

Accepted Manuscript

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PII: S0043-1354(17)30378-0

DOI: [10.1016/j.watres.2017.05.018](https://doi.org/10.1016/j.watres.2017.05.018)

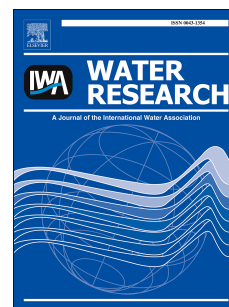
Reference: WR 12897

To appear in: *Water Research*

Received Date: 6 January 2017

Revised Date: 24 April 2017

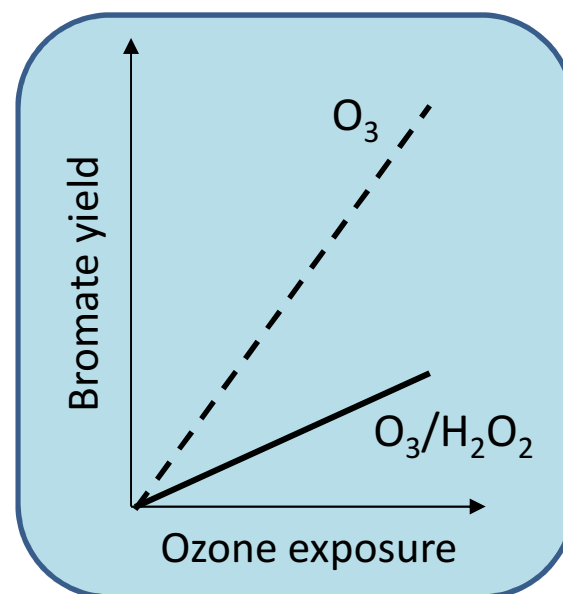
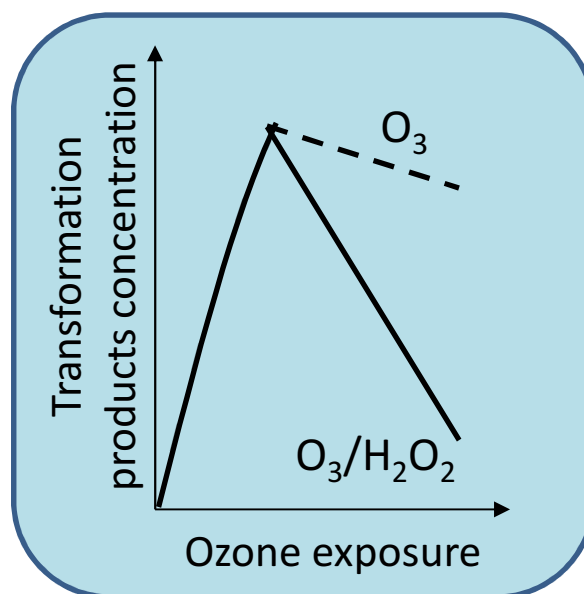
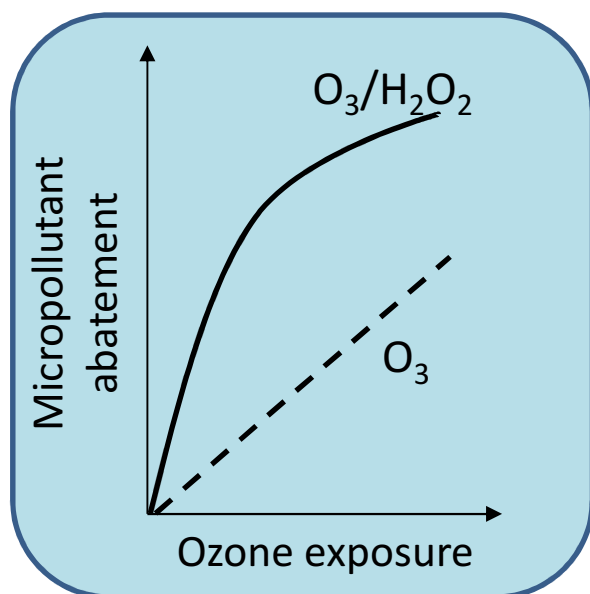
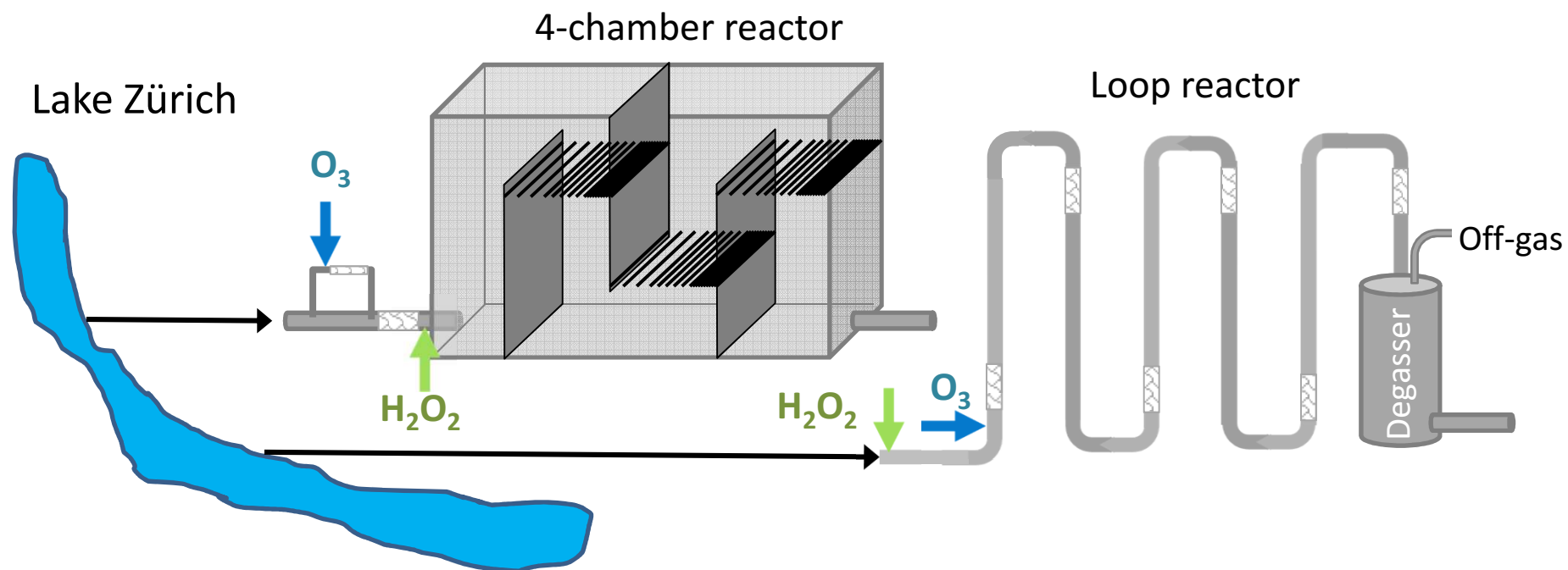
Accepted Date: 8 May 2017



Please cite this article as: Bourgin, M., Borowska, E., Helbing, J., Hollender, J., Kaiser, H.-P., Kienle, C., McArdell, C.S., Simon, E., von Gunten, U., Effect of operational and water quality parameters on conventional ozonation and the advanced oxidation process O_3/H_2O_2 : Kinetics of micropollutant abatement, transformation product and bromate formation in a surface water, *Water Research* (2017), doi: 10.1016/j.watres.2017.05.018.

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Effect of operational and water quality parameters on conventional ozonation and the advanced oxidation process O_3/H_2O_2 : Kinetics of micropollutant abatement, transformation product and bromate formation in a surface water

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ABSTRACT

The efficiency of ozone-based processes under various conditions was studied for the treatment of a surface water (Lake Zürich water, Switzerland) spiked with 19 micropollutants (pharmaceuticals, pesticides, industrial chemical, X-ray contrast medium, sweetener) each at $1 \mu\text{g L}^{-1}$. Two pilot-scale ozonation reactors ($4\text{-}5 \text{ m}^3 \text{ h}^{-1}$), a 4-chamber reactor and a tubular reactor were investigated by either conventional ozonation and/or the advanced oxidation process (AOP) $\text{O}_3/\text{H}_2\text{O}_2$. The effects of selected operational parameters, such as ozone dose ($0.5\text{-}3 \text{ mg L}^{-1}$) and H_2O_2 dose ($\text{O}_3:\text{H}_2\text{O}_2 = 1:3\text{-}3:1$ (mass ratio)), and selected water quality parameters, such as pH ($6.5\text{-}8.5$) and initial bromide concentration ($15\text{-}200 \mu\text{g L}^{-1}$), on micropollutant abatement and bromate formation were investigated. Under the studied conditions, compounds with high second-order rate constant $k_{\text{O}_3} > 10^4 \text{ M}^{-1} \text{ s}^{-1}$ for their reaction with ozone were well abated ($>90\%$) even for the lowest ozone dose of 0.5 mg/L . Conversely, the abatement efficiency of sucralose, which only reacts with hydroxyl radicals ($\bullet\text{OH}$), varied between 19 and 90%. Generally, the abatement efficiency increased with higher ozone doses and higher pH and lower bromide concentrations. H_2O_2 addition accelerated the ozone conversion to $\bullet\text{OH}$, which enables a faster abatement of ozone-resistant micropollutants. Interestingly, the abatement of micropollutants decreased with higher bromide concentrations during conventional ozonation due to competitive ozone-consuming reactions, except for lamotrigine, due to the suspected reaction of HOBr/OBr^- with the primary amine moieties. In addition to the abatement of micropollutants, the evolution of the two main transformation products (TPs) of hydrochlorothiazide (HCTZ) and tramadol (TRA), chlorothiazide (CTZ) and tramadol *N*-oxide (TRA-NOX) respectively, was assessed by chemical analysis and kinetic modelling. Both selected TPs were quickly formed initially to reach a maximum concentration followed by a decrease of their concentrations for longer contact times. For the studied conditions, the TP's concentrations at the outlet of the reactors ranged from 0-61% of the initial parent compound concentration, CTZ being a more persistent TP than TRA-NOX. Finally, it was demonstrated in both reactors that the formation of bromate (BrO_3^-), a potentially carcinogenic oxidation by-product, could be controlled by H_2O_2 addition with a general improvement on micropollutant abatement. Post-treatment by granular activated carbon (GAC) filtration enabled the reduction of micropollutants and TPs

concentrations but no changes in bromate were observed. The combined algae assays showed that water quality was significantly improved after oxidation and GAC post-treatment, driven by the abatement of the spiked pesticides (diuron and atrazine).

Keywords: Surface water, AOP O_3/H_2O_2 , micropollutants, transformation products, bromate, ozonation reactors

1. Introduction

The production of drinking water has become an important challenge, particularly in densely populated areas with limited clean water resources (Schwarzenbach et al. 2010). In this context, impaired surface waters are often the only available water resources. Their treatment usually requires a multi-barrier approach to fulfill the standards in terms of particle removal, disinfection, micropollutant and organic matter abatement, and organoleptic quality (Crittenden et al. 2012). One option is the use of a succession of oxidation and adsorptive filtration steps (Rosario-Ortiz et al. 2016). The type, the design and the order of the differing treatment steps are case-specific and strongly depend on the water quality.

Oxidation-based processes implemented in drinking water treatment processes were originally applied for disinfection purposes (Schwarzenbach et al. 2010). In Switzerland, an ozonation step is commonly used for the production of drinking water from lake water (Kaiser et al. 2013, von Sonntag and von Gunten 2012) and is known to abate efficiently many micropollutants such as pesticides, pharmaceuticals, cyanotoxins and taste and odor compounds (Huber et al. 2003, Ikehata and Gamal El-Din 2005a, b, Ikehata et al. 2006, Onstad et al. 2007, Peter and von Gunten 2007). During ozonation, two reactive species are involved, *i.e.*, ozone and hydroxyl radicals ($\bullet\text{OH}$) formed during the decomposition of ozone in water (Hoigné and Bader 1975, Staehelin et al. 1984, Staehelin and Hoigné 1982, von Sonntag and von Gunten 2012). Ozone reacts readily with electron-rich moieties (direct reaction), while hydroxyl radicals are much less selectively reacting with most organic compounds in an almost diffusion controlled reaction (second-order rate constants in the range of 10^9 - $10^{10} \text{ M}^{-1}\text{s}^{-1}$) (von Sonntag and von Gunten 2012). Thus, $\bullet\text{OH}$ can abate ozone-resistant compounds. Hydrogen peroxide may be added during ozonation to enhance the ozone decomposition rate to hydroxyl radicals (Staehelin and Hoigné 1982) resulting in an advanced oxidation process (AOP $\text{O}_3/\text{H}_2\text{O}_2$, hereafter only AOP). Even though the rate of $\bullet\text{OH}$ formation can be enhanced, the yield compared to conventional ozonation remains quite constant (Acero and von Gunten 2001). Under realistic treatment conditions, micropollutants are not fully mineralized by ozone and/or $\bullet\text{OH}$ reactions but degraded to transformation products (TPs). There is a growing concern about TPs because of their unknown structures and their potential biological effects. Recent reviews revealed transformation pathways from the reactions of

ozone with micropollutants (Hübner et al. 2015, Lee and von Gunten 2016, von Sonntag and von Gunten 2012). For amines, typically a formation of the corresponding *N*-oxides/hydroxylamines and/or dealkylated compounds has been observed (Benner and Ternes 2009a, Benner and Ternes 2009b, Borowska et al. 2016, Lange et al. 2006, Lester et al. 2013, Zimmermann et al. 2012). Olefinic and aromatic compounds usually lead (i) either to hydroxylated compounds or (ii) to aldehydes from the cleavage of C-C double bonds and thereafter to carboxylic acids (Deborde et al. 2008, Müller et al. 2012, Mvula and von Sonntag 2003, Ramseier and von Gunten 2009).

In addition to mechanistic aspects, the evolution of the effects of transformation product mixtures are relevant (Prasse et al. 2015). Though recent studies showed ozone-treated water may have negative effects on specific toxicity endpoints (Stalter et al. 2010a, Stalter et al. 2010b), ozonation was demonstrated to generally improve water and wastewater quality (Bourgin et al. 2013, Dodd et al. 2006, Margot et al. 2013, Mestankova et al. 2012).

Furthermore, ozonation can lead to the formation of oxidation/disinfection by-products. During water treatment, the reactions of ozone and hydroxyl radicals with bromide and its oxidation products leads to bromate (BrO_3^-) formation (Haag and Hoigné 1983, von Gunten and Hoigné 1994), which is classified as a potential human carcinogen (Kurokawa et al. 1990). For this reason, a drinking water standard/guideline value was set to $10 \mu\text{g BrO}_3^- \text{ L}^{-1}$ (Commission Directive 2003, U.S. EPA 2006, WHO 2011). A post-treatment showed limited bromate removal, except filtration through fresh granular activated carbon (Asami et al. 1999, Kirisits et al. 2000, L. Bao et al. 1999, Legube 1996). Therefore, bromate formation must be mitigated during oxidation. A key intermediate in the formation of BrO_3^- is HOBr/OBr^- (von Gunten and Hoigné 1994). In H_2O_2 -based AOPs, HOBr/OBr^- reacts competitively (i) with the oxidant species to bromate, (ii) with the natural organic matter to bromo-organic compounds and (iii) with $\text{H}_2\text{O}_2/\text{HO}_2^-$ ($k_{\text{HOBr},\text{HO}_2^-} = 7.6 \cdot 10^8 \text{ M}^{-1} \text{ s}^{-1}$) to bromide (von Gunten and Oliveras 1997). Based on the reaction of HOBr with hydrogen peroxide and a lower ozone exposure compared to conventional ozonation (leading to a reduced disinfection efficiency), bromate formation is lower in the AOP (von Gunten and Oliveras 1997), but not entirely suppressed (von Gunten and Oliveras 1998).

The aim of this study was to compare two ozone-based processes (conventional ozonation and the AOP) in two pilot-scale reactors (a conventional 4-chamber reactor and a tubular reactor) for the treatment of a

Swiss surface water (Lake Zürich water) in terms of efficiency of micropollutant abatement and bromate formation. The abatement of a selection of environmentally-relevant, spiked micropollutants with various reactivities with ozone was investigated for differing operational conditions and water quality parameters, *i.e.*, O₃ and H₂O₂ doses, influent bromide concentrations and pH, and was quantified based on reaction kinetics. In addition, the formation of two transformation products and bromate was monitored. Furthermore, the fate of ozone-resistant micropollutants and the selected transformation products were studied over a post-filtration with granular activated carbon. Finally, bacteria luminescence inhibition and algal photosynthesis and growth bioassays were performed to evaluate the water quality after oxidative treatment and after post-treatment with granular activated carbon.

2. Material and methods

2.1 Water quality parameters

The raw water from Lake Zürich (from a depth of about 30 m and at a distance of about 500 m from the lakeshore) was continuously fed into the pilot plant, where it was membrane-filtered (ultrafiltration) before ozonation. The water quality parameters were relatively stable over the experimental period (November 2013-April 2014, see Table S1). The term R_{ct} defined as the ratio of •OH exposure to ozone exposure (Elovitz and von Gunten 1999) was determined to be constant over this period ($R_{ct} = 10^{-8}$).

2.2 Chemicals and preparation of stock solution

Nineteen environmentally-relevant micropollutants with differing physical-chemical properties (molecular weight, hydrophobicity, pK_a , structures, reactivity with ozone; see Tables S2-S4) were chosen. Benzotriazole (BZT), carbamazepine (CBZ), diclofenac (DIC), hydrochlorothiazide (HCTZ), *N,N*-Diethyl-*m*-toluamide (DEET), diuron (DIU), metoprolol (MET), phenazone (PHE), primidone (PRI), sucralose (SUC), sulfamethoxazole (SMX), tramadol (TRA) and trimethoprim (TRI) were obtained from Sigma-Aldrich (Buchs, Switzerland); atrazine (ATZ), lamotrigine (LAM) and valsartan (VAL) from TCI Europe (Zwijndrecht, Belgium); bezafibrate (BZF) and gabapentin (GAB) from Toronto Research Chemicals (Toronto, ON); and iopromide (IOP) from LGC Standards (Wesel, Germany). The two monitored ozone transformation products, chlorothiazide (CTZ) and tramadol *N*-oxide (TRA-NOX), were obtained from Sigma-Aldrich and LGC Standards, respectively. For some

compounds, second-order rate constants for their reaction with ozone were experimentally determined as described in Text S1 and Fig. S1. The rate constants are compiled in SI, Table S4.

A stock solution was prepared by dissolving the 19 parent compounds (each at 1 mg L^{-1}) in ultrapure water overnight. To enhance the solubility of the majority of the compounds, the pH was adjusted to 7 with 1 M NaOH and the solution was heated to 40°C .

Potassium indigo trisulfonate, sodium bromide and hydrogen peroxide (35% (w/w) in H_2O) were obtained from Sigma-Aldrich (Buchs, Switzerland).

2.3 Pilot-scale ozonation reactors

Two ozonation reactors were investigated in this study, a 4-chamber reactor and a tubular reactor. The reactors were fed with membrane-filtered Lake Zurich water spiked with the 1 mg L^{-1} micropollutant stock solution to get inlet concentrations of about $1 \text{ } \mu\text{g L}^{-1}$ for each micropollutant. The bromide inlet concentration in Lake Zürich water was approximately $15 \text{ } \mu\text{g L}^{-1}$ or adjusted to 50, 100 or $200 \text{ } \mu\text{g L}^{-1}$ by dosing a $200 \text{ mg Br}^- \text{ L}^{-1}$ aqueous solution of sodium bromide. The raw water pH (7.8-8.2) was occasionally adjusted to a different pH in the range of 6.5-8.5 by the addition of 37% (w/w) hydrochloric acid or 30% (w/w) sodium hydroxide aqueous solutions.

2.3.1 4-chamber ozonation reactor

The first pilot-scale ozonation reactor consisted of 4 chambers with a total volume of 2.2 m^3 (Kaiser et al. 2013) operated at $4 \text{ m}^3 \text{ h}^{-1}$ (Fig. S2). Each chamber was equipped with tubular obstacles to improve the hydraulics in the reactor to approach a plug-flow behavior. After inlet water enrichment with micropollutants and, if necessary bromide and/or pH modifications, 10% of the flow was diverted to a side stream, where ozone, produced from oxygen gas by an ozone generator (Ozonía, Switzerland), was injected. After ozone dosing, the water passed through a static mixer and the ozone-enriched side stream was mixed again into the full stream by a second static mixer to get the appropriate ozone doses ($0.5\text{--}3 \text{ mg O}_3 \text{ L}^{-1}$ corresponding to approximately $0.5\text{--}3 \text{ g O}_3/\text{g DOC}$). The reactor was used for both the conventional ozonation and the AOP. For the AOP, an aqueous solution of hydrogen peroxide (1 g L^{-1}), prepared from a 35% hydrogen peroxide solution (Sigma-Aldrich, Switzerland), was spiked after addition of ozone in the main stream with differing $\text{O}_3\text{:H}_2\text{O}_2$ ratios (w/w): 3:1, 1:1, 1:2 and 1:3. In

addition to the inlet (INF) and the outlet (EFF, hydraulic residence time of 33 min), 3 sampling points (SP1-3) were assessed at hydraulic residence times of about 8.3, 16.5 and 24.8 min, respectively. A post-treatment step with granular activated carbon followed the ozonation reactor and is described in Text S2.

2.3.2 Tubular ozonation reactor

A second ozonation reactor, called tubular reactor hereafter, consisted of a pipe ($V = 9$ L) and a degassing chamber ($V = 33$ L) and was operated at a flow rate of $5 \text{ m}^3 \text{ h}^{-1}$ (Fig. S3). In contrast to the 4-chamber reactor, it was only operated as an AOP system with injection of hydrogen peroxide, micropollutants and bromide (if applicable) at the influent. Ozone-enriched gas ($75\text{-}150 \text{ g O}_3 \text{ m}^{-3}$) was directly injected ($30\text{-}100 \text{ L h}^{-1}$) into the main stream to achieve an ozone dose of $0.5\text{-}3 \text{ mg O}_3 \text{ L}^{-1}$, corresponding to approximately $0.5\text{-}3 \text{ g O}_3/\text{g DOC}$. After injection, the transfer of ozone gas to the aqueous phase was enhanced by various static mixers placed at regular distances in the tube. In addition to the inlet (INF), 5 sampling points (SP 1-5) were placed at regular hydraulic residence time intervals (*ca.* 1.2 second between the sampling points). After SP5, the treated water remained in a degassing contact chamber for about 25 s to strip oxygen and residual ozone. The off-gas was directed into an activated carbon column for a catalytic decomposition of ozone to oxygen. A final sampling point (EFF, hydraulic residence time of 31 sec) was placed at the outlet of the degassing contact chamber.

2.4 Chemical analyses

2.4.1 Determination of ozone concentrations, ozone exposures and hydroxyl radical exposures

Ozone and H_2O_2 concentrations were monitored at the differing sampling points (SI, Text S3). Since both reactors behave like plug-flow reactors, ozone exposure ($\int [\text{O}_3] \text{dt}$) was determined from the area under the measured ozone depletion curves, at the sampling points in the reactors where ozone was measured (Kaiser et al. 2013). Additionally, $\bullet\text{OH}$ exposure ($\int [\bullet\text{OH}] \text{dt}$) was calculated from the abatement of an ozone-resistant compound, sucralose, according to equation (1):

$$\int [\bullet\text{OH}] \text{dt} = -\ln([\text{SUC}]/[\text{SUC}]_0)/k_{\bullet\text{OH},\text{SUC}} \quad (1)$$

where $[SUC]_0$ and $[SUC]$ are the respective concentrations of sucralose at times 0 and t , and $k_{\bullet OH, SUC}$ is the second-order rate constant for the reaction of sucralose with $\bullet OH$ ($k_{\bullet OH, SUC} = 1.5-1.6 \cdot 10^9$) (Keen and Linden 2013, Toth et al. 2012).

2.4.2 Quantification of micropollutants and kinetic modeling

For the quantification of micropollutants in water samples, a 100 mL sample was taken from the reactors, quenched with sodium sulfite (1.5 mL, 1.5 M) and stored at 4 °C. If the micropollutant measurements were not carried out within 2 weeks, samples were frozen at -20 °C and thawed before sample preparation. After filtration through a 13-mm syringe filter (regenerated cellulose membrane, 0.45 μm porosity, Infochroma), 20 mL aliquots were spiked with 5 ng of internal standards methanolic solution (Table S5) and enriched by online SPE through a cartridge filled with Oasis HLB (top layer, 9 mg, Waters) and a mixture (bottom layer, 9 mg, 1:1:1.5, w/w/w) of Strata-X-AW (anion exchanger, Phenomenex), Strata-X-CW (cation exchanger, Phenomenex) and ENV+ (Biotage). The cartridges were conditioned online successively with acetonitrile and 2 mM ammonium acetate in ultrapure water and loaded for sample enrichment (see Jeon et al. (2013) for more details on the analytical method). The sample was rinsed with an ammonium acetate solution and back-flush eluted with a methanolic solution containing 0.1% formic acid (Optima LC/MS grade, Fisher Scientific). The eluate was mixed with 0.1% formic acid in ultrapure water and transferred to the LC system and separated on an Atlantis T3 column (3 μm particle size, i.d. 3.0 x 150 mm, Waters) guarded with a pre-column and an online filter. Elution in the HPLC column was performed with both 0.1% formic acid in ultrapure water and methanol (300 $\mu L min^{-1}$) at 30 °C. Detection was performed with electrospray ionization (ESI) in positive and negative modes simultaneously using a ThermoScientific Q-Exactive high-resolution mass spectrometer at a resolution of 70,000. External mass calibration was performed and mass accuracy of the measurements was in general better than 5-8 ppm. For quality control, multiple blank (ultrapure water), blind samples (internal standards in ultrapure water) and calibration standards (500 ng L^{-1} in ultrapure water) for each micropollutant were regularly analyzed. The limits of quantification ranged from 1-50 ng L^{-1} (SI, Table S5) and recoveries were $100 \pm 4\%$. The software Kintecus (Ianni 2015) was used to perform kinetic

model calculations to simulate the fate of 3 parent compounds (LAM, HCTZ and TRA) and their major
TPs (CTZ and TRA-NOX) during conventional ozonation (SI, Text S4, Tables S6-S7).

2.4.3 Bromine species

For the quantification of bromide and bromate, samples (250 mL) were collected in a bottle containing
1-3 mL of a potassium indigo trisulfonate solution (6.2 g L^{-1}) to quench ozone. As described previously
(Salhi and von Gunten 1999), both Br^- and BrO_3^- were measured by ion chromatography followed by
combined detection: conductivity for bromide determination and post-column reaction with potassium
iodide with UV detection at 352 nm for bromate determination. The quantification limits were $2.1 \text{ } \mu\text{g L}^{-1}$
for bromide and $0.6 \text{ } \mu\text{g L}^{-1}$ for bromate.

2.5 Ecotoxicological evaluation of samples after ozone-based processes

Ecotoxicological effects were assessed in a bacteria luminescence inhibition and combined algal
bioassays as described in SI, Text S5 with selected samples (Table S8).

3. Results and discussion

3.1 Abatement of micropollutants

3.1.1 Role of ozone dose on micropollutant abatement

The abatement of micropollutants was investigated at differing ozone doses ($0.5\text{-}3 \text{ mg O}_3 \text{ L}^{-1}$) in both
reactors (Figs. 1a-d). At the lowest ozone dose (0.5 mg L^{-1}), 10 compounds (DIC, CBZ, TRI, SMX,
PHE, HCTZ, TRA, MET, DIU and BEZ) were well abated ($>87\%$) in the conventional ozonation
process, although ozone was not completely consumed (13% residual, Table S9). Ozone and $\bullet\text{OH}$
exposures were high enough (Table S9) to abate these compounds, due to their high reactivity with
ozone and $\bullet\text{OH}$: apparent second-order rate constants for the reactions with ozone (k_{O_3}) and $\bullet\text{OH}$ (k_{OH})
are $\geq 10^4 \text{ M}^{-1} \text{ s}^{-1}$ and $5.0 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$, respectively (Table S4). Their extents of abatement were increasing
with increasing k_{O_3} . For compounds with low k_{O_3} ($<10^2 \text{ M}^{-1} \text{ s}^{-1}$), the extent of abatement depends more
strongly on k_{OH} rather than on k_{O_3} . The abatement of micropollutants also increased with increasing
ozone doses (Fig. 1, increasing ozone doses from a-d). Fig. 2 shows the abatement of four ozone

recalcitrant micropollutants (*i.e.*, PRI, LAM, ATZ and SUC) as a function of ozone consumed for all ozone doses (*i.e.*, difference between ozone dose and residual ozone), at each sampling point in the reactor. Independently of the initial ozone dose, the micropollutants were abated to the same extent for the same ozone consumption, because of similar ozone and $\bullet\text{OH}$ exposures (Table S9). It is noteworthy that the maximum ozone consumption did not exceed 0.9 mg L^{-1} , even for an ozone dose of $3 \text{ mg O}_3 \text{ L}^{-1}$. Therefore, a large fraction of the applied ozone is leaving the reactor for conventional ozonation, potentially leading to $\bullet\text{OH}$ formation in the activated carbon filter (Sánchez-Polo et al. 2005). In contrast, for the AOP systems ($\text{O}_3\text{:H}_2\text{O}_2$ mass ratio 1:3, (w/w)), dissolved ozone was almost instantaneously converted to $\bullet\text{OH}$. In this case, ozone exposure was very low and the oxidation was almost exclusively driven by $\bullet\text{OH}$. Even though, $\bullet\text{OH}$ is more reactive than ozone, it is also less selective and is consumed to a large extent in many competing reactions with *e.g.*, the natural organic matter (NOM). Therefore, the ozone-reactive compounds are not anymore preferentially attacked under these conditions. This explains why the abatement of some compounds (HCTZ, TRA, MET, DIU, BZF) was significantly lower in the AOP compared to conventional ozonation (Fig. 1). Conversely, ozone-resistant compounds, *e.g.*, SUC and IOP, were abated more efficiently in the AOPs because their abatements are controlled by $\bullet\text{OH}$ under these conditions. Independently of the reactor, all 19 micropollutants were abated in AOP by more than 87% at $3 \text{ mg O}_3 \text{ L}^{-1}$, while only 7 compounds were abated to this level at $0.5 \text{ mg O}_3 \text{ L}^{-1}$ (Fig. 1).

3.1.2 Role of bromide concentration for micropollutant abatement

The concentration of bromide in drinking water resources may vary widely in the range of $\mu\text{g L}^{-1}$ to mg L^{-1} (Flury and Papritz 1993, Magazinovic et al. 2004, Salhi and von Gunten 1999, Soltermann et al. 2016). In Lake Zürich water, the background bromide concentration is relatively low (approximately $15 \mu\text{g L}^{-1}$). Therefore, in certain experiments, bromide was dosed to cover a wider range of up to $\sim 200 \mu\text{g L}^{-1}$. The influence of bromide on micropollutants abatement is shown in Fig. 3, while bromate formation is discussed later in section 3.3. For conventional ozonation at a high ozone dose (3 mg L^{-1}), the abatement of ozone-reactive compounds, *e.g.*, HCTZ and TRA, was not affected by varying bromide concentrations. For the more persistent compounds, the abatement generally decreased with increasing

bromide concentrations. For instance, PRI and SUC were abated by 90% and 42%, respectively at the background bromide concentration, whereas the abatement efficiency was reduced to 55% and 19%, respectively, at a bromide concentration of 200 $\mu\text{g L}^{-1}$. The ozone profiles are not affected significantly by bromide, which is expected from the low reactivity of bromide with ozone (Haag and Hoigné 1983). Furthermore, the fraction of $\bullet\text{OH}$ scavenged by bromide is low, even at the highest bromide concentration (Table S10). Therefore, it is unclear what causes this effect and further investigations are needed. In the case of LAM, the opposite effect was observed with a significantly higher extent of abatement with increasing bromide concentrations, *i.e.*, 79% abatement at 15 $\mu\text{g Br}^{-1} \text{ L}^{-1}$ and 92% abatement at 200 $\mu\text{g Br}^{-1} \text{ L}^{-1}$. Due to the presence of two primary amine ($-\text{NH}_2$) groups in its structure, LAM reacts with both ozone ($k_{\text{O}_3, \text{LAM}} = 4 \text{ M}^{-1} \text{ s}^{-1}$ at pH 7, see Table S4) and with HOBr/OBr $^{-}$ (pK_a 8.8) formed during the oxidation of Br^{-} (equation S1 in Text S6, $k_{\text{O}_3, \text{Br}^{-}} = 160 \text{ M}^{-1} \text{ s}^{-1}$) (Haag and Hoigné 1983). The second order rate constants for the reactions of HOBr with amine-containing compounds are in the range 10^4 - $10^5 \text{ M}^{-1} \text{ s}^{-1}$ at circumneutral pH (Heeb et al. 2014). A kinetic model (Table S6, Fig. S4) confirms that a bromide concentration up to 100 $\mu\text{g Br}^{-1} \text{ L}^{-1}$ does not significantly influence LAM abatement. However, at higher bromide concentrations (200 $\mu\text{g Br}^{-1} \text{ L}^{-1}$), LAM elimination is significantly enhanced. Even though the model does not exactly predict LAM abatement, the trend of the HOBr/OBr $^{-}$ effect is evident and shows an involvement of bromine in the abatement of LAM. For the AOPs, the abatement of micropollutants remained high, typically >90%, with no significant influence of the bromide concentration (Fig. 3b-c). Due to the presence of H_2O_2 , the contribution of Br^{-} on $\bullet\text{OH}$ scavenging is expected to be less significant than in conventional ozonation. Furthermore, in high excess of hydrogen peroxide, HOBr is quickly reduced to bromide, wherefore, no effect on the abatement of bromine-reactive micropollutants such as LAM is expected.

3.1.3 Effect of pH on micropollutant abatement

The pH was varied in the range of 6.5-8.5 to determine its influence on micropollutant abatement under typical drinking water treatment conditions (Fig. 4). During conventional ozonation at a high ozone dose (3 $\text{mg O}_3 \text{ L}^{-1}$), the compounds with moderate/high ozone reactivity and/or high $\bullet\text{OH}$ reactivity, *i.e.*, DIC, SMX, CBZ, TRI, HCT, PHE, TRA, MET, BEZ, were abated to >99%, independently of the pH. For the

more ozone-resistant compounds, the abatement was generally increasing at higher pH (Fig. 4a). This is firstly because of the enhanced conversion of O_3 to $\bullet OH$ at higher pH: the reactivity of DOM with ozone increases due to the deprotonation of many functional groups, which leads to a higher reactivity towards ozone and concomitantly a higher conversion rate to $\bullet OH$ (Nöthe et al. 2009). Under our conditions, it was confirmed that the extent of ozone consumption/conversion in the reactor increased with increasing pH (22%, 31% and 38% at pH 6.5, 7.8 and 8.5, respectively, Table S11). In addition, most of the studied compounds have at least one pK_a value in the pH range 4-11 (see Table S2), and may therefore dissociate at least partially at circumneutral pH, what increases their reactivity with ozone with increasing pH (Table S4) (von Sonntag and von Gunten 2012). Overall, the $\bullet OH$ formation and exposure increased at higher pH (Table S11), promoting the abatement of ozone-resistant compounds. Furthermore, the deprotonation of target compounds enables a faster direct ozone reaction.

For the AOP in the 4-chamber reactor, the micropollutant abatement was driven almost exclusively by the oxidation by $\bullet OH$ and was pH independent (Fig. 4b). The $\bullet OH$ exposures, deduced from sucralose abatement (equation 1 in section 2.4.1), were similar for all pH values (Fig. 4b), while the reactivity of micropollutants with $\bullet OH$ was also assumed to be independent of pH. Conversely, in the tubular reactor, ozone was more stable (Table S12). This means that the oxidative abatement of micropollutants can occur by both O_3 and $\bullet OH$ and the abatement efficiency depends on the pH (Fig. 4c). At pH 6.5, only 5 compounds (DIC, CBZ, TRI, LAM and PRI) were abated to >99% until the outlet. Ozone consumption was very low: at the outlet, even after degassing, an ozone residual of 2.25 mg L^{-1} was still present, corresponding to 75% of the initial ozone dose. At $pH \geq 7.5$, 15 micropollutants, *i.e.*, all except PHE, ATZ, IOP and SUC, were abated to >99%. Consequently, due to short hydraulic residence times in the tubular reactor, a relatively high pH is necessary to consume the dosed oxidant completely and to obtain a maximum abatement. This is also confirmed by the higher $\bullet OH$ exposures at higher pH (Table S12).

3.2 Formation of transformation products

3.2.1 Effect of ozone dose

Hydrochlorothiazide yields predominantly chlorothiazide by direct reaction with ozone (Borowska et al. 2016), while tramadol forms tramadol *N*-oxide with a high yield (Zimmermann et al. 2012). Their

formation and fate were evaluated during conventional ozonation ($0.5\text{--}3\text{ mg O}_3\text{ L}^{-1}$) in the 4-chamber reactor (Fig. 5). The fate of the investigated TPs is expressed as the ratio of the TP concentration to the initial concentration of the corresponding parent compound, *e.g.*, $[\text{CTZ}]/[\text{HCTZ}]_0$ for CTZ. A kinetic model calculation of the evolutions of CTZ and TRA-NOX formation for the four applied ozone doses is presented in SI, Fig. S5. At SP1, both TRA and HCTZ were completely abated even at the lowest ozone dose of $0.5\text{ mg O}_3\text{ L}^{-1}$. Maximum TP concentrations were detected at SP1 followed by a decrease for longer contact times. For an ozone dose of 0.5 mg L^{-1} , 75% of the initial HCTZ concentration was detected as CTZ at SP1. In contrast, only 35% of TRA was detected as its main ozone transformation product TRA-NOX. TP concentrations were also the highest at SP1 for higher ozone doses. However, the TP concentrations at this sampling point decreased with increasing ozone doses. For instance, for an ozone dose of $3\text{ mg O}_3\text{ L}^{-1}$, the CTZ concentration was only 20% of the initial HCTZ concentration at SP1. The investigated transformation products are more resistant towards ozone attack than their parent compounds because only the latter contain an ozone-reactive site (Zimmermann et al. 2012, Borowska et al. 2016). The apparent second-order rate constants at pH 7 for the reaction of ozone with HCTZ and TRA are $8\cdot 10^4$ and $2.2\cdot 10^3\text{ M}^{-1}\text{ s}^{-1}$, respectively. For CTZ, the second order rate constant is $1.5\text{ M}^{-1}\text{ s}^{-1}$ (Borowska et al. 2016), and TRA-NOX is assumed to react as fast with ozone as the protonated tramadol amine species, *i.e.*, $77\text{ M}^{-1}\text{ s}^{-1}$ (Zimmermann et al. 2012), since the rest of the molecule remains unchanged. Based on these relatively low second order rate constants for the reactions of the TPs with ozone, it can be concluded that the further abatement of the TPs after their formation is also affected by $\bullet\text{OH}$ oxidation. CTZ and TRA-NOX have similar second-order rate constants for their reactions with $\bullet\text{OH}$ ($5.7\cdot 10^9$ and $6.3\cdot 10^9\text{ M}^{-1}\text{ s}^{-1}$, respectively, Table S4). The lower second order rate constants for both the reactions of CTZ with O_3 and $\bullet\text{OH}$ explain why it is more persistent to further abatement than TRA-NOX. TRA-NOX was completely abated at the outlet of the reactor at an ozone dose of 2 mg L^{-1} , while CTZ was still present (7% of the initial HCTZ concentration).

Overall, the experimental results are in agreement with expectations of the kinetic model, which shows an instantaneous formation of CTZ and TRA-NOX to reach a maximum relative concentration in $<20\text{ s}$, followed by a slow decrease for longer ozone contact times (Fig. S5).

During the AOP in the 4-chamber reactor, the oxidative transformation of both parent compounds was also almost immediate and complete for an ozone dose ≥ 1 mg O₃ L⁻¹ (Fig. S6). No ozone residual was detected at SP1 for any ozone dose, explaining why the abatement of micropollutants did not increase with increasing contact time. TPs also reached a maximum concentration at SP1 and their concentration stayed constant thereafter due to the lack of residual oxidant. For an ozone dose of 0.5 mg O₃ L⁻¹, CTZ and TRA-NOX were measured at the outlet at concentrations corresponding to 48% and 16% of the initial concentrations of the parent compounds, respectively. However, with higher ozone doses, the TP concentrations at the outlet decreased significantly to only 1% of HCTZ for CTZ at 3 mg O₃ L⁻¹, whereas TRA-NOX was not detected anymore at the outlet for ozone doses ≥ 2 mg L⁻¹. Consequently, the concentration of the investigated TPs was lower for the AOP compared to conventional ozonation at the same ozone dose. This is due to a shift from a direct ozone reaction to hydroxyl radical transformation products, which were not identified in this study.

In contrast to the 4-chamber reactor, in the tubular reactor, the abatement of the parent compounds occurred stepwise (Fig. 6). This is due to a stepwise dissolution of ozone by multiple static mixers. The abatement of HCTZ and TRA increased with higher O₃ exposure (due to higher residence time and/or higher ozone dose, SI Table S13) and higher •OH exposure, ranging from 17-78% for ozone doses of 0.5-3 mg L⁻¹ at SP1 and reached 91-100% abatement at the outlet. For an ozone dose of 0.5 mg L⁻¹, the concentrations of CTZ and TRA-NOX gradually increased almost over the entire reactor to reach 62% and 23% of the initial concentrations of the parent compounds, respectively (at EFF for CTZ and at SP5 for TRA-NOX). At this low ozone dose, the production of TPs from the oxidation of the parent compounds is more important than their further oxidation by •OH. For an ozone dose of 1 mg L⁻¹, the TPs concentrations only increased up to SP2. From SP3 to SP5, the abatement of HCTZ and TRA was already >80% and the TPs concentrations were at a pseudo steady state with *ca.* 40% for CTZ and 16% for TRA-NOX. After SP5 (additional 25 sec residence time in the degasser), the parent compounds were completely abated. Hence, no more TPs were formed and a further oxidation occurred, leading to a significant decrease of their concentrations. Parent compounds were markedly abated at SP2 for an ozone dose of 2 mg L⁻¹ (>92% abatement) and at SP1 for an ozone dose of 3 mg L⁻¹ (>77% abatement),

and therefore, the relative concentrations of TPs were generally decreasing from this point to non-detect at the outlet of the reactor.

3.2.2 Effect of pH

The fate of the parent compounds and the transformation products during the AOP in the tubular reactor at three pH values (6.5, 7.5 and 8.5) is presented in Fig. 7. CTZ accumulated along the treatment at pH 6.5 and its concentration reached 27% of the initial HCTZ concentration at the outlet, where HCTZ was eliminated by 91%. This indicates that the formation of this TP is still significant with a relatively low abatement by $\bullet\text{OH}$, mainly because at pH 6.5, the reaction between ozone and hydrogen peroxide to produce $\bullet\text{OH}$ is very slow (Staehelin and Hoigné 1982). At pH 7.5, the relative CTZ concentration increased to ~30% of the initial HCTZ concentration at SP2, where HCTZ abatement was 75% and reached a plateau up to SP4 (93% HCTZ abatement). For higher contact times, the produced CTZ was very low and the CTZ concentration decreased to 3% of the initial HCTZ concentration. For the experiments at pH 8.5, where HCTZ was quickly abated (93% at SP1), the maximum CTZ concentration was observed at SP1 (30% of initial HCTZ) and then decreased quickly to $\leq 1\%$ of the initial HCTZ at SP4.

Similarly, TRA-NOX accumulated during the treatment at pH 6.5, but only up to SP5 to reach a relative concentration of 3% before decreasing to 2% after the degasser. At the pHs 7.5 and 8.5, TRA-NOX reached a maximum of 7% relative to TRA at SP2 and SP1. Thereafter, the TRA-NOX concentration decreased to <LOQ until the reactor outlet (Fig. 7b).

Overall, at higher pH, the reactivity of HCTZ and TRA with ozone increases, leading to a faster oxidation to the known TPs. Therefore, depending on pH, the maximum concentration of the studied TPs was observed at differing residence times: the maximal concentration was observed at SP1 for pH 8.5, while it was observed at SP5 or EFF for pH 6.5. At higher pH, TPs are also abated more efficiently, because of their higher reactivity with ozone (higher degree of dissociation) and higher $\bullet\text{OH}$ exposures (Table S12). This explains why the concentrations of the studied TPs decrease more rapidly at higher pH.

3.3 Bromate formation

3.3.1 Effect of ozone dose

The formation of bromate was first investigated at the background bromide concentration of $15 \mu\text{g L}^{-1}$ for 4 ozone doses in both reactors for conventional ozonation and the AOPs. The mechanism of bromate formation during ozonation of bromide-containing waters is described in Text S6. Based on previous studies, hydrogen peroxide addition is known to mitigate bromate formation (Pinkernell and von Gunten 2001). For an ozone dose of 0.5 mg L^{-1} , the formation of bromate was insignificant ($<0.4 \mu\text{g L}^{-1}$), even for conventional ozonation in the 4-chamber reactor (Fig. 8). For higher ozone doses ($>1 \text{ mg O}_3 \text{ L}^{-1}$), bromate concentrations at the outlet increased linearly with increasing ozone doses. Consequently, with respect to drinking water standards, Lake Zürich water can be treated by conventional ozonation with a maximum ozone exposure of *ca.* 0.06 M s (*i.e.*, $48 \text{ mg L}^{-1} \text{ min}$), corresponding to the exposure at the outlet for an applied ozone dose of $2 \text{ mg O}_3 \text{ L}^{-1}$ (Fig. 8 and Fig. S7). However, this implies an ozone residual of 1.2 mg L^{-1} (Table S9), which will decompose later in the post-treatment, possibly yielding more bromate. This potential issue is discussed in Text S7.

In both AOP systems (at $\text{H}_2\text{O}_2\text{:O}_3$ mass ratio, 3:1), bromate formation was similar (*i.e.*, $0.4\text{-}0.7 \mu\text{g L}^{-1}$ at $1 \text{ mg O}_3 \text{ L}^{-1}$ and $2.6\text{-}2.9 \mu\text{g L}^{-1}$ at $3 \text{ mg O}_3 \text{ L}^{-1}$) but significantly lower than for conventional ozonation (Fig. 8). In presence of H_2O_2 , the intermediate HOBr/OBr^- can be reduced to Br^- , but more importantly, the ozone residual concentration is minimal, which results in a low formation of BrO^\bullet , a decisive intermediate in the combined ozone-hydroxyl radical pathway for bromate formation (von Gunten and Oliveras 1997, 1998, von Sonntag and von Gunten 2012).

3.3.2 Effect of bromide concentration

The bromate formation at high ozone doses ($3 \text{ mg O}_3 \text{ L}^{-1}$) was also evaluated with differing influent bromide concentrations ($15\text{-}250 \mu\text{g L}^{-1}$) (Fig. S8). In conventional ozonation with $3 \text{ mg O}_3 \text{ L}^{-1}$, bromate concentration already exceeded the drinking water standard in natural Lake Zürich water with $15 \mu\text{g L}^{-1} \text{ Br}^-$ ($13.7 \mu\text{g BrO}_3^- \text{ L}^{-1}$, 53% yield, *i.e.* ratio $\text{mol BrO}_3^- \text{ L}^{-1} / \text{mol Br}^- \text{ L}^{-1}$) and increased significantly with increasing bromide levels to a bromate concentration of $72 \mu\text{g L}^{-1}$ for $197 \mu\text{g L}^{-1}$ bromide (23% yield). In the two AOP systems ($3 \text{ mg O}_3 \text{ L}^{-1}$, $9 \text{ mg H}_2\text{O}_2 \text{ L}^{-1}$), similar bromate concentrations and bromide conversion efficiencies ($9 \pm 1\%$) were observed at identical conditions. Again, BrO_3^- formation was

significantly mitigated in presence of H_2O_2 . Overall, in terms of bromate mitigation for similar AOP conditions, the performance of both reactors was quite similar.

3.3.3 Effect of hydrogen peroxide dose

Fig. 9 presents the bromate yield as a function of the abatement of selected ozone-resistant micropollutants (PRI, LAM, ATZ, SUC) for differing conditions, including conventional ozonation in the 4-chamber reactor or the AOP in both reactors with various H_2O_2 doses. Fig. 9 shows similar trends for the four compounds. As discussed above, conventional ozonation led to both a poor oxidation of ozone-resistant compounds and a high bromate formation. For example, selected micropollutants were abated by 19-92% at $3 \text{ mg O}_3 \text{ L}^{-1}$, while the bromate yield was 23% (symbols (+) in Figs. 9a-d).

In the AOPs, a slight increase of $\bullet\text{OH}$ scavenging contribution by H_2O_2 was expected (Table S15). However, it was not significant enough to result in a decreased micropollutant abatement: The micropollutant abatement at the outlet was similar for all H_2O_2 doses, *i.e.*, 83-91% abatement for sucralose and 91-100% abatement for the other compounds, except for $\text{O}_3:\text{H}_2\text{O}_2$, 3:1 (w/w) in the tubular reactor (61-94% abatement). In this case, the oxidation was not complete: A residual of $1.5 \text{ mg O}_3 \text{ L}^{-1}$ was measured at the outlet (Table S14).

Both AOP systems showed similar bromate yields for a given relative micropollutant abatement: for instance, at an $\text{O}_3:\text{H}_2\text{O}_2$ of 1:3 (w/w), atrazine and sucralose were abated 92% and 83%, respectively, with a bromate yield of 7.7% in the 4-chamber reactor (EFF), while a respective 90% and 81% abatement and a bromate yield of 7.9% were observed in the tubular reactor (SP4) (Figs. 9c-d). Compared to conventional ozonation, for a comparable micropollutant abatement, AOPs result in a significant bromate mitigation. For instance, sucralose was abated by 17% at $\text{O}_3:\text{H}_2\text{O}_2$, 3:1 (w/w) in the tubular reactor with a bromate yield of only 1.6% (SP1) compared to a bromate yield of 23% for a 19% abatement in conventional ozonation (Fig. 9d).

During the initial phase of the treatment in the tubular reactor (INF to SP2), the slopes of the micropollutant abatement vs. bromate yield curves were similar, independent of the H_2O_2 dose. For instance, for $\text{O}_3:\text{H}_2\text{O}_2$, 1:3 (w/w), a slope of 22.9 (94% primidone abatement for a 4.1% bromate yield) was observed, while it was 24.4 (39% primidone abatement for a 1.6% bromate yield) for $\text{O}_3:\text{H}_2\text{O}_2$, 3:1

(w/w) (Fig. 9a). Therefore, in the studied range ($1\text{--}9\text{ mg H}_2\text{O}_2\text{ L}^{-1}$), at the beginning of the treatment (up to SP2), micropollutant abatement and bromate yield increased proportionally with H_2O_2 doses. After SP2, the slope decreased for every compound and H_2O_2 dose: Bromate formation increased faster than micropollutant abatement, compared to the initial phase.

Consequently, a $\text{O}_3\text{:H}_2\text{O}_2$ ratio of 1:3 (w/w) seems to be the best condition for an efficient micropollutant abatement and bromate mitigation for a moderate cost increase (Fig. 9). However, the H_2O_2 residual is generally high, close to the dosed concentration, since only a small fraction reacts with ozone. Therefore, it has to be guaranteed that H_2O_2 is properly removed during post-treatment (see section 3.4).

3.4 Post-treatment with granular activated carbon

The granular activated carbon (GAC) filtration step can eliminate very efficiently ozone (no residual after 2 min contact in 10 cm depth) and H_2O_2 . For instance, in the effluent of the AOP at $3\text{ mg O}_3\text{ L}^{-1}$ and $9\text{ mg H}_2\text{O}_2\text{ L}^{-1}$, the concentration of H_2O_2 dropped from 7.9 to 0.3 mg L^{-1} after 4 min contact in 20 cm depth (Text S7, Fig. S9). Additionally to the removal of H_2O_2 , the GAC post-treatment enabled to remove organic compounds (parent compound residuals and TPs) (Text S7, Fig. S10). The elimination of organic compounds varied between 37% and 98%, depending on the compound and the contact time. These results are discussed in more details in SI, Text S7.

3.5 Evaluation of water quality after treatment

Water quality was evaluated by 2 bioassays. First, a bacteria luminescence inhibition test (Escher et al. 2008) was implemented for the assessment of general, non-specific toxicity. This assay potentially targets all the chemicals bacteria are sensitive to. However, the response was too close to the quantification limit to draw any conclusions (Text S8, Table S8). The second test, the combined algae assay (photosynthesis and growth rate inhibition) (Schreiber et al. 2007), targets more specifically photosystem II-inhibiting herbicides, such as diuron and atrazine, both spiked in this study. Non-spiked samples showed low or no activity. In the spiked samples, similar activities were found before treatment ($766\text{--}839\text{ ng DEQ L}^{-1}$), as expected based on similar spiking mixture composition. After treatment (ozonation or AOP), a significant decrease of the activity was observed ($15.8\text{--}92.6\text{ ng DEQ L}^{-1}$) before it was completely removed after GAC. More details are provided in SI (Text S8, Fig. S11 and Table S16).

4. CONCLUSIONS

Lake Zürich water was treated by conventional ozonation and the AOP $\text{O}_3/\text{H}_2\text{O}_2$ for the abatement of micropollutants in two reactor systems. Conventional ozonation led to moderate abatements of ozone-resistant compounds, even for high ozone doses of $3 \text{ mg O}_3 \text{ L}^{-1}$. The AOPs in a 4-chamber reactor and in a tubular reactor showed better results, the two reactors having quite similar performances. For ozone-resistant compounds, the abatement was significantly enhanced in the AOPs compared to conventional ozonation, due to a faster transformation of ozone to hydroxyl radicals.

Simultaneously to the abatement of micropollutants, the evolution of two transformation products (TPs, *i.e.*, chlorothiazide from hydrochlorothiazide and tramadol *N*-oxide from tramadol) was measured for all operational conditions and could be adequately simulated by a kinetic model considering the second order rate constants for all reactions with ozone and $\bullet\text{OH}$. Both TPs were formed initially with significant yields relative to the abated parent compounds, however, for prolonged treatment a decrease in their concentrations was observed due to further oxidation. At the highest ozone dose (3 mg L^{-1}), the selected TPs were not detected after the AOP treatment.

Due to its low bromide concentration of about $15 \text{ } \mu\text{g L}^{-1}$, Lake Zürich water can be treated by conventional ozonation with a dose of up to $2 \text{ mg O}_3 \text{ L}^{-1}$ and a hydraulic residence time of 33 min without exceeding the drinking water standard for bromate ($10 \text{ } \mu\text{g L}^{-1}$). The AOPs in the two reactor systems yield significantly less bromate and can be applied for micropollutant abatement for higher bromide concentrations of up to $200 \text{ } \mu\text{g/L}$.

Investigations by algal growth and photosynthesis inhibition bioassays showed an improvement along the treatment chain (ozone-based process followed by GAC).

Overall, the tested AOPs $\text{O}_3/\text{H}_2\text{O}_2$ in two reactor systems were able to significantly abate micropollutants without violating the drinking water standards for bromate even for high bromide levels, however, with a limited disinfection efficiency of the AOP compared to conventional ozonation.

ACKNOWLEDGEMENT

This study was funded by the EU-FP7 project DEMEAU “Demonstration of promising technologies to address emerging pollutants in water and wastewater” (Grant Agreement no. 308339). Ewa Borowska was financially supported by the SCIEX- Scientific Exchange Program NMS.CH within the project MICROZO “Fate of organic micropollutants in advanced treatment of wastewater with ozone” (Project code 12.333). The authors thank Andrea Schifferli from the Swiss Centre for Applied Ecotoxicology Eawag-EPFL for the measurement of the bioassays.

SUPPLEMENTARY INFORMATION

Additional information is presented in the Supplementary Information (Texts S1-S8, Tables S1-S16 and Figs. S1-S11).

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662 List of figure captions

663 Fig. 1. Comparison of the effects of ozone doses - (a) 0.5 mg O₃ L⁻¹, (b) 1 mg O₃ L⁻¹, (c) 2 mg O₃ L⁻¹ and (d)
 664 3 mg O₃ L⁻¹ - on the abatement of micropollutants (sorted by decreasing apparent second-order rate constants
 665 for their reaction with ozone at pH 7) in the 3 differing systems: (white bars) conventional ozonation in the
 666 4-chamber reactor, (grey bars) AOP O₃/H₂O₂ in the 4-chamber reactor and (black bars) AOP O₃/H₂O₂ in the
 667 tubular reactor. Experiments for both AOP systems were carried out with an initial O₃:H₂O₂ mass ratio of 1:3
 668 (w/w). pH: 7.8, initial bromide concentration: 15 µg L⁻¹.

669 Fig. 2. Abatement efficiency during conventional ozonation of selected micropollutants ((a) primidone, (b)
 670 lamotrigine, (c) atrazine and (d) sucralose) as a function of the consumed ozone at the sampling points (INF,
 671 SP1, SP2, SP3, EFF, SI Fig. S2) at pH 7.8 for various ozone doses: (◇) 0.5 mg O₃ L⁻¹, (■) 1 mg O₃ L⁻¹, (▲)
 672 2 mg O₃ L⁻¹, and (●) 3 mg O₃ L⁻¹.

673 Fig. 3. Comparison of the effects of bromide concentrations – (white): background bromide concentration
 674 (15 µg L⁻¹), (light grey shaded): 50 µg L⁻¹, (dark grey shaded): 100 µg L⁻¹, (black): 200 µg L⁻¹ - on the
 675 abatement of selected micropollutants in the 3 differing systems: (a) conventional ozonation in the 4-
 676 chamber reactor, (b) AOP O₃/H₂O₂ in the 4-chamber reactor, and (c) AOP O₃/H₂O₂ in the tubular reactor.
 677 Ozone dose: 3 mg L⁻¹, hydrogen peroxide dose (if applicable): 9 mg L⁻¹ (O₃:H₂O₂ ratio of 1:3 (w/w)).

678 Fig. 4. Comparison of the effects of pH – (white): pH 6.5, (grey): pH 7.8 (for conventional ozonation) or pH
 679 7.5 (for AOPs), (black): pH 8.5 – on the abatement of selected micropollutants during (a) conventional
 680 ozonation in the 4-chamber reactor, (b) AOP O₃/H₂O₂ in the 4-chamber reactor, and (c) AOP O₃/H₂O₂ in the
 681 tubular reactor. Ozone dose: 3 mg L⁻¹, hydrogen peroxide dose (if applicable): 9 mg L⁻¹ (O₃:H₂O₂ ratio of 1:3
 682 (w/w)). Inlet bromide concentrations: ca. 200 µg L⁻¹.

683 Fig. 5. Evolution of parent compounds (left y-axis), (a) hydrochlorothiazide (HCTZ) and (b) tramadol
 684 (TRA), and their respective ozone transformation products (right y-axis), chlorothiazide (CTZ) and tramadol
 685 N-oxide (TRA-NOX), during conventional ozonation of lake water for differing ozone doses. Parent
 686 compounds (bars) and transformation products (symbols): (white and ◇): 0.5 mg O₃ L⁻¹, (light grey and ■):

687 1 mg O₃ L⁻¹, (dark grey and ▲): 2 mg O₃ L⁻¹, and (black and ●): 3 mg O₃ L⁻¹. INF, SP1, SP2, SP3, EFF:
 688 sampling points at hydraulic residence times of 0, 8.3, 16.5, 24.8 and 33 min (SI, Fig. S2). pH 7.8.

689 Fig. 6. Evolution of parent compounds (left y-axis), (a) hydrochlorothiazide (HCTZ) and (b) tramadol
 690 (TRA), and their respective ozone transformation products (right y-axis), chlorothiazide (CTZ) and tramadol
 691 N-oxide (TRA-NOX), along the AOP treatment of lake water in the tubular reactor (O₃:H₂O₂, 1:3 (w/w)) for
 692 various ozone doses. Parent compounds (bars) and transformation products (symbols): (white and ◇): 0.5
 693 mg O₃ L⁻¹, (light grey and ■): 1 mg O₃ L⁻¹, (dark grey and ▲): 2 mg O₃ L⁻¹, and (black and ●): 3 mg O₃ L⁻¹.
 694 INF, SP1, SP2, SP3, SP4, SP5 and EFF: sampling points at residence times of 0, 1.2, 2.4, 3.6, 4.8, 6 and 30 s
 695 (SI Fig. S2). pH 8.2.

696 Fig. 7. Evolution of parent compounds (left y-axis), (a) hydrochlorothiazide (HCTZ) and (b) tramadol
 697 (TRA), and their respective ozone transformation products (right y-axis), chlorothiazide (CTZ) and tramadol
 698 N-oxide (TRA-NOX), along the AOP treatment of lake water in the tubular reactor (O₃:H₂O₂, 1:3 (w/w)) for
 699 various pH values. Parent compounds (bars) and transformation products (symbols): (white and ◇): pH 6.5,
 700 (grey and ■): pH 7.5, and (black and ▲): pH 8.5. Ozone dose: 3 mg L⁻¹, hydrogen peroxide dose: 9 mg L⁻¹.
 701 INF, SP1, SP2, SP3, SP4, SP5 and EFF: sampling points at respective residence times of 0, 1.2, 2.4, 3.6, 4.8,
 702 6 and 30 s (Fig. S2).

703 Fig. 8. Comparison of bromate concentrations at the outlet of the differing reactors as a function of the ozone
 704 dose (0.5-3 mg L⁻¹): (◇) conventional ozonation in the 4-chamber reactor, (▲) AOP in the 4-chamber
 705 reactor, (●) AOP in the tubular reactor. Initial bromide concentration: 15 µg L⁻¹, O₃:H₂O₂, 1:3 (w/w).
 706 Bromate drinking water standard: 10 µg L⁻¹.

707 Fig. 9. Comparison of the effect of H₂O₂ dose on the abatement of selected micropollutants - (a) primidone,
 708 (b) lamotrigine, (c) atrazine and (d) sucralose - as a function of the bromate yield (mol BrO₃⁻ L⁻¹/mol Br⁻ L⁻¹)
 709 during conventional ozonation in the 4-chamber reactor (+) and the AOPs in the 4-chamber reactor (open
 710 symbols) and the tubular reactor (closed symbols). (◆,◇) O₃:H₂O₂, 3:1 (w/w), (■,□) O₃:H₂O₂, 1:1 (w/w),
 711 (▲,△) O₃:H₂O₂, 1:2 (w/w), and (●,○) O₃:H₂O₂, 1:3 (w/w). For the 4-chamber reactor, samples were taken
 712 at INF, SP2 and EFF: sampling points at hydraulic residence times of 0, 16.5 and 33 min, respectively. For

the tubular reactor, samples were taken at INF, SP2, SP4 and EFF: sampling points at hydraulic residence times of 0, 2.4, 4.8 and 30 s, respectively. Ozone dose: 3 mg L⁻¹, pH: 8.2, Br⁻: 200-250 µg L⁻¹. The bromate yield obtained for the AOP in the 4-chamber reactor at O₃:H₂O₂, 1:1 (w/w) is considered as an outlier.

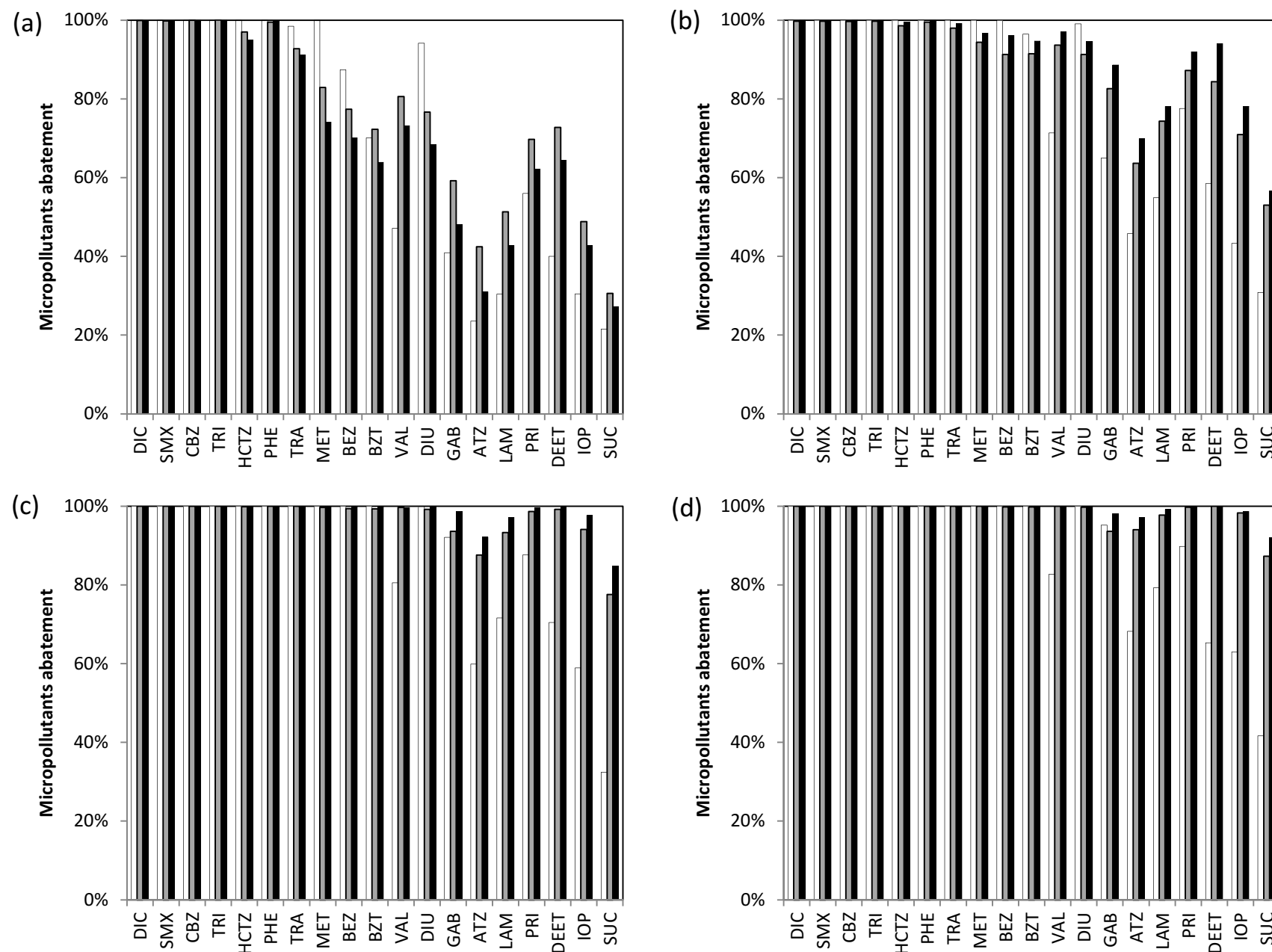


Fig. 1. Comparison of the effects of ozone doses - (a) 0.5 mg O_3 L⁻¹, (b) 1 mg O_3 L⁻¹, (c) 2 mg O_3 L⁻¹ and (d) 3 mg O_3 L⁻¹ - on the abatement of micropollutants (sorted by decreasing apparent second-order rate constants for their reaction with ozone at pH 7) in the 3 differing systems: (white bars) conventional ozonation in the 4-chamber reactor, (grey bars) AOP O_3/H_2O_2 in the 4-chamber reactor and (black bars) AOP O_3/H_2O_2 in the tubular reactor. Experiments for both AOP systems were carried out with an initial $O_3:H_2O_2$ mass ratio of 1:3 (w/w), pH: 7.8, initial bromide concentration: 15 μ g L⁻¹.

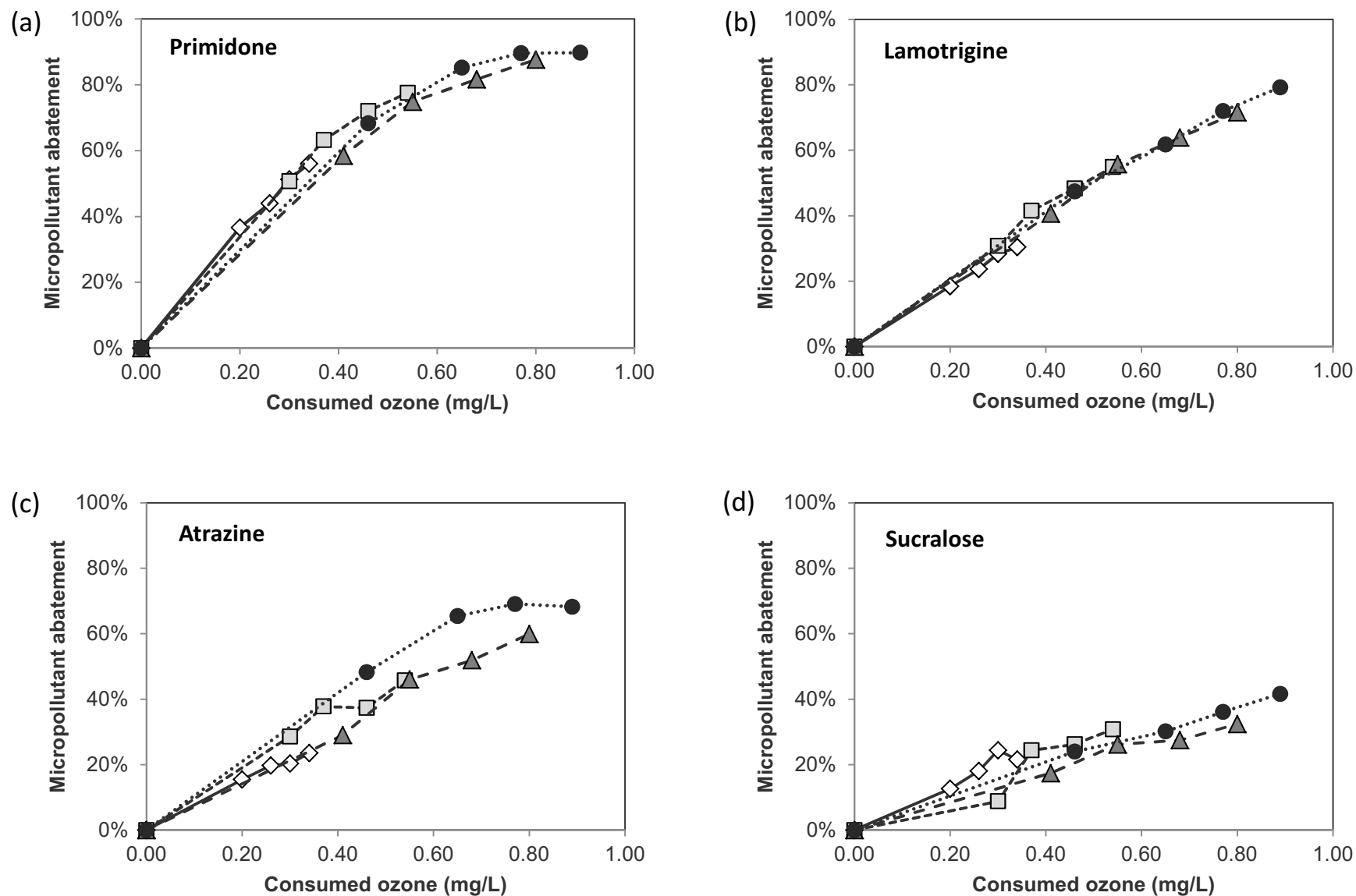


Fig. 2. Abatement efficiency during conventional ozonation of selected micropollutants ((a) primidone, (b) lamotrigine, (c) atrazine and (d) sucralose) as a function of the consumed ozone at the sampling points (INF, SP1, SP2, SP3, EFF, SI Fig. S2) at pH 7.8 for various ozone doses: (\diamond) 0.5 mg O₃ L⁻¹, (\square) 1 mg O₃ L⁻¹, (\triangle) 2 mg O₃ L⁻¹, and (\bullet) 3 mg O₃ L⁻¹.

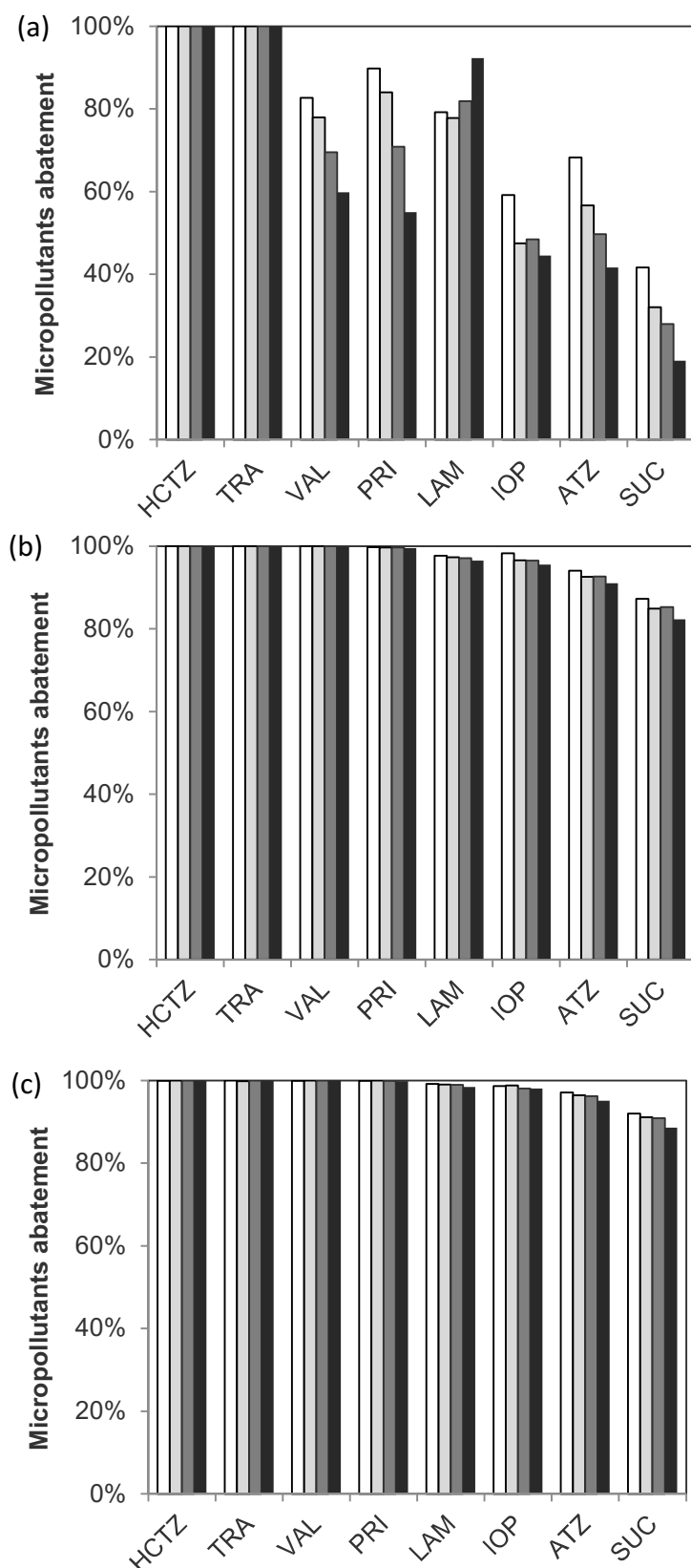


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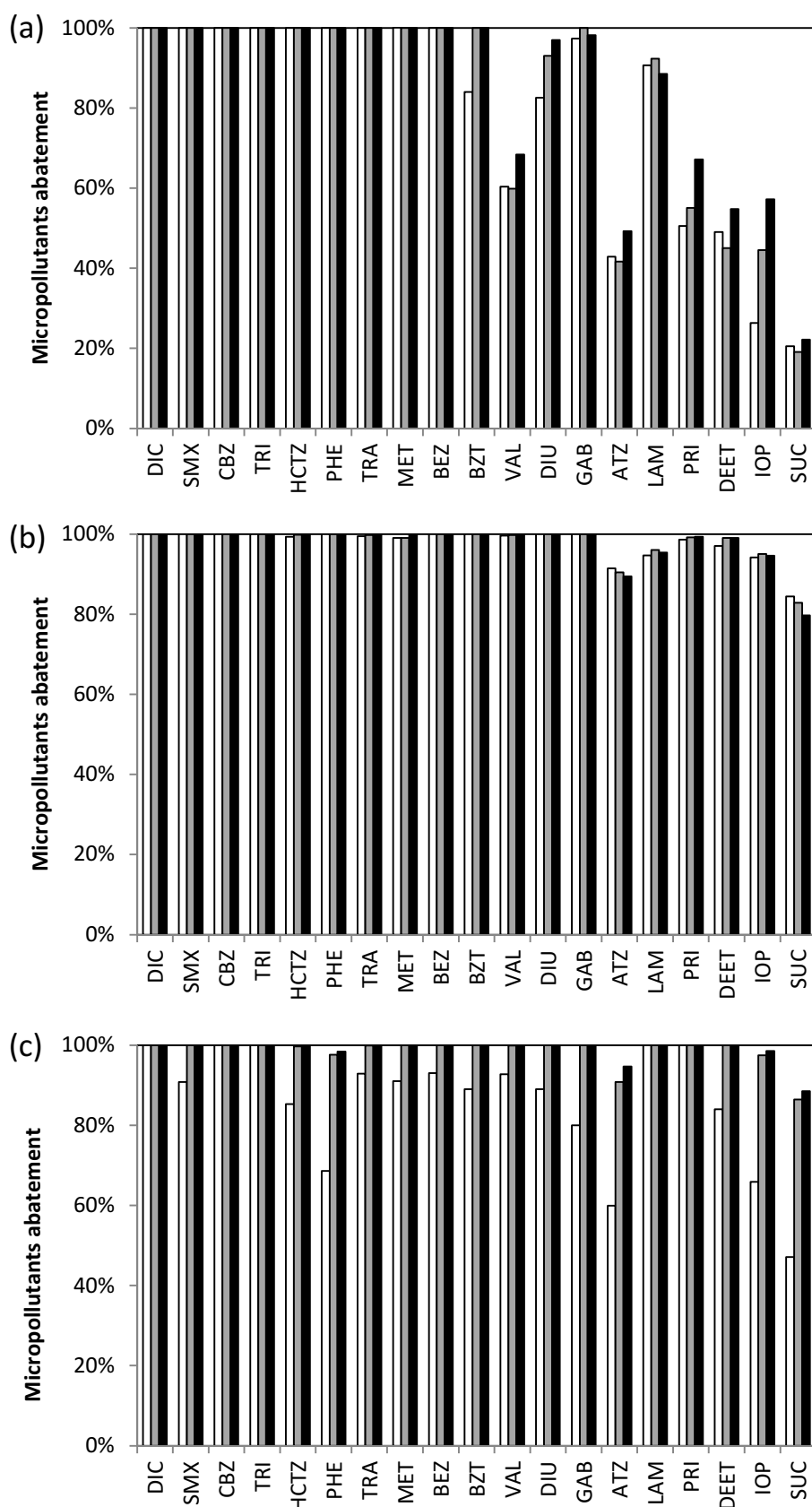


Fig. 4. Comparison of the effects of pH – (white): pH 6.5, (grey): pH 7.8 (for conventional ozonation) or pH 7.5 (for AOPs), (black): pH 8.5 – on the abatement of selected micropollutants during (a) conventional ozonation in the 4-chamber reactor, (b) AOP O_3/H_2O_2 in the 4-chamber reactor, and (c) AOP O_3/H_2O_2 in the tubular reactor. Ozone dose: 3 mg L⁻¹, hydrogen peroxide dose (if applicable): 9 mg L⁻¹ ($O_3:H_2O_2$ ratio of 1:3 (w/w)). Inlet bromide concentrations: *ca.* 200 µg L⁻¹.

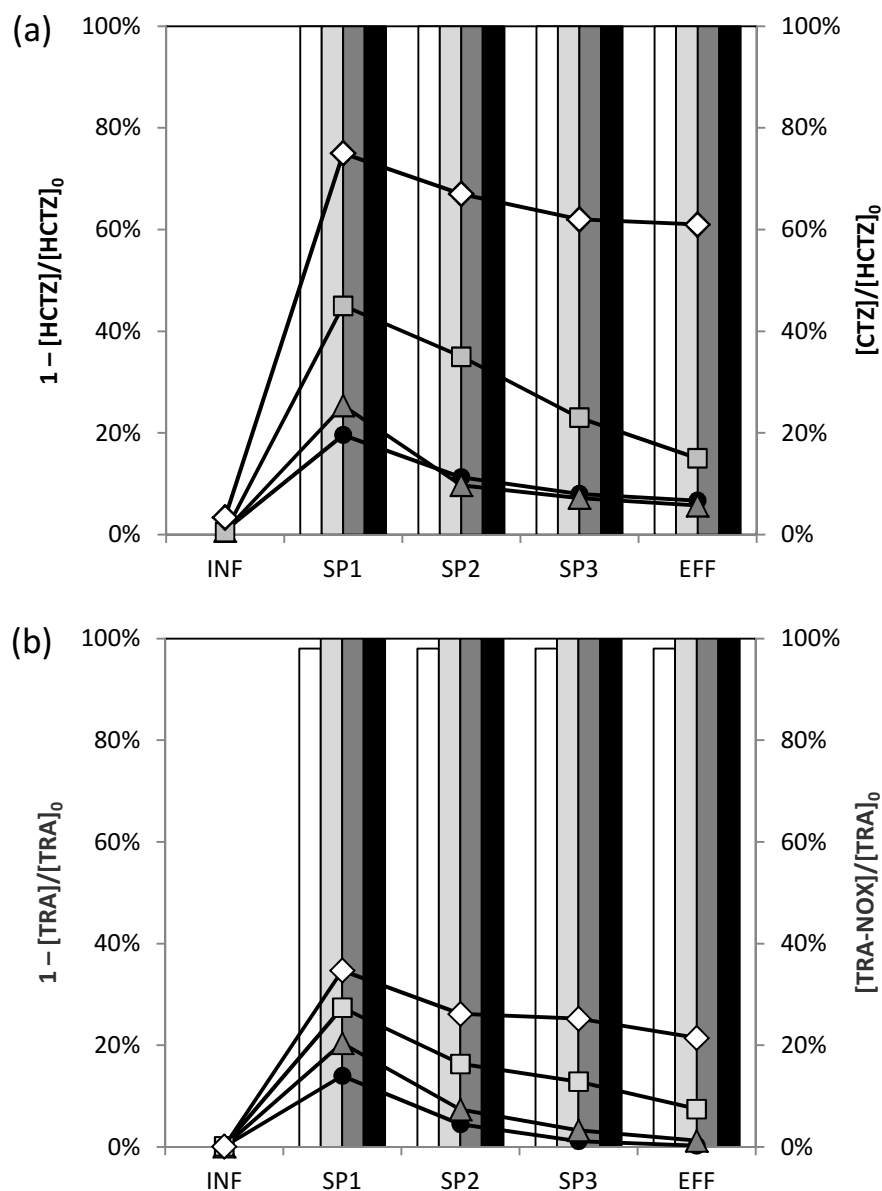


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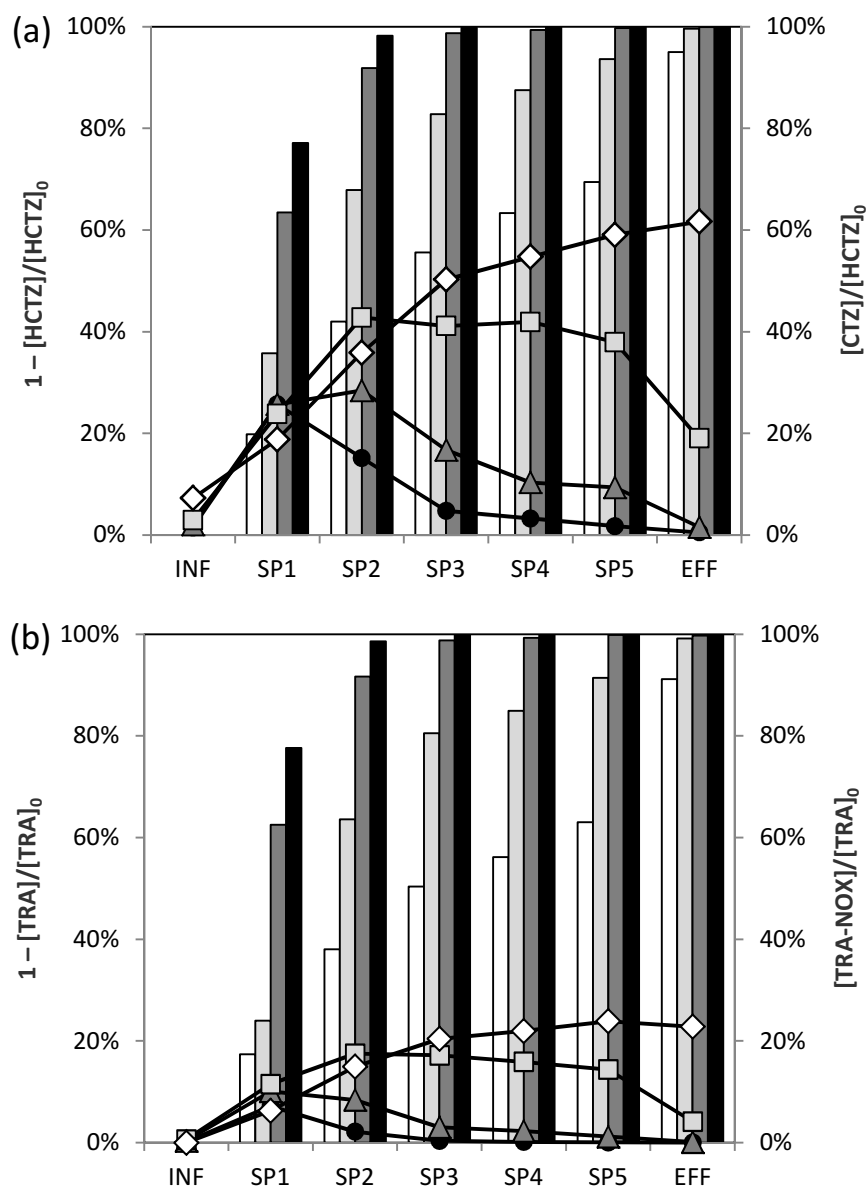


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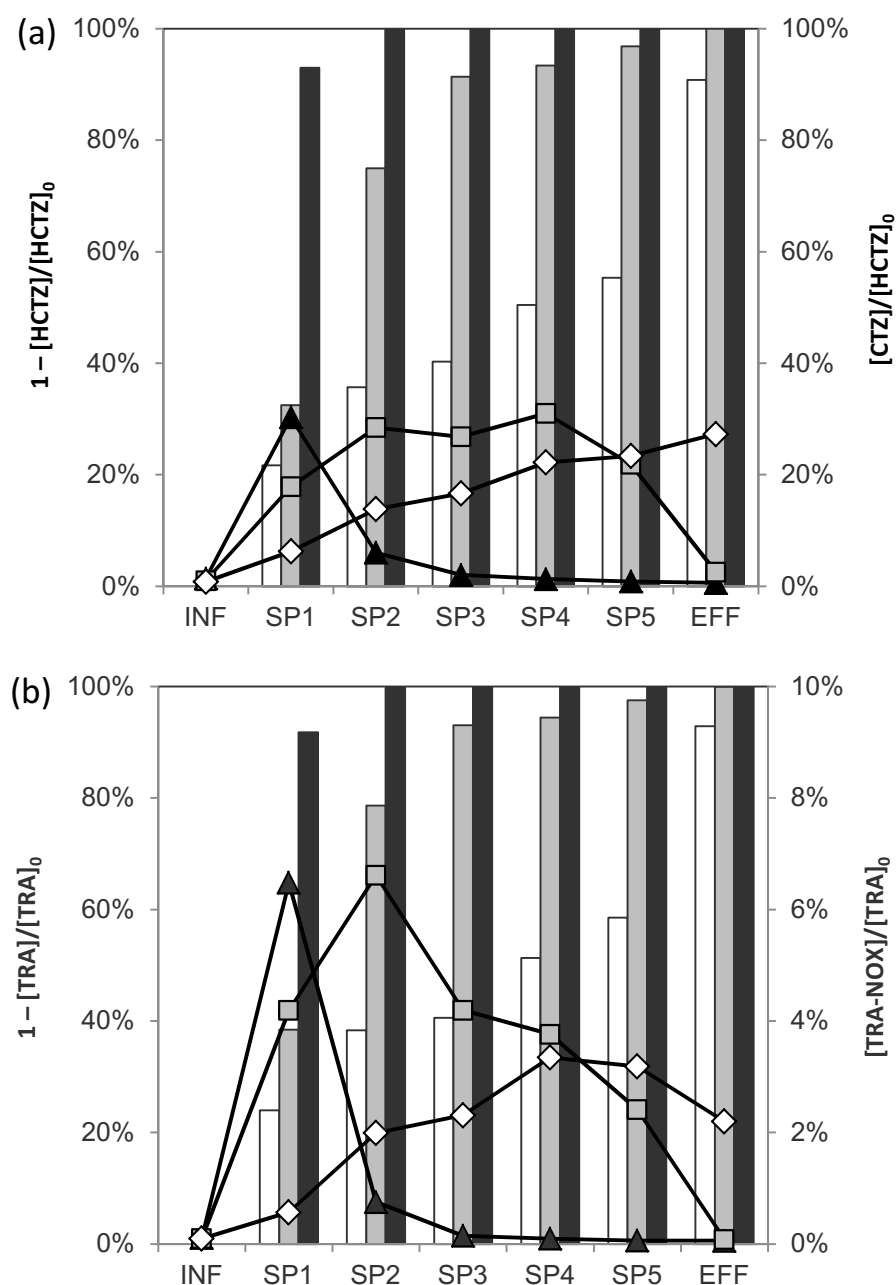


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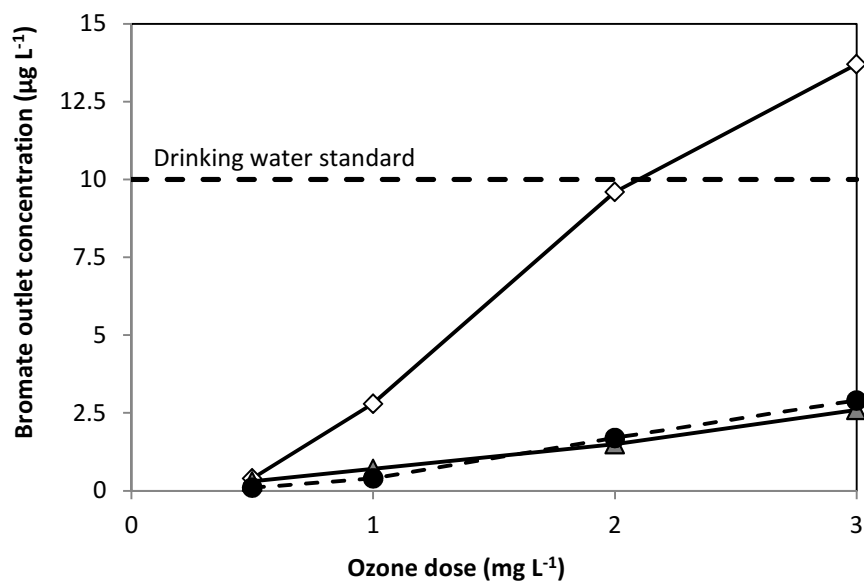


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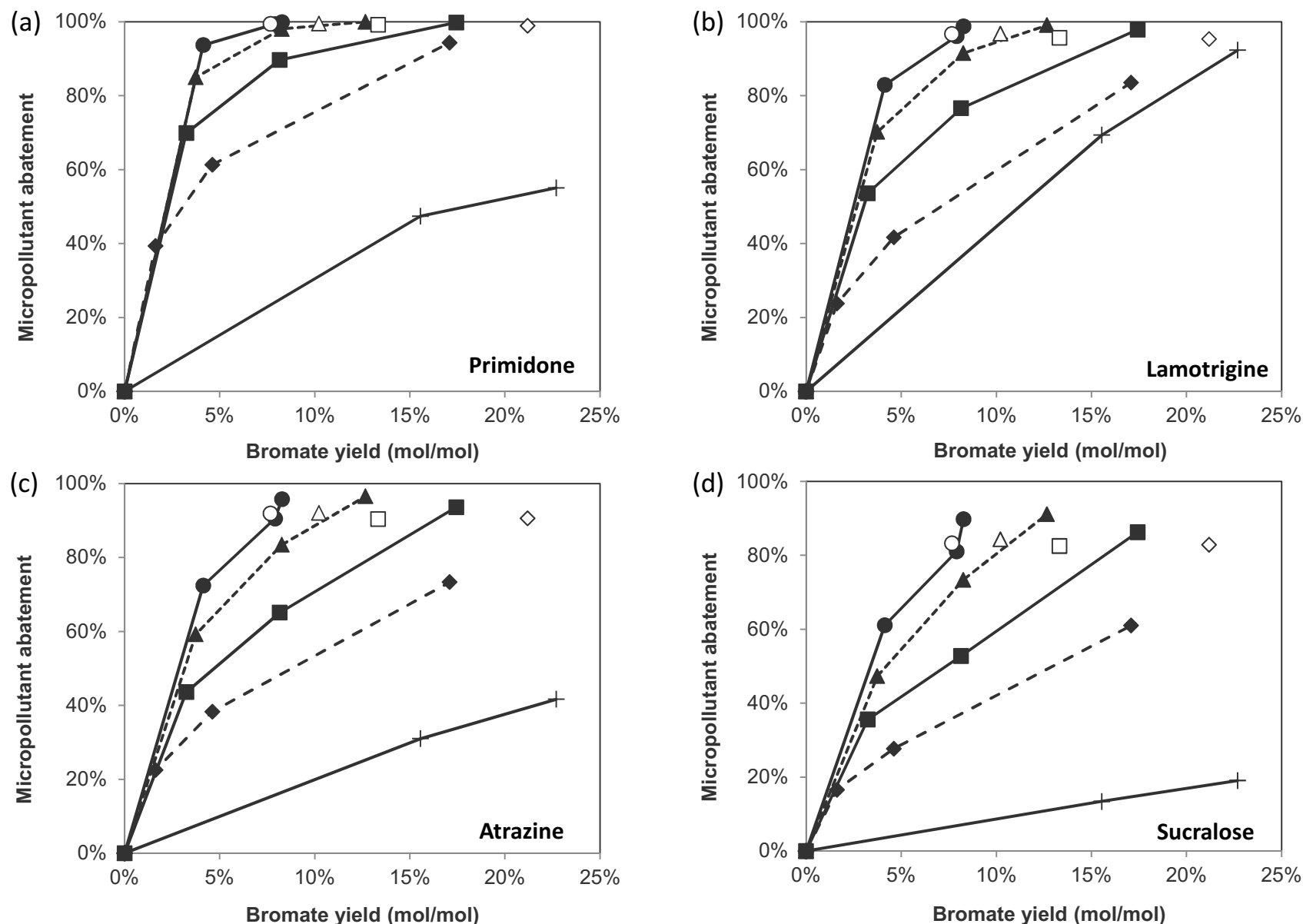


Fig. 9. Comparison of the effect of H_2O_2 dose on the abatement of selected micropollutants - (a) primidone, (b) lamotrigine, (c) atrazine and (d) sucralose - as a function of the bromate yield ($\text{mol BrO}_3^- \text{ L}^{-1} / \text{mol Br}^- \text{ L}^{-1}$) during conventional ozonation in the 4-chamber reactor (+) and the AOPs in the 4-chamber reactor (open symbols) and the tubular reactor (closed symbols). ($\blacklozenge, \blacklozenge$) $\text{O}_3:\text{H}_2\text{O}_2$, 3:1 (w/w), (\blacksquare, \square) $\text{O}_3:\text{H}_2\text{O}_2$, 1:1 (w/w), ($\blacktriangle, \triangle$) $\text{O}_3:\text{H}_2\text{O}_2$, 1:2 (w/w), and (\bullet, \circ) $\text{O}_3:\text{H}_2\text{O}_2$, 1:3 (w/w). For the 4-chamber reactor, samples were taken at INF, SP2 and EFF: sampling points at hydraulic residence times of 0, 16.5 and 33 min, respectively. For the tubular reactor, samples were taken at INF, SP2, SP4 and EFF: sampling points at hydraulic residence times of 0, 2.4, 4.8 and 30 s, respectively. Ozone dose: 3 mg L^{-1} , pH: 8.2, Br^- : $200\text{--}250 \mu\text{g L}^{-1}$. The bromate yield obtained for the AOP in the 4-chamber reactor at $\text{O}_3:\text{H}_2\text{O}_2$, 1:1 (w/w) is considered as an outlier.

Highlights:

- The abatement of 19 micropollutants was studied by ozonation and the AOP O_3/H_2O_2
- The effects of O_3 , H_2O_2 and bromide doses and pH were investigated in two reactors
- Micropollutant abatement was generally higher in the AOP compared to ozone
- The yield of two monitored transformation products ranged from 0-61%
- Bromate formation was significantly mitigated in presence of H_2O_2