydrophobic acid and 10% hydrophobic base/neutral fractions. However, the hydrophobic fraction showed barely any change with ozonation. Although biological treatment after the 1st ozonation removed the hydrophilic fraction, a significant decrease in hydrophobic acid was not noted in the 2nd and further ozonations. This result indicates that the hydrophobic acid fraction in the secondary effluent was not susceptible to ozone, which was the reason why the multi-stage ozonation-biological treatment process was not effective for the secondary effluent.

Mechanism of BDOC production

To clarify the role of each fraction in BDOC production, the multi-stage ozonation-biological treatment process was conducted separately on hydrophobic acid and hydrophilic fractions from Minaga reservoir water. Figure 5 shows BDOC production after ozonation in the multi-stage ozonation-biological treatment process for hydrophobic acid and hydrophilic fractions, respectively. Initially, the hydrophobic acid fraction contained about 3% of BDOC. After the 1st stage ozonation, BDOC in the hydrophobic acid fraction increased to 30% and the mineralized DOC was about 6.5% of total DOC. Moreover, the 2nd and the 3rd ozonation of hydrophobic acid after biological treatment could produce additional BDOC. On the other hand, the hydrophilic fraction contained 22% of BDOC before ozonation. BDOC production in the hydrophilic fraction was remarkable only during the 1st ozonation, whereas little BDOC was produced in the 2nd and the 3rd ozonation.

As shown in Figure 5, ozone could oxidize both hydrophobic acid and hydrophilic fractions and produce significant amounts of BDOC in the first stage of ozonation. Although further ozonation produced more BDOC from the hydrophobic acid fraction after the removal of BDOC by biological treatment, little BDOC was produced from the hydrophilic fraction. It is most likely that further BDOC production in the multi-stage ozonation-biological treatment process, in comparison with the single-stage ozonation-biological treatment process, was mainly attributed to the decrease in the hydrophobic acid fraction.

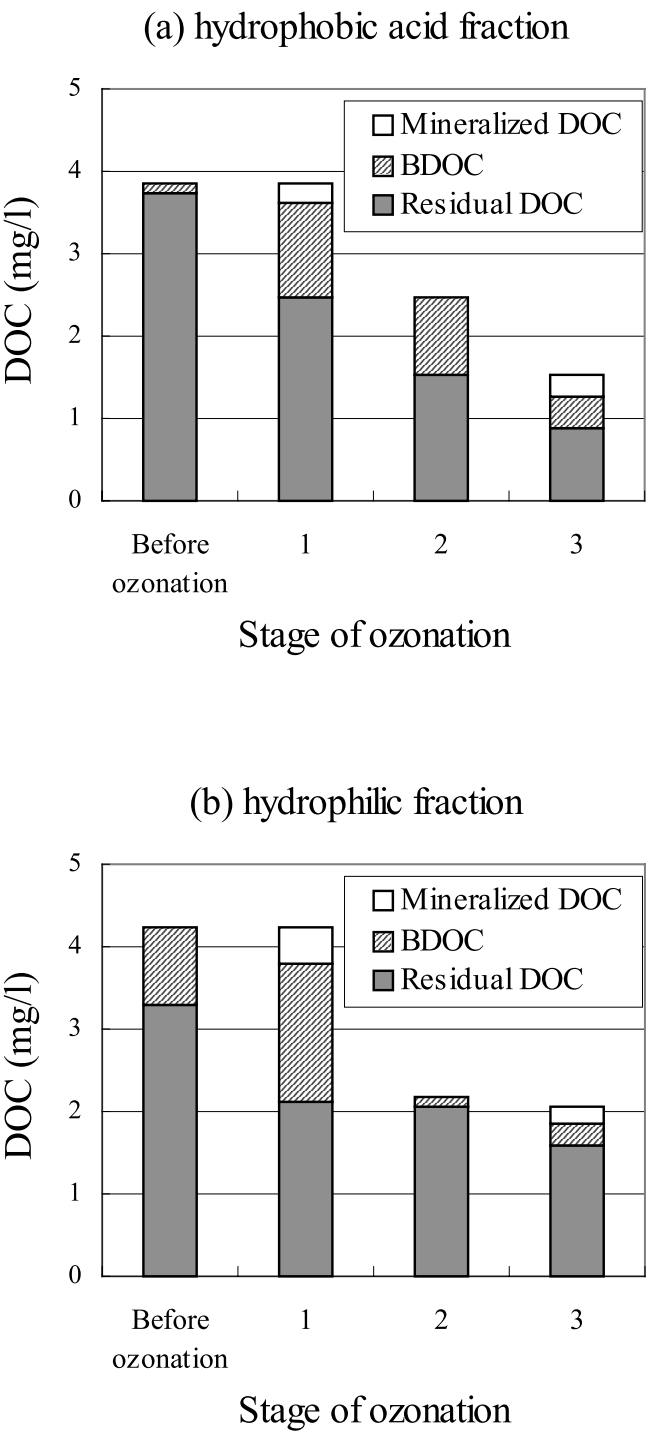

Figure 5 | BDOC production in the hydrophobic acid and hydrophilic fractions of the Minaga reservoir water after each stage of ozonation by the multi-stage ozonation-biological treatment process.

SUMMARY AND CONCLUSIONS

The multi-stage ozonation-biological treatment process was evaluated by comparing the performance of DOC removal from two water sources using the conventional single-stage and the multi-stage ozonation-biological treatment processes. Characteristic changes in DOC during these treatment processes were also evaluated by biodegradability and hydrophilicity. The water sources used

in this study were Minaga reservoir water and secondary effluent from a domestic wastewater treatment plant. The specific conclusions derived from this study are as follows:

1. In the multi-stage ozonation-biological treatment process, more BDOC was produced in comparison with the single-stage ozonation-biological treatment process by the removal of BDOC produced by ozonation and, consequently, more DOC was removed from the raw water. The improvement in DOC removal in the multi-stage ozonation-biological treatment process was mainly attributed to the decrease in the hydrophobic acid fraction in the raw water.
2. Higher DOC removal was obtained from Minaga reservoir water than the secondary effluent, both in the single-stage and the multi-stage ozonation-biological treatment processes, because the DOC in the secondary effluent was less susceptible to ozone.

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