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Optimizing Micropollutant Removal by Ozonation; Interference of Effluent Organic Matter Fractions

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ABSTRACT

Ozonation for micropollutant removal from wastewater treatment plant effluent is energy and cost-intensive because of competition between background organic matter and micropollutants. This study aims to elucidate the interference of different organic matter fractions during the ozonation of micropollutants. Wastewater treatment plant effluent was fractionated using membranes and XAD-8 resin. All membrane and resin fractions were spiked with 18 micropollutants (2 μg/L) and ozonated with 0.25, 0.5 and 1 g O_3/g TOC. Results show that these fractions differ in their interference with the ozonation of micropollutants. Interference was lower in the smallest size fraction (<1 kDa) than in all other fractions for micropollutants with low and medium ozone reactivity. The hydrophobic neutrals and hydrophilics resin factions showed a high interference for ozonation of micropollutants with medium and high ozone reactivity, respectively. The four parameters that were analyzed (specific UV absorbance at 254 nm, fluorescence, chemical oxygen demand and nitrite) could not elucidate the differences in micropollutant removal. Still, we conclude that understanding the type of organic matter present in the matrix, is essential to optimize micropollutant ozonation and other tertiary micropollutant removal treatments.

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Ozone; micropollutants; effluent organic matter; resin fractions; membrane fractions

Introduction

All over the world, micropollutants (MPs) are detected in various types of water systems, such as surface water, groundwater and wastewater (Philip, Aravind, and Aravindakumar 2018; Yang et al. 2017). The presence of MPs in these water systems raises concerns regarding ecosystems and human health (Kidd et al. 2007; Krzeminski et al. 2019; Oaks et al. 2004; Polesel, Plósz, and Trapp 2015). Both human population and the consumption of chemicals like pharmaceuticals are increasing, hence the discharge of MPs into the environment will also increase. Therefore, the precautionary principle should be applied to reduce emissions of MPs into the environment (Kriebel et al. 2001).

Wastewater treatment plants (WWTPs) are suitable places to intercept and reduce emissions into the environment because they are important point sources of MPs. Conventional WWTPs remove part of the MPs present in wastewater via adsorption to sludge and biological degradation, but cannot remove all MPs (Eggen et al. 2014; Luo et al. 2014). Hydrophilic and biorecalcitrant MPs can be removed in a tertiary treatment step, for instance, ozonation or activated carbon filtration (Boehler et al., 2012; Bourgin et al. 2018; Margot et al. 2013). However, these tertiary treatments are often associated with high energy use and high costs.

The high energy requirement for ozonation of WWTP effluent results from competition of other organic matter (OM) with MPs for reaction with ozone. All of the OM in WWTP effluent can react with ozone and MPs only form a small fraction of the total. In general, the total effluent organic matter (EfOM) concentrations (in the range of mg/L) are 10^3 to 10^6 times higher than target MP concentrations (in the range of ng – μg/L). Hence, required ozone doses are based on EfOM concentrations, using specific ozone dosages such as g O_3/g TOC or g O_3/g COD, and not on MP concentrations (Ekblad et al. 2018; Hansen et al. 2016a; Lee et al. 2013; Nilsson et al. 2017). Both TOC and COD are bulk parameters that mainly give information about the quantity of EfOM. However, also the type of OM in WWTP effluent strongly affects the reactivity of OM with ozone (P. Jin et al. 2016; Qi et al. 2018; Westerhoff et al. 1999). Still, EfOM composition and its interactions with the ozonation of MPs are poorly understood. Insight in these processes is key to improve the energy and cost efficiency for ozone treatment to remove MPs from WWTP effluent.

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In order to gain insight in the composition of EfOM, it can be fractionated by, for example, particle size using membranes, or by functional groups using resins. Additionally, fingerprinting methods such as LC-OCD or novel MS-based fingerprinting can be used to elucidate EfOM structure (Her et al. 2002; Qiu et al. 2020). Although, for fingerprinting techniques, it is not possible to collect different parts of the OM separately and conduct experiments regarding their specific behavior. Previous studies found that EfOM fractions have different reactivity toward ozone. Gonzales, Peña, and Rosario-Ortiz (2012) showed that size fractions have different ozone reactivity and OH· formation potential. Resin fractionation experiments showed that hydrophobic-neutral and -acid compounds are removed during ozonation, while hydrophilic compounds are produced (P. Jin et al. 2016; Qi et al. 2018). Still, it is not clear if and if so how differences in ozone reactivity of EfOM fractions affect the ozonation of MPs.

We hypothesize that the type of EfOM affects the efficiency of MP ozonation, whereas currently, only the quantity of EfOM is taken into account for the ozonation of MPs in WWTP effluent. To investigate this hypothesis, WWTP effluent was fractionated using both membrane and resin-based fractionation methods. Produced fractions were diluted to a standardized TOC level to ensure that effects of the type were compared and not the quantity of the EfOM. Standardized fractions were spiked with a mix of MPs and ozonated with four different ozone doses. In addition to the MP concentrations, several parameters were analyzed to understand the differences in OM composition between the fractions: fluorescence, specific UV absorbance at 254 nm (SUVA), chemical oxygen demand (COD) and nitrite. Additionally, the size fractions were analyzed using liquid chromatography coupled to organic carbon detection (LC-OCD) to give more insight in their composition, since these fractions provided the most interesting results. The results are discussed in the context of improving MP removal by ozonation of WWTP effluent.

Materials and methods

Wastewater treatment plant effluent

A volume of 5 L of WWTP effluent was collected from the WWTP in Bennekom, the Netherlands. This WWTP is designed for organic carbon and biological nutrient removal and treats approximately 1,000 m^3/h municipal wastewater per hour (35.000 P.E.). The effluent was collected on a dry day to minimize dilution by rainfall and stored in a glass Schott bottle, wrapped in aluminum foil at 4 °C until further use. The WWTP effluent was used for the membrane experiment 1 week after sampling and for the resin experiment 3 months after sampling.

Micropollutants

The MP mix used for this study contained 18 MPs dissolved in methanol: 2.4D, 4 & 5 methylbenzotriazole, BAM, bentazone, benzotriazole, carbamazepine, chloridazon, desphenyl-chloridazon, dimetridazole, furosemide, iopamidol, irbesartan, mecoprop, metoprolol, propranolol, sotalol, sulfamethoxazole and trimethoprim (Table A1, Appendix A). The MPs are organized in three classes based on their ozone reactivity: class I – high ozone reactivity ($kO_3 > 10^4$ M^{-1} s^{-1}), class II – medium ozone reactivity ($10^2 > kO_3 > 10^4$ M^{-1} s^{-1}) and class III – low ozone reactivity ($kO_3 < 10^2$ M^{-1} s^{-1}) (Table A2 in Appendix A). Note that, to the authors' best knowledge, kO_3 values for four of the used MPs (Bentazone, Chloridazon, Desphenyl-Chloridazon and 2.4 D) are not available in the literature. Therefore, these four MPs were placed in the three classes solely based on the removal observed in our study, and interpretation of their classification should be done with caution.

Fractionation

Two fractionation methods were used: fractionation with membranes to separate fractions based on particle size and fractionation with XAD-8 resin to separate fractions based on functional groups. Cross-flow filtration using three hollow fiber membranes with a molecular weight cutoff of 1.08, 11.4 and 99.8 kDa was used to separate the effluent sample into four size fractions. In addition to the size fractions, a sample of unaltered effluent (later referred to as 'Total') and effluent that was passed through a 0.45 µm membrane (later referred to as 'Filter') were included in the experiment. Two liter of 0.45 µm filtered effluent was circulated through the cross-flow setup (Figure A1, Appendix A). For each of the following steps, the effluent was circulated until at least 200 mL of permeate was collected. First, the permeate was collected of the 1.08 kDa membrane (F4). Second, the 1.08 kDa membrane was replaced with the 11.4 kDa membrane, and the permeate was collected (F3). Finally, the permeate from the 99.8 kDa membrane was collected (F2) and the remaining liquid in the circulating setup was collected (F1) (Figure A2, Appendix A).

The resin fractionation procedure was adjusted from Imai et al. (2002) and Qi et al. (2018) (Figure A3,

Appendix A). Fractionation using XAD-8 resin combined with acidity adjustments was used to fractionate the effluent sample into four resin fractions: hydrophilics (HI), hydrophobic acids (HOA), hydrophobic neutrals (HON) and hydrophobic bases (HOB). In addition to the resin fractions, a sample of non-fractionated effluent ('Total') was included in the experiment. First, 3.1 g of XAD-8 resin (wet weight) was washed subsequently with demi water, 0.1 M KOH and 0.1 M HCl to reduce background OM release from the resin. The washed resin was placed in a 50 mL syringe and flushed with 20 mL of demi water, which was collected as a blank for the experiments. Next, 400 mL of 0.45 μm filtered effluent sample was eluted through the resin and collected as the first eluate for later use. The resin was washed with 200 mL 0.1 M HCl in demi water and the second eluate was collected (HOB). The first eluate was adjusted to pH 2, flushed through the resin again and collected as HI. The resin was washed with 200 mL of 0.1 M KOH and collected (HOA). Finally, the resin was washed with 100 mL of methanol. The methanol was evaporated in a flow cabinet overnight after which the non-evaporated organics were dissolved in 200 mL MQ water (HON). After fractionation, all resin fractions were adjusted to pH 7. All pH adjustments mentioned above were done with 1 M HCl or 1 M KOH in demi water.

Ozonation experiment

Prior to the ozonation, all fractions were diluted to a TOC concentration of 3.7 mg/L. For each fraction, 27 μL of MP mix was added to a glass beaker the methanol was evaporated under a gentle flow of nitrogen gas in a flow cabinet for half an hour. After all, methanol was evaporated, the diluted fractions were added to the glass beakers with MPs to reach final MP concentrations of approximately 2 μg/L per MP and the beakers were shaken to dissolve the MPs.

Each diluted and spiked fraction was split into four equal parts of 40 mL and each part was transferred into a 50 mL Greiner tube. The spiked fractions were ozonated at different doses: 0, 0.25, 0.5 and 1 g O_3/g TOC. The ozone was added using an ozone stock (as described in (Zucker et al. 2016)) with a concentration of approximately 45 mg O_3/L. Ozone stock was prepared by guiding pure oxygen gas through an Anseros COM-AD ozone generator and into a cooled modified Schott bottle (Figure A3, Appendix A). After saturating the ozone stock, it was transferred from the Schott bottle into a clean glass beaker and from there pipetted into the samples. A beaker with ozone stock was used to pipet no more than 6 times to limit the effect of evaporation of ozone from the ozone stock. The first and sixth pipetting was used to measure ozone concentration with the indigo method, in order to calculate the exact amount of ozone dosed (Table B3, Appendix B).

Analyses

Ozone concentration in the ozone stock was analyzed using the indigo method based on Bader and Hoigné (1985). For each measurement, 1 mL of indigo trisulfonate stock (0.97 mM) and 0.5 mL of H_3PO_4 stock (1.5 mM) were added to a 25 mL volumetric flask. 1 mL of ozone stock was added and the flask was shaken briefly to let the ozone react with the indigo. Afterward, the volumetric flask was filled up to 25 mL with MQ water and absorbance was measured at 600 nm. Similarly, a reference was made without ozone stock. Using the reference, ozone concentration was calculated using Equation 1:

$$[O_3] = \frac{V_f \Delta A}{f b V_t} [\mathrm{mg/L}] \qquad [1]$$

where $[O_3]$ is the ozone concentration in solution (mg/L), V_f is the volume of the volumetric flask, ΔA is difference in absorbance between the reference indigo solution and the indigo reference with ozone stock added, f is the ratio between absorbance change and ozone concentration (ε/O_3 in L/cm/mg), b is the path length of the cuvette in cm and V_t is the volume of the individual sample (ozone stock) added to V_f .

MPs were analyzed using liquid chromatography coupled to high-resolution accurate-mass mass spectrometry (LC-HRAM-MS). The LC consisted of an Ultimate 3000 coupled through a Hesi II electrospray source to a QExactive Orbitrap MS (Thermo Scientific, San Jose, CA, USA). Sample volumes of 50 μL were injected onto a phenyl-hexyl column, oven temperature at 35 °C. Elution flow was set to 0.3 mL/min with a gradient of the following two eluents (A): UPLC-MS quality water with 1% formic acid (v/v) and (B): UPLC-MS quality acetonitrile with 1% formic acid (v/v), both UHPLC grade, purchased from Actu-All (The Netherlands). The gradient applied was: 0–0.5 min stable at 0% B, 0.5–13 min linear increase of eluent to 80% B, 13–16 min stable at 80% B, 16–17 min linear decrease to 0% B, 17–23 min stable at 0% B. Micropollutants were detected in positive ionization and negative mode using electrospray. Full-scan windows were applied for each MP. The following MS conditions were applied: spray voltage 3.5 kV, sheath and sweep gas flowrates 48 and 2, respectively, capillary temperature 256 °C, aux gas heater temperature 413 °C and resolution 70000. MS was calibrated for each series according to manufacturer protocol using a Pierce™ LTQ Velos ESI Positive Ion Calibration Solution (Thermo Scientific). Peak identification and quantification were done with Thermo Xcalibur (version 2.2) software.

Fluorescence intensity analyses were based on Jin et al. (2019). A Perkin Elmer Luminescence Spectrometer LS50B was used to scan the following ranges: emission from λ_{em} 280–550 nm with 0.5 nm intervals and excitation from λ_{ex} 220–480 nm with 10 nm intervals. The slit width for both emission and excitation was 5 nm and the scanning speed was 1300 nm/min. Region integration was done based on Chen et al. (2003), to calculate the fluorescence in five regions: Region I indicating tyrosine like proteins (ex 220–250 nm, em 280–325 nm), Region II indicating tryptophan like proteins (ex 220–250 nm, em 325–380 nm), Region III indicating fulvic-like compounds (ex 220–250 nm, em 380–550 nm), Region IV indicating microbial by-products (ex 250–400 nm, em 280–3380 nm) and Region V indicating humic-like compounds (ex 250–400 nm, em 380–550 nm) (Figure A4, appendix A). The StaRdom package in R was used to remove and interpolate the Rayleigh scattering bands for the emission excitation matrices.

Total organic carbon (TOC) was analyzed with the non-purgeable organic carbon method on a TNM-L TOC analyzer (Shimadzu). Ultraviolet absorbance at 254 nm (UV_{254}) was analyzed using an Infinite M200 Pro multimode plate reader (Tecan). Specific ultraviolet absorbance (SUVA) was calculated by dividing the UV_{254} values by the TOC values. Chemical oxygen demand (COD) and nitrite concentrations were analyzed with dr. Hach-Lange kits, LCK 1414 and LCK 341, respectively. Size fractions were analyzed using LC-OCD to quantify biopolymers, chromatographic DOC, hydrophobic organic carbon, humic acids, low molecular weight acids and low molecular weight neutrals. The LC-OCD used a Toyopearl HW-50S column and was coupled with both a UV and an organic nitrogen detector (Figure A5, Appendix A).

Results and discussion

Fractionation

To investigate the effect of differences in organic matter type in WWTP effluent on the ozonation of MPs, the effluent was fractionated with two methods: membrane based fractionation to produce four size fractions (Figure 1A) and XAD-8 resin-based fractionation to produce four functional group based fractions (Figure 1B).

Fractionation with membranes produced four size fractions with larger (F1) to smaller (F4) EfOM. Due to the used fractionation process, smaller molecules can still be present in the larger fractions. The TOC of F1 was highest, followed by F2, F4 and F3 (Figure 1A). This is different compared to Gonzales, Peña, and Rosario-Ortiz (2012) who found that for each of the four effluents they fractionated, 75% of the DOC was present in the fraction smaller than 10 kDa. In our case, the sum of F3 and F4 is only 46% of the 'Total' TOC. This difference could be due to the use of different effluents or due to the different type of membrane separation that was applied. We used cross-flow filtration whereas Gonzales, Peña, and Rosario-Ortiz (2012) used dead-end filtration. Cross-flow filtration results in less fouling of the membrane resulting in the high TOC recovery rate of 97%. The disadvantage of the technique is that part of the small particles or molecules can end up in the larger

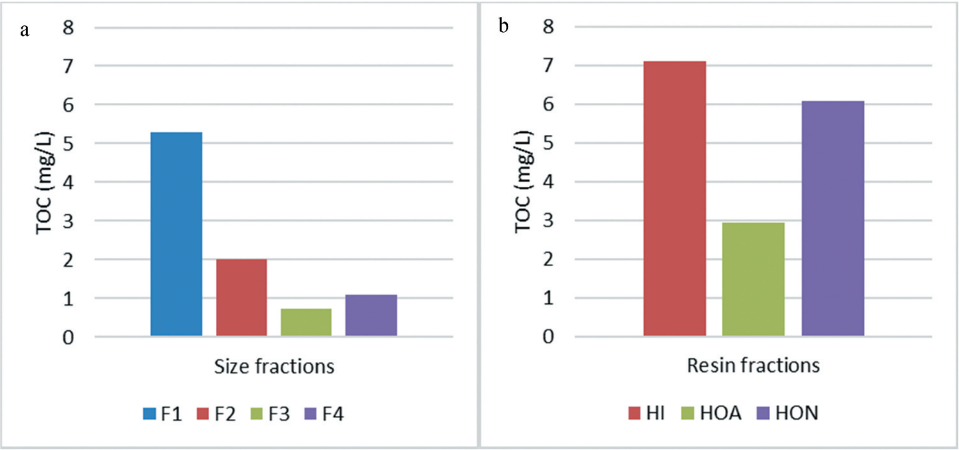


Figure 1. Composition of complete wastewater treatment plant effluent: size fractions (A) and resin fractions (B). The TOC of the resin fraction HOB was lower than the TOC of the blank, therefore this fraction is not included in the figure.

fractions, resulting in a slight overestimation of the large fractions and underestimation of the small fractions.

Fractionation with resin also produced four fractions: hydrophilics (HI), hydrophobic acids (HOA), hydrophobic neutrals (HON) and hydrophobic bases (HOB). The TOC of the HOB fraction was lower than the TOC of the blank, therefore this fraction is not included in further analysis. The HI fractions were the largest based on TOC, followed by the HON fraction and the HOA fraction (Figure 1B). Other studies using resin fractionation found similar effluent compositions (Imai et al. 2002; P. Jin et al. 2016; Qi et al. 2018; Zhang et al. 2008). One difference we found, is that the HON fraction had a higher TOC than the HOA fraction, whereas the other studies found the opposite. This difference could be explained by variation between effluents from different WWTPs was added. The TOC recovery of the resin fractionation was close to 100% (102%), similar to that of P. Jin et al. (2016), which indicates that OM was not lost or released from the resins. This means that the used washing, sorption and desorption steps onto and from the resin were appropriate to prevent loss of OM during the fractionation process.

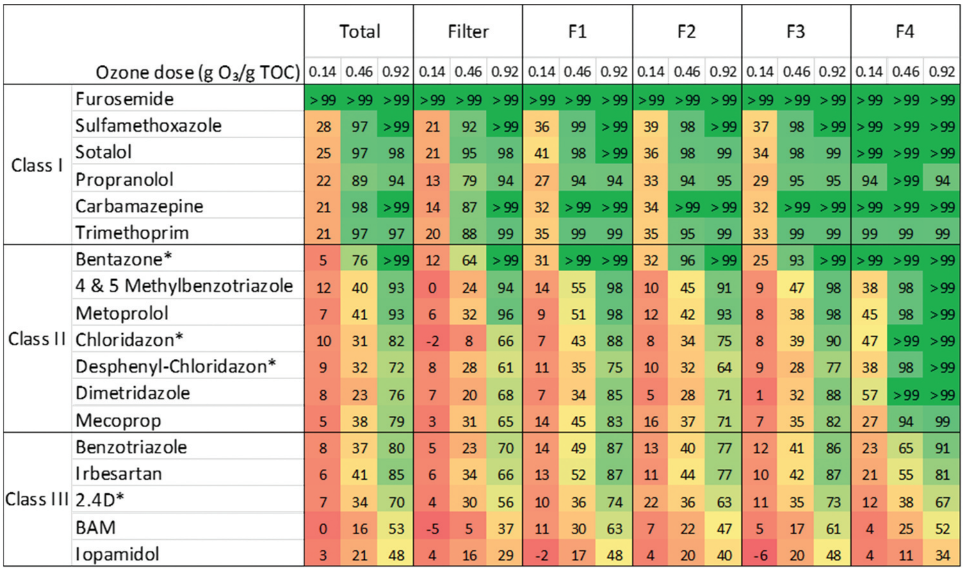
Micropollutant removal

The smallest size fraction (F4) showed the highest MP removal compared to the other size fractions (Figure 2). This higher removal was only observed for class I and class II MPs, but not for the MPs with low ozone reactivity in class III. The five MPs in class III (Benzotriazole, Irbesartan, 2.4D, BAM and Iopamidol) showed similar removal in all size fractions. This shows that the OM in F4 is less reactive with ozone than most MPs, resulting in high removal of class I and class II MPs in this fraction. Only class III MPs are less reactive with ozone than the OM in F4, resulting in similar removal behavior of these compounds in all size fractions.

The resin fraction HI showed lower removal of class III MPs compared to the other resin fractions and similar removal of class II and class III compounds (Figure 3). This indicates that OM from the HI fraction interferes more with the removal of MPs with low kO_3 ($<10^2$ M^{-1} s^{-1}). The resin fraction HON showed lower removal of class II MPs than all other resin fractions and lower removal of class III MPs than the resin fractions 'Total' and HOA. The HON fraction interferes more with the ozonation of class II MPs than other resin fractions.

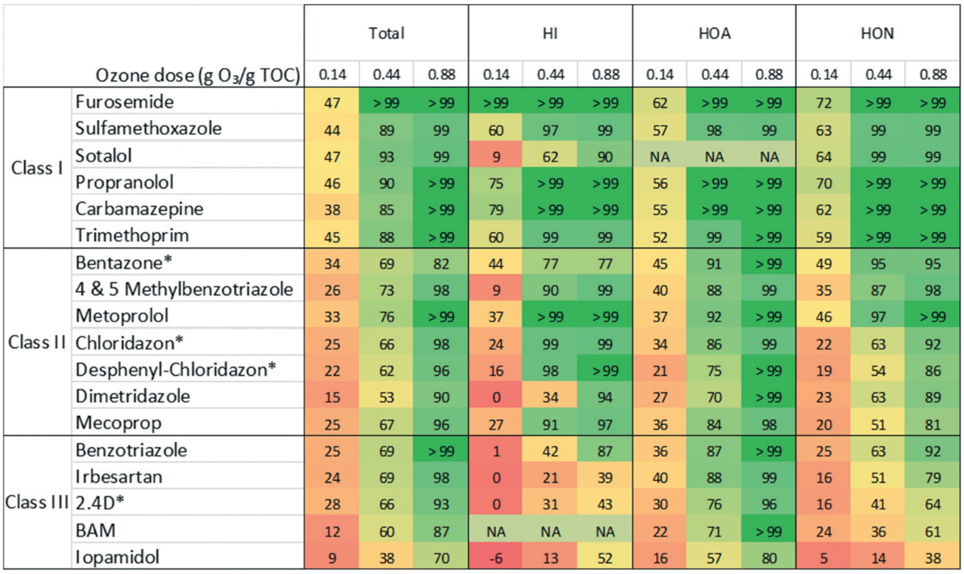
MP removal in the 'Total' sample was consistently higher in the resin experiment than in the membrane experiment. This was not expected because the 'Total' sample was taken from the same batch for both experiments. This can be explained by the difference in storage time of the water prior to the experiments, which was longer for the resin fractionation than for the membrane fractionation experiments, as discussed further in paragraph 3.3.

Observed differences in interference of MP ozonation were not consistent for all analyzed MPs. Grouping the MPs in classes based on their kO_3 values shows that



		Total			Filter			F1			F2			F3			F4		
	Ozone dose (g O_3/g TOC)	0.14	0.46	0.92	0.14	0.46	0.92	0.14	0.46	0.92	0.14	0.46	0.92	0.14	0.46	0.92	0.14	0.46	0.92
Class I	Furosemide	>99	>99	>99	>99	>99	>99	>99	>99	>99	>99	>99	>99	>99	>99	>99	>99	>99	>99
	Sulfamethoxazole	28	97	>99	21	92	>99	36	99	>99	39	98	>99	37	98	>99	>99	>99	>99
	Sotalol	25	97	98	21	95	98	41	98	>99	36	98	99	34	98	99	>99	>99	>99
	Propranolol	22	89	94	13	79	94	27	94	94	33	94	95	29	95	95	94	>99	94
	Carbamazepine	21	98	>99	14	87	>99	32	>99	>99	34	>99	>99	32	>99	>99	>99	>99	>99
	Trimethoprim	21	97	97	20	88	99	35	99	99	35	95	99	33	99	99	99	99	99
Class II	Bentazone*	5	76	>99	12	64	>99	31	>99	>99	32	96	>99	25	93	>99	>99	>99	>99
	4 & 5 Methylbenzotriazole	12	40	93	0	24	94	14	55	98	10	45	91	9	47	98	38	98	>99
	Metoprolol	7	41	93	6	32	96	9	51	98	12	42	93	8	38	98	45	98	>99
	Chloridazon*	10	31	82	-2	8	66	7	43	88	8	34	75	8	39	90	47	>99	>99
	Desphenyl-Chloridazon*	9	32	72	8	28	61	11	35	75	10	32	64	9	28	77	38	98	>99
	Dimetridazole	8	23	76	7	20	68	7	34	85	5	28	71	1	32	88	57	>99	>99
	Mecoprop	5	38	79	3	31	65	14	45	83	16	37	71	7	35	82	27	94	99
Class III	Benzotriazole	8	37	80	5	23	70	14	49	87	13	40	77	12	41	86	23	65	91
	Irbesartan	6	41	85	6	34	66	13	52	87	11	44	77	10	42	87	21	55	81
	2.4D*	7	34	70	4	30	56	10	36	74	22	36	63	11	35	73	12	38	67
	BAM	0	16	53	-5	5	37	11	30	63	7	22	47	5	17	61	4	25	52
	Iopamidol	3	21	48	4	16	29	-2	17	48	4	20	40	-6	20	48	4	11	34

Figure 2. Heatmap with micropollutant removal (%) at three different ozone doses (0.14, 0.45 and 0.93 g O_3/g TOC) in the size fractions. Micropollutants were divided in three classes: class I – high ozone reactivity ($kO_3 > 10^4$ M^{-1} s^{-1}), class II – medium ozone reactivity ($10^2 > kO_3 > 10^4$ M^{-1} s^{-1}) and class III – low ozone reactivity ($kO_3 < 10^2$ M^{-1} s^{-1}). The color scale is from red (0% removal) to green (100% removal). For micropollutants with an *, kO_3 values were not found in literature so the division of these compounds into the classes is solely based on the results of our study.



		Total			HI			HOA			HON		
	Ozone dose (g O_3/g TOC)	0.14	0.44	0.88	0.14	0.44	0.88	0.14	0.44	0.88	0.14	0.44	0.88
Class I	Furosemide	47	>99	>99	>99	>99	>99	62	>99	>99	72	>99	>99
	Sulfamethoxazole	44	89	99	60	97	99	57	98	99	63	99	99
	Sotalol	47	93	99	9	62	90	NA	NA	NA	64	99	99
	Propranolol	46	90	>99	75	>99	>99	56	>99	>99	70	>99	>99
	Carbamazepine	38	85	>99	79	>99	>99	55	>99	>99	62	>99	>99
	Trimethoprim	45	88	>99	60	99	99	52	99	>99	59	>99	>99
Class II	Bentazone*	34	69	82	44	77	77	45	91	>99	49	95	95
	4 & 5 Methylbenzotriazole	26	73	98	9	90	99	40	88	99	35	87	98
	Metoprolol	33	76	>99	37	>99	>99	37	92	>99	46	97	>99
	Chloridazon*	25	66	98	24	99	99	34	86	99	22	63	92
	Desphenyl-Chloridazon*	22	62	96	16	98	>99	21	75	>99	19	54	86
	Dimetridazole	15	53	90	0	34	94	27	70	>99	23	63	89
	Mecoprop	25	67	96	27	91	97	36	84	98	20	51	81
Class III	Benzotriazole	25	69	>99	1	42	87	36	87	>99	25	63	92
	Irbesartan	24	69	98	0	21	39	40	88	99	16	51	79
	2.4D*	28	66	93	0	31	43	30	76	96	16	41	64
	BAM	12	60	87	NA	NA	NA	22	71	>99	24	36	61
	Iopamidol	9	38	70	-6	13	52	16	57	80	5	14	38

Figure 3. Heatmap with micropollutant removal (%) at three different ozone doses (0.14, 0.45 and 0.93 g O_3/g TOC) in the resin fractions. Micropollutants were divided in three classes: class I – high ozone reactivity ($kO_3 > 10^4\ M^{-1}\ s^{-1}$), class II – medium ozone reactivity ($10^2 > kO_3 > 10^4\ M^{-1}\ s^{-1}$) and class III – low ozone reactivity ($kO_3 < 10^2\ M^{-1}\ s^{-1}$). The color scale is from red (0% removal) to green (100% removal). For micropollutants with an *, kO_3 values were not found in literature so the division of these compounds into the classes is solely based on the results of our study.

EfOM fractions interfere only with MPs in specific classes. To illustrate, differences in interference of the smallest size fraction (F4) were only observed for class I and class II MPs, while interference in F4 was similar to interference in the fraction 'Total' for class III MPs (Figure 2). Additionally, differences in interference observed in the resin fractions HON and HI were only observed for class II and class III MPs, respectively (Figure 3). This means that the interference of OM during ozonation of MPs does not only depend on the type of OM, but also on the ozone reactivity of the MPs themselves.

Uncertainties introduced in the different experimental steps were less than 5% for the individual steps. TOC recoveries of the fractionation steps were 100% (102% and 97%), which means that OM loss during the fractionation procedures was negligible. For the ozonation step, the standard deviation in the measured ozone dose was always less than 5% of the applied dose (Table B3, Appendix B). Finally, the average R2 of the standard curves for MP measurements were close to 1 (0.996 for membrane and 0.994 for the resin fractions), illustrating that the MP quantification is reliable. Finally, the different ozone doses served as replicates for each other in the ozonation and analysis steps and confirm the observed differences between the fractions.

Generally, only the quantity of EfOM is used as indication for the interference of EfOM with MP ozonation. To illustrate, EfOM quantity (DOC) is often used to determine the required ozone dose (Hansen et al. 2016a; Lee et al. 2013; Nilsson et al. 2017). Our results show that also the type of EfOM is important to consider for the ozonation of MPs. For example, class I and class II MP removal was over 3 times higher in the smallest membrane fraction (F4) compared to the membrane fraction 'Total' (Figure 2). Furthermore, in the resin fractions, class III MP removal was 1.3 lower for HON and 2 times lower for HI, when compared to the 'Total'. This shows that, at the same DOC concentration, different types of OM have different interference with MP ozonation. Therefore, additional research is needed into the variations of EfOM type in WWTP effluents, for example, spatial and temporal variation, and their effect on MP ozonation.

Understanding of the complex EfOM in effluents can confirm which OM fractions and characteristics interfere with the ozonation of which MPs. For example, WWTP effluent can be screened for the type and characteristics of EfOM to decide whether the effluent is suitable for ozone treatment, or other treatment should be considered. Moreover, insight in the characteristics of highly interfering EfOM can be used to develop online sensors to control ozone dosing and prevent over- and underdosing. Finally, this insight can aid the optimization of treatments preceding ozonation treatment, e.g. conventional WWTPs or small specialized treatment modules. A pre-treatment that reduces the most interfering OM fractions and characteristics, will result in a lower energy and cost demand for the ozone treatment.

Organic matter characteristics

Three parameters were used to characterize the EfOM in the analyzed fractions: specific UV absorbance at 254 nm (SUVA) as indication for double bonds and aromatic compounds, fluorescence as indication for humic- and fulvic-like organics and protein-like compounds (Carstea et al. 2016), and COD as indication for total oxidizable potential in the samples. In addition to the three EfOM parameters, we analyzed nitrite because it can scavenge ozone and affect MP removal (Nilsson et al. 2017). We aim to use these analyses to get insight in the compositional differences of the fractions.

SUVA

SUVA correlated well to the applied ozone dose, showing a decrease with increase in ozone dose in all fractions (Figure 4). This indicates that SUVA values are a strong tool to monitor and screen ozone reactions, which is in line with other studies (Bahr et al. 2007; Westerhoff et al. 1999; Wittmer et al. 2015). The size fraction 'Total' showed 1.8 times higher SUVA values than the resin fraction 'Total'. The most likely reason for this was instabilities in the TOC measurement, used for the dilutions of the fractions, as explained further in paragraph 3.4.

Similar SUVA values of 2.4 ± 0.14 L/mg TOC/m were found in most size fractions at the zero ozone doses. The smallest fraction, F4 with compounds smaller than 1 kDa, was the only exception to this and showed a lower SUVA of 0.19 L/mg TOC/m. Another study that used membranes to fractionated four different WWTP effluent found similar SUVA values, but did not find lower SUVA values in their smaller than 1 kDa fractions (Gonzales, Peña, and Rosario-Ortiz 2012). This indicates that the nature of the smaller than 1 kDa fraction in our study is very different from the respective fractions of (Gonzales, Peña, and Rosario-Ortiz 2012). An explanation for this could be different source waters for the WWTPs from which the effluents were taken.

The resin fractions 'Total', HI and HOA showed similar SUVA values around 1.3 L/mg TOC/m. The HON fraction showed a lower SUVA of 0.39 L/mg TOC/m and also hardly any decrease in SUVA with increasing ozone dose. Qi et al. (2018) also found that SUVA of the HON fraction does not change after ozonation. This indicates that UV_{254} absorbing compounds, for example, aromatic compounds, in the HON fraction of WWTP effluents generally are not reactive with ozone, unlike most other UV_{254} absorbing EfOM (Stapf, Miehe, and Jekel 2016).

Fluorescence

The highest fluorescence was found in region III and region V in most samples (Figure 5). These regions indicate the presence of humic- and fulvic-like compounds, respectively (Chen et al. 2003). None of the analyzed samples showed fluorescence around in region I, and little fluorescence was observed in regions II and IV, this indicates the absence of protein-like compounds (Carstea et al. 2016). A clear decrease in fluorescence with increasing ozone dose was found in both the size fractions and the resin fractions (Figure B6, B7 and B8 in Appendix B).

Approximately 1.2 times higher fluorescence values were found in the resin fraction 'Total' compared to the size fraction 'Total'. This difference could be caused by lower SUVA values in the size fractions (Figure 5).

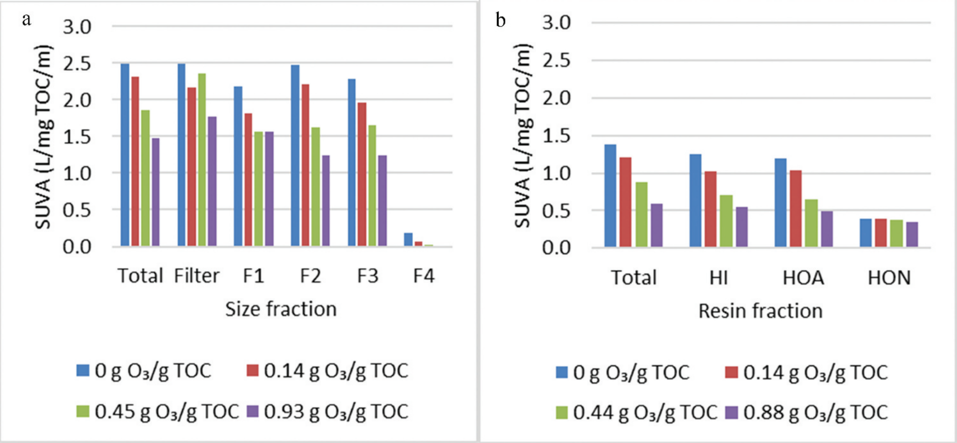


Figure 4. SUVA measurements in different effluent organic matter fractions at four ozone doses for the size fractions (A) and resin fractions (B).

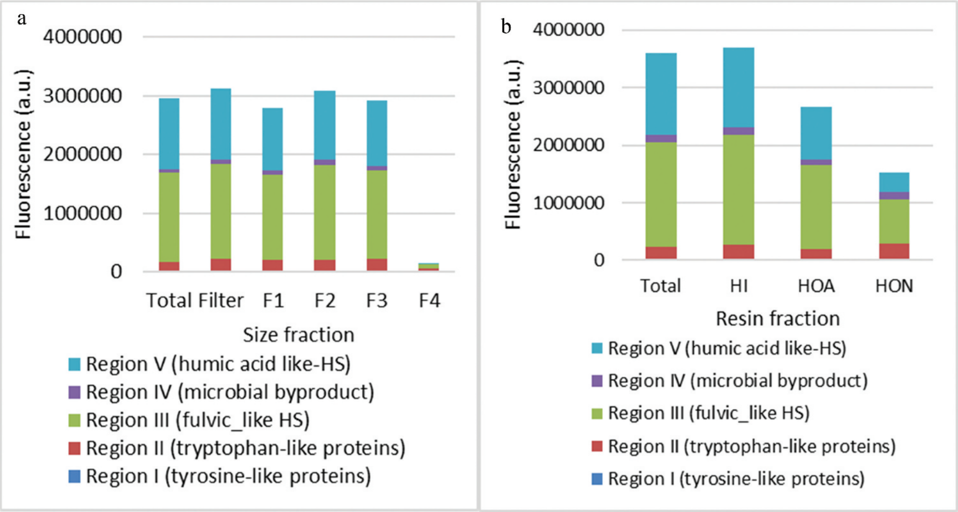


Figure 5. Fluorescence measurements in the size fractions (A) and resin fractions (B) without ozone addition.

Lower SUVA causes a lower inner filter effect and therefore higher fluorescence values in the resin fractions. The inner filter effect is absorption of part of the emitted fluorescence during fluorescence measurement by particles or molecules in the sample. This causes the measured fluorescence to be lower than the actual fluorescence of a sample. The inner filter effect is stronger in samples with high absorption values (Kubista et al. 1994).

Most non-ozonized size fractions showed similar fluorescence intensities (Figure 5). The smallest size fraction (F4) is the only exception and shows almost no fluorescence. For the resin fractions at zero ozone doses, 'Total' and HI showed similar fluorescence intensities. Organic matter in the HOA fraction showed lower fluorescence, mainly at the humic-like compounds peak, and the HON fraction showed lower fulvic- and humic-like content than the 'Total' and the HI. The low fluorescence intensities in size fraction F4 and resin fractions HON and HOA indicate that these three fractions contain less fulvic- and humic-like compounds than the other studied fractions.

We observed a decrease in SUVA with increasing ozone dose in almost all fractions (Figure 4). This should also have resulted in a decrease in inner filter effect and therefore an increase in fluorescence. However, the opposite was found: a decrease in fluorescence with increasing ozone dose (Figure B7, Appendix B). This indicates that fluorescent groups are faster depleted than UV$_{254}$ absorbing groups and therefore either less abundant or more reactive with ozone than UV$_{254}$ absorbing groups.

COD

COD decreased with ozone dose for all size and resin fractions except for the size fraction 'Filter' (Figure 6). The observed decrease in COD was similar to the absolute ozone concentration dosed (0.5, 1.6 and 3.3 mg O$_3$ /L relating to the low medium and high doses, respectively). Approximately 2.3 times lower COD values in the resin fraction 'Total' than in the size fraction 'Total'. This is probably due to instabilities in the NPOC measurement used for the dilutions as explained in paragraph 3.3 – SUVA.

A more than three times higher COD was measured in the size fraction 'Filter' at the highest ozone dose compared to the zero ozone dose. This COD value of 35 mg O$_2$/L was confirmed by duplicate measurements at different days by different people, and cannot be explained. Therefore, this value is not presented in Figure 6.

COD measured in the resin fraction HON was approximately two times higher than in the 'Total', HI and HOA fractions, indicating that the HON fraction contains many unsaturated groups that have higher COD. This is because more saturated organic molecules, with less double bonds, have higher COD values than unsaturated groups. The low saturation in the HON fraction is confirmed by the low SUVA values of this fraction (Figure 4), as SUVA mainly detects saturated bonds, for example, in aromatic groups.

Nitrite

A rapid decrease of nitrite concentrations was observed with increasing ozone dose in the size fractions (Figure 7). In all size fractions except 'Filter', nitrite was removed by ozonation to below the detection limit of 0.051 mg NO$_2$/L at the highest ozone doses. Surprisingly, nitrite concentrations in the smallest size fraction (F4) were below the detection limit at the zero ozone dose. We did not expect that the naturally present

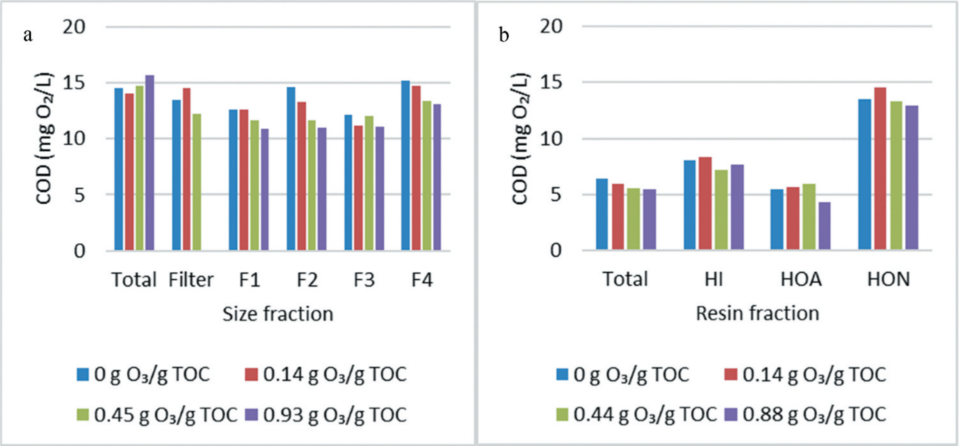


Figure 6. COD measurements in different effluent organic matter fractions at four ozone doses for the size fractions (A) and resin fractions (B). For the size fractions, several samples were measured twice to confirm the stability of the analysis, averages are presented.

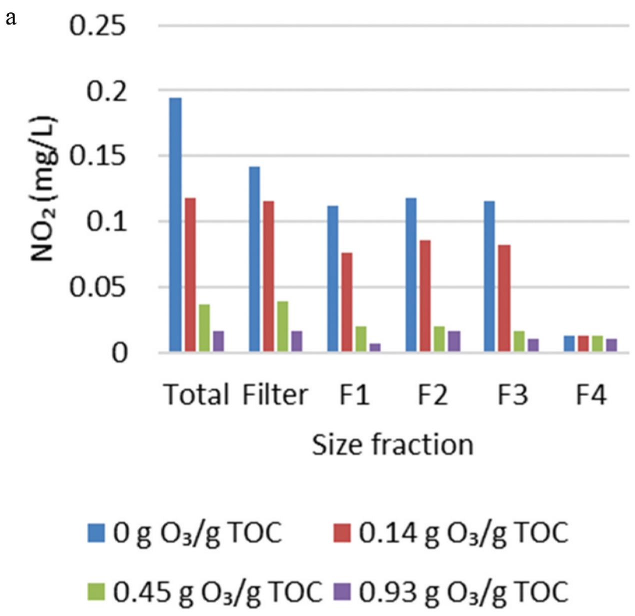


Figure 7. Nitrite measurements in different size fractions at four ozone doses. Results for the resin fractions are not shown because they were all below the detection limit of 0.05 mg NO_2/L.

nitrite would be rejected by the membrane with cutoff 1.08 kDa since nitrite molecules are more than 20 times smaller (0.046 kDa). Possibly, nitrite was rejected due to interactions of nitrite with positively charged compounds.

There are compounds that have a stronger affinity for ozone than nitrite. At the lowest ozone dose of 0.14 g O_3 /g TOC or 0.5 mg O_3/L, not all nitrite was removed from the fractions, even though 0.05 mg O_3/L would theoretically be sufficient for the complete oxidation of the nitrite that was present. This indicates that ozone reacts first with other compounds in the effluent, before reacting with nitrite. These other compounds are most likely organic because a decrease in SUVA was also observed at the lowest ozone dose (Figure 4). Moreover, reduction in MP concentrations was also observed at the lowest ozone dose (Figures 2 and Figure 3). After reaction with these other compounds, nitrite is completely removed, as was observed at the two highest ozone doses.

Nitrite levels in all of the resin fractions were below the detection limit of 0.05 mg NO_2/L. We assume that this lack of nitrite in the resin fractions is caused by longer storage time of the effluent before use. Samples for the resin and membrane fractionation experiments were taken from the same batch that was stored at 4 °C. The resin experiment was done three months after the membrane experiment, during this time, biological nitrification depleted all nitrite in the resin fractionation samples.

LC-OCD

The size fractions were further analyzed using LC-OCD to quantify biopolymers, chromatographic DOC, hydrophobic organic carbon, humic acids, low molecular weight acids and low molecular weight neutrals (Figure B9, Appendix B). No trends in any of these components with increasing ozone dose were observed. The smallest size fraction F4 showed the most differences with the other analyzed fractions at the zero ozone doses. This fraction contained very few biopolymers: 28 μg C/L in F4 compared to 310 ± 85 μg C/L for the other size fractions, very few humic acids: 41 μg C/L in F4 compared to 1890 ± 208 μg C/L for the other size fractions and many low molecular weight neutrals: 2560 μg C/L in F4 compared to 650 ± 98 μg C/L for the other size fractions. Biopolymers and humic acids are large molecules that were retained by the 1 kDa membrane, while the small low molecular weight neutrals could easier pass through (Huber et al. 2011). The hydrophobic organic carbon was approximately 12% of the total DOC of the unfractionated effluent, which is typical for EfOM (Huber et al. 2011).

Relations between MP removal and EfOM characteristics

The size fraction F4 and the resin fraction HON showed the largest differences in MP removal and concentrations of the other parameters at zero ozone doses compared to the other fractions. The size fraction 'Total' and the resin fraction 'Total' showed consistent differences in the measured parameters, which was not expected because they were taken from the same effluent. These three fractions are further analyzed below combining all measured parameters to give more insight in their constituents. Finally, we analyze which of the measured parameters can be used to explain the observed differences in MP removal.

Totals

We expected both 'Total' samples to behave similarly because both samples were taken from the same batch of effluent, stored in a 4 °C room. The size fraction 'Total' showed more than three times higher fluorescence and SUVA values and more than two times lower COD values than the resin fraction 'Total'. We did not expect these differences because both 'Total' samples were taken from the same batch. We expect that these differences are due to the difference in storage time before the experiments as also discussed in paragraph 3.3.

Size fraction F4

Higher removal of class I and II MP's was observed in the smallest size fraction (F4) compared to the other fractions. This indicates that the EfOM in this fraction interferes less with ozonation of ozone reactive MPs than the EfOM in other fractions. Organic matter in F4 also showed very low fluorescence, SUVA and nitrite, while the OM in this fraction had similar COD levels as other size fractions. LC-OCD analysis showed that this fraction contains mainly low molecular weight neutrals and no humic acids or biopolymers. The lack of humic compounds is confirmed by the SUVA and fluorescence measurements. Low SUVA values indicate the absence of aromatic groups, which are unsaturated (Westerhoff et al. 1999). Because F4 has similar overall saturation as other size fractions, but a lower aromaticity content, this fraction must contain other types of unsaturated groups, such as alkenes.

Another study that used membrane fractionation on four different effluents found that the EfOM fraction <1 kDa has a higher ozone reaction coefficient than the other fractions of <10 kDa, <5 kDa and <3 kDa (Gonzales, Peña, and Rosario-Ortiz 2012). Our study shows a high MP removal in the <1 kDa fraction (F4). This indicates that the highly reactive EfOM in this fraction stimulates MP ozonation. However, the SUVA values of the <1 kDa in our study were lower than those of Gonzales, Peña, and Rosario-Ortiz (2012), 0.2 and 1.8 ± 0.22 L/mg C/m, respectively. This indicates that the OM in the <1kDa fraction in our study was different from that in the respective fractions of Gonzales, Peña, and Rosario-Ortiz (2012).

Resin fraction HON

The OM in the resin fraction HON has low fluorescence and SUVA, and high COD values. SUVA in the HON fraction also did not decrease with increasing ozone dose as was seen in the other fractions. Despite this, we did not observe high MP removal in the HON fraction, which was expected because of the low fluorescence and SUVA values. The high COD values indicate that OM in this fraction contains OM with a lower level of saturation, which matches with the low SUVA values. Another study that ozonated and fractionated WWTP effluent also found low and stable SUVA values in the HON fraction (Qi et al. 2018). P. Jin et al. (2016) found a more than twofold decrease in UV_{254} absorbance at their lowest ozone dose of 0.42 g O_3/g TOC and stable SUVA with higher ozone doses. This shows that the HON fraction is made up of a very different type of OM than the other fractions, while it only shows slight differences in MP removal.

Explaining parameters

Because the smallest size fraction (F4) showed low interference with the ozonation of MPs and low SUVA, fluorescence and nitrite values, all three parameters can be used to explain the low interference in this fraction. This indicates that effluents with low fluorescence, SUVA and nitrite values need less ozone to reach the same MP removal. Moreover, other studies find that UV_{254} absorbing compounds and nitrite are highly reactive with ozone and are therefore likely to interfere with MP ozonation (Nilsson et al. 2017; Stapf, Miehe, and Jekel 2016). On the other hand, all resin fractions showed nitrite levels below detection limit and MP removal in these fractions was not as high as in F4 of the size fractions. Therefore, our results indicate that the OM characteristics have a larger effect on MP ozonation than nitrite concentrations. Furthermore, fluorescence values in the resin fraction 'Total' were approximately two times higher than fluorescence values in the size fraction 'Total', whereas MP removal was higher in the resin fraction 'Total'. This indicates that fluorescence is not a suitable parameter to explain the observed differences in MP removal. Finally, low

SUVA correlates with high MP removal in most samples. The only exception to this rule is the resin fraction HON, that had low SUVA values and did not have lower MP removal other resin fractions. Therefore, we conclude that none of the measured parameters are sufficient to predict all variation in MP removal by ozonation.

Conclusions

In general, the quantity of organic matter is important for ozonation of micropollutants. Our study shows that micropollutant removal is also affected by the type of organic matter (different organic matter fractions). Comparing all size fractions, the smallest size fraction (<1 kDa) had the lowest interference with the ozonation of micropollutants. For the resin fractions, hydrophobic neutrals and hydrophilics had higher interference than other resin fractions. This shows that size and resin fractionation give insight in the type of organic matter, which provides understanding in the interference of organic matter during micropollutant ozonation. Further research on effluents of various matrix compositions is needed to study the consistency of this interference in effluents of different origins.

The degree of interference by organic matter fractions depends on the ozone rate constants of individual micropollutants. For micropollutants with high and medium ozone rate constants, the smallest size fraction (<1 kDa) had low interference on their removal. This and other size fractions had the same interference for micropollutants with low ozone rate constants. The higher interference in the resin fractions hydrophobic neutrals and hydrophilics only occurred for micropollutants with medium and high ozone rate constants, respectively. Therefore, when studying the interference of the type of organic matter on the ozonation of micropollutants, micropollutants must be grouped based on their ozone rate constants.

The four parameters: specific UV absorbance at 254 nm, fluorescence, chemical oxygen demand or nitrite were used to elucidate the composition of organic matter in the fractions. Still, these four parameters were insufficient to predict the differences in micropollutant removal in the various fractions. Therefore, other characterization methods are needed to understand and predict the interference of organic matter with micropollutant ozonation. To conclude, understanding of the type of organic matter in wastewater is essential to optimize micropollutant ozonation from, for example, wastewater treatment plant effluent. Insight in the type of organic matter can be used to decide which effluents are suitable to implement ozonation and to determine the required ozone dose for specific effluents.

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Declaration of interests

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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