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Iodate and iodo-trihalomethane formation during chlorination of iodide-containing waters: Role of bromide.

Justine Crique^{a,b}, Sebastien Allard^b, Elisabeth Salhi^a, Cynthia A. Joll^b, Anna Heitz^b and Urs von Gunten^{a,c,d*}.

- a. Eawag, Swiss Federal Institute of Aquatic Science and Technology, CH-8600, Dübendorf, Switzerland.
- b. Curtin Water Quality Research Centre, Curtin University, G.P.O. Box U1987, Perth, WA 6845, Australia.
- c. School of Architecture, Civil and Environmental Engineering (ENAC), Ecole Polytechnique Fédérale de Lausanne (EPFL), CH-1015 Lausanne, Switzerland.
- d. Institute of Biogeochemistry and Pollutant Dynamics, ETH Zentrum, CH-8092 Zürich, Switzerland.

* corresponding author: urs.vongunten@eawag.ch
Phone: +41 58 765 5270

Abstract

The kinetics of iodate formation is a critical factor in mitigation of the formation of potentially toxic and off flavour causing iodoorganic compounds during chlorination. This study demonstrates that the formation of bromine through the oxidation of bromide by chlorine significantly enhances the oxidation of iodide to iodate in a bromide-catalysed process. The pH-dependent kinetics revealed species specific rate constants of $k(\text{HOBr} + \text{IO}^-) = 1.9 \times 10^6 \text{ M}^{-1} \text{ s}^{-1}$, $k(\text{BrO}^- + \text{IO}^-) = 1.8 \times 10^3 \text{ M}^{-1} \text{ s}^{-1}$ and $k(\text{HOBr} + \text{HOI}) < 1 \text{ M}^{-1} \text{ s}^{-1}$. The kinetics and the yield of iodate formation in natural waters depend mainly on the naturally occurring bromide and the type and concentration of dissolved organic matter (DOM). The process of free chlorine exposure followed by ammonia addition revealed that the formation of I-THMs, especially iodoform, was greatly reduced by an increase of free chlorine exposure and an increase of the Br^-/I^- ratio. In water from Great Southern River (with a bromide concentration of 200 $\mu\text{g/L}$), the relative I-incorporation in I-THMs decreased from 18 to 2% when the free chlorine contact time was increased from 2 to 20 minutes (chlorine dose 1 $\text{mg Cl}_2/\text{L}$). This observation is inversely correlated with the conversion of iodide to iodate, which increased from 10 to nearly 90%. Increasing bromide concentration also increased the conversion of iodide to iodate: from 45 to

nearly 90% with a bromide concentration of 40 and 200 $\mu\text{g/L}$, respectively and a prechlorination time of 20 min, while the I-incorporation in I-THMs decreased from 10 to 2%.

Introduction:

Iodide in source waters is rapidly oxidized to hypiodous acid during oxidation and disinfection with chlorine, monochloramine and ozone.¹⁻⁴ During oxidative water treatment, hypiodous acid (HOI) is formed and can be further oxidized to iodate (IO_3^-) or react with NOM to form iodo-organic compounds as disinfection by-products (DBPs).^{5,6} It has been shown that iodo-trihalomethanes (I-THMs) are more toxic than their brominated and chlorinated analogues and iodoacetic acid has been found to be the most genotoxic DBP identified to date.^{7,8} Moreover, I-THMs, especially iodoform, were associated with a characteristic medicinal taste and odor which may appear in finished drinking water.⁹ In fact, these compounds have low odor threshold concentrations ranging from 0.03 to 8.9 $\mu\text{g/L}$, with the lowest concentration being for iodoform.¹⁰ The occurrence of I-THMs and iodo-acids has been studied and these compounds were found in most finished drinking waters when the iodide levels in the corresponding source waters were between 0.4 and more than 100 $\mu\text{g/L}$.⁸ The formation of iodoorganic compounds is favored in waters containing a high iodide concentration and, among existing disinfection processes, it was shown that chloramination leads to the highest concentrations of iodo-DBPs.^{5,8,9,11,12} In a survey of the occurrence of DBPs in the United States, the highest I-THM concentration was observed for a simultaneous addition of chlorine and ammonia.¹¹ Another survey showed the relationship between the formation of I-THMs and the free chlorine contact time, with shorter contact times inducing a higher formation of I-THMs.⁸ These observations are related to the further oxidation of HOI, the first oxidation product of I^- , which determines the fate of iodine compounds in oxidative treatment. Only ozone and chlorine oxidize HOI and IO^- to IO_3^- , iodate formation does not occur with monochloramine. Iodate is the desired sink of iodide in drinking water treatment. In contrast to bromate, iodate has been conferred a “Generally Recognized as Safe” status by the United States Food and Drug Administration.¹³

Chlorine species oxidize HOI by a combination of second- and third-order reactions ($k''(\text{HOCl} + \text{HOI}) = 8.2 \text{ M}^{-1} \text{ s}^{-1}$; $k'''(\text{HOCl} + \text{HOCl} + \text{HOI}) = 8.3 \times 10^4 \text{ M}^{-2} \text{ s}^{-1}$ and $k''(\text{ClO}^- + \text{HOI}) = 52 \text{ M}^{-1} \text{ s}^{-1}$).⁴ It has been shown that an increasing chlorine dose caused a reduced level of iodinated organic by-products due to the formation of iodate.⁶ However, the kinetics of the formation of iodate by chlorine is quite slow (half-life of iodide around 40 min for a chlorine concentration of 1 mg/L) and on this basis it is difficult to explain these observations. Usually natural waters containing high concentrations of iodide also contain elevated concentrations of bromide.⁸ During chlorination, bromide is oxidized to HOBr (Table 2, Eq. 19).¹⁴ Bromine has generally a higher reactivity than chlorine. For example, the reaction rate of bromine with phenolic compounds has been found to be 10^3 times higher than that for chlorine.¹⁵⁻¹⁸ Several studies considering the effect of the presence of bromide during chlorination focus only on the differences in the extent of formation of halogenated compounds.^{6,19-22} In this study we investigate the influence of bromide on the kinetics of iodate formation during chlorination of iodide-containing natural and synthetic waters. Furthermore, the effect of DOM type and concentration on iodate formation was studied. Finally, the effect of the bromide concentration on the mitigation process for iodo-organic compounds, based on free chlorine followed by ammonia addition was investigated in natural waters.

Materials and Methods

Chemicals. All reagents used were of the highest purity. HOBr was produced through the oxidation of Br^- by HOCl from a NaOCl stock solution (Sigma Aldrich) of 1.29 M (determined by iodometry²³). Br^- was added in a slight stoichiometric excess of $1.05 \times [\text{HOCl}]$. The concentration of the HOBr stock solution ($7 \times 10^{-2} \text{ M}$) was determined by photometry ($\epsilon_{329\text{nm}}(\text{BrO}^-) = 332 \text{ M}^{-1} \text{ cm}^{-1}$; after adjusting the pH of the solution to 11).¹⁵ Experiments were performed in ultra-pure water (Barnstead Nanopure (Skan); TOC <0.2 mg/L; 18.2 mΩ cm). pH was controlled by 5 mM phosphate, borate or carbonate buffers.

Natural waters. Five natural waters were collected in Switzerland and in Western Australia. Their key water quality characteristics are summarized in Table 1. The collected waters were filtered through 0.45 μm membranes before storage at 4 $^{\circ}\text{C}$. To allow a comparison of iodate formation for the different waters, they were diluted to obtain the same DOC concentration (1.2 mg C/L) and then spiked in order to achieve the same final concentration of iodide (50 $\mu\text{g/L}$; 0.4 μM) and bromide (100 $\mu\text{g/L}$; 1.25 μM). The pH was adjusted to 8.0 and, for the waters from Great Southern River, North West Reservoir and Great Southern Reservoir, in which deviations of pH during chlorination occurred, a phosphate buffer (5 mM) was added.

Table 1

Ions and trihalomethane analysis. Br^- and IO_3^- analysis were performed in both laboratories by ion chromatography (Dionex ICS 3000) on an AG-S9 column. Low quantification limits for iodate were obtained by a post-column reaction with UV/Vis detection of I_3^- at 288 nm.²⁴ The quantification limits were 10 and 1 $\mu\text{g/L}$ for Br^- and IO_3^- , respectively. Iodide was determined by an ion-selective electrode (Orion 96-53 Combination iodide electrode) for the Swiss waters and by ion chromatography for the Australian waters, with a quantification limit of 10 $\mu\text{g/L}$. Most of the iodate samples were analysed at least twice, an average of the values was determined, the standard deviation of the method was around 5%.

Trihalomethanes (I-THMs and THM4) were analyzed by a headspace solid-phase microextraction-gas chromatography-mass spectrometry (SPME-GC-MS).²⁵ The error bars (Figure 5 and S7-9) represent the values obtained by a repetition of the analysis on each sample. More detailed information for each compound (detection, quantification limits and reproducibility) can be found in a previous publication.²⁵

Chlorination/bromination experiments. Experiments were performed at 24 ± 1 $^{\circ}\text{C}$ in a 500 mL batch reactor equipped with a dispenser. The oxidant concentration was measured using the colorimetric method based on diethyl-p-phenylene diamine (DPD).²³ Small volumes of

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sodium hypochlorite or hypobromite stock solutions were added at $t = 0$ to the different water samples and aliquots of reaction solutions were withdrawn after 15 s - 5 h and added to an excess ($20 \times$) of sodium sulfite solution to quench the oxidants before iodate analysis. Aliquots were also added to a DPD/phosphate buffer mixture to determine residual oxidant concentrations. To determine the rate constants for the reaction of HOBr with HOI, triplicate experiments were performed under pseudo first order conditions by measuring the formation of iodate in the presence of an excess of bromine ($[HOBr/BrO^-] = 2 \mu M$ and $[I^-] = 0.1 \mu M$), the pH range was 5.4 to 11.5.

Chlorine-ammonia experiments for trihalomethane mitigation

The natural water was diluted and spiked with aliquots of stock solutions of iodide and bromide to achieve a dissolved organic carbon (DOC) concentration of 1.2 mg C/L and desired concentrations of 50 $\mu g/L$ and from 40 to 200 $\mu g/L$, respectively for I^- and Br^- . The reactions were initiated in 100 mL batch reactors by the addition of chlorine to yield 1 mg/L as Cl_2 . At different reaction times (0, 2, 5, 10, 20 min), an aliquot of ammonium chloride solution ($10 \times$ molar excess compared to the initial chlorine concentration) was added to quench the residual chlorine by the formation of monochloramine. After 24 hours, samples were withdrawn for iodate and trihalomethane measurements. The iodate concentrations measured after the different reaction time by quenching with sulfite and after 24 hours after addition of NH_4Cl were identical. Experiments without addition of NH_4Cl (i.e. 24 h chlorination) were also performed for comparison.

Results and Discussion

Effect of bromide on the kinetics of iodate formation during chlorination

The oxidation of iodide by chlorine has been studied previously.² The first step is the oxidation of I^- to HOI and is very fast.³ This reaction occurs immediately, then 2 additional moles of HOCl per mole of HOI are consumed to yield IO_3^- . Figure 1 shows the effect of bromide on iodate formation, chlorination experiments were performed in the presence of various concentrations of bromide (*i.e.* ultrapure water; $[I^-]_0 = 1 \mu M$ (127 $\mu g/L$); $[HOCl]_{tot,0} = 4 \mu M$; pH 7; with $[Br^-]$ from 0 to 2 μM (up to 160 $\mu g/L$)). The kinetics of the decrease of the oxidant concentrations are shown in SI (Figure S1) and represented as the sum of $[HOCl]_{tot} + [HOBr]_{tot} + [HOI]_{tot}$; with $[HOX]_{tot} = [HOX] + [XO^-]$, $X = Cl, Br, I$.

Figure 1

As demonstrated in Figure 1, the presence of bromide significantly enhances the kinetics of iodate formation compared to chlorination alone. Half of the iodide was oxidized to iodate after 360, 35 and 13 min, for bromide concentrations of 0, 0.5 and 2 μM , respectively. The much higher rate of iodate formation by HOBr (Figure 1a) (half-life of iodide of 4 and 360 min for oxidation by bromine or chlorine, respectively) explains the enhancement observed in presence of bromide during chlorination. This is due to the formation of HOBr by oxidation of Br^- by HOCl (Eq. 19) followed by the reaction of bromine with HOI. Moreover, according to Figure 1b, the kinetics of iodate formation by bromine is pH-dependent, with the slowest rate occurring at low pH (7.0). With increasing pH the rate reached a maximum before decreasing again at higher pH.

Kinetics and stoichiometry of iodate formation from iodide by HOBr

The stoichiometry of the reaction of $HOBr/BrO^-$ with HOI/IO^- to iodate was investigated as a function of pH and at molar ratios of $[HOBr]_{tot}: [I^-] = 4:1$. Considering the consumption of the

oxidant (HOBr/BrO⁻) and its self-decay in water, it was found that 3.0 ± 0.2 mol of HOBr/BrO⁻ were consumed per mol of I⁻ oxidized to IO₃⁻ (SI, Figure S2). According to the stoichiometry and the mass balance showing quantitative formation of iodate from iodide, it can be assumed that no stable intermediates or IO₄⁻ were formed. Therefore, it can be hypothesized that the reaction pathway of formation of iodate through oxidation of iodide by bromine is similar to the one proposed for chlorine (Eqs.1-3).⁴

X = Cl, Br

The kinetics of the first step of iodide oxidation by HOBr, *i.e.*, the formation of HOI/IO⁻, has been determined previously²⁶ (Table 2, Eqs. 10 and 11). Under the conditions used, the formation of hypiodite and hypiodous acid occurs immediately. Moreover, the species specific rate constants of Eq. 3 are assumed to be high, considering that IO₂⁻ does not accumulate in solution. Therefore, the rate limiting step is the oxidation of HOI/IO⁻ by HOBr/BrO⁻ (Eq. 2) and the rate of iodate formation corresponds to the rate of the reaction (2). To determine the kinetics of the oxidation of iodine by bromine, experiments were performed under pseudo first order conditions ([HOBr]_{tot}: [I⁻] = 20). The apparent rate constant of reaction (2) can be determined as follows (Eqs. 4-8):

$$r = \frac{d[\text{IO}_3^-]}{dt} = - \frac{d[\text{HOI}]_{tot}}{dt} \quad (4)$$

where,

$$r = k''_{app} [\text{HOI}]_{tot} [\text{HOBr}]_{tot} \quad (5)$$

HOBr was introduced in a large excess, hence, [HOBr]_{tot} can be considered constant (pseudo first order conditions):

$$r = k'_{app} [\text{HOI}]_{tot} \text{ with: } k'_{app} = k''_{app} [\text{HOBr}]_{tot} \quad (6)$$

then,

$$r = - \frac{d[\text{HOI}]_{tot}}{dt} = \frac{d[\text{IO}_3^-]}{dt} = k'_{app} [\text{HOI}]_{tot} \quad (7)$$

The concentration of HOI after a time t is calculated as $[\text{HOI}]_{\text{tot},t} = [\text{HOI}]_{\text{tot},0} - [\text{IO}_3^-]_t$ with $[\text{HOI}]_{\text{tot},0} = [\text{I}^-]_0$; then,

$$\ln \frac{[\text{I}^-]_0 - [\text{IO}_3^-]_t}{[\text{I}^-]_0} = -k'_{\text{app}} t \quad (8)$$

The apparent rate constant of the reaction between iodine and bromine was obtained by measuring the kinetics of iodate formation as a function of pH from 7.0 to 11.5. The slopes of the logarithmic regression lines for the different pH (Eq. 8) (SI, Figure S3) give the value of k'_{app} . The apparent second order rate constant k''_{app} is then obtained by dividing the first order rate constant by the concentration of bromine. The derived apparent second order rate constants of the reaction between iodine and bromine species as a function of the pH are plotted in Figure 2.

Figure 2

The variation of the apparent second order rate constants shows a maximum at the mean of the two pKa values ($1/2(\text{pKa}_1 + \text{pKa}_2) = 9.6$) of the involved species HOBr and HOI ($\text{pKa}_1(\text{HOBr}/\text{BrO}^-) = 8.8$; $\text{pKa}_2(\text{HOI}/\text{IO}^-) = 10.4$). This behaviour is common for the reaction of two compounds HA and HB if either the protonated form HA reacts with the deprotonated form B^- , or conversely, A^- reacts with HB.²⁷ From a kinetic point of view, the two reactions ($\text{BrO}^- + \text{HOI}$ and $\text{HOBr} + \text{IO}^-$; Eqs. 14 and 14a, Table 2) cannot be distinguished since they have the same pH dependence. Rather than considering the two reactions in parallel, it is usually assumed that only one of the two pathways is important. From a chemical point of view, HOBr is a stronger electrophile and IO^- is a stronger nucleophile. Therefore, the reaction of HOBr with IO^- (Table 2, Eq. 14) is considered as the dominant pathway for the reaction of the bromine with the iodine species. Nevertheless, at low or high pH, $\text{HOBr} + \text{HOI}$ or $\text{OBr}^- + \text{IO}^-$, respectively, might also be important reactions (see below). Consequently, the reactions considered to represent this reaction step are Eqs. 13-15 (Table 2).

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3 220 The species specific rate constants were determined by a non-linear least-square regression
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5 221 with the experimental rate constants determined as a function of the pH (SI, Text S1). The
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7 222 regression curve is represented in Figure 2 and is in good agreement with the profile of the pH-
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9 223 dependent experimental data. The species specific second order rate constants were
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11 224 determined to be $k(\text{HOBr}/\text{IO}^-) = 1.9 \times 10^6 \text{ M}^{-1} \text{ s}^{-1}$ and $k(\text{BrO}^-/\text{IO}^-) = 1.8 \times 10^3 \text{ M}^{-1} \text{ s}^{-1}$. Based on
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13 225 this model, the reaction between HOBr and HOI was negligible with a value tending to zero.
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15 226 For $\text{pH} < 7$, a drop of the apparent rate constant was found followed by an increase for smaller
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17 227 pH values. The increase in the apparent rate constant in more acidic conditions can be
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19 228 attributed to the formation of Br_2 . The rate constant for the reaction of Br_2 with HOI was
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21 229 estimated to be $1 \times 10^6 \text{ M}^{-1} \text{ s}^{-1}$ and this reaction becomes significant for $\text{pH} < 7$ (SI, Text S2).

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24 230 **Modeling the effect of bromide on iodate formation during chlorination**

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26 231 To validate the kinetics of iodate formation during chlorination of bromide-containing waters,
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28 232 simulations of the reaction system were carried out by a kinetic model (Software Copasi²⁸).
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30 233 The reaction model is shown in Table 2 (Eqs. 9-25).

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33 234 Table 2

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36 236 The results of the model calculation for of iodide oxidation by bromine are presented in Figure
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38 237 1b. The experiments performed in basic media were well predicted by the set of reactions
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40 238 taken into account shown in Table 2. However, the model showed a certain deviation
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42 239 compared to the experimental data obtained for $\text{pH} 7.0$. A small error on the measured pH
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44 240 value (± 0.1) can affect the kinetics of iodate formation significantly. The observed difference
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46 241 between the experiment and model calculations is therefore within the range of experimental
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48 242 error. The model was subsequently applied for modeling iodate formation during chlorination of
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50 243 iodide-containing water in the absence and presence of bromide at $\text{pH} 7$ (lines in Figure 1a)
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52 244 with good agreement with the experimental data. The increase in the rate of iodate formation in
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54 245 the presence of bromide is caused by the formation of bromine through the reaction of chlorine
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56 246 with bromide (Table 2, Eq. 19). HOBr then oxidizes HOI to IO_2^- (more rapidly than HOCl
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58 247 undertakes this oxidation) and thereby HOBr is reduced to Br^- (Table 2, Eqs. 13-15).

Therefore, bromide acts as a catalyst in the formation of iodate during chlorination. This has been shown previously for the transformation of chlorpyrifos during chlorination.³² Bromide catalysis is also known from other oxidation processes such as the enhanced ammonia oxidation during ozonation of ammonia- and bromide-containing waters, and the formation of *N*-nitrosodimethylamine during ozonation of dimethylsulfoxide- and bromide-containing waters.^{33,34}

Iodate formation during chlorination of iodide-containing natural waters

To further elucidate the reaction pathways of iodate formation, chlorination experiments were performed with two natural waters spiked with iodide ($0.40 \mu\text{M} \approx 50 \mu\text{g/L}$) and various concentrations of bromide. Bromide concentrations were in the range of natural waters from $0.19 \mu\text{M}$ ($15 \mu\text{g/L}$) up to $6.25 \mu\text{M}$ ($500 \mu\text{g/L}$). The formation of iodate is presented as a function of the oxidant exposure (sum of chlorine, bromine and iodine exposures) in Figure 3. This representation takes into account the different rates of consumption of the oxidants due to differences in the water composition.

Figure 3

According to Figure 3, as found in ultrapure water, increasing the bromide concentrations in natural waters significantly enhanced the rate of iodate formation. The experiments on both waters were performed at the same pH (8) to avoid an effect of this parameter on the kinetics of iodate formation. The main difference between the two waters was the DOC level: Lake Greifensee water (3.5 mg C/L) had a DOC concentration that was 3 times higher than the DOC concentration of Lake Zurich water (1.2 mg C/L). Comparison of Figures 3a and b shows that the rate of iodate formation was higher for the water with the lower DOC concentration at the same bromide concentration. Hypoiodous and hypobromous acids are scavenged to a higher proportion when the concentration of dissolved organic matter (DOM) is higher. This is reflected by the fact that the iodate yield in the natural waters is not 100% based on the initial

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3 276 iodide concentration. In addition to the kinetic enhancement, it is important to note that a
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5 277 higher bromide level also improves the relative conversion of iodide to iodate by lowering the
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7 278 effect of the competitive reactions with DOM. The faster reaction of bromine species compared
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9 279 to chlorine species with hypiodous acid decreases the life-time of HOI, thereby reducing its
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11 280 likelihood of reaction with DOM and favoring iodate as a sink for iodine. The stability of the
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13 281 oxidants (HOCl + HOBr + HOI) was also influenced by the bromide concentration (SI, Figure
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15 282 S4). An increase in the consumption rate of the total oxidant concentration was observed with
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17 283 increasing bromide concentration. In natural waters, this can mainly be explained by the higher
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19 284 reactivity of HOBr compared to HOCl towards DOM.^{6,35} During chlorination, a substantial
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21 285 portion of bromide disappeared and was probably incorporated into organic matter (SI, Figure
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23 286 S5). This fraction was different for the two waters and was independent of the initial bromide
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25 287 concentration. Bromide in these waters decreased about 50 and 40% based on the initial
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27 288 concentration in Lake Zurich and Lake Greifensee waters, respectively. Modeling of the effect
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29 289 of bromide on iodate formation during chlorination of iodide-containing natural waters was
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31 290 difficult due to the unknown speciation of the different oxidant species, HOCl, HOBr and HOI,
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33 291 and lack of information on the reactivity of those species with DOM which is different for each
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35 292 natural water.
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37 293 To compare the influence of the type of DOM on iodate formation, experiments with natural
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39 294 waters from different origins (lakes, reservoirs and a river from both Switzerland and Australia;
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41 295 Table 1) were performed. Chlorination experiments were conducted at pH 8.0 with the natural
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43 296 waters adjusted to the same DOC concentration (1.2 mg C/L), with iodide and bromide
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45 297 concentrations of 50 ± 2 and 105 ± 5 $\mu\text{g/L}$ (0.4 and 1.3 μM), respectively. The formation of
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47 298 iodate as a function of the oxidant exposures is presented in Figure 4.
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49 299
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51 300 Figure 4
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55 302 Despite the same experimental conditions (pH, $[\text{I}^-]$, $[\text{Br}^-]$, DOC concentration), the kinetics of
56
57 303 iodate formation varied depending on the water type. In particular, the experiment performed
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using the Great Southern Reservoir water showed completely different iodate formation. Different types of DOM have different reactivities towards hypohalous acids and are responsible for differences in extent and rate of iodate formation due to incorporation of halogens into the DOM. In fact, the kinetics of iodate formation generally decreased with increasing SUVA (SI, Figure S6). This is likely related to the more aromatic character of the organic matter (higher SUVA), which constitutes a target for quenching the moieties HOI and HOBr, thereby increasing the competition of the DOM for consumption of the HOI versus oxidation of HOI to iodate. However, the SUVA alone does not explain completely the differences in the kinetics of iodate formation. For example, Lake Zurich and Great Southern River waters showed the same trend for iodate formation but had quite different SUVA values (2.6 and 4.1, respectively). Therefore, SUVA can only serve as a very general parameter to understand the relative kinetics of iodate formation in natural waters and more detailed structural information on DOM would be needed to draw more quantitative conclusions. As noted previously, bromide incorporation into organic matter differs from one water source to another. In the five investigated waters, bromide incorporation was found to vary from 30 to 70% without any correlation to the kinetics of iodate formation (results not shown). However, the experiments performed at two DOC concentrations for Lake Griefensee (1.2 and 3.5 mg C/L) show that the kinetics of iodate formation (Figure 3b and 4) and the incorporation of bromine was related to the DOC concentration. Half of the maximum yield of iodate (*i.e.* formation of 0.2 μM of iodate) was reached for an oxidant exposure of 7 and 24 mg $\text{Cl}_2/\text{L} \times \text{min}$, for a DOC concentration of 1.2 and 3.5 mg C/L, respectively. Moreover, the incorporation of bromine into organic matter was higher for the higher organic matter content (30 and 40% for DOC concentrations of 1.2 and 3.5 mg C/L, respectively). The observations of iodate formation and bromide incorporation into organic matter indicate a significant dependence on the DOC concentration. Therefore, the conversion factor of iodide to iodate could be much lower in waters rich in organic matter.

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Formation of iodo-trihalomethanes (I-THMs)

Trihalomethane formation may serve as a model for the formation of halo-organic compounds. Chloramination with a sufficient free chlorine contact time followed by ammonia addition, rather than preformed monochloramine, has been previously suggested^{8,21,22} as a mitigation strategy for the minimization of I-DBPs, since exposure to free chlorine should promote the formation of iodate. This mitigation process was tested on one of the natural waters (Great Southern River, after dilution and spiking: [I⁻] = 50 µg/L; pH 8; DOC = 1.2 mg C/L). The free chlorine contact time was varied such that the full range of conversion of iodide to iodate (from 0 up to nearly 90%) was achieved to elucidate the optimum conditions for minimal formation of I-THMs. This was done for three different bromide concentrations (40, 100 and 200 µg/L). After a certain chlorine contact time (0, 2, 5, 10 and 20 min), ammonia was added to reduce the formation of bromo- and chloro-organic compounds. The formation of trihalomethanes, the four regulated THMs (THM4) and I-THMs, was analysed after 24 hours. Figure 5 presents the iodine incorporation into I-THMs and the corresponding iodate formation. A detailed speciation of trihalomethanes is given in SI (Figures S7 and S8). For the calculation of the incorporation of iodine, the molar concentrations of individual I-THMs were multiplied by the number of iodine atoms in the I-THM. With this value, the percentage of iodine incorporated into the I-THMs can be compared to the percentage of iodine yielding IO₃⁻.

Figure 5

Considering the monochloramination experiment (no free chlorine contact time, t = 0 min in Figure 5), only a few THM4 were formed with traces of brominated THMs, as monochloramine hardly oxidizes bromide (SI, Figures S7 and S8). Although the I-THMs were predominant in this case compared to the THM4, a relatively low incorporation of iodine into I-THMs of around 6% of the initial iodide content, independent of the bromide concentration was observed. In this process, iodoform was formed in a relatively high concentration, representing up to 90% of the

iodine incorporation into I-THMs. These results are in accordance with those previously published^{5,9,21,22,36} in which chloramination of raw waters showed substantial formation of iodoform.

The formation and the speciation of iodinated THMs depend on the free chlorine contact time and the bromide concentration. The iodine incorporation into I-THMs increased for a short chlorination time compared to chloramination but decreased for higher free chlorine exposures.

The lower formation of I-THMs with increasing free chlorine contact time was correlated with the conversion of iodide to iodate. According to Figure 5, the iodine incorporation was lowered from 18 to 2% of the initial iodide content, while the iodate concentration increased from 10 to nearly 90%, for an increase of the prechlorination time from 2 up to 20 min in the presence of 200 µg/L of bromide. Moreover, increasing concentrations of bromide clearly reduced the formation of I-THMs by favoring the formation of iodate. For the experiments performed with the highest prechlorination time, an increase of the bromide level from 40 to 200 µg/L resulted in a decrease of the iodine incorporated in I-THMs by a factor > 4 and an improvement of iodide conversion to iodate from 45 to nearly 90% of the initial iodide concentration. At the same time, the formation of Br-THMs was kept low, with a bromine incorporation between 4.5 and more than 10 times lower than the one observed during the 24h-chlorination performed under the same conditions for varying Br⁻ concentrations. The highest formation of THM4 observed for the chlorine-ammonia process occurred for the highest free chlorine contact time and highest bromide concentration. However, this concentration (9 µg/L) was significantly lower than the one observed for the 24h-chlorination (around 40 µg/L) (SI, Figure S8 and Table S1). Considering the increasing iodate formation with increasing prechlorination time (Figure 5), the higher formation of I-THMs after a short prechlorination time compared to the chloramination process was not expected.⁵ This behaviour was also noticed by Jones et al.²¹ who showed a higher formation of I-THMs by chlorination than by the chloramination process in some cases. This was attributed to the additional formation of brominated I-THMs during chlorination which are not formed during chloramination. In our experiments, the formation of brominated I-THMs effectively occurred with chlorination (SI, Figure S7) and contributed to the

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3 388 overall increase of I-THMs, but the formation of iodoform also increased with a short
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5 389 prechlorination time. As shown in a previous study,⁵ the formation of iodoform readily depends
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7 390 on the chlorination dose and exposure, decreasing with an increasing exposure. In our study,
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9 391 the highest concentrations of iodoform were observed for the smaller prechlorination contact
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11 392 times and exposures (from 0 to 5 min). Thereafter, the concentration of this product decreased
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13 393 with increasing chlorine exposure. The same trend was also observed for the highly iodinated
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15 394 compounds (CHCl₂ and CHBrI₂). Therefore, increased chlorination can limit the formation of
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17 395 the highly iodinated THMs, and especially the formation of CHI₃, which may be problematic
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19 396 due to its taste and odor.¹⁰ It can also be expected that highly toxic mono-iodinated
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21 397 compounds, such as iodo acetic acids, will behave in the same manner. However, the chlorine
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23 398 dose is an important parameter: the prechlorination exposure should be high enough to
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25 399 transform iodide into iodate and avoid the formation of high concentrations of iodinated
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27 400 compounds. In our experiments, the formation of I-THMs was decreased to a large extent after
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29 401 10 minutes for the experiment performed with the higher bromide concentration; a longer
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31 402 contact time was needed in the case of lower concentrations of bromide. Furthermore, in
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33 403 addition to the formation of I-THMs, more information is needed about the formation of other
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35 404 iodo-organic compounds, especially iodoacetic acid, under realistic conditions without omitting
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37 405 the role of bromide. During chlorination, iodate formation was controlled by HOBr even at low
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39 406 bromide levels. Considering a chlorine dose of 1 mg Cl₂/L at pH 7, a concentration of
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41 407 approximately 25 µg/L of bromide is sufficient to induce half of the iodate formation through the
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43 408 reaction of HOI with HOBr. This concentration drops to <10 µg/L for pH 8.

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46 409 **Practical implications**

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48 410 A process based on free chlorine followed by chloramine to reduce the formation of I-organics
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50 411 has been proposed in several studies.^{4,9,11,21,22,36-38} Our study reveals that bromide plays an
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52 412 important role in this process, notably by enhancing the preferred conversion of iodide to
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54 413 iodate. The balance between the formation of iodate and iodoorganic compounds formation
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56 414 depends on the water quality, *i.e.* the concentration and nature of the natural organic matter,
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58 415 the bromide concentration and the chlorine consumption rate. To determine the optimum pre-
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chlorine exposure, we propose an assessment of iodate formation. In fact, the plot of I-incorporation vs. iodate formation (SI, Figure S9) shows that, under our experimental conditions, the formation of I-THMs was minimal for a conversion of $\geq 60\%$ of iodide to iodate, independent of the bromide level. Since we have a limited data set, more information is needed to validate this procedure.

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Supporting Information Available

Two texts, one table and nine figures with further information addressing calculations and additional data. This information is available free of charge via the Internet at <http://pubs.acs.org/>.

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Table 1. Natural water characteristics.

	DOC (mg C/L)	SUVA (L/mg C.m)	I ⁻ (µg/L)	Br ⁻ (µg/L)
Lake Zurich	1.2	2.6	< 10	15
Lake Greifensee	3.5	1.8	< 10	50
North West Reservoir	2.8	1.7	31	168
Great Southern River	12.0	4.1	17	412
Great Southern Reservoir	20.0	4.9	<10	400

Table 2. Rate constants for the reactions occurring in the chlorine-bromide-iodide system.

Eq.	Reaction	Rate constants (M ⁻¹ s ⁻¹)	pKa	k''_{app} (M ⁻¹ s ⁻¹)		References
				pH 7	pH 8	
9	BrO ⁻ + H ⁺ ⇌ HOBr		8.8			29
10	HOBr + I ⁻ → HOI + Br ⁻	5.0 × 10 ⁹				26
11	BrO ⁻ + I ⁻ → IO ⁻ + Br ⁻	6.8 × 10 ⁵				26
12	IO ⁻ + H ⁺ ⇌ HOI		10.4			30
13	HOBr + HOI → IO ₂ ⁻ + Br ⁻ + 2 H ⁺	Not significant				This work
14	HOBr + IO ⁻ → IO ₂ ⁻ + Br ⁻ + H ⁺	1.9 × 10 ⁶		740	6500	This work
14a	BrO ⁻ + HOI → IO ₂ ⁻ + Br ⁻ + H ⁺	-				^a
15	BrO ⁻ + IO ⁻ → IO ₂ ⁻ + Br ⁻	1.8 × 10 ³		12	1030	This work
16	HOBr + IO ₂ ⁻ → IO ₃ ⁻ + Br ⁻ + H ⁺	High				Suggested in this work
17	BrO ⁻ + IO ₂ ⁻ → IO ₃ ⁻ + Br ⁻	High				Suggested in this work
18	ClO ⁻ + H ⁺ ⇌ HOCl		7.53			31
19	HOCl + Br ⁻ → HOBr + Cl ⁻	1550				14
20	ClO ⁻ + Br ⁻ → BrO ⁻ + Cl ⁻	9 × 10 ⁻⁴				14
21	HOCl + I ⁻ → HOI + Cl ⁻	4.3 × 10 ⁸				3
22	HOCl + HOI → IO ₂ ⁻ + Cl ⁻ + 2 H ⁺	8.2				4
23	ClO ⁻ + HOI → IO ₂ ⁻ + Cl ⁻ + H ⁺	52				4
24	HOCl + IO ₂ ⁻ → IO ₃ ⁻	High				Suggested in this work
25	ClO ⁻ + IO ₂ ⁻ → IO ₃ ⁻ + Cl ⁻	High				Suggested in this work

^aReaction 14a is not taken into account as reaction 14 describes the behaviour of these species as f(pH).

Figure 1. Kinetics of iodate formation from iodide-containing waters: a) during chlorination in presence of various concentrations of bromide or during bromination (ultrapure water, pH 7.0 $\pm$ 0.1 (phosphate buffer, 5 mM); $[I^-]_0 = 1 \mu M$; $[Br^-]_0 = 0.5$ or $2 \mu M$, $[HOBr]_0$ or $[HOCl]_0 = 4 \mu M$); b) during bromination at various pH values ($[I^-]_0 = 1 \mu M$; $[HOBr]_0 = 4 \mu M$ (phosphate, borate or carbonate buffer, 5 mM)). Symbols: experimental data; Lines: Modeling considering the reactions in Table 2 (see text).

Figure 2. pH dependence of the relative distribution of the main aqueous bromine and iodine species (grey) and the apparent second-order rate constant for the reaction of HOBr with HOI ($pK_{a1}(HOBr/BrO^-) = 8.8$; $pK_{a2}(HOI/IO^-) = 10.4$) (black) ●: experimental data; —: model calculations (see text).

Figure 3. Influence of bromide concentration on iodate formation during chlorination of iodide-containing natural waters ($[I^-]_0 = 0.4 \mu M$; $50 \mu g/L$) at pH 8.0. a) Lake Zurich water: $[HOCl]_0 = 1.0 \text{ mg Cl}_2/L$; DOC = 1.2 mg C/L ; $[Br^-]_0 = 15\text{--}500 \mu g/L$ ($0.19\text{--}6.3 \mu M$). b) Lake Greifensee water: $[HOCl]_0 = 1.8 \text{ mg Cl}_2/L$; DOC = 3.5 mg C/L ; $[Br^-]_0 = 50\text{--}510 \mu g/L$ ($0.63\text{--}6.4 \mu M$). Lines are used to guide the eye. Oxidant: $[HOCl] + [HOBr] + [HOI]$.

Figure 4. Kinetics of iodate formation for various natural waters (Table 1). Concentrations after dilution and spiking: $[I^-]_0 = 50 \pm 2 \mu\text{g/L}$ ($0.4 \mu\text{M}$); $[Br^-]_0 = 105 \pm 5 \mu\text{g/L}$ ($1.3 \mu\text{M}$); $\text{pH} = 8.0 \pm 0.1$; $\text{DOC} = 1.2 \pm 0.1 \text{ mg C/L}$; $[\text{HOCl}]_0 = 1\text{-}5 \text{ mg Cl}_2/\text{L}$. Lines are used to guide the eye.

Figure 5. Iodine incorporation into I-THMs (bars) and iodate yield (lines) for various prechlorination contact times and varying bromide concentrations for Great Southern River water (concentrations after dilution and spiking: $[I^-]_0 = 50 \mu\text{g/L}$; $[Br^-]_0 = 40, 100 \text{ and } 200 \mu\text{g/L}$; $\text{pH} 8.0$; $\text{DOC} = 1.2 \text{ mg C/L}$). Chlorine dose: $1 \text{ mg Cl}_2/\text{L}$ ($15 \mu\text{M}$), ammonia addition: $75 \mu\text{M}$. $t = 0 \text{ min}$, ammonia addition before the addition of chlorine. I-THMs were analysed after 24h to simulate contact times in distribution systems.

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