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Tradeoff between micropollutant abatement and bromate formation during ozonation of concentrates from nanofiltration and reverse osmosis processes

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ABSTRACT

Water treatment with nanofiltration (NF) or reverse osmosis (RO) membranes results in a purified permeate and a retentate, where solutes are concentrated and have to be properly managed and discharged. To date, little is known on how the selection of a semi-permeable dense membrane impacts the dissolved organic matter in the concentrate and what the consequences are for micropollutant (MP) abatement and bromate formation during concentrate treatment with ozone. Laboratory ozonation experiments were performed with standardized concentrates produced by three membranes (two NFs and one low-pressure reverse osmosis (LPRO) membrane) from three water sources (two river waters and one lake water). The concentrates were standardized by adjustment of pH and concentrations of dissolved organic carbon, total inorganic carbon, selected micropollutants (MP) with a low to high ozone reactivity and bromide to exclude factors which are known to impact ozonation. NF membranes had a lower retention of bromide and MPs than the LPRO membrane, and if the permeate quality of the NF membrane meets the requirements, the selection of this membrane type is beneficial due to the lower bromate formation risks upon concentrate ozonation. The bromate formation was typically higher in standardized concentrates of LPRO than of NF membranes, but the tradeoff between MP abatement and bromate formation upon ozonation of the standardized concentrates was not affected by the membrane type. Furthermore, there was no difference for the different source waters. Overall, ozonation of concentrates is only feasible for abatement of MPs with a high to moderate ozone reactivity with limited bromate formation. Differences in the DOM composition between NF and LPRO membrane concentrates are less relevant than retention of MPs and bromide by the membrane and the required ozone dose to meet a treatment target.

Introduction

Dense semi-permeable membranes, such as nanofiltration (NF) or reverse osmosis (RO), can be applied to simultaneously reject total dissolved solids, bacteria and viruses, salts and micropollutants (MPs) in drinking water production (Kiefer et al., 2020) or wastewater treatment (Michael-Kordatou et al., 2015; Tang et al., 2018; Warsinger et al., 2018). In RO and NF applications, solutes are physically separated at the membrane from the product stream, i.e., the permeate. Separation is based on size exclusion, electrostatic interactions between the surface of the membrane and solutes such as MPs, as well as sorption and diffusion characteristics of a compound (Shin et al., 2022; Taheran et al., 2016; Wang et al., 2014). During operation, additional effects can impact the rejection performance of the membranes, such as the applied pressure, water temperature, pH, hydrodynamic conditions in the membrane module, fouling status, membrane aging, as well as changing feed water compositions (Luo et al., 2014; Wang et al., 2014). Typically, the rejection of solutes is specific for an application and transferability is

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only limited. For example, 1H-benzotriazole (BTA) rejections were reported in the range of 16% to 42% for surface water and wastewater samples by NF membranes (Acero et al., 2015), while other studies reported rejections by RO membranes in the range of 8% to 28% in drinking water production (Brunner et al., 2020) and 70% in wastewater treatment (Loi et al., 2013). As another example, bromide (Br^-) rejection by NF membranes was found in the range of −4% to 10% in surface water treatment applications (Chellam, 2000; Listiarini et al., 2010), but can reach significantly higher extents in saline feed water streams, e.g., brackish water (Pontié et al., 2003), seawater (Harrison et al., 2007), or co-produced water (Pagès et al., 2017; Xu et al., 2008). Further information on bromide rejection by RO and NF are provided elsewhere (Watson et al., 2012).

One principal drawback of membrane applications is the production of a concentrated retentate stream, often termed "brine" or "concentrate". Here, rejected solutes such as MPs, natural and/or effluent organic matter, salts, bacteria and viruses, or process auxiliary substances such as chelating agents (antiscalants) are concentrated, depending on their specific rejection by the membrane and the water recovery. The concentrates may have to be further treated before their use or discharge to comply with regulations.

Possible treatment options for the abatement of MPs in the concentrates have been frequently discussed in literature, and they include processes such as ozonation or advanced oxidation processes, additional biological treatment or adsorption on granular or powdered activated carbon (Deng, 2020; González et al., 2016; Khan et al., 2009; Mansas et al., 2020; Pérez-González et al., 2012; Umar et al., 2015; van der Bruggen et al., 2003; Xiang et al., 2019).

Ozone (O_3) has been applied for disinfection and MP abatement for more than a century (Miklos et al., 2018; von Sonntag and von Gunten, 2012). It reacts selectively and rapidly with electron-rich moieties, such as activated aromatic compounds, olefins, neutral amines and reduced sulfur species (von Sonntag and von Gunten, 2012). In natural waters and wastewater effluents, dissolved organic matter (DOM) is usually the main consumer of O_3 (von Gunten, 2018). Hydroxyl radicals ($^{\bullet}OH$) are always formed *in situ* as secondary oxidants during ozonation by various O_3 decomposition processes (von Sonntag and von Gunten, 2012). $^{\bullet}OH$ react less selectively than ozone with second-order rate constants typically in the range of 10^9 to 10^{10} M^{-1} s^{-1}, mostly by OH-addition or by H-abstraction reactions (von Sonntag et al., 1997). In environmental applications, the steady-state or transient concentration of $^{\bullet}OH$ is determined by its main scavengers, i.e., DOM, carbonate (CO_3^{2-}), bicarbonate (HCO_3^-).

At given exposures of O_3 and $^{\bullet}OH$, the abatement of a MP depends on its second-order rate constants for reactions with O_3 ($k_{O_3,MP}$) and $^{\bullet}OH$ ($k_{\bullet OH,MP}$) (Lee and von Gunten, 2016). To facilitate a comparison between MPs with similar rate constants, they are often categorized into groups (Lee et al., 2013), i.e., (I) MPs with a high ozone reactivity ($k_{O_3,MP} \geq 10^5$ M^{-1} s^{-1}); (II) MPs with a moderate ozone reactivity (10^1 M^{-1} s^{-1} $\leq$ $k_{O_3,MP} < 10^5$ M^{-1} s^{-1}); (III) ozone resistant MPs with a high $^{\bullet}OH$ reactivity ($k_{O_3,MP} < 10^1$ M^{-1} s^{-1} and $k_{\bullet OH,MP} \geq 5 \times 10^9$ M^{-1} s^{-1}); (IV) ozone resistant MPs with a moderate $^{\bullet}OH$ reactivity ($k_{O_3,MP} < 10^1$ M^{-1} s^{-1} and 1×10^9 M^{-1} $s^{-1} \leq k_{\bullet OH,MP} < 5 \times 10^9$ M^{-1} s^{-1}); (V) MPs resistant against ozone and $^{\bullet}OH$ ($k_{O_3,MP} < 10^1$ M^{-1} s^{-1} and $k_{\bullet OH,MP} < 1 \times 10^9$ M^{-1} s^{-1}).

During ozonation of bromide (Br^-)-containing waters, bromate (BrO_3coordinates$^-$) can be formed by a complex mechanism, including both reactions with ozone and $^{\bullet}OH$ (von Gunten, 2003; von Gunten and Hoigné, 1994; von Sonntag and von Gunten, 2012). BrO_3^- is a possible human carcinogen and the WHO recommends a drinking water standard of 10 μg L^{-1} (World Health Organization, 2011). For wastewater, there is no BrO_3^- standard, but for example Switzerland proposed an environmental quality standard of 50 μg L^{-1} (Oekotoxzentrum, 2015; Soltermann et al., 2016b). Therefore, the application of ozone to abate MPs in bromide-containing concentrates is always a tradeoff between the desired MP abatement and the undesired formation of bromate. Strategies for bromate mitigation during ozone treatment are known and include, e.g., the addition of H_2O_2 (von Gunten, 2003). H_2O_2 addition results in the fast transformation of O_3 to $^{\bullet}OH$ which may reduce bromate formation due to a partial shutdown of a combined $^{\bullet}OH$ - O_3 pathway (Merle et al., 2017; von Gunten and Hoigné, 1994; von Sonntag and von Gunten, 2012). In addition, the key intermediate $HOBr/OBr^-$ ($pK_a = 8.8$ (Haag and Hoigné, 1983; Heeb et al., 2014) is reduced by reactions with H_2O_2 to Br^-, thus lowering the bromate yield (von Gunten and Oliveras, 1997). However, the addition of H_2O_2 does not necessarily imply a better tradeoff between bromate yield and MP abatement and experimental proof is required in each case to verify this strategy's success, which was outside the scope of this study.

Some studies investigated bromate formation upon ozonation of RO concentrates for MP abatement (Benner et al., 2008; Justo et al., 2013; King et al., 2020; Zhang et al., 2020) and details are provided in Table S1 in the Supporting Information (SI). All studies investigated MP abatement (and other aspects) in RO concentrates from real municipal wastewater treatment plants. Overall, the investigated concentrates had dissolved organic carbon (DOC) concentrations in the range of 22.5 to 86.7 mg L^{-1} (average: 45.6 mg DOC L^{-1}), while Br^- was present in concentrations between 1.2 to 9.64 mg L^{-1} (average: 3.0 mg Br^- L^{-1}). The molar bromate yield (η) was calculated as bromide converted to bromate upon ozone treatment in relation to the bromide concentration before ozone treatment (Eq. (1)):

$$\eta = \frac{\left(c_{BrO_3^-} - c_{BrO_3^-,0}\right) \times \frac{MW_{Br^-}}{MW_{BrO_3^-}}}{c_{Br^-,0}} \tag{1}$$

$c_{BrO_3^-,0}$ and $c_{BrO_3^-}$ (g L^{-1}) are bromate concentrations before and after ozone treatment, respectively. $MW_{Br^-} = 79.9$ g mol^{-1} and $MW_{BrO_3^-} = 127.9$ g mol^{-1} are the molecular weights of bromide and bromate, respectively. $c_{Br^-,0}$ is the bromide concentration before ozone treatment. Overall, η was reported in the range of 0.4 to 10.2% for specific ozone doses in the range of 0.17 to 1.0 mg O_3 (mg DOC)$^{-1}$ (Table S1, SI). However, only minimal data is available that allow for a systematic assessment of the tradeoff between MP abatement and bromate formation in membrane concentrates (Benner et al., 2008; Justo et al., 2013; King et al., 2020; Zhang et al., 2020).

Studies on ozonation of NF and RO concentrates from river or surface waters are lacking, despite the increasing demand for such treatment solutions (Foureaux et al., 2019; Guo et al., 2022; Jährig et al., 2018; Kiefer et al., 2020). In addition, the effect of the membrane type on the subsequent concentrate ozonation is not yet well understood. Due to different rejection performances of NF and RO with respect to DOC, HCO_3^-, CO_3^{2-}, MPs and Br^-, both the MP abatement efficiency, as well as the risk of bromate formation upon ozonation are expected to differ between different membranes. In addition, hypothetically, differences in the DOM compositions of NF and LPRO concentrates might exist if small DOM moieties are rejected by RO but not by NF and these could possibly influence, e.g., the ozone chemistry and the ensuing O_3 and $^{\bullet}OH$ exposures.

This study investigates the ozone treatment of concentrates from different NF and LPRO membranes that were applied to reject MPs in different surface water sources. Specifically, this study aims to investigate how hypothetically differing DOM compositions in NF and RO concentrates impact the abatement of MPs, the formation of bromate and the tradeoff between MP abatement and bromate formation upon ozone treatment. Two river water rapid sand filtrates (waters from River Rhine and River Wiese) and one lake water (Lake Biel) were treated with three membrane types, i.e., two NF membranes and one low-pressure RO (LPRO) membrane. Concentrates were standardized (same pH = 8.3 ± 0.1 and concentrations of DOC, total inorganic carbon (TIC) and Br^-) and spiked with seven MPs (atenolol, atrazine, 1H-benzotriazole, bezafibrate, carbamazepine, diclofenac, ibuprofen). The MPs were selected to cover a broad range of second-order rate constants for the reactions with O_3 and $^{\bullet}OH$. The concentrates were characterized by the electron donating capacity. Furthermore, the standardized concentrates were treated with various specific ozone doses in laboratory experiments. Finally, linking the membrane performance (MP rejection) with the benefits and limitations of the concentrate ozonation (abatement of MPs, formation of BrO_3^-), this study provides an overall evaluation of NF and RO membrane processes.

Materials and methods

Concentrates were produced from three different surface waters and three membranes, as further detailed below. To rule out the influence of other known parameters affecting ozonation, the concentrates were standardized before ozone treatment, i.e., the only differences between the samples were, (i) the water source, (ii) the membrane type and, (iii) the concentrations of ions other than HCO_3^-/CO_3^{2-}, Br^- and borate, which was used as a buffer.

Raw waters

All raw water samples were collected in intermediate bulk containers (IBC, material: HDPE, water volume: 0.6 m^3) and transferred without cooling to the membrane pilot plant within less than 2 h. The following sources were used (for details about the raw waters, see Table S5, SI):

1 Drinking water for the city of Basel, Switzerland and surroundings is produced by a treatment chain consisting of a raw water abstraction from the River Rhine, rapid sand filtration and subsequent soil aquifer treatment in the "Lange Erlen" area. A grab sample of the River Rhine water (RR, coordinates: 47° 34′ 35″ N, 7° 37′ 12″ E) was taken after rapid sand filtration on February 8, 2021.
2 The River Wiese flows through the Wiese valley in the southern Black Forrest in Germany and enters the River Rhine in Basel (Switzerland). In the "Lange Erlen" area in Basel, River Wiese water (RW) was abstracted from a side channel (coordinates: 47° 34′ 27″ N, 7° 37′ 10″ E). RW is used as a backup water resource for the city of Basel, Switzerland and was therefore selected for investigations. After a pilot-scale rapid sand filtration, a RW grab sample was collected on November 30, 2020.
3 The city of Biel, Switzerland and surroundings use Lake Biel as a water resource. A grab sample from the raw water intake of Lake Biel water (LB) without pretreatment was collected on March 10, 2021 (coordinates: 47° 7′ 12″ N, 7° 13′ 34″ E).

Experimental setups and procedures

Details on the selected membranes are provided in Table 1. The retentions by the membranes of Br^- and MPs present in RR without spiking were determined in bench-scale experiments with flat-sheet membranes (Figure S1, SI). The cross-flow test unit (Triple System, MMS Membrane Systems, Switzerland) was operated batch-wise for each membrane with a 2 L RR grab sample at a transmembrane pressure of 5 bar and a controlled water temperature of 25 °C. After filling the feed tank with the water sample, the operational set point was adjusted and the unit was left to stabilize for at least 1 hour, recycling the permeate back to the feed tank. Then, an initial sample of the water in the feed tank was taken for the analysis of the initial concentrations of Br^- and MPs. Concentration of the sample was started by directing the permeate into a glass beaker, which was placed on a balance (accuracy: ±0.01 g, Ohaus Scout Pro, Thermo Fisher Scientific, Germany) to measure the water recovery. Experiments were stopped at a water recovery of 75% due to experimental constraints. Samples of the final permeate and concentrate were taken. Analytical methods to determine the MP concentrations for these experiments are described elsewhere (Wünsch et al., 2021), the analytical methods for Br^- and BrO_3^- are described below. The retention of a solute i was calculated by Eq. (2) from the respective permeate ($c_{\mathrm{Permeate},i}$) and initial feed concentrations ($c_{\mathrm{Feed},0,i}$).

$$R_i = 1 - \frac{c_{\mathrm{Permeate},i}}{c_{\mathrm{Feed},0,i}} \tag{2}$$

Concentrates for the ozonation experiments were produced on a pilot-scale membrane filtration plant (Figure S2, SI) equipped with one 4″ membrane module. All membrane types described above (Table 1) were used in individual, successive runs to produce the respective concentrates. A polyphosphonic acid-based chelating agent (antiscalant) was added to all water samples in the same concentration to avoid potential scaling on the membranes (initial concentration: 2 mg L^{-1}, RPI-4000 A, Toray, Japan). Initially, the pilot plant (Figure S2, SI) was set to the desired operational set point, i.e., permeate flow of 200 L h^{-1}, water recovery of 85% (achieved by adjusting a concentrate volume flow of 35.3 L h^{-1}), and a loop volume flow before the membrane of 1 m^3 h^{-1}. The plant was left to run at least 1 hour to stabilize, recycling permeate and retentate back to the feed tank. Finally, grab samples of the retentate were collected in annealed glass bottles, diverting the full concentrate stream into the bottle. During this time, the permeate was discarded into a separate permeate tank so that the feed water was not altered by dilution with permeate.

The concentrates were standardized before ozone treatment to guarantee good comparability. The standardization protocol is described in Text S1 (SI). In brief, the concentrates were adjusted to the same pH = 8.3 ± 0.1 and concentrations of DOC, TIC, selected MPs (Table 2), bromide and borate (buffer, 10 mM). MPs were selected to represent a broad range of second-order rate constants.

Table S4 (SI) provides water quality parameters before ozonation of the different standardized concentrates. Bromate was absent in all samples before ozonation. MP concentrations in the range of 0.18 μM to 0.88 μM (Table S4, SI) were selected to avoid sample preparation by solid phase extraction. The *pseudo* first-order scavenging rate constant of the background water matrix (S) was estimated by Eq. (3).

$$S = \sum_i k_{\bullet\mathrm{OH},i} \times c_i \tag{3}$$

$k_{\bullet\mathrm{OH},i}$ and c_i are the second-order rate constants of the reaction of the $^{\bullet}OH$ scavenger i with $^{\bullet}OH$ and the concentrations of $^{\bullet}OH$ scavenger i, respectively. Typically, in surface waters, the main $^{\bullet}OH$ scavengers are carbonate ($k_{\bullet\mathrm{OH},CO_3^{2-}} = 3.9 \times 10^8$ M^{-1} s^{-1}, (Buxton et al., 1988)),

Table 1
Characteristics of the investigated membranes according to the manufacturer's specification sheets (CSM Filter, 2020a, 2020b; Toray Industries, 2021).

Membrane abbreviation	NF1	NF2	LPRO
Manufacturer	Toray	Toray	Toray
Name	NE4040	HRM	TMH20A
Membrane type and material	Thin film composite, polyamide	Thin film composite, polyamide	Cross linked fully aromatic polyamide composite
NaCl retention [%]	20 – 40 [a]	20 – 40 [b]	99.3 [c]
Permeability [L h^{-1} m^{-2} bar^{-1}]	10.0 [a]	8.8 [b]	6.9 [c]

[a] Test conditions: 5.0 bar, 25 °C, pH 6.5 to 7, 15% water recovery. [b] Test conditions: 5.2 bar, 25 °C, pH 6.5 to 7, 15% water recovery. [c] Test conditions: 6.9 bar, 25 °C, pH 7, 15% water recovery.

Table 2
Averages and standard deviations of selected dissociation constants (pK_a) and apparent second-order rate constants for the reactions of ozone ($k_{O_3,MP}$) or hydroxyl radicals ($k_{\bullet OH,MP}$) with the investigated micropollutants (MP) at pH 8.3. Underlying data and references are provided in Table S3 (SI).

Compound	pK_a	$k_{O_3,MP}$ / M^{-1} s^{-1}	$k_{\bullet OH,MP}$ / 10^9 M^{-1} s^{-1}	Group*
Atenolol (ATO)	9.6 ± 0.1	$(4.0 \pm 0.6) \times 10^4$	8.0 ± 0.5	II
Atrazine (ATZ)	4.2	$(7.0 \pm 1.3) \times 10^{\circ}$	2.3 ± 0.4	IV
Benzotriazole (BTA)	8.4 ± 0.2	$(1.8 \pm 0.4) \times 10^3$	9.2 ± 1.6	II
Bezafibrate (BZF)	3.6	$(3.3 \pm 3.9) \times 10^3$	7.8 ± 0.3	II
Carbamazepine (CBZ)	16	3.0×10^5	7.0 ± 2.7	I
Diclofenac (DCF)	4.2	1.0×10^6	9.7 ± 2.5	I
Ibuprofen (IBU)	4.9	$9.6 \times 10^{\circ}$	6.9 ± 0.5	III

*According to Lee et al. (2013) (Lee et al., 2013).

bicarbonate ($k_{\bullet OH,HCO_3^-} = 8.5 \times 10^6$ M^{-1} s^{-1}, (Buxton et al., 1988)) and dissolved organic matter ($k_{\bullet OH,DOC}$ = (0.8 to 3.3) × 10^4 L (mg C)$^{-1}$ s^{-1} with an average of 2.4 × 10^4 L (mg C/L)$^{-1}$ s^{-1}, (Brezonik and Fulkerson-Brekken, 1998; von Sonntag and von Gunten, 2012; Westerhoff et al., 2007)). Hence, the estimated *S* of the standardized concentrates was on average 1.7 × 10^5 s^{-1} (range (0.8 to 2.3) × 10^5 s^{-1}). The $^\bullet$OH scavenging rate by the spiked MPs never exceeded 0.2 × 10^5 s^{-1} and was typically < 10% of *S*. Therefore, the spiked MPs did not significantly interfere with the ozonation conditions, and the results can be transferred to real, i.e., non-spiked samples.

The standardized concentrates were ozonated at different specific ozone doses to investigate the abatement of MPs and formation of BrO_3^-. Details on the experimental standard protocol are provided in Text S2 (SI). In brief, aliquots of the standardized concentrates were filled in glass vials, subsequently ozone was added from an ozone stock solution with a known ozone concentration.

Analytical methods

The analytical methods are described in detail in Text S3 (SI) together with the limits of quantification, methods accuracies and the measurement ranges. In brief, the electron donating capacity (EDC) was measured according to a modified standard protocol (Walpen et al., 2020) by adding the radical cation of 2,2′-azino-bis(3-ethylbenzothiazoline-6-sulfonate) (ABTS$^{\bullet +}$) to dilution series of each concentrate buffered at pH 8.3 with 10 mM borate and subsequent measurement of the absorbance at 728 nm after 15 min reaction time. DOM was analyzed by size exclusion chromatography (SEC) coupled with an organic carbon detector (OCD) and an ultraviolet detector (UVD) at 254 nm (model 8b, DOC-Labor Dr. Huber, Germany). Micropollutants were measured by ultra-high pressure liquid chromatography (UHPLC) coupled with tandem mass spectrometry (MS/MS). Bromide and bromate were separated by ion chromatography (IC) and measured by an inductively coupled plasma (ICP) coupled with MS/MS.

Results and discussion

Membrane performance

The relative retentions of DOC, Br^- and MPs in bench-scale experiments with flat sheet membranes are provided in Table 3. Note that for the LPRO membrane, retentions of several MPs were reported before with the same feed water (RR raw water) at a somewhat higher transmembrane pressure, i.e., at 7 bar (Roth et al., 2021). While the DOC retentions were similar for all membranes, the membrane types strongly differ in their retentions of bromide and MPs. This means that the DOC is more efficiently concentrated in NF concentrates than Br^-. In contrast, in LPRO concentrates DOC and Br^- are concentrated to the same extent. In turn, this should make the NF concentrates more feasible than the LPRO concentrate for ozonation at similar specific ozone doses, because the relatively lower Br^- concentrations mean a lower bromate formation potential. Nevertheless, the membrane selection is typically determined by the permeate quality requirements with respect to the target MP concentrations in the permeate. To this end LPRO membranes produce a permeate with a higher quality.

Bromide is not regulated in the drinking water, because Br^- itself is not relevant for human health. Hence, higher Br^- concentrations in the NF permeate than in the LPRO concentrate are acceptable, unless the permeate is treated, e.g., with chlorine-based processes, e.g., for disinfection. In this case, higher Br^- concentrations are associated with an increased risk for the formation of bromine-containing disinfection byproducts (DBPs), which are generally more toxic than the chlorine analogues (Heeb et al., 2014; Regli et al., 2015; Wagner and Plewa, 2017). However, the risk for DBP formation is lower in the NF permeate compared to the NF feed due to the lower DOM concentrations, as DOM is the main precursor of DBPs (Sharma et al., 2014).

Table 3
Relative retentions of dissolved organic carbon (DOC), bromide (Br^-) and micropollutants (MP) by the investigated membranes (average and standard deviations). Test conditions (unless stated otherwise): River Rhine raw water (no spiking of MPs), 25 °C, 5 bar, pH 8.1, 75% water recovery. Relative measured (meas.) retentions were calculated with Eq. (2). Estimated (estim.) retentions were calculated if $c_{Permeate,i}$ of compound *i* was lower than the lowest calibrated concentration, i.e., 0.01 μg L^{-1}, with estimated permeate concentrations ($c_{Permeate,estim.,i}$) by closing the mass balance: $c_{Permeate,estim.,i} = (c_{Feed,0,i} - 0.25\ c_{Concentrate,i}) / 0.75$. $c_{Concentrate,i}$ is the retentate concentration. If $c_{Permeate,i}$ was < 0.01 μg L^{-1}, the measured retentions were calculated with $c_{Permeate,i} = 0.01$ μg L^{-1} and retentions were marked with ">".

Membrane abbreviation Solute	Molecular weight [g/mol]	NF1 Retention [%] meas.	estim.	NF2 Retention [%] meas.	estim.	LPRO Retention [1] [%] meas.	estim.
Dissolved organic carbon	–	97±0 [2]	–	96±0 [2]	–	97±0 [2]	–
Bromide	79.9	22±9	–	23±9	–	96±0	–
Metformin (MET)	129.1	34±18	–	70±8	–	95±1	–
1H-benzotriazole (BTA)	119.1	24±18	–	36±15	–	86±3 [3]	–
Diclofenac (DCF)	296.2	> 63±7 [4]	95±24	> 66±6 [4]	90±24	> 79±4	88±23
Iopromide (IPR)	791.1	> 90±1	97±11	> 90±1 [3]	100±12	> 96±0	93±11

[1] Transmembrane pressure: 5.9 bar.
[2] Values from pilot-scale test with Biel water at 85% instead of 75% water recovery.
[3] The mass balance was not closed within a 95% confidence interval of analytical uncertainties.
[4] c_{Feed} was less than three times the lowest calibrated concentration.

Table 4
Electron donating capacities (EDC) of non-standardized concentrates. All concentrates were measured at pH 8.3, buffered with 10 mM boric acid. In the first rows, EDC values and their standard errors are presented, calculated from the slopes from linear regression curves of dilution series with four dilution steps ($R^2 > 0.99$ for all, except $R^2 = 0.97$ for River Rhine concentrate of the LPRO membrane, Table S7, SI). The second rows indicate the calculated absolute EDC of the standardized concentrates, i.e., EDC multiplied with DOC concentrations reported in Table S4 (SI). Standard uncertainties calculated with the Gaussian error propagation rule are also provided.

Membrane Water Source	LPRO	NF1	NF2
River Wiese (RW)	3.8 ± 0.1 mM e^-/g C 23±2 μM e^-	3.7 ± 0.1 mM e^-/g C 23±2 μM e^-	n.a.
River Rhine (RR)	2.3 ± 0.2 mM e^-/g C 15±2 μM e^-	3.5 ± 0.1 mM e^-/g C 21±2 μM e^-	4.2 ± 0.1 mM e^-/g C 26±2 μM e^-
Lake Biel (LB)	1.8 ± 0.1 mM e^-/g C 12±1 μM e^-	2.6 ± 0.2 mM e^-/g C 16±2 μM e^-	2.6 ± 0.1 mM e^-/g C 16±1 μM e^-

n.a.: not applicable.

Characterization of standardized concentrates

The EDC was measured as a parameter determining the phenol content of DOM, which is mostly responsible for the initial ozone demand (Aeschbacher et al., 2010; Houska et al., 2021). A high EDC indicates a high concentration of O_3-reactive moieties (Walpen et al., 2020), which for a given specific ozone dose might result in a lower O_3 exposure. Results of EDC measurements of the non-standardized concentrates are shown in Table 4. The absolute EDCs of standardized concentrates, shown in the second rows of each cell in Table 4, varied within a factor of 2.2 and depended on the water source, i.e., the same order was observed for all investigated membranes: RW > RR > LB.

SEC-OCD or SEC-UVD chromatograms were not useful to detect differences between the standardized concentrates (data not shown). Minor differences were observed with respect to the water sources, which is explained by their different catchment areas. The membrane selection did not impact the SEC chromatograms.

The specific UV absorbances at 254 nm ($SUVA_{254}$) of the standardized concentrates were similar within the standard uncertainty (0.7 L mgC^{-1} m^{-1}, estimated by the Gaussian error propagation rule, Table S4, SI).

Treatment of standardized concentrates

Data of all MP abatements and molar bromate yields are provided in the "Dataset.csv" file (SI) and discussed below.

Abatement of micropollutants

The results for the abatement of MPs during ozonation are shown in Figure S3 (SI). The abatement of MPs follows the order ATZ < IBU < BZF ≈ BTA < ATO < CBZ ≈ DCF. This agrees with the order expected from the second-order rate constants for reactions of the MPs with O_3 and $^{\bullet}OH$ (Table 2). In the following, MPs with a high ozone reactivity are discussed, which are almost exclusively abated by reactions with O_3 (group I, i.e., CBZ and DCF). Then, O_3-resistant MPs are discussed, because their abatement can be mostly explained by reactions with $^{\bullet}OH$ (groups III and IV, i.e., IBU and ATZ, respectively). Finally, MPs with a moderate ozone reactivity are discussed, where both reactions with O_3 and $^{\bullet}OH$ are important for their abatement (group II, i.e., ATO, BTA and BZF).

Micropollutants with high ozone reactivity. MPs with high ozone reactivity such as CBZ or DCF (Table 2) are abated to high extents even at relatively low specific O_3 doses. Typically, these compounds are abated predominantly by direct reactions with O_3 (Lee and von Gunten, 2016). At about 0.2 mg O_3 (mg DOC)$^{-1}$, CBZ (Fig. 1A) and DCF (Figure S4A, SI) were abated by 67% to 86% and 74% to >90%, respectively, in different standardized concentrates with different raw waters. Fig. 1B and C show the differences of the relative CBZ abatements of LB and RR compared to RW, respectively, for specific ozone doses of 0.2 and 0.3 mg O_3 (mg DOC)$^{-1}$. All differences between LB or RR and RW were significantly > 0% ($p < 0.05$), which means a lower CBZ abatement in RW compared to the other water resources. The lower differences of about 5% between RW and the other water sources at a specific ozone dose of 0.3 mg O_3 (mg DOC)$^{-1}$ can be explained by the already very high relative abatements of CBZ close to 100%. No statistically significant differences were observed comparing CBZ abatements of RR and LB. Similar results were obtained for DCF at 0.2 mg O_3 (mg DOC)$^{-1}$ (Figure S4B, SI); at 0.3 mg O_3 (mg DOC)$^{-1}$, DCF was already abated to residual concentrations below the limit of quantification (Figure S4, SI). For both MPs, the membrane type did not have a statistically significant impact on their abetment in

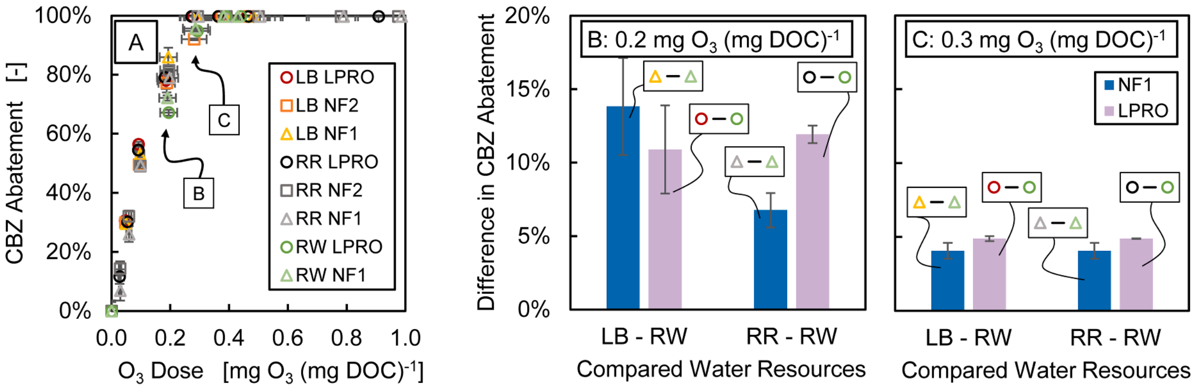

Fig. 1. A: Abatement of carbamazepine (CBZ) as a function of the specific ozone dose in standardized NF and LPRO concentrates. Error bars represent standard deviations of replicate experiments or, if no replicate experiment was conducted, calculated with the Gaussian error propagation rule. B and C: Differences in the relative abatements of CBZ in pair-wise comparisons between LB or RR and RW as reference, respectively, at specific O_3 doses of (B) 0.2 mg O_3 (mg DOC)$^{-1}$ and (C) 0.3 mg O_3 (mg DOC)$^{-1}$. Blue bars: NF concentrates; purple bars: LPRO concentrates. Error bars represent standard deviations calculated with the Gaussian error propagation rule.

standardized concentrates.

Based on the EDC values (Table 4), for a given specific ozone dose, the ozone exposures were expected to follow the order: RW < RR < LB. Therefore, a lower abatement efficiency for CBZ and DCF abatements in RW than in RR or LB can be expected, which is consistent with the obtained results in Fig. 1 and S4 (SI). This highlights that the ozone exposure was rather impacted by the water source and not by the membrane type.

Ozone-resistant micropollutants. ATZ and IBU are almost exclusively abated by reactions with $^{\bullet}$OH (Table 2). It is known that the $^{\bullet}$OH exposure can be calculated from the abatement of an ozone resistant probe compound (Acero et al., 2000; Huber et al., 2003; Hübner et al., 2013; Lee et al., 2013; Zucker et al., 2016) according to Eq. (4):

$$\ln\left(\frac{c_{\mathrm{MP}}}{c_{\mathrm{MP},0}}\right) = -k_{\bullet\mathrm{OH,MP}} \times \int c_{\bullet\mathrm{OH}}\mathrm{d}t - \underbrace{k_{\mathrm{O_3,MP}} \times \int c_{\mathrm{O_3}}\mathrm{d}t}_{\approx 0} \tag{4}$$

$c_{\mathrm{MP},0}$ and c_{MP} are the concentrations of a MP before and after ozonation, respectively. $c_{\bullet\mathrm{OH}}$ and $c_{\mathrm{O_3}}$ are the time-dependent concentrations of $^{\bullet}$OH and O_3 during ozonation, respectively.

IBU was used as a reference compound to assess the $^{\bullet}$OH exposure of the standardized concentrates. No statistically significant differences were found that indicated an impact of the membrane type or water source on the $^{\bullet}$OH exposure.

With small and similar contributions of reactions with ozone (Table 2), the ratio of $k_{\bullet\mathrm{OH,IBU}}$ / $k_{\bullet\mathrm{OH,ATZ}} = 3.0 \pm 0.6$ (standard deviation calculated by Gaussian error propagation rule) determines the expected ratio of ln abatements of these two MPs (black dashed line in Figure S5, SI). However, the average ratio of the observed second-order rate constants was 1.4, i.e., about half the expected ratio, regardless of the water source or the membrane used. No analytical issues were observed for any of the MPs discussed here, i.e., linearity of the calibrations was acceptable throughout all measurements ($R^2 > 0.995$ for all MPs) and matrix effects could be excluded from measurements of the MP recovery after spiking, both in ozonated and non-ozonated concentrates. The abatement of IBU was consistent with other MPs discussed below. Hence, ATZ was likely abated faster than expected, for unknown reasons. Further kinetic studies involving competition kinetics between ATZ and IBU are required to elucidate the reasons of this observation. Therefore, in the following, the discussions are based on IBU.

Micropollutants with moderate ozone reactivity. Three MPs with moderate ozone reactivities were investigated in this study, i.e., ATO, BTA and BZF. Their abatement is expected to occur both by reactions with O_3 and $^{\bullet}$OH. Plots of the negative natural logarithm of relative residual concentrations of BTA and BZF are shown in Fig. 2 as functions of the negative natural logarithm of relative residual concentrations of IBU as $^{\bullet}$OH reference compound. The plots indicate that significant contributions of O_3 reactions only occurred at specific ozone doses >0.5 mg O_3 (mg DOC)$^{-1}$ (highlighted data from experiments with RR standardized concentrates in Fig. 2), because below this specific ozone dose abatements of BTA and BZF did not significantly exceed the abatement expected from reactions with $^{\bullet}$OH, based IBU as $^{\bullet}$OH reference compound. Based on the significant second-order rate constants for the reactions of BZF and BTA with ozone (Table 2), a more pronounced difference would have been expected if the ozone exposures were significant for specific ozone doses <0.5 mg O_3 (mg DOC)$^{-1}$. These observations can be explained by a fast initial consumption of O_3, likely by fast reacting phenolic DOM moieties (Houska et al., 2021; Önnby et al., 2018), yielding partially $^{\bullet}$OH. Therefore, contributions of reactions with O_3 to the abatement of MPs such as BTA and BZF become more important when these DOM moieties are abated (Chon et al., 2015).

Formation of bromate

Upon ozonation, bromate can be formed from bromide by a complex reaction mechanism including both O_3 and $^{\bullet}$OH (von Gunten and Hoigné, 1994; von Gunten and Oliveras, 1998). Results for η upon ozonation of the standardized concentrates are presented in Fig. 3. For example, at a specific O_3 dose of about 0.4 mg O_3 (mg DOC)$^{-1}$, 15±2 µg BrO_3^- L^{-1} were formed on average (range: 11 to 19 µg BrO_3^- L^{-1}), corresponding to a molar bromate yield η of 2.9 ± 0.9% (range: 1.4 to 3.8%). This bromate concentration is above the drinking water standard (10 µg BrO_3^- L^{-1}), but below the proposed Swiss environmental quality standard (50 µg BrO_3^- L^{-1} (Oekotoxzentrum, 2015; Soltermann et al.,

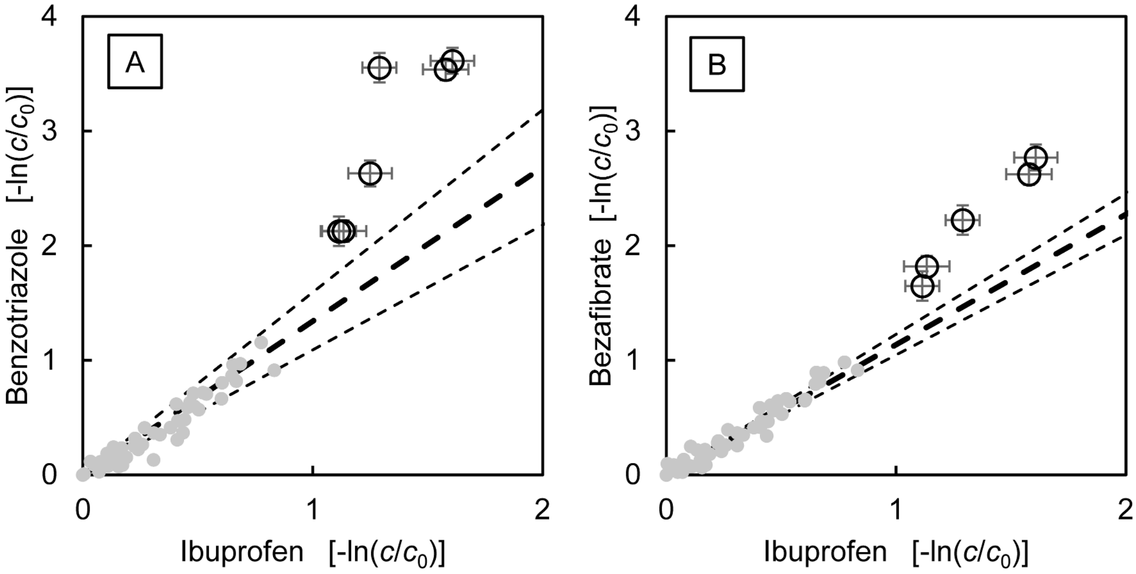

Fig. 2. Negative natural logarithm of the relative residual concentrations of (A) benzotriazole and (B) bezafibrate as functions of the negative natural logarithm of the relative residual concentrations of ibuprofen. The bold black dashed lines represent expected ratios when the abatement is explained by reactions with $^{\bullet}$OH only, utilizing the corresponding second-order rate constants for reactions of the target compounds with $^{\bullet}$OH (Table 2). Standard deviations from the second-order rate constants are also shown in normal black dashed lines. Results of the experiments with standardized concentrates at specific ozone concentrations < 0.5 mg O_3 (mg DOC)$^{-1}$ are shown as gray dots (without error bars for better readability of the plot). Experiments with specific O_3 doses > 0.5 mg O_3 (mg DOC)$^{-1}$ are shown as black open circles. Error bars of the symbols represent standard deviations.

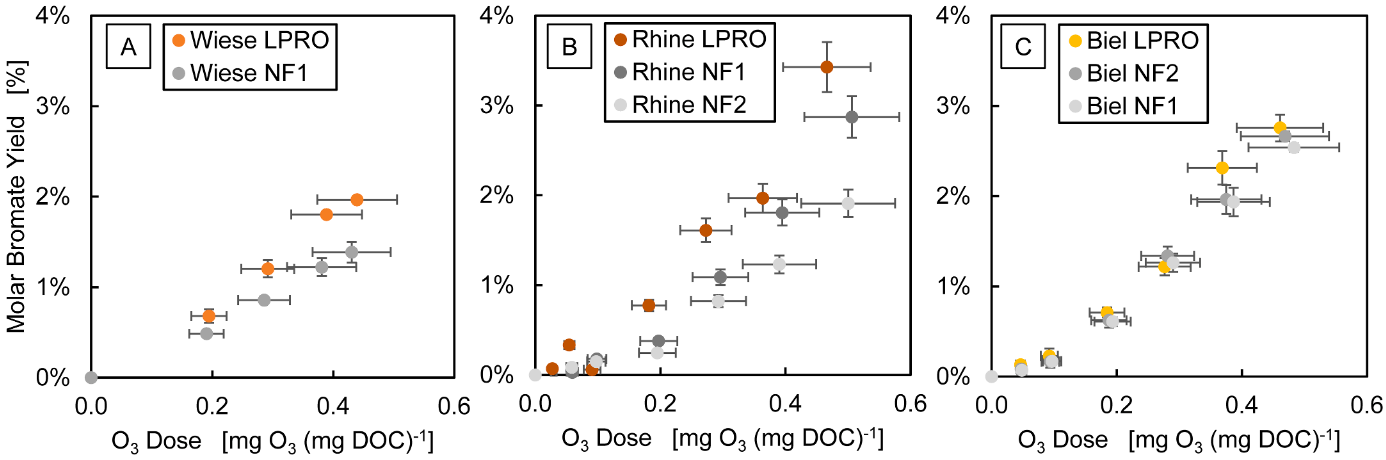

Fig. 3. Molar bromate yields as a function of the specific ozone dose for various membrane concentrates in (A) RW, (B) RR and (C) LB. The yields were calculated according to Eq. (1). The gray symbols represent the standardized nanofiltration and the colored symbols the standardized low-pressure reverse osmosis concentrates, respectively. Initial bromide concentrations: 495 to 531 µg L^{-1} (RW), 442 to 505 µg L^{-1} (RR), 474 to 517 µg L^{-1} (LB). Error bars represent standard deviations of replicate experiments (RW and LB) or, if no replicate experiment was conducted (RR), calculated with the Gaussian error propagation rule. For RR, higher specific O_3 doses ≤ 1 mg O_3 (mg DOC)$^{-1}$ are shown in Figure S6 (SI).

2016b)).

For the same water source, membrane-specific differences in molar bromate yields were observed, i.e., ozonated LPRO membrane concentrates (colored symbols in Fig. 3) typically had higher molar bromate yields than the NF membrane concentrates. On average, η of the standardized LPRO membranes was 43±51% higher than for the corresponding NF membranes at specific ozone doses in the range of 0.19 to 0.51 mg O_3 (mg DOC)$^{-1}$. Nevertheless, no statistical significance was observed except in RW at the highest specific ozone dose (>0.9 mg O_3 (mg DOC)$^{-1}$) between LPRO and NF2 (Figure S6, SI).

The observed molar bromate yields are well within the range of those reported previously for municipal wastewater RO reject streams at a specific O_3 dose of 0.45 mg O_3 (mg DOC)$^{-1}$ (Table S1, SI, (King et al., 2020)), i.e., 3.1 ± 1.5% (range: 0.8 to 4.5%). Similarly, at a specific O_3 dose of about 0.2 mg O_3 (mg DOC)$^{-1}$, η was 1.0 ± 0.4% (range: 0.5 to 1.4%), which is reasonably close to η observed by Benner et al. (2008): 1.2% at 0.17 mg O_3 (mg DOC)$^{-1}$ and 1.8% at 0.24 mg O_3 (mg DOC)$^{-1}$ (Table S1, SI, (Benner et al., 2008)). The good agreement of the results is likely fortuitous because of the differences between the standardized concentrates investigated here and the non-standardized municipal wastewater concentrates investigated by King et al. (2020) and Benner et al. (2008).

Tradeoff between micropollutant abatement and bromate formation

Fig. 4 shows the molar bromate yield in the standardized concentrates as functions of the abatement of representative MPs with high (DCF, group I) and moderate (BTA and ATO, group II) ozone reactivity and MPs of an ozone-resistant compound (IBU, group III). DCF and ATO were selected because they were studied before in ozonation of municipal wastewater RO concentrates and data was available for the corresponding bromate formation (King et al., 2020; Zhang et al., 2020). IBU was also compared with published results from diethyltoluamide (DEET) even though it has somewhat lower second-order rate constants for reactions with O_3 ($k_{O_3,\mathrm{DEET}} = 0.1\ \mathrm{M}^{-1}\ \mathrm{s}^{-1}$, (Benitez et al., 2013)) and $^{\bullet}$OH ($k_{\bullet\mathrm{OH,DEET}} = 5 \times 10^9\ \mathrm{M}^{-1}\ \mathrm{s}^{-1}$, (Song et al., 2009), i.e., group III).

Ozonation of standardized concentrates resulted in very similar abatement trends of MPs and formation of bromate for all water sources or the membrane types. Hence, even if the water source or membrane selection impacted the O_3 and $^{\bullet}$OH exposures, this did not result in a change of the tradeoff between MP abatement and bromate formation. This finding is based on the connection of bromate formation and MP abatement by combinations of ozone and $^{\bullet}$OH reactions and the corresponding exposures. The results also highlight that the small differences in the dissolved organic matter composition between NF and LPRO membrane concentrates are of minor relevance for the treatment efficiency and the tradeoff between MP abatement and bromate formation.

The data for the treatment of standardized concentrates from surface waters agree well with previously published data from non-standardized municipal wastewater RO concentrates (King et al., 2020; Zhang et al., 2020) (colored open symbols in Fig. 4) for specific ozone doses ≤ 1.0 mg O_3 (mg DOC)$^{-1}$ despite the significantly different water qualities of the ozonated samples. Fig. 4 highlights that the abatement of MPs in the standardized concentrates can be divided into three sections: (i) Low specific ozone doses ≤ 0.1 mg O_3 (mg DOC)$^{-1}$ are sufficient for MPs with a high ozone reactivity such as DCF (group I, Fig. 4A) to be abated by 50% to 60%. At a given specific ozone dose, molar bromate yields are low, with $\eta < 0.2\%$. (ii) Moderate specific ozone doses in the range of 0.1 to 0.5 mg O_3 (mg DOC)$^{-1}$ lead to an almost complete abatement of MPs with a high ozone reactivity (group I, Fig. 4A) and are sufficient to abate MPs with a moderate ozone reactivity such as ATO or BTA (group II, Fig. 4B) by up to 50% to 60%. In this range of specific ozone doses, the molar bromate yield linearly increases with the abatement of MPs and was typically < 3%. Therefore, here, bromide concentrations should be ≤ 200 µg L^{-1} in the concentrate before ozonation to limit bromate concentrations to the drinking water standard of 10 µg L^{-1} at specific ozone doses around 0.5 mg O_3 (mg DOC)$^{-1}$, i.e., which is typical for enhanced wastewater ozonation, e.g., in Switzerland. This might limit the application of the investigated treatment chain in many cases. Considering the fact that municipal wastewater RO concentrates can contain bromide in concentrations in the range of 1 to 10 mg L^{-1}, this might result in bromate concentrations around 50 to 500 µg L^{-1} (Table S1, SI), i.e., in many cases even above the proposed Swiss environmental quality standard (50 µg BrO_3^- L^{-1} (Oekotoxzentrum, 2015; Soltermann et al., 2016b)). Limiting bromate concentrations to the drinking water standard safeguards that all downstream stakeholders can produce drinking water from the river water/riverbank filtrate at any time, even in *de facto* water reuse situations, e.g., as observed in some regions of Germany (Karakurt et al., 2019). (iii) Specific ozone doses > 0.5 mg O_3 (mg DOC)$^{-1}$ are required for an almost complete abatement of MPs with a moderate ozone reactivity (group II, Fig. 4B) or to abate ozone resistant MPs such as IBU (group III, Fig. 4C) by > 50%. For these specific ozone doses, bromate formation strongly increases with increasing specific ozone dose. An ozonation of concentrates with such specific ozone doses will be challenging considering the high molar bromate yields.

Overall, concentrate ozonation with significant abatement of MPs and limited bromate formation is only feasible for MPs from groups I and

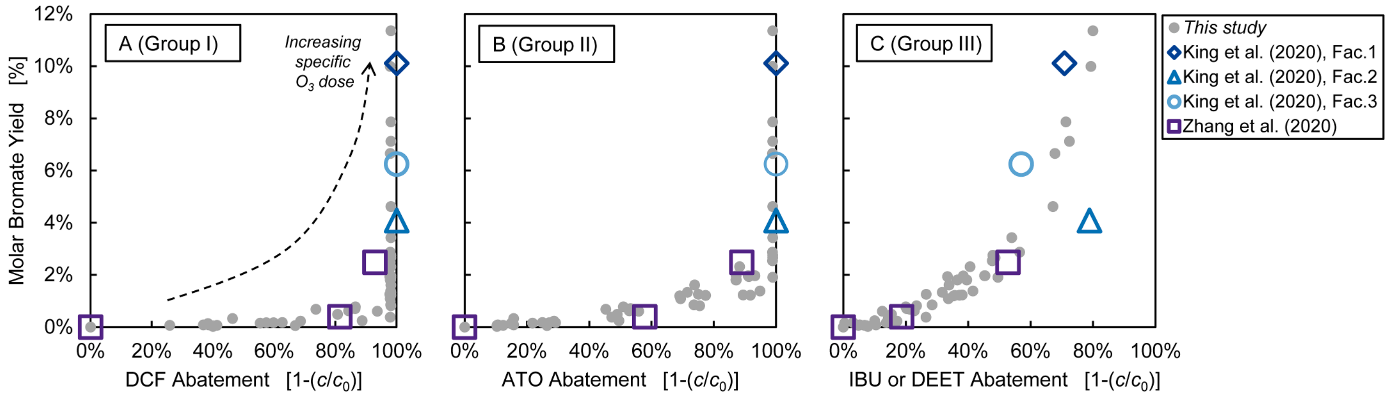

Fig. 4. Molar bromate yields as functions of the abatement of selected micropollutants, A: diclofenac (DCF); B: atenolol (ATO); C: ibuprofen (IBU) or diethyltoluamide (DEET). The dashed black arrow in subplot A indicates the course of increasing specific O_3 doses, which is valid for all subplots. Classification into groups I to III according to the respective kinetic data (Table 2, (Lee et al., 2013)). Data from this study is presented in gray filled circles (without error bars for better readability of the plots). Results of this study are compared with previously published data from ozonation of municipal wastewater reverse osmosis concentrates with colored open symbols (King et al., 2020; Zhang et al., 2020). Published abatements of DEET (Zhang et al., 2020) were used for comparison due to missing data for IBU and somewhat similar second-order rate constants, see text.

II (Fig. 4A and B).

Evaluation of NF and RO membrane processes in combination with concentrate ozonation

Ozonation of NF and LPRO concentrates were compared to assess the overall performance for MP abatement and bromate formation. Four types of MP can be distinguished conceptually in process chains consisting of a membrane treatment with a subsequent concentrate ozonation, as illustrated in Fig. 5, i.e., A, B, C and D, and discussed in Table 5 in which the types and examples of MPs are described.

Membrane treatment

Membrane treatment is evaluated by column “Treatment Step 1″ in Table 5 and reflected by the x-axis in Fig. 5. Compounds of types A or B are well retained by the membrane treatment, resulting in relatively low concentrations of these compounds in the permeate. In contrast, compounds of type C or D are retained to relatively low extents. A low retention results in relatively high concentrations of these compounds in the permeate. For this evaluation, the available experimental data with RR raw water samples was used (Table 3).

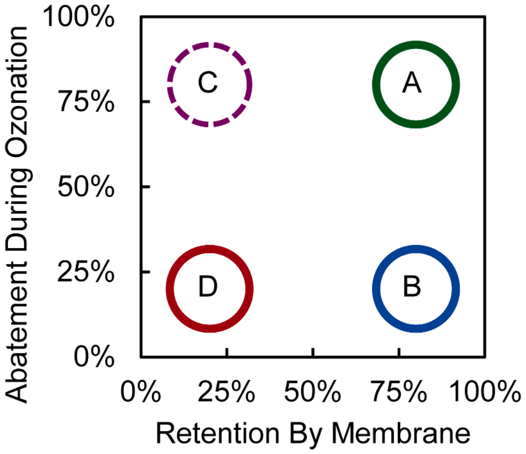

Fig. 5. Representation of different types of micropollutants (MP) in the process chain of membrane filtration represented by the MP’s retention by a dense membrane (x axis) and subsequent abatement in concentrate ozonation (y axis). The different MPs can be diverted in 4 types: A: well retained by the membrane and well abated during ozonation; B: well retained by the membrane and limited abatement during ozonation; C: poorly retained by the membrane and well abated during ozonation; D: poorly retained by the membrane and limited abatement during ozonation. For examples of such compounds and their behavior in NF and LPRO, see Table 5. Type C is shown with a dashed circle because examples of this type of compound are rare, e.g., benzotriazole in NF (Table 5), but not for reverse osmosis membranes.

Concentrate ozonation

The concentrate has to be treated for MP abatement before discharge with the corresponding necessary specific O_3 doses to comply with the local discharge limits for MPs and bromate. The abatement of the selected compounds upon ozonation of the concentrate is evaluated in Table 5 (column “Treatment Step 2″). This evaluation is based on experimental data for the abatement of BTA, DCF and IBU at specific ozone doses in the range of 0.24 to 0.61 mg O_3 (mg DOC)$^{-1}$ and the corresponding molar bromate yields for a non-standardized RW LPRO concentrate. This water source is different from membrane retention evaluation (RR), however, based on the findings presented above, it can be assumed that the MP abatement by ozonation is not significantly different for the different water sources in this study. This is not always the case because O_3 and $^{\bullet}$OH exposures can significantly vary between real water sources due to differences, e.g., in the specific NOM’s ozone reactivity, $^{\bullet}$OH yield and $^{\bullet}$OH scavenging by the water background matrix (Elovitz and von Gunten, 1999; Staehelin and Hoigné, 1985; von Sonntag and von Gunten, 2012).

The abatements of MPs in the non-standardized LPRO concentrate were comparable with those in the standardized LPRO concentrate (Text S4 and Figure S7, SI). However, the molar bromate yields in the non-standardized LPRO concentrate were only about half the yields of the standardized LPRO concentrate at comparable specific O_3 doses (Figure S8, SI). This is likely explained by the different ratios of Br^- : DOM and Br^- : S between the standardized and non-standardized concentrates and the different pH values.

The abatements of the ozone resistant MPs iopromide (IPR, group IV) and metformin (MET, group V) upon ozonation of the non-standardized LPRO concentrate were estimated based on the calculated $^{\bullet}$OH exposure from the abatement of IBU as $^{\bullet}$OH probe compound (Acero et al., 2000; Huber et al., 2003; Hübner et al., 2013; Lee et al., 2013; Zucker et al., 2016). The calculations were performed with Eq. (4) and the corresponding second-order rate constants for the reactions with $^{\bullet}$OH, i.e., $k_{\bullet \mathrm{OH,IPR}} = 0.8 \times 10^9$ M^{-1} s^{-1} (Huber et al., 2003) and $k_{\bullet \mathrm{OH,MET}} = (0.5 \pm 0.8) \times 10^9$ M^{-1} s^{-1} (average and standard deviation of three reported values, (Fu et al., 2019; Kaiser et al., 2013; Minella et al., 2017)).

For compounds of type A or C (MPs of groups I and II (Lee et al., 2013)) in Fig. 5a good abatement during ozonation of the concentrate

Table 5

Retentions in dense membranes, apparent second-order rate constants for the reactions of selected micropollutants with ozone and hydroxyl radical, experimental or predicted relative abatements of selected micropollutants during ozonation for various specific ozone doses, hydroxyl radical exposure and molar bromate yields in the non-standardized LPRO concentrate. For the retentions, the higher of the measured and estimated values reported in Table 3 was used here.

Compound	Treatment Step 1: Dense Membrane Filtration		Treatment Step 2: Ozonation of Concentrate						Evaluation	
	Experimentally determined retentions in RR raw water (pH 8.1, Table 3)		Kinetic data from the literature		Experimentally determined abatements in RW non-standardized LPRO concentrate (pH 8.6)					
	Retention [%]		Apparent second-order rate constants $[M^{-1} s^{-1}]$		Specific O_3 dose $[mg\ O_3\ (mg\ DOC)^{-1}]$					
	NF1	LPRO	$k_{O_3,MP}$	$k_{\bullet OH,MP}$ / 10^9	0.24	0.37	0.49	0.61	Type of micropollutant (Fig. 5)	Discussion
Benzotriazole (BTA)	24	86	2.5×10^3 [a]	9.2 [a]	17%	36%	53%	68%	NF1: C LPRO: A	If the low retention is sufficient for the required quality of the permeate, the concentrate treatment might be successful. Otherwise, a denser membrane has to be applied, which typically increases the subsequent bromate formation risk.
Diclofenac (DCF)	95	88	1.0×10^6 [a]	9.7 [a]	91%	98%	>99%	>99%	A	Treatment chain is well suited.
Ibuprofen (IBU)	–	–	9.6×10^0 [a]	6.9 [a]	20%	28%	38%	46%	–	–
$^\bullet$OH exposure / 10^{-11} [M s] [b]	–	–	–	–	3.2	4.7	6.9	9.1	–	–
Bromide (Br^-)	22	96	–	–	–	–	–	–	–	–
Molar bromate yield (η)	–	–	–	–	0.2%	0.4%	1.0%	1.5%	–	–
Metformin (MET) [c]	34	95	1.2×10^0 [d]	0.5 ± 0.8 [e]	2%	2%	3%	4%	NF1: D LPRO: B	The investigated treatment chain is not suited and other treatments have to be applied. Considering only the permeate quality, a denser membrane might be successful, but ozonation is not suitable to abate MPs in the retentate.
Iopromide (IPR) [c]	97	>96	8.0×10^{-1} [f]	3.3 [f]	10%	14%	20%	26%	B	High permeate quality can be achieved, but a different concentrate treatment should be considered.

[a] From Table S3 (SI); the second-order rate constant for reactions of BTA with O_3 was calculated for pH 8.6. [b] Based on the abatement of IBU as reference compound and kinetic data reported in Table 2, neglecting small contributions of O_3 reactions to the abatement of IBU. [c] Abatement upon ozonation of the concentrate was predicted for MET and IPR. Predictions are based on oxidant exposures assessed with IBU as internal probe compound and referenced kinetic data reported from the literature, using Eq. (4). [d] (Keen et al., 2014). [e] Average and standard deviation of three reported values (Fu et al., 2019; Kaiser et al., 2013; Minella et al., 2017). [f] (Huber et al., 2003).

can be expected at specific ozone doses ≤ 0.6 mg O_3 $(mg\ DOC)^{-1}$. In contrast, compounds type B or D are hardly abated during ozonation with specific O_3 doses ≤ 0.6 mg O_3 $(mg\ DOC)^{-1}$.

For an overall solution for MPs, the investigated treatment chain is well suited for type A compounds (Fig. 5) such as DCF (Table 5), because they are well retained at the membrane and abated to high extends upon ozonation. Compounds of type B (Fig. 5) such as IPR (Table 5) are well retained at the membrane, but their abatement in ozone treatment of the concentrate is limited. An additional treatment after ozonation such as activated carbon could improve the treated concentrate's quality to comply with the treatment goal (Ahn et al., 2015; Zhang et al., 2020).

Hypothetical type C compounds (Fig. 5, BTA for NF1 in Table 5) are retained to low extends by the NF1 membrane only. If retained, these compounds are well abated in the ozone treatment of the concentrate. For LPRO, there are no known compounds which fulfill these criteria. The worst case for the treatment chain are compounds of type D (Fig. 5, MET for NF1 in Table 5, no compounds for LPRO), as they are hardly retained and hardly abated by ozone treatment in the concentrate. In general, for LPRO, there are only very few examples which fulfill the criteria for type D, such as chloroform and *N*-nitrosodimethylamine (NDMA), (Marron et al., 2019).

For compounds of type C and D, the selection of a denser membrane might be suitable to improve the retention of such compounds, as in the case of BTA and MET (Table 5, compare columns "NF1" and "LPRO"). This can turn a compound type C to type A (Fig. 5, e.g., BTA in Table 5) and a compound type D to type B (Fig. 5, e.g., MET in Table 5). Nevertheless, for MET, a different concentrate treatment will be necessary, e.g., by a biological treatment (Scheurer et al., 2012; Zhang et al., 2020).

Overall assessment of process combination

Along with the retention of MPs and their abatement during ozonation of the concentrate, the retention of Br^- and the formation of BrO_3^- during concentrate ozonation is important for the assessment of the whole process train. An excessive formation of bromate might limit the application of the proposed process combination. To compare the bromate formation risk for ozonation of NF1 and LPRO concentrates, the experimentally determined Br^- retention values (Table 3) were used to calculate Br^- levels in the concentrates. Given the retention *R* of a solute *i* at the membrane, the concentration in the concentrate can be calculated according to Eq. 5:

$$c_{\text{Concentrate},i} = c_{\text{Feed},i} \times \frac{1 - (W \times (1 - R_i))}{1 - W} \quad (5)$$

$c_{\text{Feed},i}$ and $c_{\text{Concentrate},i}$ are the concentrations in the membrane feed and the concentrate, respectively. W is the water recovery, which was assumed to be 85% as in the production of the non-standardized concentrates. Bromide rejection, R_{Br^-}, is known at $W = 75\%$ for a RR sample and assumed to be the same at $W = 85\%$ for a RW sample (Table 3). As a result, the Br^- concentrations in NF1 and LPRO concentrates are $2.2 \times c_{\text{Feed},Br^-}$ and $6.4 \times c_{\text{Feed},Br^-}$, respectively. Since the bromate formation is roughly proportional to the bromide concentration, the extent of bromate formation is about three times lower in the NF1 concentrate than in the LPRO concentrate.

To estimate the bromate concentrations upon concentrate ozonation, the resulting bromide concentration was multiplied with the experimentally determined molar bromate yields. As discussed before, η of standardized NF1 concentrates were about 40% lower than the standardized LPRO concentrates, but no statistically relevant differences were found for specific O_3 doses < 0.9 mg O_3 (mg DOC)$^{-1}$. Therefore, non-standardized NF1 concentrates were assumed to have the same η as the non-standardized LPRO concentrate, which is a worst-case scenario for the NF1 concentrate treatment.

Combining this information, bromate concentrations in the NF concentrate are estimated in the range of 0.4% to 3.4% $c_{\mathrm{Feed,Br^-}} \times MW_{\mathrm{BrO_3^-}} / MW_{\mathrm{Br^-}}$, and for the LPRO concentrate in the range of 1.3% to 9.7% $c_{\mathrm{Feed,Br^-}} \times MW_{\mathrm{BrO_3^-}} / MW_{\mathrm{Br^-}}$, respectively, depending on the investigated specific O_3 dose. Estimated bromate concentrations after ozone treatment of NF1 or LPRO concentrates at the investigated specific ozone doses are shown in Figure S9 (SI) as functions of the bromide concentration in the membrane feed. To limit bromate concentrations in the treated concentrates to ≤ 10 μg L^{-1}, here, $c_{\mathrm{Feed,Br^-}}$ must therefore be < 185 μg L^{-1} or < 65 μg L^{-1} for the NF1 or LPRO membrane, respectively, for concentrate treatment with 0.61 mg O_3 (mg DOC)$^{-1}$ and without additional bromate mitigation strategies. In contrast, if Br^- is present in the membrane feed at concentrations ≤ 1.5 mg L^{-1} and ≤ 480 μg L^{-1}, here, specific O_3 doses of 0.24 mg O_3 (mg DOC)$^{-1}$ can be used in the ozone treatment of NF1 or LPRO concentrates, respectively, to limit bromate concentrations to ≤ 10 μg L^{-1} (Figure S9, SI).

Overall, the permeate quality with respect to MP concentrations is determined by the selection of the membrane. Denser LPRO membranes must be selected if only very low MP concentrations are acceptable in the permeate. However, this also considerably increases the risk of bromate formation. To limit bromate formation during the subsequent ozonation of concentrates to an acceptable level, only low to moderate specific O_3 doses can be used in the ozone treatment of the concentrate and, hence, significant abatement can only be expected for MPs with a high or moderate ozone-reactivity.

The composition of real concentrates produced by different membranes from the same water source will differ due to varying relative rejections of compounds, as described above. Therefore, in real concentrates, the pH and concentrations of DOM, HCO_3^-/CO_3^{2-} and Br^- will vary as well as concentrations of MPs. In addition, BrO_3^- is formed in a complex pathway involving both reactions with O_3 and $^{\bullet}OH$. Therefore, all water parameters affecting these oxidant exposures can ultimately result in changes of the bromate yield (Elovitz et al., 2000; von Gunten and Hoigné, 1994). Without standardization, it would be difficult to compare different concentrates in terms of the trade-off between MP abatement and BrO_3^- formation. Standardization of the concentrates allows to eliminate the above known parameters impacting MP abatement and bromate formation and therefore allows the assessment of the impact of water source and membrane type on the ozone treatment of the concentrate. However, the transferability of the obtained results to real concentrates has limitations. Nevertheless, a reasonable agreement with real concentrates was found (Fig. 4). One main finding of this study is that the selection of a NF membrane minimizes the risk of bromate formation during ozonation of concentrates due to the lower relative bromide retention by the membrane compared to a LPRO membrane. This conclusion is valid despite all limitations on transferability, as the bromate yield is roughly proportional to the bromide concentration (Elovitz et al., 2000; Soltermann et al., 2016a; von Gunten and Hoigné, 1994).

Conclusion

Concentrates of the rivers Rhine (RR) and Wiese (RW) and of Lake Biel (LB) waters were obtained from a low-pressure reverse osmosis (LPRO) membrane and two nanofiltration (NF) membranes. After standardization of the concentrates at pH = 8.3 ± 0.1 and the same concentrations of dissolved organic carbon (DOC), total inorganic carbon (TIC), bromide (Br^-) and spiked micropollutants (MPs), the impact of the membrane selection and raw water type upon ozonation was investigated. The following conclusions can be drawn:

- It was demonstrated that the water source was the main factor impacting the electron donating capacity (EDC). The expected lower ozone exposures for higher EDCs are consistent with the lower abatement of diclofenac and carbamazepine in waters with higher EDCs (RW < RR < LB).
- Upon ozonation of the standardized concentrates, the investigated MPs (atenolol, atrazine, benzotriazole, bezafibrate, carbamazepine, diclofenac, ibuprofen) were abated to different extents, in agreement with their second-order rate constants for the reactions with O_3 and $^{\bullet}OH$. The tradeoff between the desired MP abatement and undesired bromate formation was neither impacted by the water source, nor by the membrane type. Ozonation of concentrates at limited bromate formation was only feasible for MPs with a high or moderate ozone reactivity.
- An assessment of the MP abatement and bromate formed upon ozonation for non-standardized concentrates highlighted the interplay of the membrane and the subsequent concentrate treatment. The LPRO membrane had a higher retention of MPs and bromide than the investigated NF membranes. Nevertheless, for lower MP retention requirements, NF membranes might be a better choice because their concentrates will lead to lower bromate concentrations upon ozonation. The elevated bromide concentrations in NF permeates are considered not to be an issue, unless chlorine-based treatments are used, e.g., for permeate disinfection. However, the risk of brominated disinfection byproducts formation is lower in the NF permeate compared to the NF feed due to the rejection of dissolved organic matter in NF treatment, the main precursor of such compounds. In addition, the lower DOM concentrations typically allow to apply a lower chlorine dose, which additionally reduces the risk of DBP formation.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Supplementary materials

Supplementary material associated with this article can be found, in the online version, at doi:10.1016/j.watres.2022.118785.

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