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Options and limitations for bromate control during ozonation of wastewater

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Abstract

Wastewater treatment plants (WWTPs) are important point sources for micropollutants, which are harmful to freshwater organisms. Ozonation of wastewater is a powerful option to abate micropollutants, but may result in the formation of the potentially toxic oxidation by-product bromate in bromide-containing wastewaters. This study investigates options to reduce bromate formation during wastewater ozonation by (i) reducing the bromide concentration of the wastewater, (ii) lowering the ozone dose during wastewater treatment and (iii) adding hydrogen peroxide to limit the lifetime of ozone and quench the intermediates of the bromate formation pathway. Two examples demonstrate that a high share of bromide in wastewater can originate from single point sources (e.g., municipal waste incinerators or landfills). The identification of major point sources requires laborious sampling campaigns, but may facilitate the reduction of the bromide load significantly. To reduce the bromate formation by lowering the ozone dose interferes with the aim to abate micropollutants. Therefore, an additional treatment is necessary to ensure the elimination of micropollutants. Experiments at a pilot-plant illustrate that a combined treatment (ozone / powdered activated carbon) allows to eliminate micropollutants with low bromate yields. Furthermore, the addition of hydrogen peroxide was investigated at bench-scale. The bromate yields could be reduced by ~50% and 65% for a hydrogen peroxide dose of 5 and 10 mg L⁻¹, respectively. In conclusion, there are options to reduce the bromate formation during wastewater ozonation, however, they are not simple with sometimes limited efficiency.

1. Introduction

The increasing number and concentrations of micropollutants in freshwater systems are recognized as a threat for aquatic ecosystems (Schwarzenbach et al., 2006). In spite of their low concentrations (pg L^{-1} to $\mu\text{g L}^{-1}$), individual micropollutants or mixtures thereof have the potential to cause ecotoxicological effects (e.g. by interfering with the hormonal system of aquatic organisms or inhibiting the photosynthesis) (Jobling et al., 1998; DeLorenzo et al., 2001; Snyder et al., 2003; Kidd et al., 2007; Tang and Escher, 2014). The origin of micropollutants is diverse and ranges from diffuse sources (e.g., pesticides from agriculture) to point sources (e.g., pharmaceuticals and personal care products from wastewater treatment plant (WWTP) effluents) (Ternes, 1998; Nikolaou et al., 2007; Moschet et al., 2014). In consequence, strategies to reduce the discharge of micropollutants to surface waters comprise of measures at the source (reduction of the use of micropollutants) to end-of-pipe solutions such as the abatement of micropollutants in WWTPs (Joss et al., 2008; Eggen et al., 2014). Recently, the Swiss government decided to reduce the discharge of micropollutants from WWTPs by upgrading the treatment train of about 100 out of 700 Swiss WWTPs (Eggen et al., 2014). These WWTPs are required to eliminate the concentrations of a set of substances (SI, Table S9) by 80% on average over the entire treatment train (SI, Table S9; Federal Office for the Environment (FOEN) (2014)). Most WWTPs of concern will presumably install either an ozonation or an activated carbon based treatment to fulfill the requirements because numerous bench-, pilot- and full-scale studies have demonstrated the efficiency of these processes (Ternes et al., 2003; Snyder et al., 2006; Hollender et al., 2009; Lee et al., 2013; Margot et al., 2013; Altmann et al., 2014). Nevertheless, some wastewater matrices are not suitable for ozonation because of a fast ozone consumption (lowering the micropollutant elimination) or the formation of (potentially) toxic by-products upon ozonation. A test procedure was developed to identify

these wastewaters, whereof a crucial criteria is the formation of bromate during ozonation (Schindler Wildhaber et al., 2015).

Bromate is a potential human carcinogen with a drinking water standard of $10 \mu\text{g L}^{-1}$ in many countries and an environmental quality standard of $50 \mu\text{g L}^{-1}$ in Switzerland (European Council, 1998; US EPA, 2006; Oekotoxzentrum Eawag-EPFL, 2015). It is formed by the reaction of bromide with ozone and OH radicals via numerous intermediates (Scheme 1) (von Sonntag and von Gunten, 2012). For bromide levels found in municipal wastewater ($\sim 0.01\text{--}1 \text{ mg L}^{-1}$), bromate yields ($\text{mg BrO}_3^- / \text{mg Br}^-$) upon ozonation are nearly independent of the bromide concentration (Soltermann et al., 2016). The dependence of the bromate yields on the specific ozone dose is non-linear. While only low bromate yields ($< 5\%$ ($\text{mg BrO}_3^- / \text{mg Br}^-$)) were found for specific ozone doses $< 0.4 \text{ mg O}_3 / \text{mg DOC}$, bromate yields appear to increase nearly linearly with specific ozone doses $\geq 0.4\text{--}0.6 \text{ mg O}_3 / \text{mg DOC}$ (Soltermann et al., 2016). This is due to the fact, that low ozone concentrations are quickly consumed by fast reacting moieties of the dissolved organic matter (DOM). Bromate is only substantially formed, when the ozone and OH radical ($\cdot\text{OH}$) exposures are high enough to further oxidize the intermediates $\text{Br}^\cdot$ and/or HOBr/OBr^- (Scheme 1) (von Sonntag and von Gunten, 2012).

Scheme 1: Most relevant species involved in the bromate formation during the ozonation of bromide-containing waters (simplified and adapted from von Sonntag and von Gunten (2012)).

Prior to ozone application in wastewater, bromate formation was mainly an issue in the field of drinking water ozonation (von Sonntag and von Gunten, 2012). Investigations on the removal of bromate at the end of the drinking water treatment process were not fruitful, wherefore

several strategies were developed to minimize bromate formation during ozonation (von Sonntag and von Gunten, 2012). These strategies, which were all based on lowering the availability of prerequisite primary and intermediate species for bromate formation (Scheme 1), are shortly discussed:

1. *Lowering the bromide concentration.* The most straightforward approach to minimize bromate formation upon ozonation is a reduction of the bromide concentration. Recently, the awareness of bromide sources in raw waters of drinking water treatment plants increased because high bromide loads are released to surface waters from wastewater of new technologies such as shale gas production and scrubbers in coal-fired power plants (Warner et al., 2013; McTigue et al., 2014; Harkness et al., 2015). The increased bromide concentrations result in higher concentrations of brominated disinfection by-products, which (potentially) have adverse health effects (Parker et al., 2014; Regli et al., 2015). Bromide sources of wastewater have hardly been investigated. A survey on Swiss wastewaters revealed that chemical industry, special waste industry and waste incinerators are major bromide sources (Soltermann et al., 2016). Hence, an elimination of these point sources could clearly reduce the bromide load in the specific wastewaters. A bromide removal from such wastewaters would also be an option since there are multiple techniques for bromide removal (Watson et al., 2012). These techniques can be categorized in three groups: membranes (e.g., reverse osmosis, nanofiltration and electrodialysis), electro-chemical (e.g., electrolysis) and adsorptive techniques (e.g., silver-doped materials). However, all techniques are either very costly, very energy-intensive, not suitable for wastewater matrices or not efficient enough, so that they cannot be considered as practical solutions for bromide removal from wastewater.

2. *Quenching of HOBr.* Several bromate control measures based on quenching HOBr have been developed in drinking water. HOBr can be quenched by ammonia, thereby masking bromine as bromamines (Pinkernell and von Gunten, 2001; Heeb et al., 2017). In the chlorine-ammonia process bromide is oxidized to HOBr prior to ozonation and then quenched by ammonia addition, which leads to a significantly enhanced bromate minimization (Buffle et al., 2004). HOBr can also be quenched by hydrogen peroxide addition. However, because the combination of ozone with hydrogen peroxide is an advanced oxidation process (AOP) favoring hydroxyl radical formation, disinfection efficiency is significantly reduced under these conditions. Overall, the strategies for HOBr quenching developed in drinking water are less suitable for wastewater ozonation because HOBr formation (Scheme 1, pathway 2) is only a minor pathway compared to pathway 1 (Scheme 1).
3. *Lowering the $\cdot\text{OH}$ exposure (by pH-depression).* $\cdot\text{OH}$ are essential for the dominant pathways (Scheme 1, pathways 1 and 2) of the bromate formation. To lower the concentration of $\cdot\text{OH}$ might be an option for drinking water, where mainly ozone is required for disinfection. Pinkernell and von Gunten (2001) showed that lowering the pH from 8 to 6 facilitated a reduction of bromate formation in drinking water of about 60%. In contrast, for wastewater treatment, both species, ozone and $\cdot\text{OH}$, are necessary to have an optimal abatement of the whole spectrum of micropollutants, even of those with a low reactivity with ozone. Hence, the strategy to minimize bromate formation by lowering the residual $\cdot\text{OH}$ concentration by pH depression is not appropriate.
4. *Lowering the ozone exposure.* It is assumed that bromate formation during wastewater ozonation mainly occurs via the reaction pathway 1 presented in Scheme 1 because the reaction of bromide with ozone is rather slow and ozone decomposition in wastewater is faster than in drinking water (Buffle et al., 2006; von Sonntag and von Gunten, 2012). In this formation pathway, ozone is a prerequisite oxidant to oxidize Br^- to $\text{BrO}^\cdot$ and

further to BrO_3^- . It is known that ozone reacts quickly to $\cdot\text{OH}$ in the presence of H_2O_2 . This advanced oxidation process (AOP) $\text{O}_3/\text{H}_2\text{O}_2$ results in low bromate yields because of the reduced ozone exposure. However, direct ozone reactions are also desirable for the elimination of micropollutants in wastewater treatment. The effect of H_2O_2 addition on the bromate yield during wastewater ozonation has already been investigated in bench-scale experiments (Lee et al., 2016). An average reduction in the bromate formation of about 20% was found for specific H_2O_2 doses ($\text{mol H}_2\text{O}_2 / \text{mol O}_3$) of 0.5 and 1 for eight wastewaters. However, the efficiency of H_2O_2 addition for bromate mitigation depended strongly on the wastewater matrix composition.

Conclusively, bromate formation during wastewater ozonation is an emerging issue. The principal goal of wastewater ozonation in the Swiss context is to abate micropollutants. Therefore, strategies to mitigate bromate formation should not interfere with this goal to a large extent. Established solutions from the drinking water treatment field, where this problem already appeared two decades ago, are often not appropriate for wastewater treatment. Furthermore, the technical and economic feasibility at full-scale are important issues when considering bromate mitigation.

The aim of this study is to explore potential strategies to minimize the bromate formation during wastewater ozonation based on theoretical considerations and experimental results with the following investigations: (i) Two case studies show how major bromide sources were identified and eliminated in the catchments of WWTPs to considerably lower the bromide concentration in the corresponding wastewaters. (ii) The options and limitations to lower the specific ozone dose temporarily during high bromide peaks or constantly are investigated. The evolution of a bromide peak in a WWTP was modeled to define the conditions under which it might be practical to temporarily interrupt the ozonation. (iii) The combination of ozonation followed by powdered activated carbon (PAC) was studied at pilot-scale to test whether or not

163 this combined process facilitates a considerable micropollutant abatement at a low bromate
164 formation. In addition, the effect of PAC treatment on bromate yields was investigated for a
165 setting in which ozonation follows a PAC treatment. (iv) Bench-scale experiments were
166 conducted to assess the feasibility of reducing bromate formation and abatement of
167 micropollutants by the addition of H_2O_2 for various scenarios.

168

2. Materials and Methods

General information on WWTP A-E are given in SI, section E.

2.1. Sampling campaigns to identify bromide sources and the corresponding analytical methods

Two studies were performed to identify major bromide sources in the catchment of WWTP A and B. In the first study, a landfill with three compartments (A, B and C) was investigated, whereof only compartment C is still in operation. Compartment C is also the only one with two outlets (C1 and C2). To estimate bromide loads from the leachate of compartments A-C, grab samples were taken on 5 days during a period of two weeks. The annual discharge is known for all compartments. Bromide concentrations in the effluent of WWTP A, to which the wastewater of the landfill is discharged, were assessed for the same two-week period with daily composite samples. The annual bromide loads of the landfill and the WWTP were calculated from the average bromide concentrations during the sampling period and the annual discharges. Bromide concentrations were measured with ion chromatography (ICS 1100 (Dionex AG) with a LOQ of 10 $\mu\text{g L}^{-1}$.

In the second study (WWTP B), grab samples were taken at 37 points in a sewer system to identify dominant bromide sources (SI, Figure S1). To estimate the annual bromide loads from two municipal waste incinerators, bromide was measured in monthly composite samples over a period of one year (data from a previous study by Soltermann et al. (2016)). There is only data available on the annual wastewater discharges of the incinerators. The annual bromide load from WWTP B, to which the municipal waste incinerators discharge their wastewater, is estimated from 32 daily composite samples, which were taken during a period of 3 months (data from a previous study by Soltermann et al. (2016)). The discharge was measured on a

daily basis. Bromide concentrations were measured with ion chromatography (Compact IC pro (Metrohm) with a LOQ of $100 \mu\text{g L}^{-1}$.

2.2. Modelling the evolution of bromide peaks through a conventional WWTP

The evolution of a bromide peak in a WWTP was modelled with the software AQUASIM (Reichert, 1994). The model WWTP is composed of 3 compartments (primary clarifier, activated sludge tank and final clarifier), whereof each is modelled as a series of completely stirred tank reactors (Scheme 2). The WWTP was designed for 10'000 population equivalents (PE) with volumes of 25, 168 and 84 L PE^{-1} for the primary clarifier, the activated sludge tank and the final clarifier, respectively, according to the literature (Gujer, 2002). The residence time in the modelled WWTP is about 17 h assuming a wastewater input of $400 \text{ L PE}^{-1} \text{ d}^{-1}$. Furthermore, bromide was modelled as an inert substance not reacting or adsorbing during treatment.

Scheme 2: Model WWTP with dimensions according to Gujer (2002). The primary clarifier, the activated sludge tank and the secondary clarifier were modeled as a series of 2, 4 and 3 completely stirred tank reactors (CSTRs), respectively. The hydraulic residence times (Θ) of 1.5, 10 and 5 hours in the primary clarifier, the activated sludge tank and the secondary clarifier, respectively, result in a total hydraulic residence time of 16.5 h.

2.3. Pilot-plant study with ozonation and PAC treatment and the corresponding analytical methods

A pilot plant (WWTP C) with a sequencing-batch-reactor (SBR) for biological treatment, ozonation and PAC treatment was fed with municipal (90 %) and industrial wastewater (10%)

(SI, Scheme S1, Table S2). The ozonation step consisted of a column contactor in which ozone is bubbled in a counter-current mode, and a column reactor to ensure a complete ozone depletion. The residence times were about 20.5 and 12.5 minutes for the contactor and the reactor column, respectively (SI, Table S2). Ozone was produced with an ozone generator (Ozonizer S 1000, Erwin Sander Elektroapparatebau GmbH) and measured photometrically in the inlet air (ColorPlus UV, Siegrist). Additionally, the ozone concentration in the off-gas was measured periodically to confirm a complete ozone transfer in the ozone contactor and complete consumption in the ozone reactor. The PAC treatment was composed of an adsorption reactor, to which a stock solution (500 mg L^{-1}) of suspended PAC (Cabot SEA SUPER, Norit) was dosed, and a filtration unit with residence times of 12 and 24 minutes, respectively (SI, Table S2). The treatment was followed by sedimentation, from where the sludge (including PAC) is partly recycled to the SBR.

Bromate formation and the elimination of 18 micropollutants (SI, Table S5) were studied for a specific ozone dose of $0.35 \pm 0.05 \text{ mg O}_3 / \text{mg DOC}$ and a PAC dose of 10 mg L^{-1} . Composite samples were taken during 3 sampling periods of 48 hours within 10 days. Micropollutants were measured with LC-MS (1100 LC, Agilent and API 4000, Sciex; column: Waters C-18 Atlantis T3 $3 \mu\text{m}$ ($3 \times 100 \text{ mm}$); eluent: A = nanopure water 0.1% formic acid / B = methanol 0.1% formic acid, gradient from 20% B to 90% B). Bromide and bromate concentrations during the pilot-scale experiments were also measured with ion chromatography (ICS 1100, Dionex AG and 881 Compact IC Pro, Metrohm) with LOQs of $10 \mu\text{g L}^{-1}$ and $0.5 \mu\text{g L}^{-1}$ for bromide and bromate, respectively.

2.4. Bromate yields during ozonation of PAC-treated wastewater in laboratory experiments and the corresponding analytical methods

Grab samples of the effluent of WWTP D were taken at two differing days (samples 1 and 2) and filtered ($0.45 \mu\text{m}$) directly after sampling. PAC (Cabot SEA SUPER, Norit) was dosed

from a slurry (25 g L⁻¹) to the wastewater and mixed in an overhead shaker for 30 min. After sedimentation of the PAC, the supernatant wastewater was filtered again. *para*-Chlorobenzoic acid (*p*CBA) (sample 1) and carbamazepine and *p*CBA (sample 2) were spiked (1 µM) prior to ozonation. Ozonation of spiked wastewater was performed according to the procedure described in literature where an ozone stock solution (~1.3 mM) was produced by sparging ozone gas (CMG 3-3 ozone generator, Apaco AG, Switzerland) through ice-cooled, ultrapurified water (Chon et al., 2015). The ozone concentration in the stock solution was determined photometrically ($\epsilon_{260\text{nm}} = 3200 \text{ L mol}^{-1} \text{ cm}^{-1}$) (von Sonntag and von Gunten, 2012). Ozone was dosed to the vigorously stirred wastewater (400 mL) (stirring was stopped after ~30 s) and samples were taken with a dispenser from 15 s to 10 min. Ozone and $\cdot\text{OH}$ exposures were measured with the indigo method (Bader and Hoigné, 1981) and by the *p*CBA abatement (Elovitz and von Gunten, 1999), respectively. pH was measured with a 632 pH-meter (Metrohm) before and after each treatment and remained stable at 8 ± 0.15 for both samples. Carbamazepine and *p*CBA were measured with high-performance liquid chromatography (HPLC, Ultimate 3000, Dionex) with a UV-visible diode array detector (LOQ = 0.01 µM, error in measurement $\pm 5\%$ at $\lambda = 230 \text{ nm}$). Analyses were performed with an eluent consisting of acetonitrile and phosphoric acid (10 mM) (ratio 40:60, pH 2.5), at a flow rate of 0.6 mL min⁻¹ and a standard column (Cosmosil, 5C18-MS-II, 3.0 ID × 100 mm, Nacalai Tesque Inc.). Bromide and bromate were measured with IC-MS/MS (ICS400, Dionex, column: AS19-4µm, TSQ-Vantage, Thermo Scientific) (Shah et al., 2015). LOQs were 0.5 and 0.1 µg L⁻¹ for bromide and bromate, respectively. DOM measurements and fractionations were performed with size-exclusion chromatography (LC-SEC-OCD, Huber; column: TSK HW 50S, Tosoh) (Huber et al., 2011). EDC measurements were done following a method by Chon et al. (2015).

2.5. Bromate formation during ozonation in absence/presence of H₂O₂ in the laboratory and the corresponding analytical methods

The effluent of WWTP E was filtered (0.45 µm) and stored at 4 °C before the ozonation experiments. Initial DOC was measured with Shimadzu TOC-L CSH (LOQ = 0.5 mgC L⁻¹, error in measurement = 0.2 mgC L⁻¹). Ozonation of spiked wastewater (carbamazepine (2 µM), pCBA (2 µM) and bromide (100 µg L⁻¹ after spiking)) was performed by adding ozone (specific ozone doses 0–1.5 mg O₃ / mg DOC) to vigorously stirred wastewater in absence and presence of hydrogen peroxide at room temperature (22±2 °C). Samples were not analyzed before the next day to guarantee complete ozone depletion. For H₂O₂ addition after pre-ozonation with a specific ozone dose of 0.4 mg O₃ / mg DOC, post-ozonation was performed after a holding time of 3 hours. Carbamazepine, pCBA, bromide and bromate were measured as described in section 2.5.

3. Results and Discussion

In the following, the feasibilities of minimizing bromate formation by reducing the bromide concentration, by reducing the specific ozone dose or by quenching intermediates are discussed.

3.1 Elimination of bromide sources in the catchment of a WWTP

Bromate yields are almost linearly related to the bromide concentrations for typical bromide concentrations in wastewaters ($10\text{--}1000\text{ }\mu\text{g L}^{-1}$) and specific ozone doses $> 0.4\text{ mg O}_3 / \text{mg DOC}$ (Soltermann et al., 2016). Thus, a reduction of the bromide concentration typically leads to a proportional reduction of the bromate concentration. Only at extraordinarily high bromide concentrations (several mg L^{-1}), bromate yields are reduced because of an efficient scavenging of ozone and $\cdot\text{OH}$ by bromide, which hinders the full oxidation from bromide to bromate (Schindler Wildhaber et al., 2015). Under such circumstances, ozonation is an inappropriate treatment because the oxidation of micropollutants is also inefficient.

A previous study highlighted that bromide concentrations in Swiss municipal wastewaters are generally low ($< 100\text{ }\mu\text{g L}^{-1}$) unless there is a major bromide source (e.g., waste incineration, chemical or special waste industry or landfills) in their catchment (Soltermann et al., 2016). A typical specific ozone dose to substantially abate ozone-reactive micropollutants in wastewater is $\sim 0.5\text{ mg O}_3 / \text{mg DOC}$ (Lee et al., 2013). Bromate yields are commonly $\leq 5\%$ under these conditions ($\text{mg BrO}_3 / \text{mg Br}^-$) (Soltermann et al., 2016). Thus, bromate levels in the ozonated effluents of WWTPs with municipal catchments are typically far below the drinking water standard for bromate ($10\text{ }\mu\text{g L}^{-1}$). Bromide concentrations might range from $500\text{ }\mu\text{g L}^{-1}$ up to several mg L^{-1} for WWTPs with major bromide sources in the catchment, which would result in an important bromate formation. Hence, the elimination of major bromide sources in the catchment has the potential to efficiently reduce the bromate formation in such cases.

In the following, two case studies are discussed to illustrate the feasibility but also the practical limitations of this strategy:

Case study 1

WWTP A has a landfill in the catchment, where fly-ash and slag of a municipal waste incinerator are dumped. To assess the contribution of the landfill to the bromide load in the effluent of WWTP A, bromide concentrations of the leachates of the landfill compartments and of the corresponding WWTP effluent were measured (Figure 1, left). Bromide concentrations of the landfill leachates were in the range of several mg L^{-1} for all compartments, even for the compartments A and B, which are not operational anymore. The bromide concentrations were clearly lower in the WWTP effluent ($60 \pm 30 \mu\text{g L}^{-1}$). Comparing the annual bromide load of the WWTP effluent with the estimated annual bromide loads from the landfill compartments (Figure 1, right) shows that the contribution of the landfill to the total bromide load of the WWTP is about 40% (SI, Table S1). The uncertainty of this estimation is high because only a rough estimation can be done based on annual discharge measurements. Therefore, predictions on bromide concentrations of the WWTP effluent after the exclusion of the landfill from the catchment have a low precision. Only a more sophisticated sampling campaign (including discharge measurements, long-term sampling and simultaneous measurements in the WWTP) could better assess the contribution of the landfill. Nevertheless, a separate treatment (which must not be ozonation to prevent bromate formation) of the landfill leachates with a direct discharge to surface water would lower the bromide concentration of the WWTP effluent substantially. Given the rather low bromide concentration of the WWTP effluent, it is not assumed that there are other major bromide sources in the catchment.

321

322 Figure 1: Bromide concentrations (left) and loads (right) in the leachates of landfill
 323 compartments and the effluent of the corresponding WWTP A (left). Concentrations were
 324 measured in 5 grab samples (landfill) and in 14 daily composite samples during 2 weeks
 325 (WWTP A). Loads were calculated by multiplying the average concentration by the annual
 326 discharge (right).

327 *Case study 2*

328 It is planned to upgrade WWTP B with an ozonation step in future. In a previous study, it was
 329 shown that bromide concentrations in the effluent of WWTP B were $550 \pm 300 \mu\text{g L}^{-1}$ (32 daily
 330 composite samples taken during 3 months, Figure 2, left) (Soltermann et al., 2016). There are
 331 two municipal waste incinerators in the catchment of this WWTP, with bromide concentrations
 332 of $442 \pm 109 \text{ mg L}^{-1}$ and $449 \pm 165 \text{ mg L}^{-1}$ (12 monthly composite samples, Figure 2, left, data
 333 from Soltermann et al. (2016)) in their wastewater. Considering the annual wastewater
 334 discharge of the municipal waste incinerators and the estimated annual bromide load reveals
 335 that 85% of the bromide load in WWTP B originates from the municipal waste incinerators
 336 (Figure 2, right). Hence, a separated treatment and a direct discharge of the incinerator
 337 wastewater to surface water could potentially lower the bromide concentration in the effluent of
 338 WWTP B to $< 100 \mu\text{g L}^{-1}$. Such a direct discharge is only possible, if the legal discharge

criteria are fulfilled (e.g., pH, heavy metals, salt, DOC concentration, ammonium concentration and temperature).

It is unclear, whether the bromide concentration in the effluent of WWTP B really drops to $< 100 \mu\text{g L}^{-1}$ after the elimination of the contribution of the municipal waste incinerators. The uncertainty on data about the bromide loads from the municipal waste incinerators is high and this has impacts on the prediction of the bromide load. To assess, whether there are other significant bromide sources in the catchment of WWTP B, grab samples were taken at 37 points in the sewer system (SI, Figure S1). 36 out of 37 samples had bromide concentrations $< 100 \mu\text{g L}^{-1}$ and only one sample with municipal waste incinerator 2 in the sub-catchment had a bromide concentration of 41.8 mg L^{-1} . One grab sample was taken at a position where wastewater was expected to have a share of wastewater from both municipal waste incinerators. However, the bromide concentration at this point was $< 100 \mu\text{g L}^{-1}$. This can be explained by the fact that both municipal waste incinerators release their wastewaters intermittently with interruptions of several hours and days. Overall, this example illustrates previous findings that bromide discharge from major sources are often variable and a sampling campaign with grab samples only, might not be appropriate to elucidate the bromide sources (Soltermann et al., 2016). Instead longer sampling periods with composite samples would be required.

These two case studies demonstrate the potential for a substantial reduction of the bromide concentration in WWTPs by identifying major bromide sources and / or by treating and discharging their wastewater directly to surface waters. However, it is difficult to assess all important bromide sources in a catchment with certainty. This is only possible with in depth, long-term sampling campaigns in the sewer system or by precise load measurements from suspect point sources and in the WWTPs.

Figure 2: Bromide concentrations of monthly composite samples of two municipal waste incinerators and of 32 daily composite samples of the corresponding effluent of WWTP B (left) (Soltermann et al., 2016). Bromide loads of two municipal waste incinerators calculated from average bromide concentrations and the annual discharge and of the WWTP B (right).

4.2 Adapting the ozone dose for bromate mitigation

Discontinuation of ozonation during episodes with high bromide levels

WWTPs with important bromide sources in their catchments, which periodically discharge high bromide loads (e.g., chemical industry, Soltermann et al. (2016)), may consider discontinuing the ozonation during periods with high bromide concentrations. Figure 3 shows the modeled evolution of bromide peaks during a conventional wastewater treatment for various scenarios. A short bromide peak of three hours mimicking the bromide release by e.g., a special waste industry (Figures 3a) is stretched over more than one day after the entire treatment train, so that the maximum bromide concentration in the WWTP effluent is only about 20% of the initial concentration. If bromide peaks in the input are ≥ 24 hours (Figures 3b-c), the bromide concentration in the WWTP effluent reaches almost a steady-state similar to the input concentration. For all scenarios, the concentration drops to a low level within 24 hours after the bromide input stops. If peaks of 3 hours arrive in series at the WWTP (Figure 3d), e.g., from an incinerator, which releases wastewater intermittently, bromide concentrations in the primary

clarifier vary strongly with the bromide loads, whereas bromide concentrations in the activated sludge tank and the secondary clarifier are less dynamic. Again, bromide concentrations in the WWTP effluent reach a steady-state equal to the integrated bromide load if the input is constant for > 24 hours.

Conclusively, it is not practical to interrupt ozonation for short bromide peaks in the range of hours. To discontinue ozonation during longer periods (several days) with high bromide concentrations is an option, since the phase-out time after the bromide peak is relatively short (~ 1 day). This bromate mitigation strategy suffers from two main drawbacks. Firstly, regular and long interruptions of the ozonation interfere with the aim of significant, average elimination of micropollutants. Secondly, bromide peaks are not easily identified because bromide concentrations are often at the edge of the sensitivity of bromide sensors ($\sim 1 \text{ mg L}^{-1}$) or other interfering anions (e.g., chloride) give false positive signals (Shamsipur et al., 2000; Singh et al., 2006).

Figure 3: Modelled evolution of bromide peaks passing through a wastewater treatment train according to Scheme 2. (a) A short bromide peak of three hours is stretched over one day after the treatment. (b) The bromide concentration in the secondary clarifier rises almost to the concentration of the input level for a 24 h peak. (c) For a constant bromide level > 48 hours, the bromide concentration in the effluent reaches a steady-state, which is equal to the influent concentration. (d) For a series of short bromide peaks of 3 hours, the steady-state concentration in the secondary clarifier reaches the average concentration of the influent.

Combined treatment “ozonation / powdered activated carbon (PAC)” : Application of an adapted ozone dose

WWTP C aims to abate micropollutants in wastewater, which originates from a municipal ($71700 \pm 1700 \text{ m}^3 \text{ h}^{-1}$, $0.13 \pm 0.03 \text{ mg L}^{-1}$ bromide ranging from 0.08 to 0.19 mg L^{-1}) and an industrial catchment ($3400 \pm 140 \text{ m}^3 \text{ h}^{-1}$, $15.67 \pm 20.01 \text{ mg L}^{-1}$ bromide ranging from 1.2 to 74 mg L^{-1}) (SI, Table S3). Because of the high bromide concentration ($1.68 \pm 2.03 \text{ mg L}^{-1}$ bromide) of the mixed wastewater (SI, Figure S2), an ozonation of this wastewater may lead to a substantial bromate formation. A pilot-plant with a combined treatment process of ozonation followed by PAC (SI, Scheme S1) should elucidate, whether this combination facilitates the elimination of micropollutants with low bromate levels.

Bench-scale experiments from a previous study with this specific wastewater showed that bromate yields were low $< 2\%$ ($\text{mg BrO}_3^- / \text{mg Br}^-$) for specific ozone doses of $\leq 0.4 \text{ mg O}_3 / \text{mg DOC}$ (Figure 4a) (Soltermann et al., 2016). Bromate yields increased clearly for specific ozone doses $> 0.4 \text{ mg O}_3 / \text{mg DOC}$. Lee et al. (2013) grouped micropollutants (groups I-V) according to their second order rate constants with ozone and $\cdot\text{OH}$ (SI, Table S4) and measured their elimination during ozonation (Figure 4a). Contrasting the bromate yields from the bench-scale experiment with the elimination of micropollutants measured by Lee et al. (2013) reveals that for low ozone doses with bromate yields $< 1\%$, only micropollutants with high ozone

reactivity (group I, $k_{O_3, pH7} \geq 1 \times 10^5 \text{ M}^{-1}\text{s}^{-1}$) are eliminated to > 95% (Figure 4a). To abate compounds with lower reactivity (groups II-V, $k_{O_3, pH7} < 1 \times 10^5 \text{ M}^{-1}\text{s}^{-1}$) by > 95% requires an ozone dose > 0.4 mg O_3 / mg DOC and results conclusively in a higher bromate yield. Therefore, it is aimed to operate the pilot-plant at a specific ozone dose < 0.4 mg O_3 / mg DOC to minimize bromate formation. The corresponding loss in micropollutant abatement efficiency could then be compensated by a subsequent PAC treatment.

Figure 4b shows the abatement of micropollutants for a specific ozone dose of $0.35 \pm 0.05 \text{ mg } O_3 / \text{mg DOC}$ with a subsequent treatment by PAC (10 mg L^{-1}). A complete list of the 18 measured micropollutants, their second order reaction rate constants for the reactions with ozone or $\cdot OH$ and their abatements during the treatment process are given in the supporting information (SI, Tables S5-S8). The concentrations of some micropollutants were below the detection limits after the treatments, wherefore only minimum eliminations could be calculated (SI, Tables S6-S8). As predicted by Lee et al. (2013), micropollutants of group I were almost fully eliminated at the specific ozone dose of $0.35 \text{ mg } O_3 / \text{mg DOC}$. Micropollutants of group II were abated in the range 50-80%. With the additional abatement during the subsequent PAC treatment (10-20% of the initial concentration), a satisfying elimination of > 80% is reached for all substances of group II, except for acesulfame, which is known to have a low affinity to activated carbon. Micropollutants from group IV were eliminated slightly better during the ozonation in the pilot-plant than in the study of Lee et al. (2013). Furthermore, the measured bromate yield in the pilot plant of $0.3 \pm 0.1\%$ (at $0.36 \pm 0.03 \text{ mg Br}^- \text{ L}^{-1}$) for the specific ozone dose of $0.35 \pm 0.05 \text{ mg } O_3 / \text{mg DOC}$ was lower than expected ($\sim 1\%$) from the bench-scale experiment (Figure 4a). These results indicate that a combined treatment “ozonation / PAC” allows to achieve a good abatement of the micropollutants with low bromate yields. However, for some micropollutants an additional treatment with PAC has only a limited effect (e.g., acesulfame).

Figure 4: (a) Measured bromate yields for wastewater C (Soltermann et al., 2016) and % abatement of micropollutants (divided in groups I-V, Lee et al. (2013)) with differing ozone- and [•]OH-reactivity (average abatement in differing wastewaters measured by Lee et al. (2013)) as a function of the specific ozone doses. (b) Shares of ozonation and PAC treatment on the total micropollutant abatement in the combined treatment process of the pilot plant in this study (averages of 3 sampling periods). Abatements with asterisk are minimal elimination because concentrations were partly below the quantification limit after the treatment.

In comparison to an application of only activated carbon, the combined treatment (ozone / PAC) requires less activated carbon (important for operational costs) and potentially mitigates a larger group of micropollutants since they are abated by the combination of two different processes (oxidation and adsorption). A combined treatment with ozone and PAC can

potentially consist of a PAC treatment prior to ozonation. The PAC pre-treatment reduces the DOC concentration, wherefore less ozone is required for a specific ozone dose. Additionally, the micropollutant load is eliminated during the PAC pre-treatment, which leads to an only limited formation of transformation products during post-ozonation. Bromide is not expected to be substantially eliminated by PAC treatment (Watson et al., 2012). Therefore, in this study we investigated whether or not a PAC pre-treatment affects the bromate yield during ozonation.

Two grab samples (samples 1 and 2), taken at differing days, from the effluent of WWTP D were treated with differing PAC doses (0–100 mg L⁻¹) prior to ozonation (1 mg O₃ / mg DOC) (Figure 5). The DOC decreased in both samples continuously with increasing PAC doses (Figures 5a, b). Size-exclusion chromatography revealed that all fractions adsorbed almost equally, except for large fractions, which were less adsorbed (SI, Figure S3). The electron donating capacity (EDC) and the UV absorbance at 280 nm decreased in parallel to the DOC removal. Because ozone reacts primarily with electron-rich functional groups, the EDC and the UV absorbance after ozonation are clearly lower than before ozonation (Figures 5a, b). A shift towards building blocks and low-molecular weight acids and humics could be observed for the ozonated DOM (SI, Figure S4). Conclusively, the decrease of the EDC implies that the ozone consumption by DOM relative to micropollutants becomes less competitive with increasing PAC doses. However, usually, ozone is dosed proportionally to the DOC, which lowers the absolute ozone dose with increasing PAC doses.

Figure 5c shows that the bromate yield increases initially with increasing PAC doses and decreases again after a peak at around 10-20 mg L⁻¹ PAC in both samples. The same tendency was observed for the measured ozone and [•]OH exposures (Figure S5a-b). The decrease at higher PAC doses is certainly linked to the lower absolute ozone dose while the initial increase might be an effect of the decreasing EDC, which would compete for ozone during bromate formation. Figure 5d reveals that the bromate yields showed a similar correlation to the [•]OH

exposures for both samples. This was not the case for the ozone exposure (SI, S5d) where sample 2 had a clearly lower ozone exposure but similar bromate yields. This suggests that $\cdot\text{OH}$ oxidation is the limiting factor for bromate formation (Scheme 1).

Figure 5: Effect of the PAC pre-treatment (0-100 mg L⁻¹) on the DOC, the EDC and the UVA₂₈₀ of (a) sample 1 and (b) sample 2 and on (c) the bromate yield during ozonation (1 mg O₃ / mg DOC) of samples 1 and 2. (d) Bromate yields as a function of the $\cdot\text{OH}$ exposure for samples 1 and 2 with a specific ozone dose of 1 mg O₃ / mg DOC.

3.3 Bromate mitigation during ozonation by the addition of H₂O₂

It is known from drinking water treatment, that the presence of H₂O₂ partially suppresses bromate formation by the reaction of HO₂⁻ with HOBr, which is an intermediate in the bromate formation mechanism (Scheme 1, pathway 2) (von Gunten and Oliveras, 1998). In wastewater, ozone is quickly consumed and forms partially $\cdot\text{OH}$ (Buffle et al., 2006). This increased $\cdot\text{OH}$ exposure and decreased ozone exposure in comparison to drinking water ozonation may result in a shift of the main bromate formation pathway from pathway 2 to 1. During wastewater

ozonation, bromate formation via $\text{BrO}^\bullet$ (pathway 1) is most likely more favorable than via HOBr (Scheme 1). The reaction of ozone with H_2O_2 also results in lower ozone exposure. Hence, the elimination of micropollutants, which primarily react with ozone, is expected to decrease in the presence of H_2O_2 . Therefore, an optimal point for H_2O_2 addition could be after a specific ozone dose of $\sim 0.4 \text{ mg O}_3 / \text{mg DOC}$ (Hübner et al., 2015). For these conditions, micropollutants reacting quickly with ozone are expected to be substantially degraded, while bromate formation is still minimal (Figure 6) (Soltermann et al., 2016).

To investigate the feasibility of this strategy to mitigate bromate formation, wastewater of WWTP E ($\text{DOC} = 7.8 \text{ mg L}^{-1}$) was ozonated in presence/absence of H_2O_2 and by addition of H_2O_2 for specific ozone doses $> 0.4 \text{ mg O}_3 / \text{mg DOC}$ (Figure 6). The results in Figure 6a show that H_2O_2 addition affects bromate formation for doses of 5 mg L^{-1} and $10 \text{ mg L}^{-1} \text{ H}_2\text{O}_2$. These conditions might be at the edge of what is practical in WWTPs. To investigate the effect of H_2O_2 addition on the elimination of micropollutants, the abatements of compounds primarily reacting with ozone (carbamazepine, $k_{\text{O}_3} = \sim 3 \times 10^5 \text{ M}^{-1} \text{ s}^{-1}$, $k_{\text{OH}} = 8.8 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$) (Huber et al., 2003) or with $^\bullet\text{OH}$ (*p*CBA, $k_{\text{O}_3} = 0.15 \text{ M}^{-1} \text{ s}^{-1}$ (Neta et al., 1988), $k_{\text{OH}} = 5 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$) (Buxton et al., 1988) were measured for all experimental conditions. Figure 6b shows that the abatement of micropollutants primarily reacting with $^\bullet\text{OH}$ is not affected by addition of H_2O_2 . This confirms that the overall oxidation by $^\bullet\text{OH}$ is almost independent of the presence of H_2O_2 (Acero and von Gunten (2001); Hübner et al. (2015); Lee et al. (2014)). The addition of H_2O_2 for specific ozone doses $> 0.4 \text{ mg O}_3 / \text{mg DOC}$ does not interfere with the abatement of carbamazepine because this fast reacting compound is almost completely degraded at this specific ozone dose (Figure 6c). However, if H_2O_2 is dosed initially, the abatement of carbamazepine decreases slightly. For the bromate yield, there is no clear difference between an initial H_2O_2 addition or an addition after a specific ozone dose of $0.4 \text{ mg O}_3 / \text{mg DOC}$. Overall, an addition of H_2O_2 decreased bromate formation during ozonation (by 40–55 % and 65% for 5

522 and 10 mg L⁻¹ H₂O₂, respectively, at 1.5 mg O₃ / mg DOC) of this specific wastewater, while
 523 the micropollutant abatement is hardly affected for substances which have a high reactivity with
 524 ozone or react primarily with OH radicals. At an ozone dose of 0.6 mg O₃ / mg DOC, the
 525 reduction of the bromate yield was similar and slightly less pronounced (~50%) for 5 and 10
 526 mg L⁻¹ H₂O₂, respectively.

527
 528 Figure 6: (a) Bromate formation and (b, c) abatement of micropollutants ((b) pCBA and (c)
 529 carbamazepine) during ozonation of wastewater E in absence (no H₂O₂) and presence of H₂O₂

(5 and 10 mg L⁻¹) for all ozone doses (all) or starting from a specific ozone doses > 0.4 mgO₃ / mgDOC (> 0.4).

Hence, the addition of H₂O₂ to minimize bromate formation is practical, although there are several drawbacks. The required H₂O₂ doses to substantially lower the bromate formation are high but feasible and its efficiency to lower bromate formation depends on the wastewater matrix (Lee et al., 2016). Furthermore, the residual H₂O₂ concentration in the WWTP effluent must be removed by a biological treatment (e.g., sand filtration) prior to a discharge to surface waters. A biological post-treatment is required for ozonation regardless of H₂O₂ removal to eliminate ecologically toxic by-products potentially formed during ozonation (Prasse et al., 2015).

4. Conclusions

Micropollutants in WWTP effluents are an emerging issue and strategies for their elimination appear on the agenda of WWTP operators. Wastewater ozonation is approved to be a favourable technique for the abatement of micropollutants but suffers from the formation of potentially (eco)-toxicological by-products (e.g. bromate or nitrosamines) in the presence of the corresponding precursors. The by-product formation is comparable to the field of drinking water treatment, where ozonation is already state-of-the-art. Unfortunately, well-established strategies to minimize the by-product formation (i.e., bromate) in the field of drinking water are not always directly transferable to wastewater treatment.

Results of this study reveal that the addition of H_2O_2 , which efficiently lowers the bromate formation during drinking water ozonation, has the potential to reduce the bromate formation during wastewater ozonation but only at high H_2O_2 concentrations ($> \sim 5 \text{ mg L}^{-1}$). Another option to reduce the bromate formation is the elimination of major bromide sources in the sewer system. The identification of bromide sources requires detailed sampling campaigns, especially for large catchments. A preliminary assessment on bromide sources in the catchment may allow optimizing a sampling campaign. If it is not possible to reduce the bromide concentration of the wastewater to an acceptable level, the reduction of the bromate yield by lowering the specific ozone dose might be an option. This is, for instance, feasible in a process where ozonation and activated carbon are combined. If bromate formation during wastewater ozonation is high, it should also be considered to apply only adsorption-based treatment. Nevertheless, a comparison of ozonation with adsorption-based treatments or combined systems often has to include multiple aspects, such as micropollutant abatement, infrastructure and operational costs, energy demand and environmental impacts (including the production of liquid oxygen and the production and disposal of activated carbon).

565 Conclusively, several approaches are known to partly solve the upcoming problem of bromate
566 formation during wastewater ozonation, however, none of them can solve the problem for each
567 case. Therefore, it has to be decided on a case-by-case basis if an ozonation is feasible by taking
568 the strategies outlined in this paper into consideration.

569

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- Elimination of bromide sources reduces bromate formation upon wastewater ozonation
- Discontinuation of ozonation during bromide peaks is inefficient to control bromate
- A combination of ozonation with PAC allows minimizing bromate formation
- H_2O_2 addition partially suppresses bromate formation during wastewater ozonation