Vol 19 | Issue 2 | March 2019

IWA PUBLISHING

Water Supply

ISSN 1606–9749
iwaponline.com/ws

Monitoring of iodine species during water purification at a public water treatment plant in Japan

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ABSTRACT

Iodine is an essential element for humans; however, it can be toxic depending on its chemical form. A variety of toxic and non-toxic iodine species have been identified in environmental water and in the drinking water produced by public water treatment plants. Here, we examined the change of iodine species during the water treatment process at a public water treatment plant in Japan. Samples of raw water and of treated water immediately after each of eight treatment stages comprising the treatment process were collected, and a speciation analysis was conducted by means of ion chromatography– and size-exclusion chromatography–inductively coupled plasma mass spectrometry. In the raw water, iodine was found mainly as iodide or iodinated humic substances that were ultimately oxidized and transformed into iodate, a form non-toxic to humans, by two independent oxidation stages in the water treatment process – ozone treatment and chlorine treatment. No disinfection byproducts were detected at any stage of the treatment process. Fluorescence spectrometry with multivariate analysis revealed that humic substances were markedly decreased by ozone treatment, but not by chlorine treatment. The present results show that, at the plant-scale, ozone treatment is an effective means of removing toxic iodine species from raw water.

Key words | Inductively coupled plasma mass spectrometry, iodate, iodinated humic substance, ozone treatment, speciation analysis of iodine, water treatment plant

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INTRODUCTION

Chlorine treatment is a method of disinfecting water that is used as part of the water treatment processes of public water treatment plants worldwide. However, during chlorine treatment, chlorine can react with organic matter to produce carcinogenic chlorine-derived disinfection byproducts such as chloromethane and chloroacetic acid (Hua & Reckhow 2007). To address this issue, additional treatment with ozone has been proposed (Srinivasan & Sorial 2011). Ozone decomposes organic matter more readily and is less persistent than chlorine. Water treatment systems utilizing ozone treatment (hereafter 'advanced water treatment systems') are used in public water treatment plants in many developed countries, and it is reported that the addition of an ozone treatment stage to existing water treatment processes reduces the generation of chlorine-derived disinfection byproducts (Guay et al. 2005).

Iodine is a halogen element that is converted into disinfection byproducts by the water treatment process (Wang et al. 2016). In environmental water, iodine exists mainly as iodide (I^-), iodate (IO_3^-) and iodinated humic substances (Yoshida et al. 2007; Shimamoto et al. 2011). During the water treatment process, iodine species are mainly oxidized or transformed into IO_3^-, which is non-toxic to humans, by means of chlorine treatment; however, iodinated disinfection byproducts such as iodomethane and iodoacetic acid, which are more highly toxic to humans than the other halogenated disinfection byproducts, are also produced (Richardson et al. 2008; Pals et al. 2011). It has been

demonstrated experimentally that ozone transforms iodine species into IO_3^- without generating iodinated disinfection byproducts (Allard *et al.* 2013; Lee *et al.* 2015); therefore, ozone treatment is a potentially useful means of disinfecting water without increasing the amounts of iodinated disinfection byproducts in processed water.

Many studies (Hua & Reckhow 2007; Yoshida *et al.* 2007; Lee *et al.* 2015; Wang *et al.* 2016) have reported the chemical forms of halogens found in environmental water and drinking water. However, how the relative amounts of these chemical forms change during the water treatment process has not been clarified. In the present study, we examined the change in iodine species during the advanced water treatment process of a public water treatment plant located in Japan. Ion chromatography (IC)– and size-exclusion chromatography (SEC)–inductively coupled plasma mass spectrometry (ICPMS) were used to determine the chemical forms of iodine after each stage of the treatment process, and fluorescence spectrophotometry was used to determine the amount of humic substances in the water. Our results show that, at the plant-scale, ozone treatment is an effective means of removing toxic iodine species from drinking water.

MATERIALS AND METHODS

Water sample collection

The advanced water treatment process of a public water treatment plant located in Japan was examined. By using a water sampler (Norwell; Saint-Gobain, Tokyo, Japan), river water was sampled from the river 0.6 km upstream of the intake gate of the water treatment plant; drinking water supplied by the same water treatment plant was also sampled. Water at different stages of the treatment process (#1–#8 in Figure 1) was sampled in the water treatment plant, and the whole sampling process was conducted twice, in June and December 2016, because pre-chlorination was performed in December but not in June. All water samples were filtered through 0.45 μm nitrocellulose filters (Merck Millipore, Darmstadt, Germany) and then stored at 4 °C until use. Dosages of chlorination and ozonation in the water treatment plant are 1 mg L^{-1} and 0.5 mg L^{-1}, respectively, on average.

Operating conditions in ICPMS and chromatographies

An ICPMS system (7500ce, Agilent Technologies Japan, Tokyo, Japan) was used in the total iodine analysis and iodine speciation analysis with the following operating parameters: radiofrequency power, 1,550 W; plasma argon flow rate, 15 L min^{-1}; auxiliary argon flow rate, 1.0 L min^{-1}; carrier gas (argon) flow rate, 0.8 L min^{-1}; make up gas (argon) flow rate, 0.35 L min^{-1}.

A Dionex ICS-2000 instrument (Thermo Fisher Scientific, Kanagawa, Japan) equipped with an anion exchange column (Dionex IonPac AS11-HC, $\phi4 \times 250$ mm; Thermo Fisher Scientific) and a guard column (Dionex IonPac AG11-HC, $\phi4 \times 50$ mm; Thermo Fisher Scientific) was used for IC-ICPMS with the following operating parameters: injection volume, 250 μL; flow rate, 1.3 mL min^{-1}; eluent, potassium hydroxide; suppressor, Dionex ASRS-300 (Thermo Fisher Scientific). A gradient program was used: 5 mM, 0–8 min; 5–30 mM, 8–21 min; 30–50 mM, 21–26 min; 50 mM, 26–38 min; 5 mM, 38–41 min.
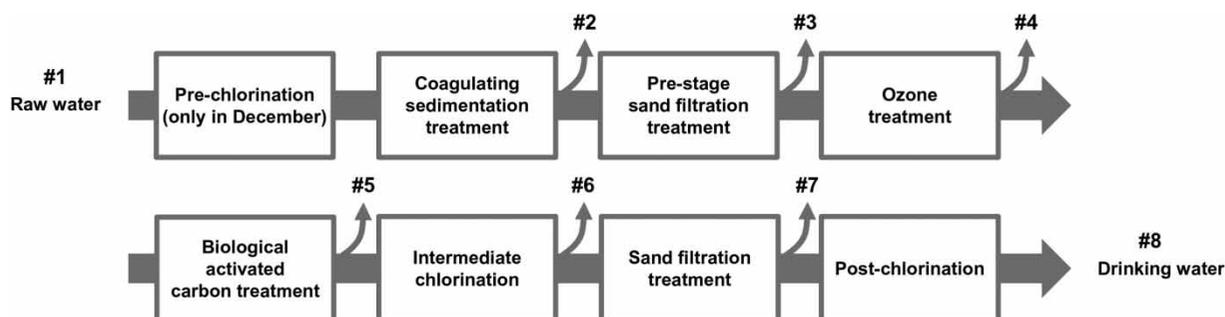
Figure 1 | Advanced water treatment process of a public water treatment plant located in Japan. Sampling points are numbered #1 to #8.

A PU-1580i instrument (JASCO, Tokyo, Japan) equipped with a multimode SEC column (Asahipak GS-320 HQ, $\phi 7.5 \times 300$ mm; Showa Denko, Tokyo, Japan) and a guard column (Asahipak GS-2G 7B, $\phi 7.5 \times 50$ mm; Showa Denko) was used for SEC-ICPMS with the following operating parameters: injection volume, 100 μL; flow rate, 0.5 mL min^{-1}; eluent, 20 mM Tris-HNO$_3$ with 0.3 wt% ethanol at pH 8.

Iodine speciation analysis and determination of total iodine content

Calibration standard solutions were prepared by dissolving commercially available chemicals in ultrapure water. Fulvic acid standard and humic acid standard, which were obtained from Japanese Humic Substances Society (Aomori, Japan), were dissolved in ultrapure water. Since humic acid is insoluble at low pH, humic acid solutions were prepared with 25% tetramethylammonium hydroxide to adjust the solution to pH 12.

The samples used for IC-ICPMS were concentrated 30-fold by means of freeze-drying (FDU-810; Tokyo Rikakikai, Tokyo, Japan) and re-dissolving in ultrapure water. The concentrated samples and untreated samples were injected into the IC-ICPMS and SEC-ICPMS systems, respectively, and the isotopes of ^{127}I were detected. To reduce the memory effect of iodine, samples and standard solutions were prepared with tetramethylammonium hydroxide to adjust the solutions to pH 12. The total concentration of iodine in the samples and standards were measured by means of ICPMS. All experiments were replicated three times.

Analysis of humic substances by using a fluorometer

Water samples and humic substance standard solutions were analyzed by using a fluorometer (F-7100; Hitachi High-Tech Science, Tokyo, Japan) and the following operating parameters: excitation wavelength, 200–600 nm; emission wavelength, 200–600 nm; sampling interval, 5.0 nm; scan speed, 60,000 nm min^{-1}, and all others remained as the default settings. The measurements were repeated twice for each sample and the mean values were used for the following analyses. The resulting three-dimensional excitation–emission matrix (EEM) data were subjected to parallel factor analysis (PARAFAC), which decomposes the peaks of EEM spectra (Yamashita *et al.* 2008). Data were analyzed by using Solo version 8.1.1 (Eigenvector Research, Inc., USA).

RESULTS AND DISCUSSION

Identification of iodine species in river water and drinking water

We first performed an iodine speciation analysis of the river water, which was sampled 0.6 km upstream of the intake gate of the water treatment plant, and of the processed drinking water by using IC-ICPMS and SEC-ICPMS. In the IC-ICPMS analysis, four peaks representing iodine compounds were detected in the river water samples and were identified as representing I$^-$, IO$_3^-$, iohexol and iopamidol by comparing the retention times with those of standard solutions and referring to the previous reports (Figure S1A; Sacher *et al.* 2005; Yoshida *et al.* 2007). In SEC-ICPMS analysis, two additional peaks (P1 and P2) were detected in the high-molecular-weight fraction of the river water (Figure S1B). (Figure S1A and S1B are available with the online version of this paper.) Previously, it was reported that iodine is contained in humic substances, which are organic high-molecular-weight compounds (molecular weight >1,000 g mol^{-1}) that are abundant in environmental water (Shimamoto *et al.* 2011). Fulvic acid and humic acid are two major soluble humic substances (Kuwatsuka *et al.* 1992). We therefore used SEC-ICPMS to examine the fulvic acid and humic acid standards, which were made from purified extracts obtained from soil (Figure S1B). A peak representing iodine was detected in the high-molecular-weight fraction of the fulvic acid standard, confirming the presence of iodine as iodinated fulvic acid. This iodinated fulvic acid was detected at the same retention time as was P2 in the river water sample, indicating that P2 represented iodinated fulvic acid. Since P1 was eluted before P2, it is likely that P1 was derived from an iodinated humic substance with a higher molecular weight than that of fulvic acid. No peak representing iodine was observed in the humic acid standard (Figure S1B). Hereafter, the peak of P1 + P2 is referred to as 'iodinated humic substances'.

We next examined the river water (stage #1 in June) and drinking water (stage #8 in June) samples by using a fluorometer, and compared the EEM patterns obtained with those of humic substance standards. Fluorescence-emitting compounds were detected in both the river water and the drinking water (Figure S2A). PARAFAC revealed that the EEM pattern for the river water (stage #1 in June) comprised two major components (components 1 and 2, Figure S2B) and one minor component (component 3, Figure S2B). (Figure S2A and S2B are available with the online version of this paper.) The EEM patterns of components 1 and 2 were identical to the EEM patterns of fulvic acid and humic acid, respectively, and these data were in good agreement with previous reports (Yamashita *et al.* 2008). The minor component (component 3) was likely derived from proteins, as suggested elsewhere (Yamashita *et al.* 2008). These results confirmed that the river water contained fulvic acid and humic acid.

Iodine speciation analysis during the water treatment process

We next conducted an iodine speciation analysis at different stages of the water treatment process of a public water treatment plant in Japan. The process at this plant comprised seven stages, and water samples were collected at each stage (Figure 1). In December, an additional hypochlorous acid treatment stage was conducted as the first stage for pre-chlorination, which is required to compensate for the decreased effect of biological purification during the winter, and therefore the water sampling was conducted twice, once in June and once in December. In June, the iodine speciation showed a drastic change after ozone treatment; I^- and iodinated humic substances were dominant until ozone treatment (#4), after which the dominant form was shifted to IO_3^- (Figure 2(a)). This indicated that I^- and iodine binding to humic substances are oxidized and transformed into IO_3^- by ozone treatment. In addition, the peak representing I^- was almost undetectable after the intermediate chlorination stage (#6), indicating that any I^- remaining after ozone treatment was completely oxidized and converted to IO_3^- by chlorine treatment.

In December, unlike in June, the iodine speciation was drastically changed by the initial treatment stages; I^- and iodinated humic substances were the most abundant forms of iodine in the raw water, but the dominant form was shifted to IO_3^- by pre-chlorination and coagulating sedimentation treatment (#2), indicating that the change in iodine form was likely a result of oxidation by pre-chlorination treatment (Figure 2(b)). I^- was further decreased by ozone treatment (#4) and was undetectable after intermediate chlorination (#6). These results demonstrated that oxidation due to ozone treatment and chlorine treatment were the main treatment stages responsible for the changes in iodine speciation during the water treatment process conducted in December.

Changes in the abundances of humic substances during the water treatment process were investigated by means of EEM analysis (Figure 3). Fluorescence intensity was markedly decreased by ozone treatment (#4, Figure 3(a)) in both June and December. Fluorescence intensities of fulvic acid and humic acid, which were estimated by PARAFAC, were greatly decreased after ozone treatment (#4, Figure 3(b)). These results indicate that humic substances were decomposed by ozone treatment. The fluorescence intensities of those humic substances were also decreased after coagulating sedimentation treatment (#2), indicating that humic substances were precipitated and removed by this treatment. The decreases in the amounts of fulvic acid and humic acid after coagulating sedimentation treatment were estimated to be 36% and 45% in June and 33% and 42% in December, respectively; the addition of a pre-chlorination stage did not affect the amount of humic substances removed. These results suggest that oxidation by chlorine treatment is not enough to decompose humic substances, but it is enough to break the chemical bonds between iodine and humic substances.

Change in the proportions of iodine species

The total amounts of iodine and of the major iodine species were quantified at the different stages of the water treatment process from the SEC-ICPMS and total iodine analysis data (Figure 4). The peaks representing iodinated humic substances and IO_3^- could not be completely separated; therefore, the concentrations of iodinated humic substances and IO_3^- were estimated from the peak area between 11.7 and 15.0 min and between 15.0 and 18.3 min, respectively (separated at the bottom of overlapped area, Figure 2).
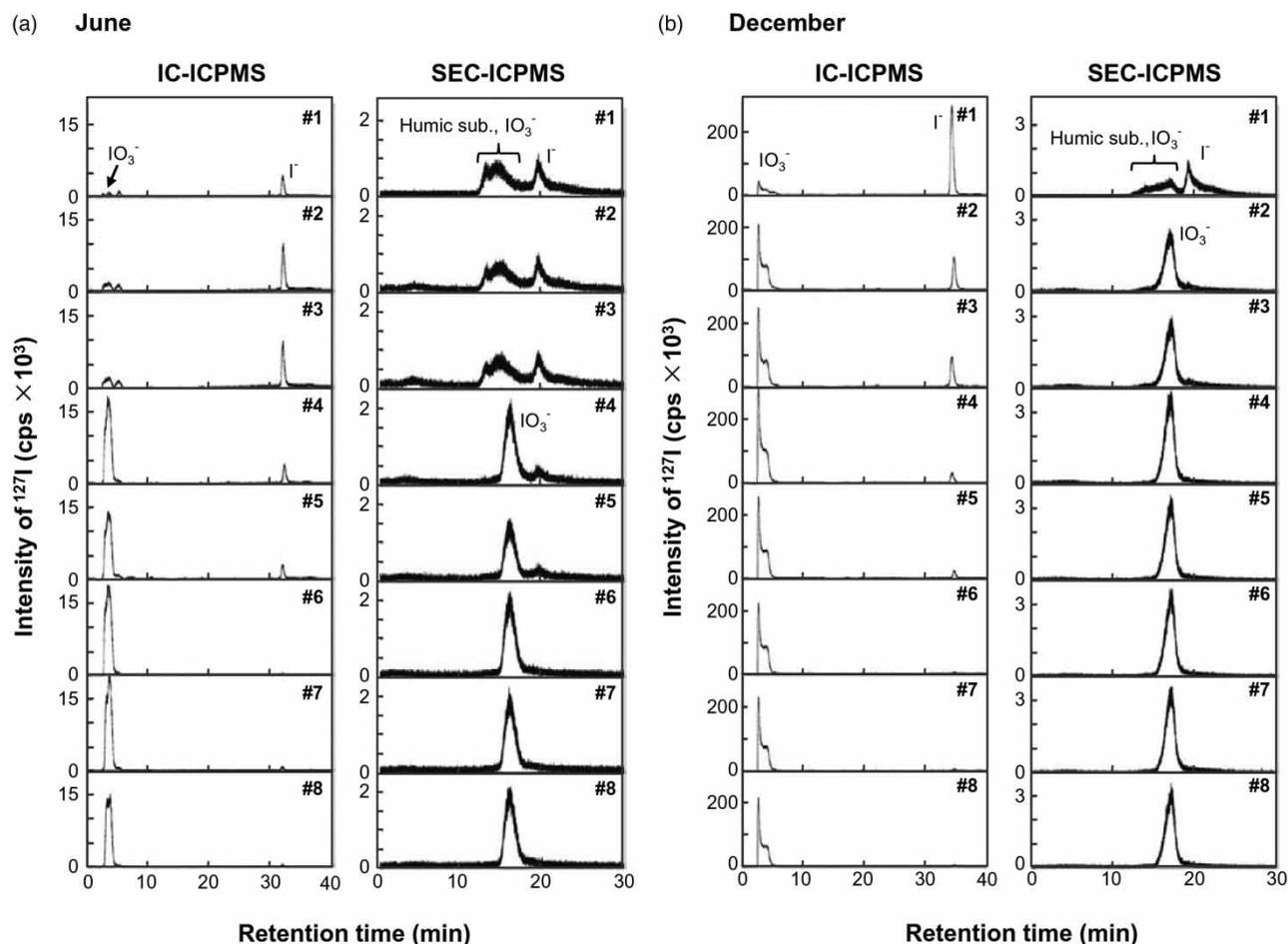
Figure 2 | Iodine speciation results for each water treatment stage. Representative data of three independent experiments are shown. IC, ion chromatography; SEC, size-exclusion chromatography; ICPMS, inductively coupled plasma mass spectrometry.

Recovery (%) was calculated as the ratio to the total iodine concentration. Iohexol and iopamidol were not taken into account in the recovery rate calculation because the peaks of those compounds were considered small enough to ignore. In the raw water, the recovery of iodine was $98 \pm 3\%$ for the samples collected in June and $99 \pm 1\%$ for the samples collected in December, confirming that all ion species could be explained in this study.

In the samples collected in June, the concentration of I^- was decreased to less than half that in the raw water by ozone treatment (#4), and it was then gradually decreased by the following treatment stages until the concentration of I^- in the drinking water was 1/8 that in the raw water. The concentration of iodinated humic substances was decreased to 1/12 that in the raw water after ozone

treatment (#4), and was decreased to an undetectable level by subsequent intermediate chlorination (#6). However, the concentration of IO_3^- was increased by 2.7 times during the water treatment process. The sum of the decrements of iodinated humic substances and I^- by ozone treatment (2.96 ng iodine mL^{-1}, from #3 to #4) was in agreement with the increment of IO_3^- (3.16 ng iodine mL^{-1}), confirming that iodinated humic substances and I^- were oxidized and transformed into IO_3^- by ozone treatment.

In the samples collected in December, the concentrations of iodinated humic substances and I^- were decreased to 1/2 and 1/3, respectively, the concentration in the raw water after chlorination and coagulating sedimentation treatment (#2), whereas the concentration of IO_3^- was increased by 2.9 times that in the raw water. A further
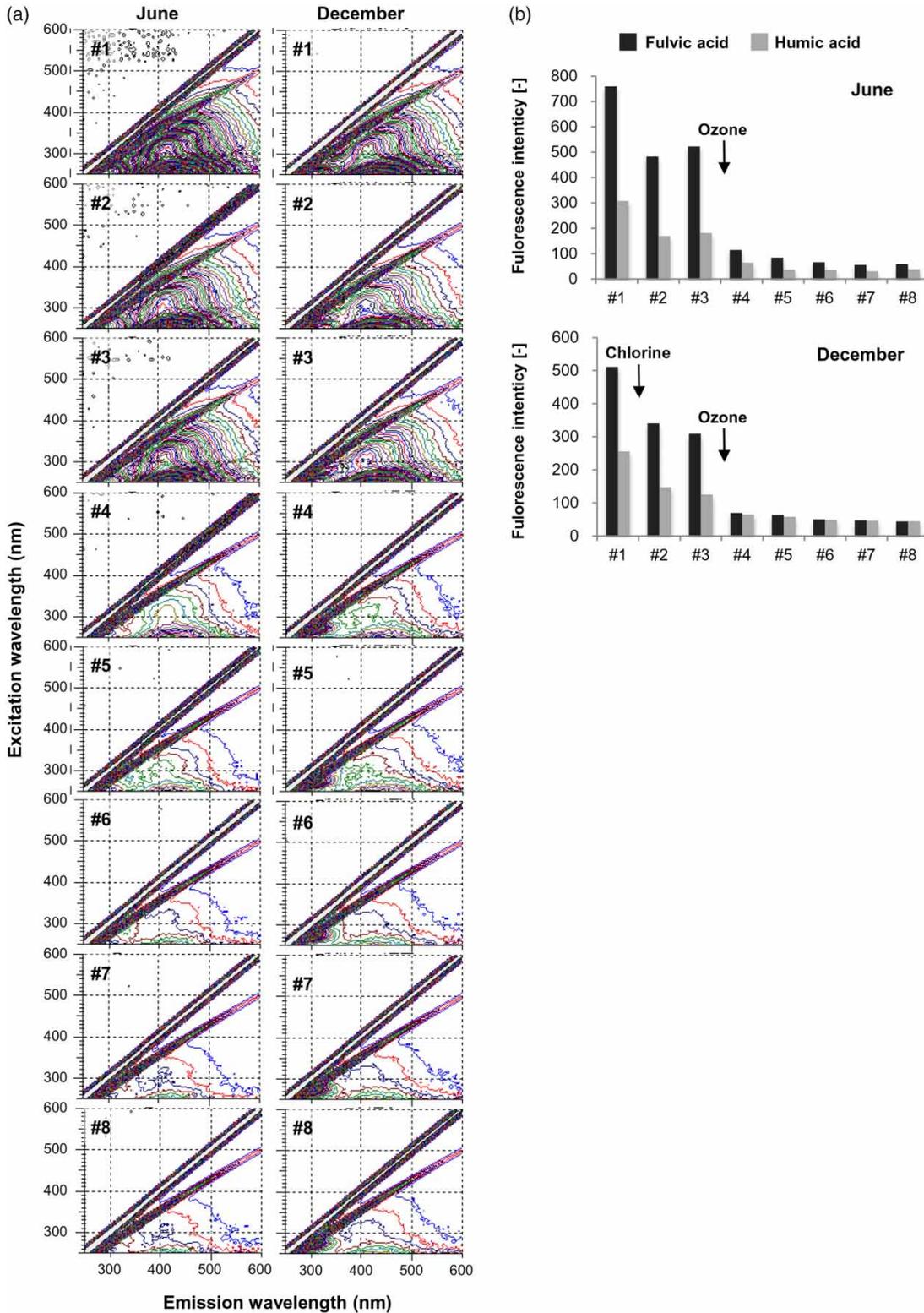
Figure 3 | Analysis of humic substances at each water treatment stage in June and in December. (a) Excitation–emission matrixes for each water treatment stage. (b) Fluorescence intensities of fulvic acid and humic acid. Values were estimated by parallel factor analysis of the excitation–emission matrixes data shown in (a). Timing of the chlorine treatment and ozone treatment is indicated with arrows.
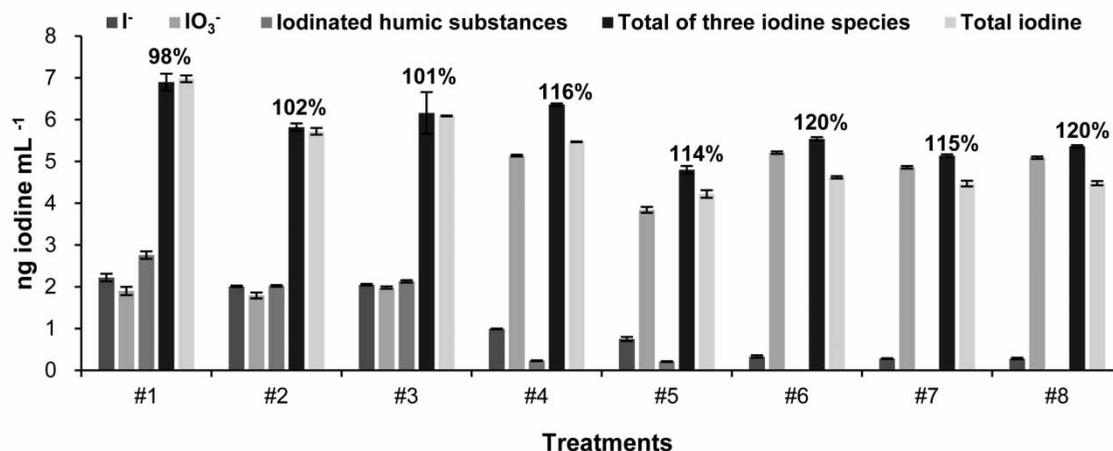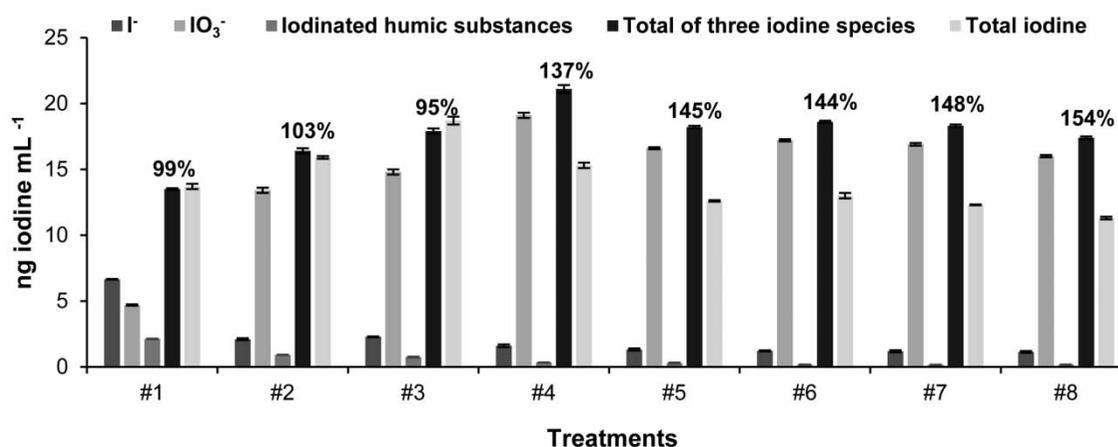
Figure 4 | Concentration of iodine species at the different treatment stages (#1–#8). Values are presented as mean ± SD of three independent experiments. Means of recovery rates ((the total concentrations of three iodine species/the total iodine concentration) ×100%) are shown above the bars of total of three iodine species. (a) June. (b) December.

reduction was observed in iodinated humic substances and I^- following ozone treatment (#4), and accordingly IO_3^- was further increased. Eventually iodinated humic substances and I^- levels in the drinking water were 1/13 and 1/6, respectively, the level in the raw water.

The present results show that I^- and iodinated humic substances in raw water are changed to IO_3^-, which is non-toxic to humans, by two independent oxidation stages in the water treatment process – ozone treatment and chlorine treatment. The results from the samples collected in December show that the pre-chlorination treatment stage accounted for oxidation of approximately half of the iodinated humic substances in the raw water. However, this pre-chlorination treatment stage did not contribute to the reduction in the

concentration of humic acid substances. These results suggest that iodine bound to humic substances is released by oxidation via chlorine treatment, but that the humic substances themselves are not decomposed (Figure S3, available with the online version of this paper). The difference in the disinfection activity between ozonation and chlorination is probably derived from the difference in oxidizability; the oxidizability of ozone is much higher than that of chlorine (Rodríguez *et al.* 2007). Although humic substances are a mixture of various compounds, it is thought that iodine bonds primarily to the aromatic rings of humic substances (Schlegel *et al.* 2006). This suggests that chlorine treatment is strong enough to remove iodine from the aromatic rings but not oxidize the humic substances themselves.

CONCLUSIONS

Here, we conducted an iodine speciation analysis during the advanced water treatment process of a public water treatment plant in Japan and found that oxidation via ozone treatment and chlorine treatment are the main stages responsible for the transformation of I^- and iodinated humic substances into IO_3^-, a harmless form of iodine to humans. In addition, our data showed that humic substances are decomposed and removed by ozone treatment. Thus, this study demonstrates that, at the plant-scale, disinfection by means of ozone treatment is an effective method for removing toxic iodine species from raw water.

REFERENCES

Allard, S., Nottle, C. E., Chan, A., Joll, C. & von Gunten, U. 2013 Ozonation of iodide-containing waters: selective oxidation of iodide to iodate with simultaneous minimization of bromate and I-THMs. *Water Research* **47** (6), 1953–1960.

Guay, C., Rodriguez, M. & Serodes, J. 2005 Using ozonation and chloramination to reduce the formation of trihalomethanes and haloacetic acids in drinking water. *Desalination* **176**, 229–240.

Hua, G. & Reckhow, D. A. 2007 Comparison of disinfection byproduct formation from chlorine and alternative disinfectants. *Water Research* **41** (8), 1667–1678.

Kuwatsuka, S., Watanabe, A., Itoh, K. & Arai, S. 1992 Comparison of two methods of preparation of humic and fulvic acids, IHSS method and NAGOYA method. *Soil Science and Plant Nutrition* **38**, 23–30.

Lee, H. J., Kim, H. H., Lee, H. & Lee, C. 2015 Reaction of aqueous iodide at high concentration with O_3 and O_3/H_2O_2 in the presence of natural organic matter: implications for drinking water treatment. *Environmental Chemistry Letters* **13** (4), 453–458.

Pals, J. A., Ang, J. K., Wagner, E. D. & Plewa, M. J. 2011 Biological mechanism for the toxicity of haloacetic acid drinking water disinfection byproducts. *Environmental Science and Technology* **45** (13), 5791–5797.

Richardson, S. D., Fasano, F., Ellington, J. J., Crumley, F. G., Buettner, K. M., Evans, J. J., Blount, B. C., Silva, L. K., Waite, T. J., Luther, G. W., McKague, A. B., Miltner, R. J., Wagner, E. D. & Plewa, M. J. 2008 Occurrence and mammalian cell toxicity of iodinated disinfection byproducts in drinking water. *Environmental Science and Technology* **42** (22), 8330–8338.

Rodríguez, E., Onstad, G. D., Kull, T. P. J., Metcalf, J. S., Acero, J. L. & von Gunten, U. 2007 Oxidative elimination of cyanotoxins: comparison of ozone, chlorine, chlorine dioxide and permanganate. *Water Research* **41** (15), 3381–3393.

Sacher, F., Raue, B. & Brauch, H. J. 2005 Analysis of iodinated X-ray contrast agents in water samples by ion chromatography and inductively-coupled plasma mass spectrometry. *Journal of Chromatography A* **1085** (1), 117–123.

Schlegel, M. L., Reiller, P., Mercier-Bion, F., Barré, N. & Moulin, V. 2006 Molecular environment of iodine in naturally iodinated humic substances: insight from X-ray absorption spectroscopy. *Geochimica et Cosmochimica Acta* **70** (22), 5536–5551.

Shimamoto, Y. S., Takahashi, Y. & Terada, Y. 2011 Formation of organic iodine supplied as iodide in a soil-water system in Chiba, Japan. *Environmental Science and Technology* **45** (6), 2086–2092.

Srinivasan, R. & Sorial, G. A. 2011 Treatment of taste and odor causing compounds 2-methyl isoborneol and geosmin in drinking water: a critical review. *Journal of Environmental Sciences* **23** (1), 1–13.

Wang, X., Wang, J., Zhang, Y., Shi, Q., Zhang, H., Zhang, Y. & Yang, M., 2016 Characterization of unknown iodinated disinfection byproducts during chlorination/chloramination using ultrahigh resolution mass spectrometry. *Science of the Total Environment* **554–555**, 83–88.

Yamashita, Y., Jaffé, R., Maie, N. & Tanoue, E. 2008 Assessing the dynamics of dissolved organic matter (DOM) in coastal environments by excitation emission matrix fluorescence and parallel factor analysis (EEM-PARAFAC). *Limnology and Oceanography* **53** (5), 1900–1908.

Yoshida, S., Muramatsu, Y., Katou, S. & Sekimoto, H. 2007 Determination of the chemical forms of iodine with IC-ICP-MS and its application to environmental samples. *Journal of Radioanalytical and Nuclear Chemistry* **273** (1), 211–214.

1 **Supplementary material**

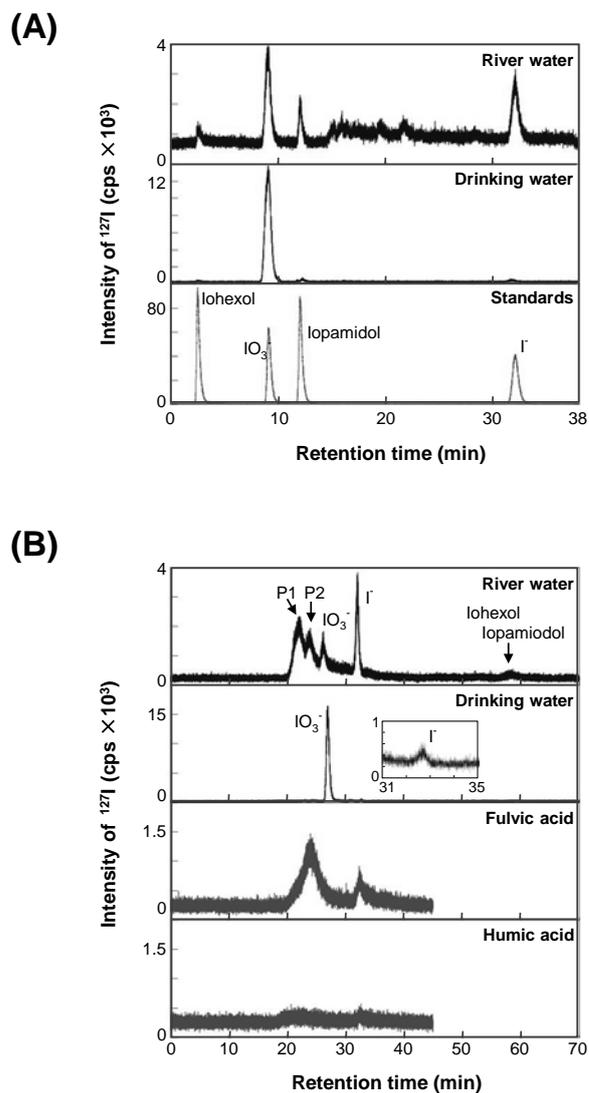2 **Figure S1** Identification of iodine species in river water and drinking water.

3

4 **Figure S2** Identification of fluorescence-emitting compounds by using parallel factor analysis.
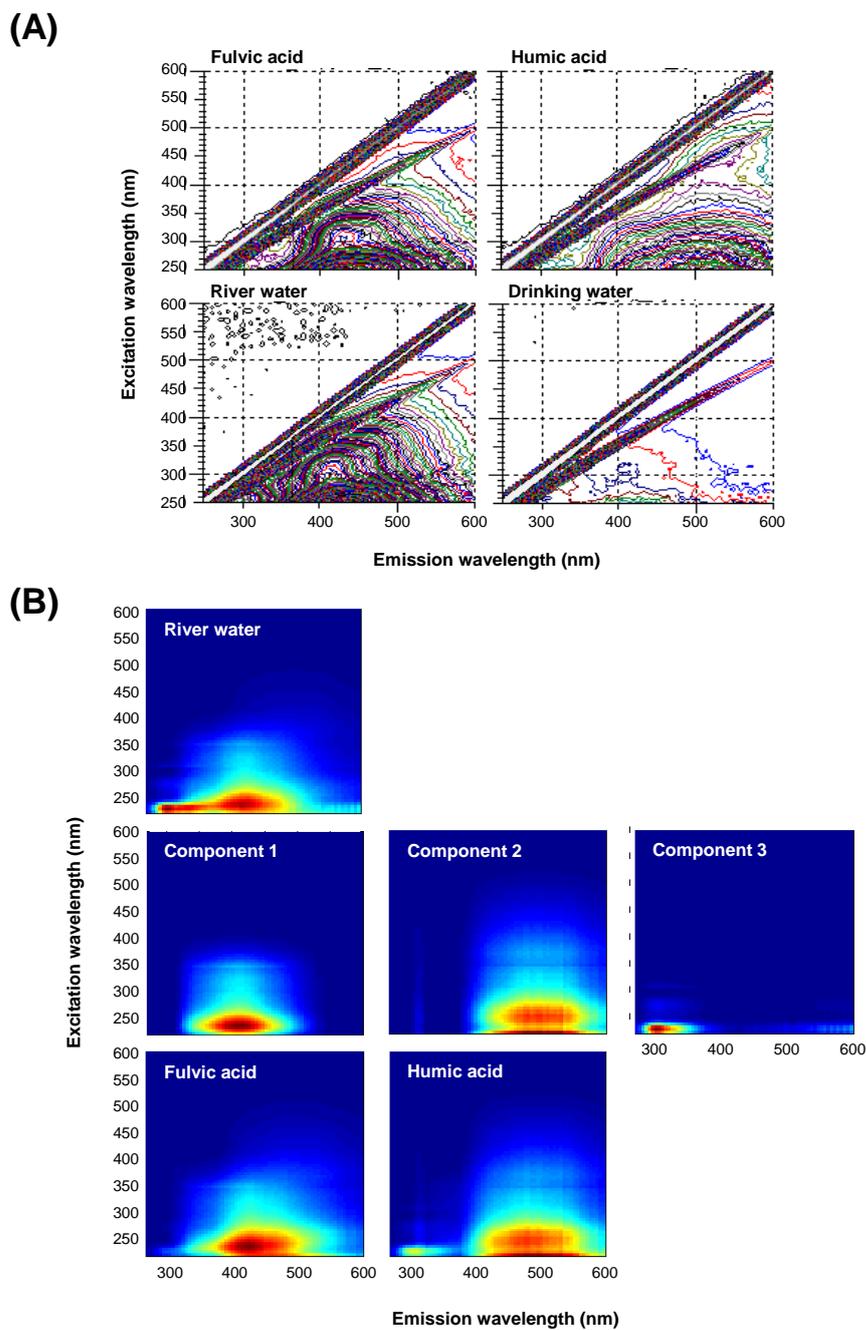
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6 **Figure S3** Hypothetical model of the change in chemical form of iodine species and humic

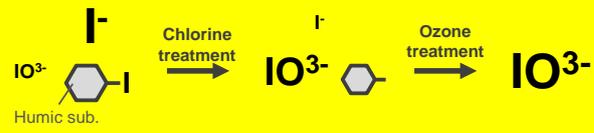7 substances during chlorine treatment and ozone treatment.

8

Figure S1 Identification of iodine species in river water and drinking water.
(A) Ion chromatography–inductively coupled plasma mass spectrometry chromatograms of iodine species in river water, drinking water, and standard solutions. (B) Size-exclusion chromatography–inductively coupled plasma mass spectrometry chromatograms of iodine species in river water, drinking water, and humic substance standard solutions.

1

(A)

(B)

Figure S2 Identification of florescence-emitting compounds by using parallel factor analysis.
(A) Excitation–emission matrix patterns were obtained for standards of two humic substances (fulvic acid and humic acid), river water (stage #1 in June) and drinking water (stage #8 in June). (B) Components in the river water (stage #8 in June) were as determined by parallel factor analysis. Data analysis was conducted by using Solo version 8.1.1 (Eigenvector Research, Inc., USA). Component 1 was identified as being fulvic acid, Component 2 as humic acid, and Component 3 was likely a mixture of proteins.

1

Figure S3 Hypothetical model of the change in chemical form of iodine species and humic substances during chlorine treatment and ozone treatment.

1