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Review

Ozonation of drinking water: Part II. Disinfection and by-product formation in presence of bromide, iodide or chlorine

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Abstract

Ozone is an excellent disinfectant and can even be used to inactivate microorganisms such as protozoa which are very resistant to conventional disinfectants. Proper rate constants for the inactivation of microorganisms are only available for six species (*E. coli*, *Bacillus subtilis* spores, *Rotavirus*, *Giardia lamblia* cysts, *Giardia muris* cysts, *Cryptosporidium parvum* oocysts). The apparent activation energy for the inactivation of bacteria is in the same order as most chemical reactions (35–50 kJ mol^{-1}), whereas it is much higher for the inactivation of protozoa (80 kJ mol^{-1}). This requires significantly higher ozone exposures at low temperatures to get a similar inactivation for protozoa. Even for the inactivation of resistant microorganisms, OH radicals only play a minor role. Numerous organic and inorganic ozonation disinfection/oxidation by-products have been identified. The by-product of main concern is bromate, which is formed in bromide-containing waters. A low drinking water standard of 10 μg l^{-1} has been set for bromate. Therefore, disinfection and oxidation processes have to be evaluated to fulfil these criteria. In certain cases, when bromide concentrations are above about 50 μg l^{-1}, it may be necessary to use control measures to lower bromate formation (lowering of pH, ammonia addition). Iodate is the main by-product formed during ozonation of iodide-containing waters. The reactions involved are direct ozone oxidations. Iodate is considered non-problematic because it is transformed back to iodide endogenically. Chloride cannot be oxidized during ozonation processes under drinking water conditions. Chlorate is only formed if a preoxidation by chlorine and/or chlorine dioxide has occured.

Keywords: Ozone; Disinfection; Disinfection by-products; Bromate; Chlorate; Iodate

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Contents

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1. Introduction

This is the second part of an article on drinking water ozonation processes dealing with disinfection and formation of disinfection by-products. The first part focussed on the oxidation kinetics and product formation for the oxidation of inorganic and organic compounds [1]. For a general introduction into ozonation processes including all aspects of oxidation, disinfection and by-product formation see [1].

Ozone is an excellent disinfectant and is able to inactivate even more resistant pathogenic microorganisms such as protozoa (e.g. *Cryptosporidium parvum* oocysts) where conventional disinfectants (chlorine, chlorine dioxide) fail. However, the ozone exposure required to inactivate these microorganisms is quite high. This may lead to the formation of excess concentrations of undesired disinfection by-products, in particular bromate, which is considered to be a potential human carcinogen. Bromate is particularly problematic because unlike many other organic by-products it is not biodegraded in biological filters which usually follow an ozonation step.

The present paper discusses the available kinetic data for the inactivation of microorganisms and how it can be applied to assess disinfection processes that occur during ozonation. The role of OH radicals for disinfection will also be assessed. Furthermore, kinetic and mechanistic information on the formation of disinfection/oxidation by-products with an emphasis on halogenates (bromate, iodate, chlorate) will be provided. In the case of bromate, an overview on bromate formation in water-treatment plants and possible options for minimization and elimination after its formation are presented.

2. Disinfection

2.1. Action of ozone

Ozone has been applied for water disinfection purposes for almost a century. A recent survey in Switzerland among water works that apply ozone has shown that for 90% of these plants the main reason for its application is disinfection [2]. Because monitoring for every pathogenic microorganism is not feasible, many countries have adopted the concept of indicator microorganisms [3]. For this purpose, fecal coliforms and *E. coli* were chosen because their presence indicates that water may be contaminated with human and/or animal wastes. Using indicator microorganisms to assess disinfection works well as long as the inactivation of the undesired pathogens is at least as efficient as the inactivation of the chosen indicator microorganisms. However, if the inactivation of indicator microorganisms is more efficient than the inactivation of pathogens, the absence of indicator microorganisms does not necessarily mean that the water is safe to drink. To overcome this problem, a process-oriented approach can be based on an estimation of the disinfectant exposure in a disinfection reactor (*ct*-concept). The disinfectant exposure (*ct*) is calculated as the time-dependent concentration of the disinfectant ($c = f(t)$) integrated for the time t of its action. It has been found that the logarithmic relative decrease of vital microorganisms is proportional to $c^n t$, according to the Chick–Watson equation (see [4] and references therein).

$$\log(N/N_0) = -kc^n t, \tag{1}$$

where N_0 is the number of microorganisms at time $t = 0$; N the number of vital microorganisms at time t; k the rate constant for the inactivation of a particular microorganism; c the concentration of a disinfectant; t the contact time; n the fitting parameter for non-first-order behavior.

In many cases, n is equal to 1 and therefore the inactivation of the corresponding microorganisms is a first-order process [5,6]. Hence, the logarithmic decrease of the relative inactivation of microorganisms is a function of a pseudo-second-order inactivation rate constant k and the *ct*-value. Typically, the assessment of disinfection is based on published *ct*-values which were measured for an inactivation of a specific microorganism by several orders of magnitude [7,8]. Because the integral *ct*-value is not easily accessible in non-ideally behaving reactors during drinking water treatment, *ct* calculations are usually performed with a conservative approach. The disinfectant concentration, c, is measured at the outlet of the reactor and multiplied with the contact time t_{10}, corresponding to the time required for 10% of an applied conservative tracer to travel through the reactor. However, in ozonation this approach is very

Table 1
Kinetics of the inactivation of microorganisms with ozone at pH 7

Microorganism	k_{O_3} ($l\,mg^{-1}\,min^{-1}$)	ct_{lag} ($mg\,min\,l^{-1}$)	k_{O_3} ($M^{-1}\,s^{-1}$)	E_{act} ($kJ\,mol^{-1}$)	T (°C)	Refs.
E. coli	130	—	1.04×10^5	37	20	[5]
B. subtilis spores	2.9	2.9	2.3×10^3	42	20	[6]
Rotavirus	76	—	6×10^4		20	[8]
Giardia lamblia cysts	29	—	2.3×10^4		25	[135]
	12^a	—	$9.5 \times 10^{3\,a}$		22	[15]
Giardia muris cysts	15.4^a	—	$1.2 \times 10^{4\,a}$	80^a	25	[136]
Cryptosporidium parvum oocysts	0.84	0.83	6.7×10^2	81	20	[14]

[a] Estimated value.

conservative and may lead to a significant underestimation of the true integral *ct* in the reactor. This may lead to excessive ozonation and correspondingly high by-products formation (see below). An overdosage of ozone is also not cost effective and should be avoided in drinking water treatment.

One way to overcome this problem is a more dynamic approach where reactor hydraulics are coupled with oxidation and disinfection kinetics [9–11]. With this approach it is possible to account for the real ozone exposure which allows a more precise assessment of the disinfection process.

While a large kinetic database for ozone reactions is available, proper kinetics of the inactivation of microorganisms have been measured only in recent years. Table 1 gives the rate constants for ozone-based disinfection processes available to date. For microorganisms which are more difficult to inactivate (e.g. *Bacillus subtilis* spores (*B. subtilis*), *Cryptosporidium parvum* oocysts (*C. parvum*)), a temperature-dependent lag-phase for disinfection is observed (ct_{lag}) which has to be taken into account [12,13,6]. In these cases, the inactivation can be modeled by a delayed Chick–Watson approach described by Rennecker et al. [4]. The rate constants for the inactivation of *Giardia lamblia* cysts given in the literature vary by a factor of two (Table 1). This degree of variability has to be accounted for in studies of the inactivation of microorganisms and may be due to differences in viability assays, different ozonation protocols and differences in the strains [15].

The data for *C. parvum* inactivation shown in Table 1 were determined by an in vitro excystation method [14]. Inactivation data for *C. parvum* from animal infectivity deviate somewhat from the data shown in Table 1 [16]. A recent pilot-scale study in which the viability was tested with animal infectivity revealed a rate constant for the inactivation of *C. parvum* similar to the value shown in Table 1 ($0.86\,l\,mg^{-1}\,min^{-1}$, [17]).

In Table 1, the apparent activation energies for the inactivation of microorganisms are also shown. The activation energies for bacteria are in a similar range as chemical reactions with ozone ($35–50\,kJ\,mol^{-1}$, [18]), whereas for protozoa (*G. muris*, *C. parvum*) they are much higher ($\approx 80\,kJ\,mol^{-1}$). No activation energies for *G. lamblia* cysts are available as yet. To assess disinfection for variable temperatures, these activation energies have to be compared to the activation energy for ozone decay. The activation energy for the decomposition of ozone in various water matrices has been determined as $65–70\,kJ\,mol^{-1}$ [19]. This means that for the same ozone dose, the degree of disinfection of bacteria and bacterial spores will be higher at lower temperatures, while it will be smaller for protozoa. This is illustrated in Fig. 1 for an ozonation experiment of River Seine water with an ozone dosage of $2\,mg\,l^{-1}$ at pH 8 and varying temperatures [20]. The results are shown for a complete depletion of ozone. The inactivation of *B. subtilis* spores was calculated from the kinetics given by Driedger et al. [6], by including the temperature dependence of the lag-phase and the rate constants. The maximum inactivation is a result from the combination of the temperature-dependent lag-phase and the inactivation rate constant. The inactivation of *C. parvum*

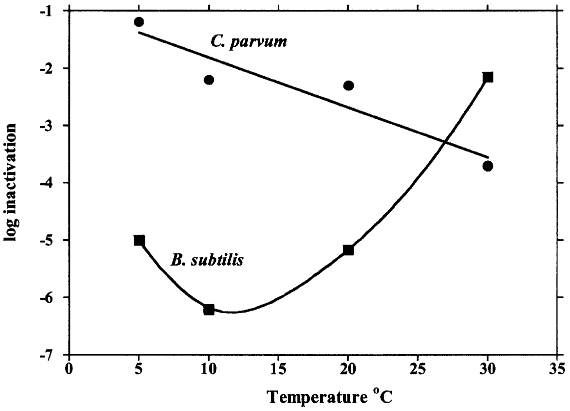

Fig. 1. Calculated temperature dependence of inactivation of *B. subtilis* spores and *Cryptosporidium parvum* oocysts in River Seine water after an ozone dosage of $2\,mg\,l^{-1}$ at pH 8. Water quality: DOC $2.4\,mg\,l^{-1}$, alkalinity 3.8 mM, pH 8.

oocysts was calculated in a similar way with the temperature-dependent kinetics given by Driedger et al. [6]. The temperature-dependent inactivation differs for the two microorganisms. Whereas for *B. subtilis* the general trend shows a less efficient inactivation for increasing temperatures, for *C. parvum* an increase in temperature leads to an increasing degree of inactivation. This inverse behavior is a result of the different activation energies for the inactivation of these microorganisms. The results shown in Fig. 1 also demonstrate that the use of *B. subtilis* spores as surrogate for the behavior of *C. parvum* oocysts is linked with several problems and that this approach can only be applied in special cases. The inactivation of *E. coli* was not plotted in Fig. 1 because it would have been out of range by many orders of magnitude due to its easier inactivation. This exemplifies the problems associated with the use of *E. coli* to assess the efficiency of disinfection processes.

2.2. Role of OH radicals

In the drinking water community, there is a frequent debate on the role of OH radicals for disinfection processes. While some authors state that ozone is the main disinfectant [21–24] others suggest that OH radicals may play an important role for disinfection [25,26]. The kinetic data shown in Table 1 together with the expected range of R_c values (ratio of the concentrations of OH radicals and ozone $R_c = [^\bullet OH]/[O_3] = 10^{-6} - 10^{-9}$, [1]) allow an estimation of the role of OH radicals during disinfection. Taking both ozone and OH radicals into account for disinfection, the following rate equation can be formulated:

$$\log(N/N_0) = -(k_{O_3} + k_{OH}R_c)\int [O_3]\,dt, \qquad (2)$$

where k_{O_3} is the rate constant for inactivation of microorganisms with ozone; k_{OH}: rate constant for inactivation of microorganisms with OH radicals.

An R_c of 10^{-8} is typical for the secondary phase of an ozonation during which most of the disinfection occurs [19]. According to Eq. (2) the rate constant k_{OH} for inactivation of *C. parvum* with OH radicals would have to be $7\times10^{10}\,M^{-1}\,s^{-1}$ for a similar disinfection efficiency as with ozone ($k_{O_3} = k_{OH}R_c$). This rate constant is about a factor of 10 above rate constants typically observed for OH radical reactions. Because the rate constants for the inactivation of the other microorganisms in Table 1 by ozone are even higher than for *C. parvum*, k_{OH} would have to be substantially higher. In advanced oxidation processes (AOP) where an R_c of 10^{-6} can be expected, OH radicals could theoretically play a certain role for *C. parvum* oocysts and *B. subtilis* spores inactivation. For the other microorganisms shown in Table 1, even in ozone-based AOPs, OH radicals will have no effect on disinfection. Therefore, the effect of OH radicals in disinfection processes can generally be neglected. In addition to these kinetic calculations, one also has to consider that the main target for inactivation of microorganisms is the DNA and not the cell wall. OH radicals would be scavenged in the cell wall and their journey to the DNA would be hampered by other cell constituents. The traveling distance of OH radicals in a cell can be estimated to be 6–9 nm [27].

3. Oxidation/disinfection by-products

Chemical disinfection processes in drinking water treatment lead to the formation of disinfection by-products that are undesired due to their potential chronic toxicity [28]. Typically, they result from the oxidation of matrix components in the water. There is an ongoing debate on the relevance of disinfection by-products compared to the risks of waterborne diseases [29,30]. Recently, the risk of infection by *C. parvum* and the development of renal cell cancer due to bromate formation in bromide-containing waters were compared for ozonation processes. It was concluded that the benefits of preventing gastroenteritis by proper disinfection outweighs health losses by premature death from renal cell cancer by a factor of 10 [31]. In developing countries, the emphasis on disinfection by-products can be detrimental, as demonstrated by the cholera epidemic in Peru in the early 1990s [32].

A recent study proposed using the by-product formation during the disinfection process to assess the disinfection efficiency [33]. This concept is based on the fact that the concentration of by-products increases by a known function with increasing exposure of a disinfectant (*ct*). Because the logarithmic disinfection efficiency is also proportional to the disinfectant exposure (*ct*), the measurement of the concentration of, e.g., bromate allows us to calculate the extent of inactivation of a certain microorganism. However, because disinfection efficiency is measured by a logarithmic scale whereas the build-up of by-products is measured on a linear scale, reactor hydraulics must be taken into account for this approach.

3.1. By-product formation in absence of bromide

During ozonation, a variety of organic by-products is formed from the oxidation of natural organic matter (NOM). Aldehydes, ketones, keto aldehydes, carboxylic acids, keto acids, hydroxy acids, alcohols and esters have been reported ([34–38] and references therein). For many of the polar non-volatile by-products there is still a lack of analytical tools [39]. Up to now, there has been no systematic study to assess the role of ozone and OH radicals in the formation of organic by-products. Also, information on the kinetics of their formation during ozonation is scarce. Some data suggests that most of the organic by-products are formed during the initial phase of an ozonation process [40]. Most of the organic by-products are readily biodegradable and may lead to an increase of the concentration of the assimilable organic carbon (AOC) [34,26,41–43]. Only a small fraction of the AOC (ca. 30%) could so far be explained by specific organic compounds [39]. To avoid fouling in the distribution system, a biological filtration step is advisable after ozonation for waters containing a DOC concentration of approximately $>1\,\mathrm{mg\,l^{-1}}$ [43]. Biological filters after ozonation are routinely applied in many drinking water treatment plants throughout the world [44–51]. Higher molecular weight oxidation by-products might not be readily reduced during biological filtration. However, there is only limited information about these products. Bromate is not degraded under typical oxic filtration conditions. Therefore, once formed it will remain in the water all the way to the tap (see below).

3.2. By-product formation in the presence of bromide

In the presence of bromide (for typical bromide levels in natural waters see below), many bromo-organic by-products such as bromoform, bromopicrin, dibromoacetonitrile, bromoacetone, bromoacetic acid, bromoalkanes, bromohydrins, etc. have been identified ([52–54] and references therein). They are all formed by the reaction of hypobromous acid (product of the reaction between bromide and ozone) with NOM ([55] see below). However, experience in many water works shows that the concentrations of these bromoorganic compounds are usually far below the current drinking water standards. This can be explained by a competition kinetics approach [56]. Therefore, the main by-product of concern in the presence of bromide is bromate (BrO_3^-). It has been found that bromate is a genotoxic carcinogen inducing, for example, renal cell tumors in rats [57]. The specific mechanism by which bromate produces tumors is not known [58]. Bromate is thought to produce its toxic response through damage that results from increased levels of lipid peroxides (LPO) or from oxygen radicals that are generated from LPO and induce DNA damage. Based on these findings, bromate was declared a potential human carcinogen which recently led to stringent drinking-water standards. The World Health Organisation (WHO) issued a guideline value of $25\,\mu\mathrm{g\,l^{-1}}$, both the European Union and the USEPA established a maximum contaminant level of $10\,\mu\mathrm{g\,l^{-1}}$ [7,59,3]. Further toxicological studies have yet to show whether there is a threshold concentration above the implemented $10\,\mu\mathrm{g\,l^{-1}}$ BrO_3^- which could be considered safe for drinking waters.

3.2.1. Bromate

3.2.1.1. Occurrence of bromide and bromate in ozonation plants. Bromide levels in natural waters are highly variable in a range of $10–1000\,\mu\mathrm{g\,l^{-1}}$ (Table 2, [60]). Both natural processes (salt water intrusion, water from special geological formations) and anthropogenic activities (potassium mining, coal mining, chemical production, etc.) may contribute to increased bromide levels in natural waters. In many waters, low levels of bromide ($<20\,\mu\mathrm{g\,l^{-1}}$) are found which are unproblematic for bromine-derived by-products. For bromide levels in the range $50–100\,\mu\mathrm{g\,l^{-1}}$, excessive bromate formation may already become a problem. However, in these waters, optimization and control options can be applied. Depending on the treatment goals, bromate formation can become a serious problem for bromide levels above $100\,\mu\mathrm{g\,l^{-1}}$.

Surveys on bromate formation in ozonation plants in numerous European countries [61–64] and the USA [65] have been carried out for water works under standard treatment conditions (grab samples). The disinfection target may vary from one treatment plant to the other. Table 2 gives a summary of the five studies performed so far. In European and US American water works, bromate formation was generally below $10\,\mu\mathrm{g\,l^{-1}}$ under these operation conditions. Only in about 6% of the more than 150 investigated water works, bromate concentrations were above $10\,\mu\mathrm{g\,l^{-1}}$. In some of these cases, optimization of the ozonation can lead to a substantial lowering of bromate formation. At the time of these studies, the target of the disinfection was inactivation of virus and/or *G. lamblia*. If a treatment

Table 2
Bromate formation in full-scale ozonation plants in Europe and the USA

Country	Number of plants	Bromide range ($\mu\mathrm{gl^{-1}}$)	Bromate range ($\mu\mathrm{gl^{-1}}$)	Number of water works $>10\,\mu\mathrm{g\,l^{-1}}$ [a]	Refs.
France	10	12–658	<2–19	2	[61]
France	32	<20–200	<2–19.6	2	[63]
Germany	4	30–150	<1–12	1	[62]
Switzerland	86	<5–50	<0.5–20	2	[64]
USA	24	2–180	0.1–40	3	[65,137,138]

[a] Once or more during survey.

goal for inactivation of *C. parvum* oocysts was implemented, the number of plants with bromate levels above 10 μg l^{-1} could increase significantly. Further full-scale tests will be necessary to draw firm conclusions.

3.2.1.2. Bromate formation during ozonation of bromide-containing waters. Bromate is formed in ozonation processes from the oxidation of bromide through a combination of ozone and OH radical reactions. Its formation includes up to six oxidation states of bromine (Table 3). Because both oxidants can act simultaneously or in sequence on various oxidation levels (Table 3), the whole reaction system is extremely complicated and highly non-linear. In the following, the various oxidation reactions are discussed in detail.

Ozone reactions. The oxidation of bromide during ozonation processes was first investigated in detail by Haag and Hoigné [55]. This study only considered direct ozone reactions and came up with the mechanism shown in Fig. 2a. The first step is an oxidation of bromide (Br^-) by ozone via an oxygen atom transfer to produce hypobromite (OBr^-). For this reaction, a second-order rate constant $k = 160\,M^{-1}\,s^{-1}$ was determined by these authors. Recently, a second-order rate constant $k = 258\,M^{-1}\,s^{-1}$ was measured [66]. The two values deviate significantly. However, because bromate formation is not only controlled by this reaction, the absolute value of this rate constant is not decisive for bromate formation (see below).

The reaction of bromide with ozone is a reversible process and occurs via a $BrOOO^-$ intermediate which can react further by two mechanisms [66]:

$$BrOOO^- \rightarrow OBr^- + O_2 \quad \text{(oxygen atom transfer)} \qquad (3)$$

$$BrOOO^- \rightarrow Br^{\bullet} + O_3^{\bullet -} \quad \text{(electron transfer)} \qquad (4)$$

The oxygen atom transfer reaction (3) is preferred over the electron transfer (4) by 402 kJ mol^{-1} and therefore is the dominant pathway [66]. In reaction (3) only about 56% of the formed oxygen is singlet oxygen

Table 3
Bromine species formed during bromate formation, oxidation states and important oxidants

Species	Chemical formula	Bromine oxidation state	Controlling oxidizing species
Bromide	Br^-	−I	O_3, $^{\bullet}OH$
Bromine radical	$Br^{\bullet}$	0	O_3
Hypobromous acid	HOBr	+I	$^{\bullet}OH$
Hypobromite	OBr^-	+I	O_3, $^{\bullet}OH$, $CO_3^{\bullet -}$
Bromine oxide radical	$BrO^{\bullet}$	+II	—
Bromite	BrO_2^-	+III	O_3
Bromate	BrO_3^-	+V	—

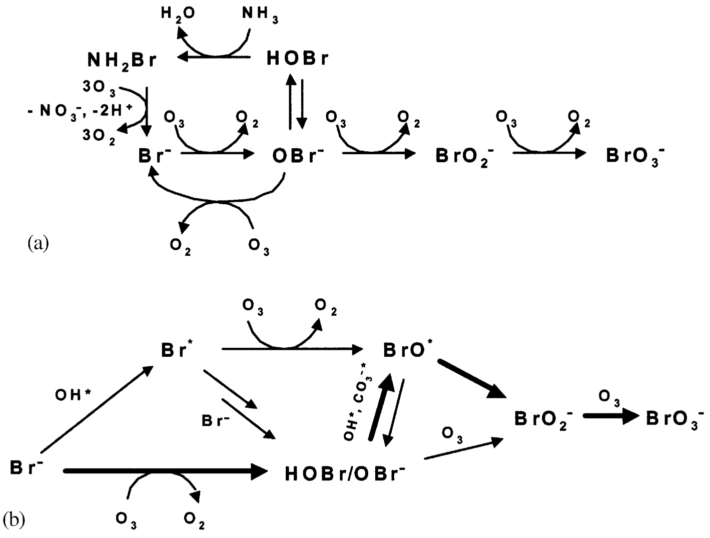

Fig. 2. Reaction scheme for bromate formation during ozonation of bromide-containing waters. (a) reactions with ozone and (b) reactions with ozone and OH radicals. The bold lines show the main pathway during the secondary phase of an ozonation process. Adapted from von Gunten and Hoigné [68].

[O_2 ($1\Delta_g$)] [67]. This can be explained by the hypothesis that the $BrOOO^-$ adduct is sufficiently long-lived to reduce the singlet oxygen yield by conversion due to a heavy atom effect [67]. In the case of iodide, this is even more pronounced (see below). The hypobromite formed is in equilibrium with hypobromous acid (HOBr) (pKa (HOBr) = 8.8–9 [55,68]. Therefore, the equilibrium $HOBr/OBr^-$ lies on the side of HOBr for typical drinking water treatment conditions (pH = 6.5–8). The kinetics of protonation reactions are fast with second-order rate constants of the order of $2 \times 10^{10}\,M^{-1}\,s^{-1}$. Considering the equilibrium constant of 10^{-9} for HOBr, this results in a deprotonation rate constant of $\sim 20\,s^{-1}$. For the further reaction of OBr^- with ozone ($400\,M^{-1}\,s^{-1}$, eqs. (5)–(7)) a maximum rate constant of $8 \times 10^{-3}\,s^{-1}$ can be calculated for an ozone concentration of $1\,mg\,l^{-1}$ (2×10^{-5} M). Therefore, the $HOBr–OBr^-$ equilibrium reaction is faster than its further oxidation by several orders of magnitude.

The oxidation of bromide by ozone to HOBr is directly applied for swimming pool water disinfection. Because ozone is unstable in water, bromide is added during ozonation to produce HOBr. In excess of bromide, the further oxidation of $HOBr/OBr^-$ can be suppressed and the resulting HOBr acts as a long-term disinfectant. OBr^- undergoes two reactions: (i) attack of ozone on the oxygen atom (5) and (6), (ii) attack of ozone on the bromine atom (7):

$$OBr^- + O_3 \rightarrow OOBr^- + O_2 \quad k = 330\,M^{-1}\,s^{-1} \tag{5}$$

$$OOBr^- \rightarrow Br^- + O_2 \tag{6}$$

$$OBr^- + O_3 \rightarrow OBrO^- + O_2 \quad k = 100\,M^{-1}\,s^{-1} \tag{7}$$

The OO–Br $^-$ intermediate from the attack of ozone on the oxygen atom leads back to bromide whereas reaction (7) leads to $O–Br–O^-$ (bromite). The rate constants for reaction (5) is $330\,M^{-1}\,s^{-1}$ and for reaction (7) it is $100\,M^{-1}\,s^{-1}$ [55]. This means that only approximately 1/4 of the "oxidized" OBr^- leads to BrO_2^- and eventually to BrO_3^-.

The successive oxidation of bromite to bromate by ozone is very fast ($k > 10^5\,M^{-1}\,s^{-1}$, [55], $8.9 \times 10^4\,M^{-1}\,s^{-1}$, [69]). Whereas Haag and Hoigné [55] describe it as a oxygen atom transfer reaction, recent studies by Nicoson et al. [69] suggest an electron transfer reaction. At a pH of 7, only about 1% of the HOBr species is present as OBr^-. This leads to an apparent second-order rate constant of $k = 1\,M^{-1}\,s^{-1}$ for its oxidation by ozone. The formation of bromite will subsequently proceed with a rate constant of only $0.25\,M^{-1}\,s^{-1}$. This is considerably smaller than the second-order rate constants for the oxidation of both bromide and bromite. Therefore, the rate limiting step for the oxidation of bromide to bromate by ozone in drinking waters is the oxidation of OBr^-, and it can be expected and is observed that HOBr will build-up during ozonation of bromide-containing waters [55,56].

OH radical reactions. In addition to the mechanism shown in Fig. 2a, there are numerous oxidation steps which occur via OH radical oxidation (Table 3). Ozone and OH radicals react in parallel or in succession leading to a strongly non-linear behavior of the system. Therefore, it is impossible to predict bromate formation intuitively. Fig 2b shows an extended reaction scheme including direct ozone reactions and secondary oxidants (OH radicals and carbonate radicals). This mechanism has been established in many studies including experimental and modeling work [52,56,58,70–79]. For a complete compilation of all reactions and their corresponding rate constants see, e.g., von Gunten and Oliveras [78], Pinkernell and von Gunten [56].

According to Fig. 2b and Table 3, OH radicals play an important role in the oxidation of bromide and $HOBr/OBr^-$. The oxidation of bromide occurs according to the following reaction sequence [80]:

$$Br^- + {}^\bullet OH \rightleftharpoons BrOH^- \quad k_+ = 1.06 \times 10^8\,M^{-1}\,s^{-1} \quad k = 3.3 \times 10^7\,s^{-1} \tag{8}$$

$$BrOH^- + H^+ \rightleftharpoons Br^\bullet + H_2O \quad k_+ = 1.06 \times 10^8\,M^{-1}\,s^{-1} \quad k = 1.36\,s^{-1} \tag{9}$$

For typical drinking water conditions, the reaction leading from bromide to the bromine radical ($Br^\bullet$) can be described by an overall rate constant of $1.1 \times 10^9\,M^{-1}\,s^{-1}$ [76].

In ozonation processes, the bromine radical can be further oxidized by ozone to the $BrO^\bullet$ radical or react with bromide to $Br_2^{\bullet-}$ and eventually to HOBr [81,78]:

$$Br^\bullet + O_3 \rightarrow BrO^\bullet + O_2 \quad k = 1.5 \times 10^8\,M^{-1}\,s^{-1} \tag{10}$$

$$Br^\bullet + Br^- \rightarrow Br_2^{\bullet-} \quad k = 10^{10}\,M^{-1}\,s^{-1} \tag{11}$$

$$Br_2^{\bullet-} + Br_2^{\bullet-} \rightarrow Br^- + Br_3^{\bullet-} \quad k = 2 \times 10^9\,M^{-1}\,s^{-1} \tag{12}$$

$$Br_3^{\bullet-} + H_2O \rightarrow HOBr + 2Br^- + H^+ \tag{13}$$

For a bromide concentration of $40\,\mu g\,l^{-1}$ ($0.5\,\mu M$) and an ozone concentration of $1\,mg\,l^{-1}$ ($20\,\mu M$), about 40% of the Br radical react through reaction (10) and 60% through reaction (11). If bromide levels are higher and/or ozone concentrations lower, the fraction of bromine radicals reacting over reaction (11) increases. Because high ozone concentrations are mostly encountered during the initial phase of an ozonation process, reaction (10) is most important during this phase (see below control strategies for bromate minimization). $BrO^\bullet$ radicals are unstable and disproportionate into $HOBr/OBr^-$ and BrO_2^-. The latter species is quickly oxidized to bromate by ozone.

The $BrO^\bullet$ radical is only formed from $Br^\bullet$ in the presence of ozone, i.e., it is not an intermediate in oxidation processes where OH radicals are the only oxidants (e.g., UV/H_2O_2 or γ-irradiation, [78]). In OH radical-based oxidation processes, $Br^\bullet$ reacts with Br^- (reaction (11)), eventually leading to $HOBr/OBr^-$ as a decisive intermediate. This has consequences for bromate formation during hydrogen-peroxide-based advanced oxidation processes (see below).

In contrast to the oxidation by ozone, which can only oxidize OBr^-, OH radicals oxidize both HOBr and OBr^- to $BrO^\bullet$ with similar rate constants ($k_{HOBr} = 2 \times 10^9\,M^{-1}\,s^{-1}$, $k_{OBr-} = 4.5 \times 10^9\,M^{-1}\,s^{-1}$, [82]). Therefore, the pH-dependent speciation of $HOBr/OBr^-$ can only change the rate of this reaction by a factor of two at the most. The oxidation of $HOBr/OBr^-$ with carbonate radicals to $BrO^\bullet$ is not well established and has only been assessed qualitatively so far [68].

Because we know the kinetics of all involved reactions, we can estimate the fraction of Br^- and $HOBr/OBr^-$ oxidized by ozone and OH radicals, respectively, if we know the ratios of the concentrations of OH radicals and ozone during an ozonation process. For the oxidation of bromide the following rate equation can be formulated:

$$-dBr^-/dt = k_1[Br^-][O_3] + k_2[Br^-][^\bullet OH] \qquad (14)$$

The ratio $R_c = [^\bullet OH]/[O_3]$ can be used to express the $[^\bullet OH]$ as a function of the $[O_3]$ [1]. This yields:

$$\begin{aligned} -\,dBr^-/dt &= k_1[Br^-][O_3] + k_2 R_c[Br^-][O_3] \\ &= [Br^-][O_3](k_1 + k_2\,R_c) \qquad (15) \end{aligned}$$

Thus, the fraction f_{OH,Br^-} of bromide reacting with OH radicals can be calculated as

$$f_{OH,Br^-} = k_2R_c/(k_1 + k_2R_c) \qquad (16)$$

An analogous calculation can be made for $HOBr/OBr^-$. However, in this case also the pH-dependent speciation of HOBr has to be considered [56]. Table 4 shows the results of such calculations. For the oxidation of bromide, the ozone reaction is the preferred pathway for a wide range of R_c values. Only for high $R_c \geqslant 10^{-7}$ a considerable fraction of bromide will be oxidized by OH radicals. Independent of the pH, such R_c values can typically be measured during the initial phase of an ozonation process [6] or in ozone-based advanced oxidation processes. For the oxidation of $HOBr/OBr^-$, a pH-dependent behavior for the importance of ozone relative to OH radicals can be calculated. Whereas at low pH oxidation occurs almost entirely by OH radicals, at higher pH values and lower R_c values, the fraction of $HOBr/OBr^-$ oxidized by ozone can be as high as 90%.

However, as the pH increases, so does the R_c. For average waters, this leads to a $\geqslant$50% fraction for the oxidation of $HOBr/OBr^-$ by OH radicals at pH 8. These calculations show clearly that the oxidation pathway for bromide and hypobromous acid/hypobromite is given largely by the ratio of the concentrations of OH radicals and ozone. For the secondary reaction phase of an ozonation process, this ratio can be strongly influenced by pH changes, i.e. the R_c can be lowered by up to a factor of 10 if the pH is lowered from 8 to 6. It has been found for River Seine water that the fraction f_{O_3} reacting with ozone for HOBr decreased from $\leqslant$40% at pH 8 to $\leqslant$15% at pH 7 and $\leqslant$5% at pH 6 [56]. The effect of pH changes on bromate formation is discussed in more detail in the context of control options for bromate formation (see below). The resulting dominant bromate formation pathway during the secondary reaction phase of an ozonation process is highlighted in Fig. 2b by thicker arrows. The first oxidation step ($Br^- \rightarrow OBr^-$) occurs via ozone, the second step ($HOBr/OBr^- \rightarrow BrO^\bullet$) via OH radicals, the third step is a disproportionation ($2\,BrO^\bullet \rightarrow OBr^- + BrO_2^-$), and the fourth step is an oxidation by ozone ($BrO_2^- \rightarrow BrO_3^-$).

In addition to the reactions shown in Fig. 2b, there are other reactions which interfere with bromate formation. First of all, the Br atom can react with NOM to form bromo-organic compounds or bromide. The rate constant for this reaction was estimated to be $10^9\,M^{-1}\,s^{-1}$ for a NOM concentration of $2 \times 10^{-6}\,M$ (based on DOC: $12\,mg\,l^{-1} = 1\,mM$, [56]). For this scenario, the reaction of $Br^\bullet$ with NOM would be of

Table 4
Fraction of ozone (f_{O_3}) and OH radicals (f_{OH}) pathway for the oxidation of bromide and $HOBr/OBr^-$ (towards bromate)

	Bromide		Hypobromous acid/ Hypobromite					
			pH 6		pH 7		pH 8	
$[OH^\bullet]/[O_3]$	f_{O_3} (%)	f_{OH} (%)	f_{O_3} (%)	f_{OH} (%)	f_{O_3} (%)	f_{OH} (%)	f_{O_3} (%)	f_{OH} (%)
10^{-7}	60	40	0.08	99.92	0.8	99.2	6	94
10^{-8}	94	6	0.8	99.2	7	93	40	60
10^{-9}	99.3	0.7	8	92	44	56	87	13

the same order of magnitude as its reaction with bromide or ozone.

In addition, there are three types of reactions interferring on the level of HOBr/OBr$^-$:

$$\mathrm{HOBr/OBr^- + NOM \rightarrow Br - NOM} \qquad (17)$$

$$\mathrm{HOBr/OBr^- + NOM \rightarrow NOM_{ox} + Br^-} \qquad (18)$$

$$\mathrm{HOBr + HO_2^- \rightarrow Br^- + H_2O + O_2} \quad k = 7.6 \times 10^8\ \mathrm{M^{-1}\,s^{-1}} \qquad (19)$$

$$\mathrm{HOBr + NH_3 \rightarrow NH_2Br + H_2O} \quad k = 8 \times 10^7\ \mathrm{M^{-1}\,s^{-1}} \qquad (20)$$

The reaction of HOBr/OBr$^-$ with NOM is of interest in connection with the potential formation of bromo-organic compounds. It may also lead back to bromide, resulting in a "catalytic" destruction of ozone. The fast reaction (19) of HOBr with HO_2^- (H_2O_2) is of particular importance in hydrogen-peroxide-based advanced oxidation processes such as O_3/H_2O_2 and UV/H_2O_2 [83]. Reaction (20) is important in ammonia-containing waters. The reaction product of the fast reaction between HOBr and NH_3 is monobromamine which is oxidized by ozone to bromide and nitrate [84]. Therefore, addition of ammonia can be used to reduce bromate formation (see control options).

Modeling of bromate formation. Because bromate formation during ozonation of bromide-containing waters is a highly non-linear process, kinetic modeling has been applied to improve mechanistic understanding and to predict bromate formation [70,79,85,68,56]. The full model consists of more than 50 coupled kinetic equations which can be solved simultaneously with a computer code such as *ACUCHEM* [86]. However, the main problem of these models is the unknown behavior of NOM both in ozone decomposition and bromate formation. To overcome the problem on the oxidant side, the experimental ozone and OH radical concentrations were introduced into the model by the R_c value. This allowed modeling bromate formation during ozonation of natural waters in laboratory systems without introducing any additional fitting parameters [56]. In an other study, kinetic modeling was applied to investigate parts of the bromate formation mechanism [78]. However, the predictive capabilities of such models for the ozonation of any water should not be overestimated. Due to the fact that the rate constants for the reactions in the bromate formation mechanism stem from various studies, predictions should preferably be used to investigate trends for changing water treatment/quality parameters. A simulation within a factor of two relative to the measured bromate concentration has to be considered satisfactory.

3.2.1.3. Bromate formation during oxidation of micropollutants in advanced oxidation processes. In advanced oxidation processes (AOPs), bromate formation is governed by oxidation processes with OH radicals. It has been shown in γ-radiolysis experiments that for systems where OH radicals are the only oxidants, HOBr is a decisive intermediate [78]. Since H_2O_2 is an important chemical in many AOPs (UV/H_2O_2, O_3/H_2O_2, Fenton reaction), the reaction of HOBr with HO_2^- back to bromide (reaction (19)) is particularly important because it is fast [83].

In the UV/H_2O_2 process, OH radicals are the only oxidants and they are produced in solutions in presence of a high excess of H_2O_2. The OH radical oxidation of bromide leads to $Br^\bullet$ which eventually forms HOBr (see above, reactions (8), (9), (11)–(13)). HOBr is then again reduced by hydrogen peroxide to Br^-. Since hydrogen peroxide is present in a large excess, the further oxidation of HOBr by OH radicals is outcompeted by its reduction. Even if a steady-state OH radical concentration in the UV/H_2O_2 process of 10^{-10} M is assumed, only a fraction (approx. 3.6%) of the total HOBr would be further oxidized and finally lead to bromate for a H_2O_2 concentration of 10 mg l^{-1}. Therefore, no bromate can be detected in the AOP UV/H_2O_2 [77,78]. However, relatively high hydrogen peroxide levels need to be applied (5–20 mg l^{-1}) because of the low efficiency of H_2O_2 photolysis. High concentrations of H_2O_2 are undesired from a toxicological point of view. In addition, hydrogen peroxide reacts quickly with chlorine applied for the distribution system. Therefore, biological filtration is necessary to remove excess H_2O_2.

In contrast to the UV/H_2O_2 process, in the O_3/H_2O_2-based AOP, bromate is still formed even if very high H_2O_2 levels are applied [78]. In this process, part of the bromate formation occurs via the Br atom which is oxidized to the $BrO^\bullet$ radical by ozone (reaction (10)). This species is not reduced by H_2O_2 [78]. Hence, in the AOP O_3/H_2O_2 there is a trade-off between a more efficient oxidation of the target micropollutant and bromate formation.

Table 5 shows an example of the oxidation of atrazine in a full-scale water treatment plant [75] and methyl tert-butyl ether (MTBE) in a laboratory study [87] and the connected bromate formation. Results are shown for conventional ozonation or the AOP O_3/H_2O_2 for waters containing about 50 µg l^{-1} bromide.

The two experiments shown for the full-scale water treatment plant demonstrate the beneficial effect of an accelerated O_3/H_2O_2-based AOP. For the same ozone dose, the oxidation of atrazine increases from 42% to 75% if the process is changed from conventional ozonation to the AOP. This is due to a faster transformation of ozone into OH radicals. In the conventional ozonation process, the ozone residual concentration at the outlet of the reactor was

Table 5
Oxidation of micropollutants and bromate formation

Oxidation of atrazine in a full-scale plant [75] (*pH* 7.6, *DOC* 2 mg l^{-1}, *alkalinity* 4 mM)			
	ozone 1.6 mg l^{-1}	ozone/H_2O_2 1.6/0.5 mg l^{-1}	
% elim. atrazine	42	75	
Bromate[a] (μg l^{-1})	19	4	
Oxidation of MTBE in laboratory system [87]			
	ozone 2 mg l^{-1}	ozone/H_2O_2 2/0.7 mg l^{-1}	ozone/H_2O_2 4/1.4 mg l^{-1}
Lake Zürich water (*pH* 7, *DOC* 1.4 mg l^{-1}; *alkalinity* 2.5 mM *OH scavenging rate constant*: 5.6×10^4 s^{-1})			
% elim. MTBE	39	46	71
Bromate[(b)] (μgl^{-1})	15.1	8.8	16.8
Well water Porrentruy (*pH* 7, *DOC*: 0.8 mg l^{-1}; *alkalinity* 5 mM) *OH scavenging rate constant*: 6.2×10^4 s^{-1})			
% elim. MTBE	28	37	65
Bromate[b] (μg l^{-1})	20.7	12.5	33.5

Initial bromide concentrations:
[a] 45 μg l^{-1}.
[b] 50 μg l^{-1}.

0.65 mg l^{-1}, whereas it was 0.1 mg l^{-1} for the AOP. Due to this higher degree of ozone transformation, the OH radical oxidation capacity for the AOP is significantly higher. Bromate formation decreases drastically from 19 to 4 μg l^{-1} from conventional ozonation to the AOP.

This decrease is due to the reduction of HOBr by H_2O_2/HO_2^- (Eq. (19)). However, even in presence of H_2O_2, bromate formation is not zero. This is due to the oxidation of the Br atom by ozone (reaction (10)).

The laboratory experiments for MTBE oxidation in the two waters in Table 5 basically show similar features. For a constant ozone dose and a complete transformation of ozone, the addition of H_2O_2 slightly increases the elimination percentage of MTBE and decreases bromate formation. A higher ozone dose increases the elimination percentage of MTBE but also increases bromate formation. Both waters shown in Table 5 (MTBE) have approximately the same OH radical scavenging rate constant. It is composed of the OH radical scavenging by NOM and carbonate/bicarbonate. This is reflected in similar oxidation percentage of MTBE for similar ozone dosages. It is an indication that the OH radical oxidation in both waters is fairly similar. For an ozone dose of 2 mg l^{-1}, approximately 40% of the MTBE can be oxidized, whereas for 4 mg l^{-1} it is approximately 70%. As a negative trade-off, bromate formation increases significantly if the ozone dose is increased. In addition, the absolute level of bromate is markedly higher in the high-alkalinity water (well water) than in the water with the lower alkalinity (lake water). This is due to the reaction of carbonate radicals with OBr^- [68]. Therefore, the application of the AOP O_3/H_2O_2 has to be carefully evaluated for high-alkalinity waters to avoid excessive bromate formation.

Both the oxidation of atrazine and MTBE have shown that it is possible to oxidize micropollutants efficiently with the O_3/H_2O_2-based AOP. However, in turn, the process must be optimized with regard to bromate formation. This is of particular importance if the rate constants for the micropollutants that need to be oxidized are relatively low. This is certainly the case for MTBE ($k_{OH} = 1.9 \times 10^9\ M^{-1}\,s^{-1}$, [87]). For micropollutants with higher second-order rate constants for reactions with OH radicals, the oxidation can be carried out to a higher degree without violating the drinking water standard for bromate. This is shown with the oxidation of atrazine ($k_{OH} = 3 \times 10^9\ M^{-1}\,s^{-1}$, [88]) where a lower ozone dose already leads to a similar degree of oxidation (75%). In this case the bromate level still remains low (4 μgl^{-1}).

3.2.1.4. Balance between bromate formation and disinfection in bromide-containing waters. The occurrence of more resistant pathogens such as *C. parvum* oocysts leads to a demand for increased *ct*'s for their inactivation. In waters with bromide levels above 50 μg l^{-1}, bromate formation may exceed the drinking water standard of 10 μg l^{-1} under certain treatment conditions [89,90]. One of the decisive factors is the temperature of the treated water. Both the efficiency of inactivation of microorganisms (Table 1) and bromate formation increase with increasing temperature. Therefore, it has to be tested whether lower or higher temperatures lead to a better performance with regard to the overall

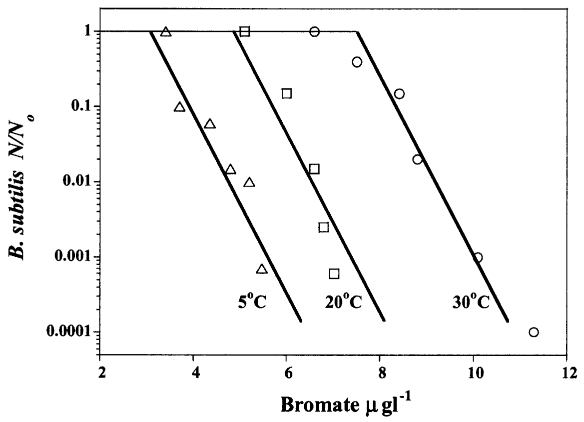

Fig. 3. Inactivation of *B. subtilis* spores and bromate formation during ozonation of Lake Zürich water at temperatures 5°C, 20°C and 30°C ($[Br^-]_o = 30\,\mu g l^{-1}$, pH = 7, DOC = $1.4\,mg l^{-1}$, alkalinity 2.5 mM).

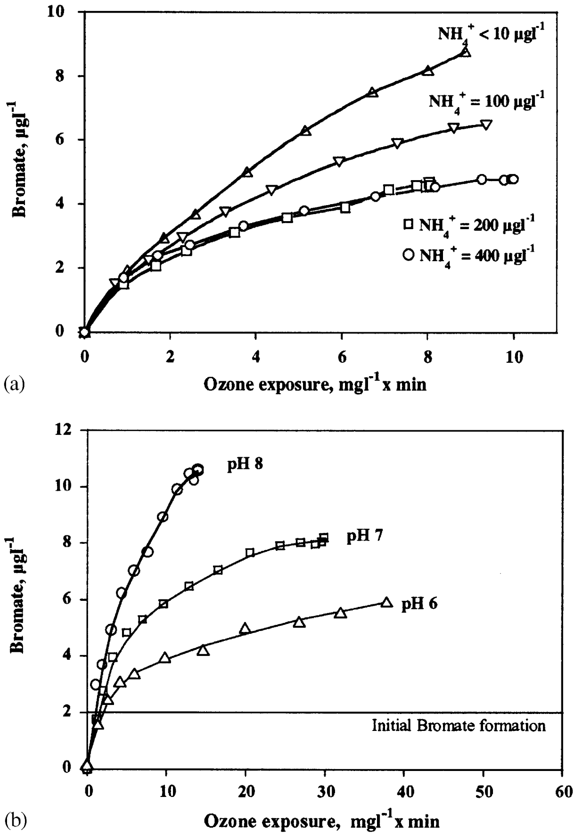

Fig. 4. Bromate minimization during ozonation processes: a) Lake Zürich (LZ) water (Switzerland), addition of ammonia, b) River Seine (RS) water (France) pH depression (8–6). Water quality parameters and experimental conditions: LZ: DOC $1.4\,mg l^{-1}$, alkalinity 2.5 mM, pH = 8, $T = 20°C$, $[O_3]_o = 1.5\,mg l^{-1}$, $[Br^-]_o = 50\,\mu g l^{-1}$; RS: DOC $2.4\,mg l^{-1}$, alkalinity 3.8 mM, $T = 10°C$, $[O_3]_o = 2\,mg l^{-1}$, $[Br^-]_o = 50\,\mu g l^{-1}$, $[NH_4^+] = 126\,\mu g l^{-1}$. Adapted from Pinkernell and von Gunten [56].

process (sufficient disinfection with low bromate). Fig. 3 shows a comparison of bromate formation and inactivation of *B. subtilis* spores for 5°C, 20°C and 30°C [6].

It can be seen that the initial phase is decisive for the overall process. During this phase, bromate increases quickly because of the importance of OH radical reactions. However, inactivation of *B. subtilis* does not occur due to the lag-phase. Therefore, the critical factor will be the bromate formed during the lag-phase of the inactivation. In the example shown in Fig. 3, higher temperatures are more critical because initial bromate formation under these conditions is very fast. This outrules the shorter lag-phase for inactivation at these temperatures. To overcome these problems, it might be necessary to use control options to minimize bromate formation.

3.2.1.5. Strategies for bromate minimization. To solve the problem of excessive bromate formation, several treatment options have been tested, namely ammonia addition, pH depression, OH radical scavenging and scavenging or reduction of HOBr [91,92,56]. It turns out that only the first two options, namely ammonia addition and pH depression, are feasible in drinking water treatment [93,56]:

- Ammonia addition does not alter the ozone stability and therefore, oxidation and disinfection processes remain unchanged. Ammonia only interferes by reacting with HOBr (reaction (19)), the decisive intermediate of the bromate formation mechanism [94]. Fig. 4a shows the effect of ammonia on bromate formation in Lake Zürich water which was spiked to a bromide level of $50\,\mu g l^{-1}$. It is shown that this measure has no influence on bromate formation during the initial phase of ozonation (ozone exposure $\leqslant 2\,mg l^{-1}$ min). As discussed above, during this ozonation phase a large fraction of bromide is oxidized by OH radicals leading to the bromine atom which is further oxidized to $BrO^\bullet$ by ozone. $BrO^\bullet$ does not react with ammonia and therefore, the reaction proceeds towards bromate. Only part of this pathway leads to the formation of $HOBr/OBr^-$ which is necessary for the effeciency of the ammonia addition. Fig. 4a also shows that ammonia addition is only effective up to a certain concentration (in this case $200\,\mu g l^{-1}$). A further increase of ammonia beyond this concentration does not show an improvement in bromate minimization [56]. It has been suggested that the reaction between HOBr and NH_3 is a base-catalyzed equilibrium reaction which still leaves a fraction of $HOBr/OBr^-$ to be further oxidized to bromate [56]. Therefore, this method is not efficient in waters that already contain medium to high levels of ammonia. Because even small ammonia concentrations show a positive effect, this could be an economical way of minimizing bromate formation.

- Lowering the pH is another effective method for bromate minimization (Fig. 4b). This influences bromate formation by shifting the HOBr/OBr$^-$ equilibrium towards HOBr and increasing the ozone exposure relative to OH radical formation. As a consequence, for a certain ozone exposure the OH radical exposure decreases with decreasing pH. This means that for similar disinfection targets the overall oxidant exposure (ozone and OH radicals) will be smaller at a lower pH, leading to a lower bromate formation. Because the oxidation of HOBr/OBr$^-$ is dominated by OH radicals under almost all treatment conditions, a decrease of pH will lead to less formation of bromate if normalized to a certain ozone exposure. The effect of pH on the contribution of direct ozone reaction is expected to be small. Similar to the addition of ammonia, this measure also does not lead to a reduction of the initial bromate formation. The initial fast transformation of ozone into OH radicals is almost independent of the pH. This leads to a similar initial bromate formation for various pH values (Fig. 4b). Due to the longer lifetime of HOBr under depressed pH conditions, there may be a trade-off between lower bromate formation and higher total organic bromine (TOBr) formation [93]. In high-alkalinity waters, pH depression might be expensive because large amounts of carbon dioxide have to be added to the water.

Overall, ammonia addition and reasonable pH depression may lead to a 50% decrease of bromate formation. This might be a feasible control option for waters containing bromide levels between 50 and 150 $\mu g\,l^{-1}$.

3.2.1.6. Bromate elimination during drinking water treatment. Once bromate is formed, its elimination is difficult. Most of the research has concentrated on bromate removal by activated carbon filtration and microbiological procsses such as BAC or slow sand filtration. Ozonation is frequently followed by these processes to remove biodegradable organic compounds. However, other process such as UV irradiation and addition of iron were also investigated:

- It has been demonstrated in several studies that new granular activated carbon (GAC) is able to reduce bromate to bromide [95–98]. However, there is a consensus in the literature that the change from GAC to biologically active carbon (BAC) results in a decrease of the rate of bromate reduction. Also the presence of NOM or high concentrations of other anions decrease the ability of GAC to reduce bromate. Bromate elimination in BAC was observed in the laboratory under conditions of low oxygen concentrations ($<2\,mg\,l^{-1}$, [99]). However, this effect was not observed in full-scale plants, mainly due to the high oxygen concentrations after ozonation. The oxygen concentrations are especially high if ozone is produced from oxygen. Therefore, bromate reduction in activated carbon filters has only limited applicability after ozonation.
- The reduction of bromate by iron(II) was tested in laboratory systems [100,101]. Bromate was reduced by Fe(II) to bromide in the pH range of drinking waters. As expected, the rate of bromate reduction increases with decreasing pH. Relatively high Fe(II) doses ($>10\,mg\,l^{-1}$) are required to obtain a sufficient reduction rate. Iron (II) adsorbed to iron(III)(hydr)-oxides enhances the rate of reduction of bromate significantly under anoxic conditions [102]. However, for both the homogeneous and the heterogeneous process, the presence of dissolved oxygen is problematic because it competes with bromate as an oxidant for Fe(II). Therefore, the addition of Fe(II) does not appear to be a feasible option for bromate reduction after ozonation.
- It was demonstrated that UV irradiation of bromate-containing solutions with low-pressure mercury lamps ($\lambda = 255\,nm$) leads to its reduction to hypobromous acid and finally bromide [100]. However, the required UV exposures were much higher than those typically required for disinfection processes. It was recently demonstrated that the inactivation of *C. parvum* oocysts by two and three orders of magnitude required a UV exposure of 10 and 25 $mJ\,cm^2$, respectively [103]. To achieve a reduction of 50 $\mu g\,l^{-1}$ bromate to approximately 25 $\mu g\,l^{-1}$, the UV exposure ranged from 250 to 550 $mJ\,cm^{-2}$ depending on the lamp type (low vs. medium pressure, [104]). To reduce bromate from 50 to $<10\,\mu g\,l^{-1}$, exposures above 1000 $mJ\,cm^2$ were required [100]. This is about a factor of 100 higher than doses required for disinfection. Therefore, this process will be restricted for economical reasons.

3.2.2. Bromo-organic compounds

Only few studies have been carried out to establish the kinetics of reactions (17) and (18) [105,106,56].

The formation of bromo-organic compounds is controlled by the competition of reactions (17) and (18) with the oxidation of HOBr/OBr$^-$ with ozone and OH radicals. In addition, HOBr/OBr$^-$ and O_3 compete for similar structures in the NOM. A comparison of the kinetics of the reaction of HOBr and ozone with organic model compounds in combination with the fact that the concentration of ozone is always much higher than the concentration of HOBr allows the conclusion that only a minor fraction of HOBr, reacts via reactions (17) and (18) [56]. In addition, we know from the analogous reaction of chlorine with NOM that only a minor fraction (a few percent) of the halogen adds to NOM [107]. Therefore, it is expected that the formation of bromo-organic compounds during ozonation is of minor importance. This is in agreement with findings from water works, where bromoform was $<5\,\mu\mathrm{g\,l^{-1}}$ in 37 out of 38 ozone treatment plants [63]. This is far below the drinking water standards of the European Union ($\Sigma\,\mathrm{THM} = 100\,\mu\mathrm{g\,l^{-1}}$) and the USEPA ($\Sigma\,\mathrm{THM} = 80\,\mu\mathrm{g\,l^{-1}}$) [7,3]. In the same study, in one water with extremely high concentrations of $\mathrm{DOC} > 6\,\mathrm{mg\,l^{-1}}$, bromoform was found to be between 30 and $73\,\mu\mathrm{g\,l^{-1}}$. Part of the organic bromine will also bind to higher molecular weight organic material from NOM. Westerhoff et al. [85] have shown in laboratory experiments that this fraction can make up between 1% and 8% of the initial bromide concentration. However, these higher molecular weight bromine compounds are currently not regulated.

3.3. By-product formation in iodide-containing waters

Iodide concentrations in natural waters are usually fairly low ($<10\,\mu\mathrm{g\,l^{-1}}$). However, due to special geological formations or seawater intrusion, iodide concentrations can reach levels of $\geqslant 50\,\mu\mathrm{g\,l^{-1}}$ [114]. The oxidation of iodide by ozone is very fast with a second-order rate constant $k = 1.2 \times 10^9\,\mathrm{M^{-1}\,s^{-1}}$ [66] and occurs via an oxygen atom transfer. It leads to hypoiodite ($\mathrm{OI^-}$) which is in equilibrium with hypoiodous acid (HOI) (Fig. 5). In the case of iodide, only about 12% of the formed oxygen is singlet oxygen [$\mathrm{O_2}$ ($^1\Delta_g$)] which confirms the explanation of a long-lived intermediate adduct ($\mathrm{I\text{-}OOO^-}$). This reduces the singlet oxygen yield by conversion due to a heavy atom effect [67]. For drinking waters, $\mathrm{OI^-}$ accounts only for a very small fraction of the overall HOI concentration ($pK_a = 10.4$, [108]). Similar to the case of bromine, the $\mathrm{OI^-}$/HOI intermediate can undergo several reactions. It is shown in Fig. 5 that it can be further oxidized to iodate, disproportionate to iodate and iodide, and it can react with NOM to form iodo-organic compounds [1 0 9]. Disproportionation of HOI is a very slow process under drinking-water treatment conditions. Therefore, this process is insignificant for the lifetime of HOI [108]. Among the iodinated organic compounds, iodoform is most undesired because of its low organoleptic threshold concentration which is between 0.3 and $1\,\mu\mathrm{g\,l^{-1}}$ [110,111]. Iodoform leads to an unpleasant medicinal taste and odor in drinking waters. Under typical drinking water treatment conditions, HOI does not react with ammonia [109].

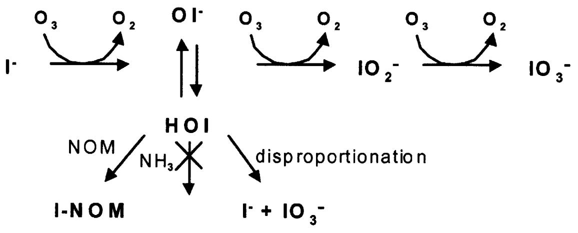

Fig. 5. Iodate formation during ozonation of iodide-containing waters.

For drinking waters, iodate is the desired sink. Unlike bromate it is not considered a carcinogenic risk [112] because it is quickly reduced to iodide in the body [113]. In contrast to aqueous bromine and chlorine, both HOI ($k = 3.6 \times 10^4\,\mathrm{M^{-1}\,s^{-1}}$) and $\mathrm{OI^-}$ ($k = 1.6 \times 10^6\,\mathrm{M^{-1}\,s^{-1}}$) are quickly further oxidized to iodate by ozone [114]. Therefore, OH radical oxidations can be neglected in the case of iodine. The oxidation of the I(+I) species by ozone occurs predominantly via HOI for pH $\leqslant 8$. Only at pH > 8 the oxidation of $\mathrm{OI^-}$ contributes significantly to the overall oxidation process. The lifetime of $\mathrm{HOI/OI^-}$ in ozonation processes is in the order of ms. Therefore, the reaction of HOI with NOM can be ruled out.

In the case of chlorination and especially chloramination processes, HOI is sufficiently long lived to react with NOM. The further oxidation of HOI is either slow (chlorine) or does not occur (chloramin) [115,116,109,117]. Therefore, the risk for iodoform formation is substantially higher under these treatment conditions.

3.4. Chlorine-derived by-products

Chloride is not oxidized by ozone. Also, the oxidation of chloride to Cl radicals by OH radicals can be neglected under typical drinking water conditions (circumneutral pH, [82]). The oxidation of chloride by OH radicals is analogous to the oxidation of bromide. The formation of $\mathrm{Cl^{\cdot}}$ and $\mathrm{OH^-}$ is given by a pH-dependent equilibrium [80]:

$$\mathrm{Cl^-} + {}^{\bullet}\mathrm{OH} \rightleftharpoons \mathrm{ClOH^-}$$
$$k_+ = 4.3 \times 10^9\,\mathrm{M^{-1}\,s^{-1}}$$
$$k_- = 6 \times 10^9\,\mathrm{s^{-1}} \tag{21}$$

$$\mathrm{ClOH^-} + \mathrm{H^+} \rightleftharpoons \mathrm{Cl^{\bullet}} + \mathrm{H_2O}$$
$$k+ = 2 \times 10^{10}\,\mathrm{M^{-1}\,s^{-1}}$$
$$k_- = 1.6 \times 10^5\,\mathrm{s^{-1}} \tag{22}$$

Reaction (21) has a very fast back reaction which leads to small steady-state concentrations of $\mathrm{ClOH^-}$. In addition, its further reaction (22) to $\mathrm{Cl^{\bullet}}$ and $\mathrm{H_2O}$ depends on the pH. Taking both reactions (21) and (22) into account, the rate constant for the oxidation of chloride by $^{\bullet}OH$ to Cl atoms is about $10^3\,M^{-1}\,s^{-1}$ at pH 7 and increases by a factor of 10 per pH unit decrease. For this reason, it only becomes important at $pH<3$.

Thus, inorganic chlorine-derived by-products are only formed during ozonation if a water is pretreated with chlorine or chlorine dioxide prior to ozonation. Fig. 6 shows the oxidation processes that can occur during ozonation of chlorine-containing waters. The processes are analogous to the bromine and iodine chemistries with the difference that they start from the Cl(+I) oxidation state. In the first step of the oxidation, ozone transfers an oxygen atom to hypochlorite. Hypochlorous acid which is in equilibrium with hypochlorite ($pK_a = 7.5$) is not oxidized by ozone [118]. The attack on hypochlorite can occur either at the chlorine atom or at the oxygen atom, leading to chlorite (ClO_2^-) and chloride (Cl^-), respectively. The oxidation of chlorite by ozone is fast, with the formation of chlorine dioxide [69,119]. It is a rare case of an electron transfer reaction between an inorganic compound and ozone. In excess of ozone, chlorine dioxide is then quickly further oxidized to chlorine trioxide (ClO_3) which reacts with chlorine dioxide to chlorate (ClO_3^-) the end product of the oxidation by ozone (see bottom of Fig. 6). The overall second-order rate constant for the oxidation of hypochlorite by ozone is $140\,M^{-1}\,s^{-1}$ with $110\,M^{-1}\,s^{-1}$ leading to chloride and $30\,M^{-1}\,s^{-1}$ leading to chlorite [118,119]. The rate constant for the oxidation of OCl^- with ozone is relatively small. Therefore, it is possible for both ozone and chlorine to be present simultaneously. The oxidation of chlorite with ozone to chlorine dioxide has a second-order rate constant of $8.2\times10^6\,M^{-1}\,s^{-1}$ [69]. Chlorine dioxide reacts with ozone with a second-order rate constant of $1.05\times10^3\,M^{-1}\,s^{-1}$ [120]. If ozone is present in large excess over chlorite, ClO_3 may be the main product. It is unstable in water and disproportionates to ClO_3^- and ClO_4^- [121].

OH radicals can also play a significant role for the oxidation of chlorine to chlorate (Fig. 6). The second-order rate constant for the oxidation of OCl^- with OH radicals to the ClO radical is $9\times10^9\,M^{-1}\,s^{-1}$ [122]. No value is available in literature for HOCl. Considering only the oxidation of OCl^- by ozone and OH radicals, the fraction f_{O_3} of the total HOCl reacting with O_3 can be calculated to be 60% ($R_c = [^{\bullet}OH]/[O_3] = 10^{-8}$). This fraction is independent of the pH and corresponds approximately to the f_{O_3} for HOBr at pH 8 (Table 3). If there is a fast reaction of HOCl with OH radicals, f_{O3} will decrease and will become pH dependent. As shown in Fig. 6, the further oxidation of chlorite with OH radicals ($k_{OH,ClO_2^-} = 4.2\times10^9\,M^{-1}\,s^{-1}$) leads to chlorine dioxide and then to chlorate ($k_{OH,ClO_2^-} = 4.2\times10^9\,M^{-1}\,s^{-1}$) [120]. For conventional ozonation processes these reactions are not important. The direct reactions with ozone are much faster. Based on this finding the reaction between ozone and chlorine was used to calibrate a full-scale ozonation reactor during conventional ozonation [9]. A shock prechlorination was applied and the chlorate formation was measured in the ozonation reactor. A combination of hydraulic modeling with reaction kinetics allowed the assessment of the ozone concentration and, in turn, the disinfection and oxidation processes in this particular reactor [9].

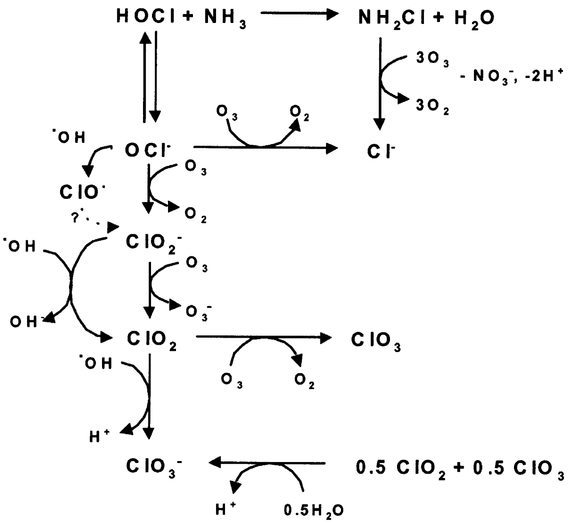

Fig. 6. Oxidation of chlorine species to chlorate during ozonation. (a) processes involving hypochlorite and (b) oxidation of chlorine dioxide.

Similar to HOBr, HOCl reacts quickly with NH_3 to form monochloramine, which is oxidized by ozone to nitrate and chloride. Because chloride is not oxidized during ozonation, the presence of ammonia completely prevents the formation of chlorate (Fig. 6).

Possible adverse health effects from chlorate are not well established to date. The WHO gives no guideline value for drinking water, however, it does suggest that chlorate should be kept as low as possible until more toxicological information is available [59]. In Switzerland, the drinking water standard for chlorate is $200\,\mu g\,l^{-1}$ [123].

3.5. *Effect of ozonation on precursors for chlorination by-products*

The reactions of ozone with NOM may lead to a partial removal of precursors of trihalomethanes (THM), total organically bound halogens (TOX), trichloroacetic acid and dichloroacetonitrile. After pre-ozonation, these post-chlorination by-products may be reduced by 5–75% ([124,125,8] and references therein). However, precursors of dichloroacetic acid were not altered and precursors for 1,1,1-trichloroacetone even increased [124]. Also, in the case of trichloronitromethane, an increase of its formation was found in a chlorination after preozonation [126]. The increase of precursors of disinfection by-products can be explained by the formation of intermediate species by partial oxidation processes (e.g., formation of phenolic compounds from the oxidation of aromatic compounds by OH radicals, formation of methyl ketones from the oxidation of olefines with ozone, [127]).

It has been shown that the presence of carbonate, a scavenger for OH radicals, enhances the removal of precursors of chlorination by-products [125,8]. Since carbonate is an inhibitor for the decomposition of ozone by the radical chain reaction it enhances the lifetime of ozone. Therefore, for a given ozone dose the effect of carbonate can be explained by a higher ozone exposure. This is a strong indication that the precursor removal is caused by direct ozone reactions. It has been demonstrated that resorcinol- and phenol-type entities or β-ketoacids and β-diketones are important precursors for chlorination by-products [128–131]. These structures also react quickly with ozone [132]. It has been shown that the formation of trihalomethanes after ozonation was primarily reduced during the initial phase of chlorination of natural water. This was attributed to a preoxidation of resorcinol-type entities, β-ketoacids or β-diketones by ozone [134].

Ozonation could be a powerful pretreatment step to remove precursors of *N*-nitrosodimethylamine (NDMA) which can be formed in distribution systems during chloramination. Mechanistic studies show that NDMA is formed from a reaction of monochlormaine with dimethylamine or other amines [133]. Ozone reacts quickly with secondary amines and, therefore, these precursors are efficiently eliminated [134].

4. Conclusions

Ozone is the most efficient chemical disinfectant currently applied in drinking water treatment. Even for microorganisms such as protozoa which are difficult to inactivate with other disinfectants, ozone provides adequate inactivation with reasonable doses and contact times. The only restrictive factor in this context is a proper inactivation of *C. parvum* oocysts while complying with regulations for by-products.

Disinfection by-products include (non-)brominated organic compounds and the inorganic compounds bromate, iodate (and chlorate). Most of the low-molecular weight non-brominated organic by-products are mineralized during biologically activated carbon filtration, which is typically performed after an ozonation process. Therefore, they are of minor concern. Information is lacking on higher molecular weight organic by-products. The extent of formation of brominated organic compounds is usually small, because the bromination process occurs in competition with an ozone attack. Bromate is currently the by-product that causes most concern due to its potential carcinogenicity. Because of the low drinking water standards ($10\,\mu g l^{-1}$), an optimization of the ozonation process is required in certain cases to minimize its formation. Once formed, its removal is non-economical. The best bromate minimization strategies appear to be lowering of the pH or ammonia addition. Iodate, quantitatively formed by oxidation of naturally occurring iodide by ozone, is of no toxicological concern. It is rapidly metabolised after ingestion. Chlorate is only formed during ozonation if a preoxidation of the water with chlorine and/or chlorine dioxide is applied. The toxicological impact of chlorate is unclear and more studies are required to permit regulation.

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