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Removal of Organic Micropollutants and Microplastics via Ozonation Followed by Granular Activated Carbon Filtration

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Abstract: Discharge from Wastewater Treatment Plants (WWTPs) can result in the emission of organic micropollutants (OMPs) and microplastics (MPs) into the aquatic environment. To prevent this harmful release, a pilot plant consisting of an ozonation followed by a granular activated carbon (GAC) filter was operated at a WWTP in Germany, and its side-effects on the concentrations of nitrogen (N) and phosphorous (P) compounds were measured. Over 80% of OMPs and transformation products were removed during the operating time (around 6000 bed volumes) no matter the ozone dose (from around 0.1 to 0.5 mg_{O3}/mg_{DOC}), except for Diatrizoic acid, whose breakthrough appeared at 3500 BV. Formation of the oxidation by-product, NDMA, increased with higher ozone doses, but the concentration remained below 100 ng/L. Bromate was formed at a higher ozone dose (>0.4 mg_{O3}/mg_{DOC}) but at a low concentration—below 10 µg/L. The MP particles detected in the inflow (PE, SBR, PP, and PS) were effectively eliminated to a high degree, with a removal rate of at least 92%. Carbon parameters (COD, DOC, and SAC_{254}) were removed further by the pilot plant, but to different extents. As expected, nitrate was formed during ozonation, while nitrite's concentration decreased. Further, nitrite decreased and nitrate increased within the GAC filter, while ammonium was eliminated by at least 90%. Total P concentration decreased after the pilot, but the concentration of PO_4-P increased.

Keywords: advanced oxidation process; emerging pollutants; microplastics; organic trace substances; wastewater effluent; adsorption; oxidation by-products; transformation products; bromate; NDMA

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1. Introduction

Wastewater Treatment Plants (WWTPs) are identified as point sources of organic micropollutants and microplastics in receiving waters [1–3], as conventional WWTPs are not designed to eliminate these substances. The term organic micropollutants (OMPs) describes substances that occur in very low concentrations (µg/L) in wastewater, such as personal care products, hormones, pharmaceuticals, and pesticides. Emitted by WWTP effluents, they can trigger harmful effects on freshwater fauna in terms of growth and migration [1]. Wastewater-derived OMPs have been widely detected in aquatic ecosystems, as many of them are polar, non-volatile, and poorly biodegradable, and are subject to governmental regulation. According to the adopted text from the Urban Wastewater Treatment Directive (UWWTD 91/271, version from 10 April 2024) of the European Commission, an OMP removal step will be mandatory for all large WWTPs (≥150,000 population equivalent) and additionally for certain WWTPs in water-sensitive areas with ≥10,000 population equivalent after 2045 [4]. The elimination of micropollutants will be determined according to the size of the plant using up to two samples per month and should not go under 80%. Therefore, there is an urgent need to implement advanced quaternary treatment for OMP removal at WWTPs.

Microplastics (MPs) are another material group of concern in aquatic systems. In comparison to OMPs, MPs are eliminated to a high extent in conventional WWTPs (>95%) [5,6]. However, the remaining parts can still be harmful to the fauna because they degrade through weathering and break down into smaller so-called nanoplastics [7]. MPs are defined as solid thermoplastic polymer particles (as the main component) with any size between 1 and 1000 µm, including chemical additives [8]. Several incubation studies have shown that the presence of MPs in aquatic environments and soils can affect multiple biological processes, e.g., reproduction, metabolism, and growth, negatively [9–12]. However, research in this field is still in its early stages, and assessing the toxicity of the polymer components in MPs, compared to the additives, requires further investigations. MPs are probably ingested by different aquatic species along freshwater food chains and in turn jam their gastrointestinal tracts [13,14]. In addition, MPs can operate as vectors for other pollutant groups such as persistent organic pollutants, heavy metals [15,16], and on-top organic micropollutants [17].

As OMPs are not removed to a high extent at conventional WWTPs, various processes have been developed and tested over the last 20 years to remove OMPs from wastewater. Oxidative processes such as ozonation and adsorption on granular activated carbon (GAC) have been shown to be promising and are already operated on a full scale in Switzerland and Germany (two in Germany, one in Switzerland), but are rarely used in combination [18,19]. In a certain range, the elimination of OMPs can be increased by adding a higher amount of ozone to the water. Generally, ozonation does not lead to complete mineralization. Depending on the ozone dose, oxidation by-products are produced to different extents, which can be toxic to the environment [20]. For example, 2,6-dichloroaniline, which occurs during the ozonation of Diclofenac, is classified as toxic to aquatic life by the European Chemical Agency [21]. N-Nitrosodimethylamine (NDMA) is a well-known oxidation by-product from the group of Nitrosamines. It is cancerogenic and comes from several precursors but can be eliminated through biological post-treatment [22]. On the contrary, Bromate, which can be formed at high ozone doses ($>0.4\ \mathrm{mg_{O3}/mg_{DOC}}$) in the presence of relevant concentrations of Bromide (>100 µg/L) [20,23–25], is not removed by post-treatment [26]. Bromate is possibly carcinogenic to humans as well, has a drinking water limit of 10 µg/L [27,28], and has been proven to negatively affect the reproduction rate of model planktonic organisms [28]. GAC is usually installed in fixed-bed filters and can serve as post-treatment. Wastewater components can be adsorbed onto the large surface of activated carbon and are thus removed from the water at a high yield. If the cleaning performance of OMP adsorption decreases with the loading of the GAC filter, the activated carbon must be replaced and reactivated.

Treating the WWTP effluent with a combination of oxidative (ozonation) and subsequent adsorptive (GAC) processes is an effective setup to degrade and eliminate OMPs [29–31]. In addition to the increased broadband effect, the combination of the two processes has further benefits. Besides the additional adsorption of OMPs in wastewater effluent, GAC filters can also remove several transformation products resulting from ozonation, like the nitrosamines group [32,33]. Thus, lower ozone doses (around 0.1–0.3 $\mathrm{mg_{O3}/mg_{DOC}}$ instead of 0.6–0.8 $\mathrm{mg_{O3}/mg_{DOC}}$ for stand-alone ozonation) can be used [34], which can prevent the formation of unwanted toxic by-products such as bromate and NDMA. Micropollutant adsorption on activated carbon also becomes more efficient with pre-ozonation, making the organic background matrix more hydrophilic [11,12]. At the same time, ozonation enriches the water with oxygen and degradable organic substances, both available for the formation of a biofilm. Biological processes in the GAC filter contribute to further removal of micropollutants and their transformations products too [35]. Furthermore, prior ozonation extends the lifetime of the GAC, which is advantageous since reactivation and replacement of activated carbon is expensive and increases the carbon footprint of the usage of GAC [36]. Böhler et al. [37] successfully conducted micropollutant removal by a GAC filter with prior low-dose ozonation after 80,000 treated-bed volumes. This is around four factors more than using stand-alone GAC filters [38].

The particulate nature of MPs favors their mechanical removal through filtration or floatation [39]. Large-scale GAC filters in operation at WWTPs demonstrate high removal potential of total solids (81–87%) [40], indicating a positive effect on MPs removal as well. Moreover, the ozonation of MP particles with organic matter coatings prior to GAC filtration can lead to further reduction in the surface charge of these particles [41], thereby enhancing their adsorption. Although WWTPs are not the primary transport pathway for MPs, where most are retained and accumulated in sewage sludge (>97%) [3,42,43], further treatment steps have high potential for reducing the remaining MP load preventing the production of nanoplastics in freshwater after release of the WWTP-treated water into the environment.

The adopted text from the Urban Wastewater Treatment Directive outlines that nitrogen (N) and phosphorus (P) limits will be strengthened for large treatment plants effluents ($\geq$150,000 population equivalents) [4]. Another question therefore arises as to whether an additional treatment stage for OMP and MP elimination can still have a synergistic effect and further remove N and P components as well as carbon (C) parameters further. During ozonation, nitrite is known to react quickly, forming nitrate (NO_3^-) and oxygen (O_2) as major final products [44]. As it reacts in a ratio of about 1 g O_3 per g NO_2^- [31], an additional ozone input is needed to oxidize nitrite and ensure sufficient ozone for the oxidation of OMPs. Therefore, a sometimes recommended approach is to correct the ozone dose for nitrite consumption [29,31,45]. For ammonium, ozonation has had no or only a slight influence [46,47], or a decrease was monitored [48,49]. Phosphorus (P) parameters are not studied in detail, but total P-concentration seems not to change during ozonation [46,47]. Carbon parameters (C) such as spectral absorption at 254 nm (SAC_{254}) and dissolved organic carbon (DOC) are, on the contrary, well studied during ozonation [29,50,51], but the chemical oxygen demand (COD) is studied more rarely [50]. As OMPs are a (small) part of these sum parameters, DOC is used to normalize the ozone dosage (mg_{O3}/mg_{DOC}). However, the SAC_{254} is often applied instead of the DOC as substitute parameter, e.g., for plant control, because it is easy to measure in-line and reduction of SAC_{254} correlates well with the elimination of micropollutants through ozonation [52–55]. In GAC filter treatment studies, DOC is also frequently measured and reduced up to 50% by adsorption and biodegradation [48,49,56–58]. SAC_{254} is reduced further in GAC filter treatment [58], and again, SAC_{254} is a suitable control parameter for GAC filters breakthrough as the correlation with micropollutants is high [56]. Ammonium concentrations can be reduced better through nitrification in the GAC filter if water is oxygen rich after an ozonation [46,48,49]. Nitrite concentrations can both de- or increase through GAC filter treatment due to either further or incomplete nitrification [46,48,49]. GAC filters are also used for P-elimination in combination with precipitants. Then, low P concentrations can be reached in the effluent of the GAC filter [59,60]. No negative influence on precipitation through ozonation has been noticed [61].

This paper presents the performance of ozonation followed by GAC filtration in a pilot plant installed on a German WWTP, operated primarily to remove OMP, for removing MP and conventional C, N, and P parameters. In addition, this paper also presents the results of the formation and potential removal of toxic by-products formed during ozonation (bromate, NDMA) and of one transformation product (2,6-Dichloraniline) from the OMP Diclofenac.

OMP elimination is already well studied in the combination of ozonation and GAC filtration [31,33,58,62,63], but only a few studies have reported the effects on oxidation by-products and C, N, and P parameters as well [49,64,65]. In particular, synergy effects on N and P compounds will become relevant regarding stricter demands in the Urban Wastewater Treatment Directive in the future [4]. Furthermore, no literature has been found to date regarding the removal of MP through both ozonation and GAC filter treatment steps. Hence, the combined removal of both substance groups OMP and MP (1–1000 µm) as well as the side effect removal of C, N, and P parameters using ozonation followed by GAC-filtration is very promising and has not yet been investigated in parallel.

2. Materials and Methods

2.1. Experimental Site

2.1.1. Pilot Plant Set-Up and Wastewater Effluent

A pilot plant, consisting of ozonation and GAC filtration for the removal of OMP was set up at the WWTP Kaiserslautern in Germany as part of the Eloise Project [31]. This pilot plant was also used to investigate the elimination of micro-plastics and C, N, and P parameters. The WWTP is designed for a population equivalent of 240,000 and treats the wastewater from the city and the surrounding area of Kaiserslautern in a mechanical and biological treatment system with targeted removal of nitrogen and phosphorous. Two hospitals are located in the catchment area, and the city is predominantly drained in a combined sewer system.

The influent of the pilot plant was supplied from the effluent of the secondary clarifiers of the WWTP. Main characteristics are listed in Table 1. Water temperature in the effluent was between approx. 11.5 and 19 °C in the sampling period in May to October 2021 (measured every 2 h, *n* = 2207), while the pH was between 6.99 and 7.93 (*n* = 19). The effluent was transported to the pilot plant with a submerged pump through a by-pass hose with an average flow rate of 1 m^3/h to a first buffer tank (Tank 1 in Figure 1).

Table 1. Concentration of wastewater parameters in the effluent of the secondary clarifiers of the WWTP Kaiserslautern, from May to October 2021. Number of samplings: 22 (only 20 for DOC, only 18 for P_{tot} and PO_4-P, only 19 for pH), 24 h composite samples, time- and flow-proportional. Temperature measured by Stadtentwässerung Kaiserslautern AöR, *n* = 2207 in May–October 2021, every 2 h.

Parameter	Average Concentration ± Standard Deviation	Parameter	Average Concentration ± Standard Deviation
DOC	7.50 ± 0.82 mg/L	COD	20.73 ± 3.63 mg/L
SAC_{254}	13.30 ± 3.22 m^{-1}	NO_3–N	3.04 ± 1.40 mg/L
NO_2–N	0.20 ± 0.08 mg/L	NH_4–N	1.38 ± 0.65 mg/L
P_{tot}	0.27 ± 0.07 mg/L	PO_4–P	0.13 ± 0.09 mg/L
Temperature	16.5 ± 1.4 °C	pH	7.49 ± 0.25

The ozone generator (custom-made, Kaufmann Umwelttechnik GmbH, Wehr, Germany) produces ozone at a maximum rate of 6 g/h from oxygen (gas flow rate from 10 to 80 L/h) taken from oxygen bundles of 12 gas cylinders (50 L each) with a maximal pressure of 200 bar, purity ≥99.5% (Ref. I1001V12R2A001, Air Liquide Deutschland GmbH, Düsseldorf, Germany) with a silent corona discharge. A Programmable Logic Controller (PLC) panel collects data (water flow, ozone concentration in feed gas, gas temperature) and controls all sensors of the ozonation plant. The ozone is mixed with the WWTP effluent through a venturi injector (3/4″ injector from Mazzei, Bakersfield, USA, model 0684) at full flow. The pipe carrying the mixed ozone and wastewater is fed directly to an ozone reactor (cylinder with 47 cm diameter and a height of 1.6 m, about 28 L, hydraulic retention time: 1.7 min) where reactions can take place. Figure S6 in Supplementary Materials shows the fine bubbles in the column. The ozone production was regulated via the frequency with a consistent gas flow (gas flow: 31.5 ± 0.4 NL/h; ozone concentration: 25–123 g/Nm^3). Specific ozone doses ranging from 0.1 to 0.5 mg_{O3}/mg_{DOC} were targeted during the operation process. For this purpose, a constant mean DOC concentration was assumed, and a fixed amount of ozone was added to the water. Because of variations in the DOC concentrations in the WWTP effluent, specific ozone doses ranged from 0.09 to 0.53 mg_{O3}/mg_{DOC} were reached (recalculated with measured values after each experiment). However, the ozone doses presented in this paper were calculated without correcting for nitrites consumed by ozone (specific ozone dose = Transferred ozone dose/[DOC]).

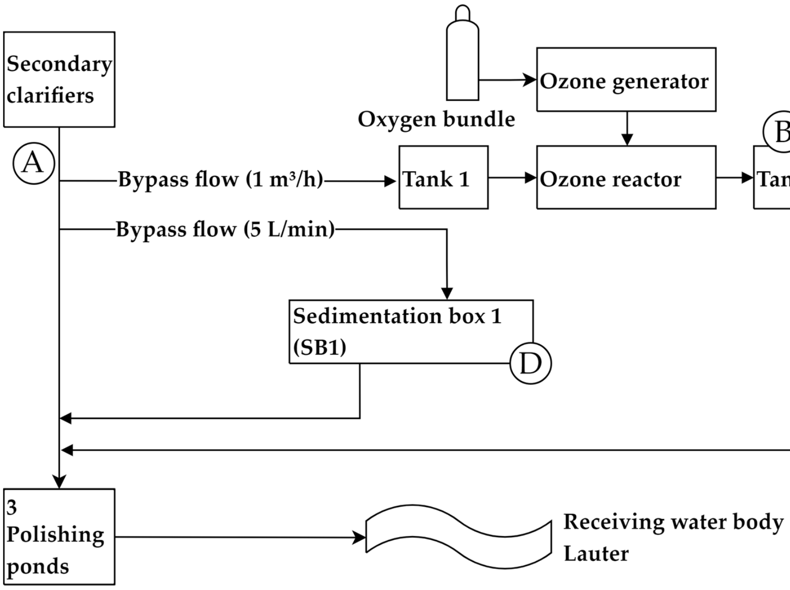

Figure 1. Scheme of pilot plant steps. A, B, C, D, and E designate the sampling points.

The ozonated wastewater is then channeled into a second tank (Tank 2 in Figure 1), which is connected to a residual ozone destructor (activated carbon). Buffer tanks 1 and 2, the ozone generator, and the ozone reactor were housed in a container that was air-conditioned at 17 °C. From tank 2, the ozonated wastewater is further pumped (BBA Pump, Model B40 BVGMC) to the subsequent GAC filter, which was located outside the container. Water flows from the top to the bottom and continuously feeds a third tank (Tank 3 in Figure 1).

The GAC filter consists of a 5.4 m-high gray PVC column (column is not transparent to avoid sun related algae growth) with an inner diameter of 488 mm (Figure S1). The GAC filter bed is 2.7 m-high and is filled with 500 L lignite and black-coal-based carbon with a grain size range of 0.60–2.36 mm (Hydraffin AR 8 × 30 Donau Carbon GmbH, Frankfurt, Germany), which is retained at the bottom by a 13-nozzle plate. A water flow of 1 m^3/h corresponds to an Empty Bed Contact Time (EBCT) of 30 minutes and a filter velocity of 5 m/h. Water flow rate, EBCT, and filter velocity varied across different experiments (see Table 2). Two pressure sensors (Cerabar M PMC51, Endress and Hauser, Weil am Rhein, Germany) continuously measure water pressure above and in the bed during all operation phases. All data are collected in a LabVIEW program (version 2016), which also controls the automatic valves, feeding pump (B40 BVGMC, BBA Pumps, Doetinchem, the Netherlands), backwashing pump (B50 BVGMC, BBA Pumps, the Netherlands), and an air compressor. In the event of filter clogging, a backwash cycle was manually initiated using filtered water from Tank 3 and compressed air upwards the column. Used backwash water was then fed back into the effluent canal of the WWTPs secondary clarifiers.

Table 2 shows the different settings of the pilot plant operated during the experiment for the removal of OMP. For each of the OMPs, one transformation product and ozone by-product (detailed pollutants that have been measured are explained in Section 2.2) were analyzed at least one time. Settings of samples taken of MP and C, N, and P parameters are also given in Table 2. The sampling strategy is described in Section 2.2.

Table 2. Operation modes of the pilot plant and overview of samples taken before and during experimental phase. OMP screening: long list of organic micropollutants analyzed for the selection of OMP (see Section 2.2), performed before experimentation time; OMP short list: short list of organic micropollutants for regular analysis during experimentation time (indicator substances); TP: transformation products; OBP: oxidation by-products; C, N, P parameters: carbon, nitrogen, and phosphorus parameters; MP: microplastics; 2012/13 marked with *.

Water Flow Rate	Ozone Dose	EBCT	Filter Velocity	Number of Samples					
$[\mathrm{m}^3/\mathrm{h}]$	$[\mathrm{mg}_{\mathrm{O3}}/\mathrm{mg}_{\mathrm{DOC}}]$	[min]	[m/h]	OMP Screening	OMP Short List	TP	OBP	C,N,P	MP
0.75	0.50	40	4.00	-	2	1	1	4	
0.75	0.20	40	4.00	-	2	1	1	5	
0.90	0.50	33	4.80	-	2	2	1	2	
0.90	0.20	33	4.80	-	2	1	1	2	
0.90	0.10	33	4.80	-	4 *	1	1	5 *	
1.10	0.20	27	5.86	-	2	-	1	2	
1.00	0.40	30	5.00	-	-	-	-	-	2
Sampling points (in accordance with Figure 1)				A	A B C	A B C	A B C	A B C	D E
Sampling process				----------24 h composite samples----------					2 to 3 weeks with sedimentation boxes
Period of sampling				March–November 2020	---------May–October 2021--------				April–May 2021
Total number of sampling				6	14	6	6	20	2

2.1.2. Monitoring and Sampling Strategy

In order to select a few OMPs for regular sampling (OMP short list) during the experimentation time (Section 2.2 explains the selection process), a long list of OMPs (screening) was analyzed six times from March to November 2020. During the experiment, sampling took place from April to October 2021 in two phases: microplastics from April to May 2021; OMP and C, N, and P parameters from May to October 2021. An overview of the sampling strategy of the experiment is given in Table 2.

Samples for OMP and C, N, and P parameters were taken at one (for OMP screening) and three sampling points (for OMP short list and C, N, and P parameters) using automatic samplers (two samplers from Maxx GmbH, Rangendingen, Germany, Model SP5 S, A and B in Figure 1; one from Endress + Hauser, Weil am Rhein, Germany, Model asp-station d 2, C in Figure 1). To ensure corresponding samples, the second sampler after ozonation (B in Figure 1) was set to start 45 min after the first sample in the effluent canal of the secondary clarifiers (A in Figure 1). The third sampler after the GAC filter (C in Figure 1) began one hour after the second sampler. The 24-hour composite samples were taken (every 30 min at 100 mL) and stored at 4 °C in each sampler before being transported in brown glass bottles for OMPs analysis and in plastics bottles for C, N, and P parameter analysis. Sampling for the OMPs and standard parameters was conducted from 28 May to 26 October 2021.

For microplastics sampling, two 3-chamber stainless-steel sedimentation boxes (SBs) (600 × 450 × 250 mm) (UGT GmbH, Müncheberg, Germany) (Figure S2) were installed to sample a bypass flow from both the effluent of secondary clarifiers and the effluent of GAC filter (Figure 1). The use of SBs enables integrative long-term sampling of solid particles in surface water streams or WWTPs effluents by directing the flow through a zigzag-shaped path against baffle plates attached to the ceiling and bottom of the SB. This design, combined with a sudden reduction in flow velocity, enhances particle retention [66]. To maximize solid particles retention in the SB, the flow rate was maintained at a maximum of 5 L/min during the sampling of both streams [67]. The ozonation plant and GAC filter were operated continuously at a flow rate of 1000 L/h (16.6 L/min) during the MP-sampling period. To achieve the recommended inflow rate of 5L/min, a 3/4″ gate valve was installed between the GAC filter and the SB (Point E in Figure 1). Additionally, a submerged pump (FlatOne 6000 INOX, T.I.P. GmbH, Waibstadt, Germany) was installed in the effluent canal of the secondary clarifiers to feed the SB at point D. A similar 3/4″ gate valve was installed between the pump and SB (D) to regulate the flow to 5 L/min [68].

The initial sampling strategy planned to feed both SBs to operate continuously over 14 days. However, due to multiple pump clogging, continuous sampling was not feasible. Instead, flow volumes into the SBs were calculated based on the operational period of the ozonation plant. As a result, average polymer concentrations were used to compare emissions and removal rates rather than the absolute polymer loads.

From 14 April to 25 May 2021, two sampling cycles were executed, lasting 15 and 14 days, respectively. During the first cycle, approximately 110 m^3 of effluent from secondary clarifiers and 115 m^3 from the GAC filter were sampled by SB_1 and SB_2. During the second cycle, SB_1 sampled approximately 127 m^3, while SB_2 sampled 75 m^3 only.

2.2. Analytical Methods and Choice of Analyzed Pollutants

2.2.1. Organic Micropollutants

In order to select OMP for the main investigations (see Figure 2) six screenings of organic micropollutants were performed in 2020 (see Table 3) using 24-hour composite samples in the effluent of the secondary clarifiers (Sample point A in Figure 1). Four samples were taken during dry weather (with <1 mm precipitation in the previous two days) and two during rainy weather. For these screenings, 47 OMPs were selected based on the A list from the micropollutants competence center Baden-Württemberg in Germany [69]. The substances include different substance groups (pharmaceuticals and metabolites, X-ray contrast media, estrogen, pesticides, corrosion inhibitors, etc.) along with additional bromide. The analyzed OMP and their concentrations are listed in Table S1.

The following aspects were considered when selecting the OMP for the short list: occurrence of the substance in samples, potential removability of the substance during ozonation and by GAC filtration, ecological relevance of the substance, key parameters from the literature for comparability of experimental results, and including a broad range of substances that are either well or poorly eliminated by ozonation and GAC filtration. Ozone by-products and transformation products formed during ozonation were additionally selected to measure their formation and possible elimination by the GAC filter.

Based on the screenings (Table S1), only substances with measured concentrations above the limit of quantification (LOQ) in at least four of the samples (2/3 of data points; (a) in Figure 2) were considered for further analysis. This excludes 12 substances from the main investigations, for example, all the perfluorinated tensides. Other substances were excluded if they did not meet at least 3 of the 5 criteria ((b)–(f) in Figure 2).

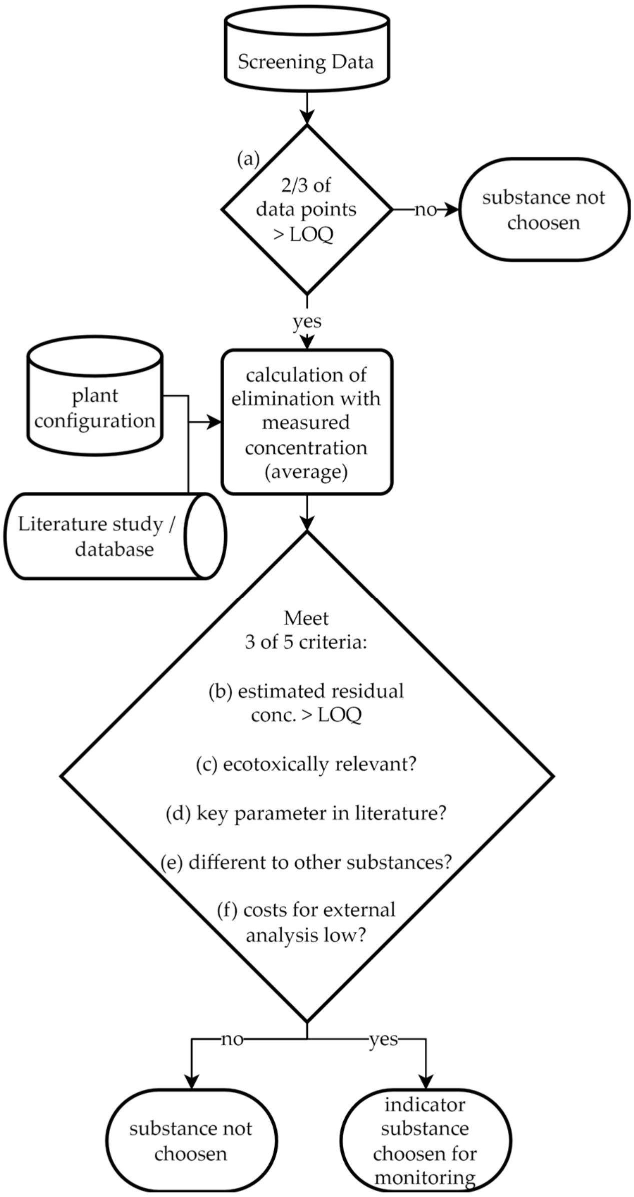

Figure 2. Decision matrix for the selection of organic micropollutants for regular screening in the pilot plant with ozonation and GAC filtration (short list) based on a broader micropollutant screening and literature data. LOQ: limit of quantification.

A literature review was conducted to collect the removal values for substances through ozonation and GAC filtration (sources see Table 3). These values and the measured average concentrations in the effluent of the secondary clarifiers from the screenings were used to calculate whether the substances remained quantifiable after ozonation or after the combination of ozonation and GAC filtration ((b) in Figure 2).

To address the ecotoxicology potential ((c) in Figure 2), the measured concentration of each substance was compared to ecotoxicological quality criteria given by stakeholders, inter alia, environmental quality norm, PNEC (Predicted No Effect Concentration), and the Watch List contaminants of emerging concern. Although measurements were conducted in a WWTP effluent, concentrations near limit values are alarming for small receiving rivers. Carbamazepine was detected in concentrations higher than an environmental quality norm [70,71], so this substance was selected for further investigations.

To place our results in the context of the literature, substances that are frequently mentioned in the literature were selected ((d) in Figure 2).

Steps (e) and (f) (Figure 2) take into account that the selection of substances should be as broad as possible, but also economically feasible. Breadth achieved by two aspects: different eliminations (refer to the literature already used in step (b)) and substances from different substance groups ((e) in Figure 2). The elimination potential for ozone and GAC was classified as good (>70%), moderate (40–70%), and low (<40%). For example, X-ray contrast media are classified as moderately eliminable through ozonation and adsorption on GAC, while Diclofenac and Carbamazepine are well eliminated in both processes (sources see Table 3).

Table 3 shows the criteria and the final list of indicator substances (OMP short list) that have been regularly measured. The pesticide Diuron was widely used in Germany as a biocide for facades, from where it is rinsed off during rain events and transported by rainwater to the WWTP, especially shortly after application [72]. Its use has been prohibited since 2011 in Germany [73] because its concentrations decrease gradually; it was found in all WWTP effluent samples from previous measurement campaigns from 2012/13 (see Table S2). As Diuron is listed as a priority substance under the European Directive 2013/39/EU [74], it was taken in the OMP short list to verify if it is still present. In addition, even though it did not meet the selection criteria, Iopromide was also included because it could be analyzed with minimal additional effort along with the other X-ray contrast media. All samples were analyzed by an external lab (Technologiezentrum Wasser Laboratory, Karlsruhe, Germany), which also conducted the screening analyses, according to [75]. The limits of quantification (LOQs) for the OMPs in the screening (Table S1) were different from the LOQ (0.02 µg/L for all OMPs) in the regular analyses of the OMP short list.

In addition, ozonation by-products and transformation products were considered and measured during the pilot plant's operation. Bromate was selected as ozonation by-product since bromide was detected at an average concentration of 114 µg/L during the screenings conducted in 2020 (Table S1). Likewise, NDMA is a well-known cancerogenic ozonation by-product that forms during the ozonation process from various substances. A widespread predecessor substance known in groundwater is DMS (N.N-Dimethylsulfamide) [22,76], and it was also selected. NDMA and DMS were regularly monitored after ozonation and downstream the GAC filter. One transformation product from diclofenac, 2,6-Dichloroaniline, was selected for monitoring because it is listed as toxic for the aquatic life and has been shown to have a higher toxicity than diclofenac and its other transformation products [21,77,78]. Desmethyl diuron (DCPMU), a transformation product of Diuron, was also measured [79]. These substances are representative of the large number of newly formed compounds that occur in the wastewater after ozonation and are known transformation products occurring in the ozonation, which impact human health and aquatic life. They were also analyzed by the same external lab that analyzed the OMP (Technologiezentrum Wasser Laboratory, Karlsruhe, Germany). Table S3 gives details about analytical methods and LOQs of these substances.

Table 3. Result and criteria for the selection of organic micropollutant indicator substances for the pilot plant based on the screenings in 2020 and 2012/13 (2012/13 marked with *). x: criteria applicable; blank: criteria not applicable; n.d.: not defined. TCEP: Tris-(2-chorethyl)-phosphat; TCPP: Tris2-(chlorpropyl)-phosphat; DTPA: Pentetic acid (diethylenetriaminepentaacetic acid); EDTA: Ethylenediaminetetraacetic acid; NTA: Nitrilotriacetic acid; PFBA: Perfluorobutanoic acid; PFOA: Perfluorooctanoic acid; PFBS: Perfluorobutane sulfonic acid; PFOS: Perfluorooctane sulfonate; AHTN and HHCB: polycyclic musks; DEET: Diethyltoluamide; DMS: N.N-dimethylsulfamide; NDMA: N-Nitrosodimethylamine; DCPMU: Desmethyl diuron. For sources, see the Table.

Substance Group	**Substance**	**Indicator Substance**	**% >LOQ**	**Key Parameter in Literature**	**Elimination by Ozonation**	**Elimination by Activated Carbon**	**Concentration > LOQ**		**Relevant for Receiving Water**
							After O_3	**After O_3 + GAC**	
				[4,69,80,81]	[31,47,49,58,62,82–86]	[34,40,47,49,57,58,62,82,85–89]			[70,71,74,90–94]
Pharmaceuticals and Metabolites	10,11-Dihydro-10,11-dihydroxy-carbamazepine	x	100		n.d	n.d	n.d	n.d	n.d.
	Azithromycin		100		good	good	x		
	Bezafibrate		83		moderate	good			x
	Candesartan	x	100	x	moderate	moderate	x	x	n.d.
	Carbamazepine	x	100	x	good	good	x		x
	Ciprofloxacin		100		good	good			x
	Clarithromycin	x	100	x	good	good	x		x
	Dehydrato-Erythromycin A		17		n.d	n.d	n.d	n.d	n.d.
	Diclofenac	x	83	x	good	good	x		x
	Erythromycin A		33		moderate	moderate			
	Gabapentin		100		low	low	x	x	
	Guanylurea		100		n.d	moderate	n.d	n.d	n.d.
	Hydrochlorothiazide	x	100	x	moderate	good	x	x	n.d.
	Ibuprofen		50	x	moderate	good			
	Irbesartan		100	x	moderate	good	x		
	Metformin		100		low	good	x	x	
	Metoprolol	x	100	x	moderate	good	x	x	x
	Sulfamethoxazole	x	100	x	good	moderate			x
Estrogen	17-alpha-Ethinylestradiol		50		n.d	good	n.d	n.d	x
	17-beta-Estradiol		100		n.d	good	n.d	n.d	x
	Estrone		100		good	good	x		
Flame retardant	TCEP		33		n.d	moderate	n.d	n.d	
	TCPP		100		moderate	moderate	x	x	

Table 3. *Cont.*

Substance Group	Substance	Indicator Substance	% >LOQ	Key Parameter in Literature	Elimination by Ozonation	Elimination by Activated Carbon	Concentration > LOQ		Relevant for Receiving Water
							After O_3	After O_3 + GAC	
				[4,69,80,81]	[31,47,49,58,62,82–86]	[34,40,47,49,57,58,62,82,85–89]			[70,71,74,90–94]
Complexing agent	DTPA		100		n.d	low	n.d	n.d	n.d.
	EDTA		100		n.d	low	n.d	n.d	
	NTA		0		n.d	low	n.d	n.d	n.d.
Corrosion inhibitors	4-Methylbenzotriazole	x	100	x	moderate	good	x		
	5-Methylbenzotriazole	x	100	x	moderate	good	x	x	
	Benzotriazole	x	100	x	moderate	good	x		x
Perfluorinated tenside	PFBA		50		n.d	moderate	n.d	n.d	n.d.
	PFBS		17		n.d	low	n.d	n.d	n.d.
	PFOS		50		n.d	moderate	n.d	n.d	x
	PFOA		33		n.d	moderate	n.d	n.d	n.d.
Pesticide	Carbendazim		33		good	good			
	DEET		33		moderate	moderate	x	x	x
	MCPP (Mecoprop)		67	x	moderate	moderate			x
	Terbutryn		50	x	moderate	good			x
	Diuron	x	100 *		good	good	x		n.d.
	Glyphosate		100 *		n.d	n.d	n.d	n.d	n.d.
X-ray contrast media	Diatrizoic acid	x	100	x	low	low	x	x	n.d.
	Iohexol	x	100	x	moderate	moderate	x	x	
	Iomeprol	x	100	x	moderate	moderate	x	x	
	Iopamidol	x	100	x	moderate	moderate	x	x	
	Iopromide	x	17	x	low	moderate	x		
Synthetic fragrance	AHTN		83		n.d	good	n.d	n.d	n.d.
	HHCB		100		n.d	good	n.d	n.d	n.d.
Synthetic sweetener	Acesulfame		100		moderate	low	x	x	
	Cyclamate		50		n.d	n.d	n.d	n.d	n.d.
	Sucralose		100		low	moderate	x	x	
other chemicals	Melamine		100		n.d	low	n.d	n.d	n.d.

Table 3. *Cont.*

Substance Group	**Substance**	**Indicator Substance**	**% >LOQ**	**Key Parameter in Literature**	**Elimination by Ozonation**	**Elimination by Activated Carbon**	**Concentration > LOQ**		**Relevant for Receiving Water**
							After O_3	**After O_3 + GAC**	
				[4,69,80,81]	[31,47,49,58,62,82–86]	[34,40,47,49,57,58,62,82,85–89]			[70,71,74,90–94]
				Additional substances:					
Educt NDMA	DMS								
Transformation products	2,6-Dichloroaniline NDMA DCPMU								
Oxidation by-products	Educt: Bromide Product: Bromate								

2.2.2. Microplastics

The water inside the SBs (≈46 L) was homogenized; sieved into five fractions >1000, 1000–500, 500–100, 100–50, and 50–5 µm; sterilized; and dried at 80 °C. The MP analysis is based on identification and quantification of the polymer content by thermo-extraction/detection–gas chromatography/mass spectrometry (TED–GC/MS) generating a polymer type and mass as output. The following polymer types were routinely screened due to their intensive use and production in Europe [95]: Polyethylene (PE), Polypropylene (PP), Polystyrene (PS), Polyamide (PA), Polyethylene terephthalate (PET), Polymethyl methacrylate (PMMA), and Styrene–butadiene rubber (SBR). SBR is also included in the MP term because of a similar particle formation process, although the authors acknowledge that SBR is an elastomer and hence not officially included in the MP definition. Details about TED–GC/MS equipment, measuring conditions, marker molecules, and detection limits can be found in the literature [96,97]. Quantification was conducted using standard addition or external calibration. For quality assessment, an injection standard (13C labeled PS) was used. The results of the thermal analysis were provided for each detected polymer in µg polymer/µg dry sieve residue in the sample. The average concentration of MP during sampling cycle was then calculated using Equations (1)–(3).

$$C_{m,total} = \sum_{x=1}^{k} C_{m,x} \tag{1}$$

$$C_{m,x} = C_{m,x,y1(\mu\mathrm{m})} + \cdots + C_{m,x,yn(\mu\mathrm{m})} \tag{2}$$

$$C_{m,x,y} = \frac{m_{x,y} \times m_{s,y}}{V_s} \tag{3}$$

where

- k: number of detected polymers;
- C_m, *total*: mean concentration of all detected polymers in sample in [µg/m^3];
- $C_{m,x}$: mean concentration of polymer x in sample in [µg/m^3];
- $C_{m,x,y}$: mean concentration of polymer x in size fraction y (µm) in [µg/m^3];
- $m_{x,y}$: mass concentration of MP x in analyzed subsample of size fraction y (µm) in [µg/µg];
- $m_{s,y}$: total mass of sediments of size fraction y (µm) in [µg];
- V_s: treated WW volume that streamed into SBs during sampling cycle [m^3].

The average concentrations of MP [µg/m^3] in both cycles and streams were used to test the MP removal efficiency of the ozonation plant and GAC filter.

2.2.3. C, N, and P Parameters

C, N, and P parameters were analyzed in the 24-hour composite samples. While total phosphorus (P_{tot}) and COD were determined from the homogenized sample, the samples for determining nitrate–nitrogen (NO_3–N), nitrite–nitrogen (NO_2–N), ammonium–nitrogen (NH_4–N), phosphate–phosphorus (PO_4–P), Spectral Absorption Coefficient (SAC_{254}), and DOC were filtered beforehand using syringe filters with a 0.45 µm pore size regenerated cellulose membrane (Minisart, Sartorius AG, Göttingen, Germany), pre-washed with ultrapure water. The concentrations of COD, NO_3–N, NO_2–N, NH_4–N, PO_4–P, and P_{tot} were measured using a UV/VIS spectrometer (DR5000, Hach Lange GmbH, Düsseldorf, Germany) with cuvette test (LCK 1414 for 5–60 mg/L COD, LCK 339 for 0.23–13.5 mg/L NO_3–N, LCK 341 for 0.015–0.6 mg/L NO_2–N, LCK 304 for 0.015–2.0 NH_4–N, LCK 349 for 0.05–1.5 mg/L PO_4–P, and Ptot. Hach Lange GmbH, Düsseldorf, Germany). The SAC at λ = 254 nm (SAC_{254}) was also measured using the same spectrometer. A Total Organic Carbon (TOC) analyzer (Vario TOC Cube, Elementar, Langenselbold, Germany) was deployed to measure the concentration of DOC in the filtered samples. Before filtering the wastewater, a blank with filtered ultrapure water was measured for each filter to wash carbon out of the filters (c(DOC) = 0.53 ± 0.23). The DOC from the blanks was then subtracted from the samples' DOC. Changes in C, N, and P parameter concentrations were calculated for ozonation and combination of ozonation and GAC filter from the measured concentrations.

2.2.4. Removal Calculations for Organic Micropollutants and CNP Parameters

OMPs and C, N, and P parameters removal was calculated (see Equation (4)) for the ozonation step and after the combination of ozonation and GAC filter from the measured concentrations for the corresponding samples as the flow was constant. Concentrations below the LOQ were assumed to be 0.5 × LOQ. Concentrations before ozonation had to be >5 × LOQ to avoid errors over 10% according to Sauter et al. 2021 [98]; otherwise, they were not included in the elimination calculations.

$$R_i = \left(1 - \frac{C_{i,out}}{C_{i,in}}\right) \times 100 \qquad (4)$$

where

- i: name of the substance measured;
- R_i: removal of the substance in [%];
- $C_{i,out}$: concentration of the substance in the outflow of the process step in [μg/L] for organic pollutants, transformation products, and ozonation by-products and in [mg/L] for standard parameters;
- $C_{i,in}$: concentration of the substance in the inflow of the process step in [μg/L] for organic pollutants, transformation products, and ozonation by-products and in [mg/L] for standard parameters.

3. Results

3.1. Removal of Organic Micropollutants

In total, 14 of the 16 micropollutants from the OMP short list were found in all samples during the sampling period in the influent of the pilot plant (see Table S4). The exceptions were Iopromide and Diuron. Although Iopromide was only included in the list as a supplement (see Section 2.2.1), it was still found in 10 of out 14 samples. Diuron (and its corresponding transformation product, Desmethyl Diuron) was not detected above the LOQ and was therefore not included in the elimination calculations (Sections 3.1.1 and 3.1.2).

3.1.1. Removal Through Ozonation

Specific ozone doses ranging from 0.1 to 0.5 mg_{O3}/mg_{DOC} were targeted throughout the experiments. Figure 3 shows the mean values and standard deviation for the removal of organic micropollutants within the ozonation step for different ozone doses. The values were calculated for each substance, each substance group, and for all micropollutants.

Although the elimination is highly substance-specific, it is evident that the removal of all OMPs increases with a higher specific ozone dose. Considering the mean value for all micropollutants in sum, 60% elimination is achieved with 0.5 mg_{O3}/mg_{DOC}, while it amounts to approximately 22% and 12% for the doses of 0.2 and 0.1 $mg_{O3}/mg_{DOC,}$ respectively. At all ozone doses, the elimination of all pharmaceuticals and metabolites as a group is higher than that of corrosion inhibitors and the X-ray contrast media.

The highest removal was reached for the group of pharmaceuticals with over 80% as mean value of all substances at an ozone dosage of 0.5 mg_{O3}/mg_{DOC}. Four of the seven substances in this group (Carbamazepine, Diclofenac, Hydrochlorothiazide, and Sulfamethoxazole) achieved at least 80% removal with the highest specific ozone dose. Carbamazepine and Diclofenac were almost completely removed, reaching nearly 100%. Candesartan and Metoprolol were eliminated with at least 70% removal at the highest specific ozone dose. However, DCBZ was the most challenging to remove from the pharmaceutical group, with only 60% elimination at the highest specific ozone dose. At lower ozone doses, the pharmaceuticals were removed to a lower extent. Even at the lowest specific ozone dose, Diclofenac and Carbamazepine were at least removed by 40%, whereas the removal range for all other pharmaceuticals was between 0 and 14%.

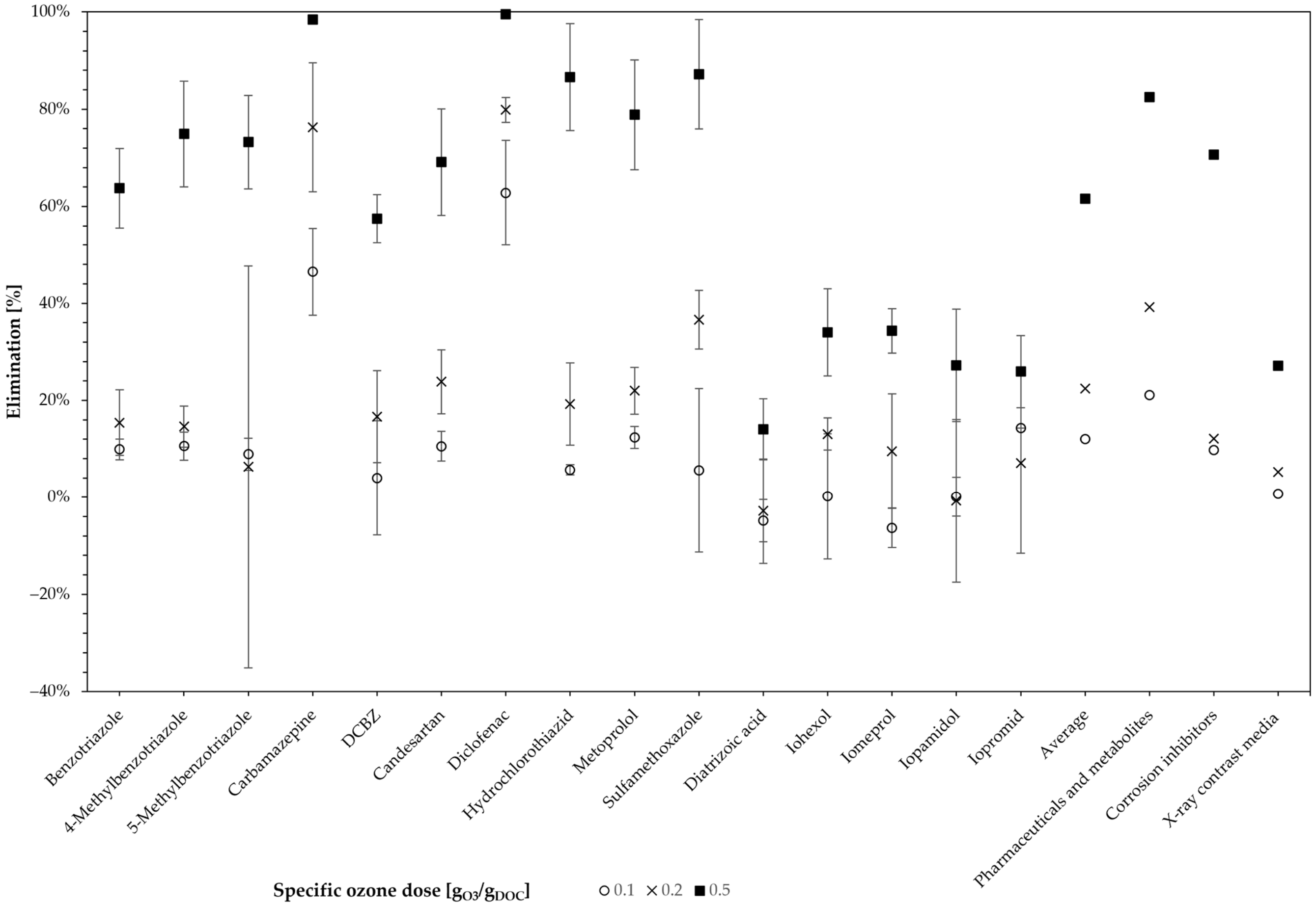

Figure 3. Elimination of organic micropollutants through ozonation depending on the specific ozone dose. An average of four samples was taken for each specific ozone dose with their standard deviation (n = 4 for each specific ozone dose, except for Iopromide, which could not be found in the four samples and had too-small concentrations for calculation of elimination in two samples (0.1: n = 1; 0.2: n = 3; 0.5: n = 2). Averages calculated from the mean eliminations of all OMP and for each substance group (pharmaceuticals and metabolites, corrosion inhibitors, X-ray contrast media). DCBZ= 10,11-Dihydro-10,11-Dihydroxycarbamazepine.

The removal of the corrosion inhibitors group was similar for both the entire group and the individual substances. At 0.1 and 0.2 mg_{O3}/mg_{DOC}, the elimination remains under 20%. At a specific ozone dose of 0.5 mg_{O3}/mg_{DOC}, the removal efficiency reached approximately 70%.

As expected, the X-ray contrast media group (Iohexol, Iomeprol, Iopamidol, and Iopromid) showed the lowest removal. Even at the highest dose of 0.5 mg_{O3}/mg_{DOC}, less than 30% was removed. At the lower ozone doses, their elimination ranged between 0 and 13%. Diatrizoic acid less successfully reduced during the ozonation process. Even at the highest ozone dose, only 14% was removed.

Figure 3 shows that the calculation of the removal of some substances, like the X-ray contrast media, DCBZ, Sulfamethoxazole, and 5-Methylbenzotriazol, give negative values at the two lower specific ozone doses. Concentrations of these OMPs before and after ozonation were very similar at the lower ozone doses, and due to measurement inaccuracy, it led to negative values. The concentrations of OMPs and their eliminations were also very low, so small inaccuracies could have a significant impact.

The measurements in the effluent of the ozone reactor clearly show that low ozone dosages (0.1 and 0.2 mg_{O3}/mg_{DOC}) had only a slight effect on the removal of the micropollutants on average, while increasing the dosage to 0.5 mg_{O3}/mg_{DOC} resulted in significantly higher elimination rates of about 60% removal alone in the single treatment step considering all substances. Other parameters, such as pH, did not appear to have a significant impact on the removal, as it remained relatively constant in the wastewater, with an average of 7.49 ± 0.25. It is assumed that the impact of the other parameters in the wastewater matrix and experimental design had a higher impact, as suggested by the literature [99].

3.1.2. Removal with the Combination of Ozonation and Granular Activated Carbon

Following the ozonation, the wastewater in the pilot plant was further treated in the GAC filter (see Table S4). During ozonation, organic micropollutants were already eliminated to a certain extent. Most of the substances were almost completely eliminated (concentrations were below the LOQ) during the operation period of 6000 bed volumes, regardless of the ozone dose previously used. Over the approximately 6000 bed volumes treated, elimination efficiencies of over 95% were achieved for all substances except Diatrizoic acid and Iopromide. Figure 4 presents the OMP breakthrough curves over the whole investigation phase only for the X-ray contrast media. Even the relatively poorly eliminated substances, such as the X-ray contrast media Diatrizoic acid, Iohexol, Iomeprol, and Iopamidol, were nearly completely eliminated at a load of up to approximately 3500 bed volumes. The elimination efficiency was therefore very high, independent of the previously used ozone dose. Over the ca. 6000 bed volumes treated, elimination efficiencies of over 95% could be reached for all substances except Diatrizoic acid and Iopromide. Iopromide's elimination was still quite effective, with values ≥87% throughout the entire investigation period. Diatrizoic acids' elimination, in contrast to all other substances, decreases substantially from around 3500 treated-bed volumes with a sharp drop to ca. 55% at 4750 treated-bed volumes. In the subsequent samples, the elimination returned to about 70%, suggesting that this drop was an anomaly, presumably because of the significantly lower concentration (2.7 µg/L at this day, average concentration amounts 6.9 µg/L) in the ozonation feed wastewater on that sampling day. A detailed breakthrough curve with operation modes can be found in the Supplementary Data (Figure S5).

As shown in Section 3.1.1, the elimination performance of a low ozone dose alone is insufficient for most of the OMPs studied here. In combination with the GAC filter, they were nevertheless removed with a very high efficiency. Due to this high elimination, with values mostly below the LOQ, the influence of the ozone dose or residence time in the GAC filter (EBCT) could not be determined within the limited bed volume of 6000 and the fact that only one GAC filter was operated.

3.1.3. Removal of By-Products Generated from Ozonation: Bromate, Nitrosamine (NDMA), and Transformation Product of Diclofenac

As shown in Section 3.1.1, ozone reduced the concentrations of organic micropollutants. However, the decrease in the concentration of the original substance does not necessarily indicate that it has been mineralized. For some substances, such as Diclofenac, it is known that transformation products (TPs) are formed during ozonation. Three TPs were analyzed in the pilot plant at various ozone concentrations. Additionally, the results for NDMA, the formation of bromate from bromide, and its removal in the GAC post-treatment are presented below. All results for transformation products and oxidation by-products can be found in Table 4.

NDMA was present in the secondary clarifiers' effluent at very low concentrations (c = 0.002–0.003 µg/L) in five out of seven samples. It was formed during ozonation at all investigated ozone concentrations except on one sampling day. At higher specific ozone dose, the concentration of NDMA increased up to 0.039 µg/L, particularly with higher ozone dose (around 0.5 mg_{O3}/mg_{DOC}). One of its possible educts, DMS, was found in only one out of seven samples collected. Its concentration remained constant before and after the ozonation (0.025 µg/L), indicating that the formation of NDMA does not depend on the DMS concentration. DMS concentration decreased after GAC filtration to 0.018 µg/L. Although a part of NDMA is eliminated in the subsequent GAC treatment, the remaining concentration of 0.010 µg/L is consistently higher than in the secondary clarifiers' effluent of the corresponding sample. No correlation between the residual time in the filter (EBCT) and the decrease in NDMA concentration was observed.

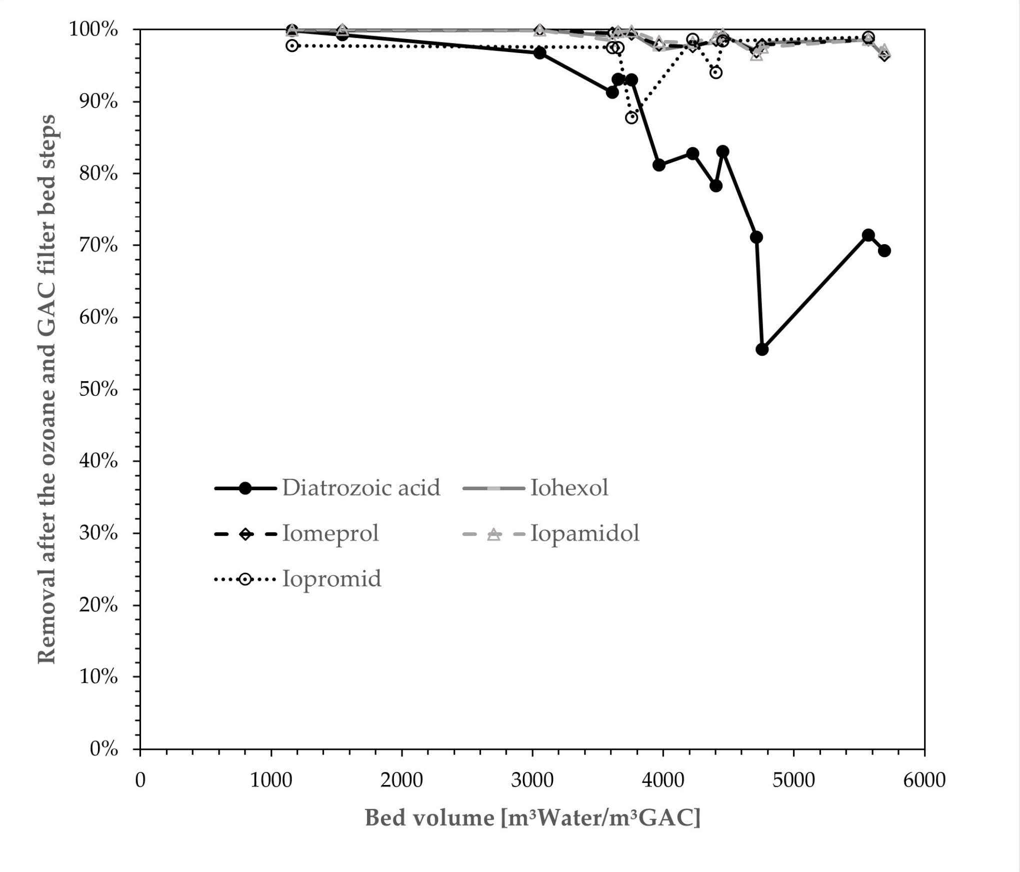

Figure 4. Breakthrough curves of X-ray contrast media, after ozonation and additional GAC filtration. Various ozone doses (0.1 to 0.5 mg_{O3}/mg_{DOC}) and different EBCTs (from 27 to 40 min) have been applied.

Regarding the transformation products from Diclofenac, 2,6-Dichloraniline was not detected in secondary clarifiers' effluent but is formed through ozonation at specific ozone dose from 0.5 mg_{O3}/mg_{DOC} to low concentrations between 0.054 and 0.068 µg/L. It was no longer detectable after the GAC filter (c(LOQ) = 0.05 µg/L).

Low doses of ozone were used in the investigations to prevent the formation of toxic by-products, such as Bromate from Bromide. Bromide concentrations remained nearly constant throughout the treatment steps (c = 130–160 µg/L). Bromate was detected only once at a specific ozone dose of 0.5 mg_{O3}/mg_{DOC}, but still at a very low concentration (c = 3.3 µg/L) in the effluent of the ozonation. The bromate concentration then decreased to 2.9 µg/L in the effluent of the GAC filter.

Table 4. Concentration of ozone by-products and transformation products before treatment in the pilot plant (secondary clarifiers' effluent), after ozonation, and after GAC filtration. Dry weather conditions, specific ozone dose from 0.1 to 0.5 mg_{O3}/mg_{DOC}, and EBCT 27–40 min. n.d.: no data; LOQ: limit of quantification; DMS: N.N-Dimethylsulfamide; NDMA: N-Nitrosodimethylamine.

		Secondary Clarifiers' Effluent						Ozonation						GAC					
Specific Ozone Dose	**EBCT**	**Bromide**	**Bromate**	**DMS**	**NDMA**	**Diclofenac**	**2,6-Dichloroaniline**	**Bromide**	**Bromate**	**DMS**	**NDMA**	**Diclofenac**	**2,6-Dichloroaniline**	**Bromide**	**Bromate**	**DMS**	**NDMA**	**Diclofenac**	**2,6-Dichloroaniline**
mg_{O3}/mg_{DOC}	**min**	**µg/L**	**µg/L**	**µg/L**	**µg/L**	**µg/L**	**µg/L**	**µg/L**	**µg/L**	**µg/L**	**µg/L**	**µg/L**	**µg/L**	**µg/L**	**µg/L**	**µg/L**	**µg/L**	**µg/L**	**µg/L**
0.09	33	n.d.	n.d.	<LOQ	0.002	2.20	<LOQ	n.d.	n.d.	<LOQ	0.005	0.79	<LOQ	n.d.	n.d.	<LOQ	0.003	<LOQ	<LOQ
0.13	33	140	<LOQ	n.d.	n.d.	n.d.	n.d.	140	<LOQ	n.d.	n.d.	N.d.	n.d.	140	<LOQ	n.d.	n.d.	n.d.	n.d.
0.17	33	140	<LOQ	<LOQ	<LOQ	2.10	<LOQ	140	<LOQ	<LOQ	<LOQ	0.37	<LOQ	140	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ
0.19	27	130	<LOQ	n.d.	n.d.	n.d.	n.d.	130	<LOQ	n.d.	n.d.	n.d.	n.d.	130	<LOQ	n.d.	n.d.	n.d.	n.d.
0.23	40	140	<LOQ	0.025	0.003	1.30	<LOQ	140	<LOQ	0.025	0.005	0.23	<LOQ	140	<LOQ	0.018	0.003	<LOQ	<LOQ
0.23	33	n.d.	n.d.	<LOQ	0.002	2.00	<LOQ	n.d.	n.d.	<LOQ	0.002	0.47	<LOQ	n.d.	n.d.	<LOQ	0.002	<LOQ	<LOQ
0.44	33	n.d.	n.d.	<LOQ	0.002	1.80	<LOQ	n.d.	n.d.	<LOQ	0.006	<LOQ	<LOQ	N.d.	n.d.	<LOQ	0.009	<LOQ	<LOQ
0.45	33	160	<LOQ	<LOQ	0.003	1.80	<LOQ	150	3.3	<LOQ	0.019	<LOQ	0.068	150	2.9	<LOQ	0.010	<LOQ	<LOQ
0.49	40	160	<LOQ	<LOQ	<LOQ	1.70	<LOQ	160	<LOQ	<LOQ	0.039	<LOQ	0.054	160	<LOQ	<LOQ	0.006	<LOQ	<LOQ

3.2. Removal of Microplastics

PE, PP, PS, and SBR were identified as polymer types within the suspended particulate matter. The results of the two sampling cycles indicate that the average MP concentrations in the effluent of secondary clarifiers were 373 µg/m^3 during cycle 1 and 167 µg/m^3 during cycle 2. After passing through the combined ozonation and GAC filtration, 99% and 92% of MP particles were further removed, reducing concentrations to approximately 3.5 µg/m^3 and 14 µg/m^3, respectively (Figure 5).

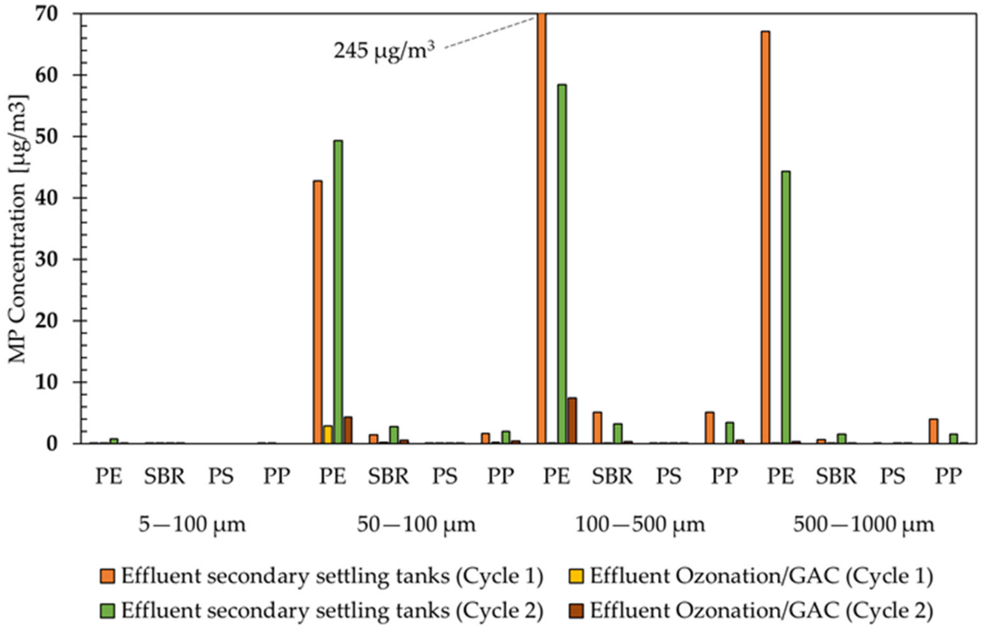

Figure 5. Concentrations of all detected polymers within their size fractions in the effluent of secondary clarifiers and GAC filter, cycles 1 and 2 [µg/m^3].

PE was the most abundant polymer, representing an average of 93% and 87% of the total concentration before and after combined removal, respectively. PP accounted for 3.5% and 6% and SBR for 3% and 6% (Figure 5). Considering the particle size distribution (PSD) before the combined removal of MPs, particles within the size fraction 100–500 µm were the most abundant, representing 54% of all polymers, followed by 500–1000 µm and 50–100 µm size fractions, representing 24% and 22%, respectively. However, the PSD after the combined removal showed a different trend. The size fraction 50–100 µm became the most abundant, representing 67% of all polymers, followed by 100–500 µm fraction, with only 30% representation. Nonetheless, both size fractions ended up with similar concentrations of approximately 4.2 µg/m^3 each (Figure S3). This shift in PSD was also observed in the TS content after the combined ozonation/GAC treatment step, where the 100–500 µm size fraction lost its dominance to the 50–100 µm size fraction (Figure S4).

3.3. C, N, and P Parameters

C, N, and P parameter concentrations are also affected by the treatment process. Table 5 shows the elimination of several substances during ozonation and combined ozonation and GAC treatment for each sampling day. For some parameters, no clear trend can be discerned from the data, while for others, trends or tendencies can be identified.

Table 5. Removal of C, N, and P parameters through ozonation and GAC filtration dependent on the specific ozone dose and the concentrations of DOC and NO_2-N in the secondary clarifiers' effluent. DW = dry weather, RW = rainy weather. n.d. = no data. Light gray: EBCT 27 min; medium gray: EBCT 33 min; black: EBCT 40 min.

Specific Ozone Dose	Weather Conditions	EBCT	Secondary Clarifiers' Effluent		Removal Through Ozonation [%]								Removal Through Ozonation and GAC Filtration [%]							
			DOC	NO_2–N																
mg_{O3}/mg_{DOC}		min	mg/L	mg/L	DOC	SAC_{254}	COD	P_{tot}	PO_4–P	$NO_2{}^-$-N	$NO_3{}^-$-N	$NH_4{}^+$-N	DOC	SAC_{254}	COD	P_{tot}	PO_4-P	$NO_2{}^-$-N	$NO_3{}^-$-N	$NH_4{}^+$-N
0.09	DW	33	8.73	0.21	27	13	32	11	−35	23	−30	−13	52	75	59	10	−213	96	−190	99
0.09	DW	33	8.44	0.21	25	−1	0	−7	−19	15	−37	−25	51	84	50	12	−99	96	−180	99
0.12	RW	33	7.68	0.35	22	7	−7	−15	−61	21	−17	8	51	74	56	0	−392	90	−106	99
0.13	RW	33	7.23	0.35	27	10	11	−4	0	34	−27	15	54	76	68	27	−376	95	−330	100
0.15	RW	40	7.52	0.20	4	15	4	6	−23	66	−15	6	62	79	78	25	−55	70	−90	96
0.17	DW	33	9.57	0.20	30	13	0	−10	−21	48	−14	−11	52	77	62	5	−29	96	−48	97
0.18	RW	40	6.95	0.17	0	19	2	−3	−42	67	−5	−32	69	85	75	−4	−92	96	−15	99
0.19	DW	40	8.36	0.28	29	16	−6	−8	−14	46	−6	−7	56	78	64	20	−3	97	−39	99
0.19	DW	27	7.76	0.27	30	14	−16	−1	−67	48	−10	−8	59	76	58	17	−75	97	−48	100
0.20	DW	27	7.36	0.32	26	15	8	−26	−37	49	−17	0	54	82	69	3	−64	98	−60	99
0.23	RW	40	5.81	0.10	−6	n.d.	5	−6	−60	70	−19	−19	67	n.d.	64	−8	−402	93	−81	99
0.23	DW	33	7.50	0.20	30	12	2	−25	−29	13	−8	−44	62	81	66	9	−69	9	−43	94
0.23	DW	40	6.67	0.24	25	16	10	−8	0	48	−4	−26	67	87	72	10	−124	97	−54	99
0.24	RW	40	6.07	0.21	−4	15	10	16	−18	50	−18	11	71	87	85	20	3	75	−101	98
0.44	DW	33	8.23	0.15	23	38	2	−13	−29	88	−13	−17	49	79	52	1	−72	95	−50	99
0.45	DW	33	7.63	0.20	21	45	7	−9	−14	96	−13	−16	56	84	65	3	−154	85	−35	99
0.49	DW	40	7.98	0.13	1	n.d.	12	−10	−46	94	−21	−9	71	n.d.	71	2	−283	94	−51	97
0.51	DW	40	7.64	0.08	3	n.d.	9	−5	−9	91	−5	8	71	n.d.	70	25	−17	91	−21	99
0.52	RW	40	7.02	0.14	7	41	58	−32	−45	95	1	7	79	87	92	31	−125	95	−10	96
0.53	DW	40	6.67	0.09	−1	41	4	−5	−32	92	−2	−11	71	91	86	21	14	92	−15	98

Carbon parameters (DOC, SAC_{254}, and COD) are mostly removed in the ozonation to varying extents. A correlation between increasing ozone dose and decreasing concentration in the effluent of the ozone reactor was observed only for SAC_{254}. Table 5 shows that the GAC filter has an additional positive effect on the organic carbon elimination. SAC_{254} shows the better elimination, with at least 75% removal at the outflow of the GAC filter. COD elimination varies after ozonation, but no clear pattern is evident, as the fluctuations are high for all ozone doses used. However, mean concentration of COD was 20 mg/L in the influent of the pilot plant and 19 mg/L after the ozonation (see Table 5), indicating that there is hardly any difference in the COD concentration through ozonation. In the GAC filter, COD concentration is reduced by at least 50%.concentration is at least 50%. Regardless of the ozone dose or weather conditions, COD removal is more effective with a longer contact time in the GAC filter (EBCT = 40 min). DOC showed a similar trend to COD during ozonation. DOC can slightly increase (6%) or decrease (up to 30%) regardless of the ozone dose applied, within the average decrease of around 16%. However, weather conditions may have an impact, as the elimination was higher when weather was dry than in rainy weather (see Section 4.2.3). The GAC filter allows for further elimination of DOC (at least 49%), and like COD, a higher removal (56 to 79%) is achieved with a longer EBCT (40 min).

The concentration of total P did not change consistently in ozonation (mean concentration of 0.277 mg/L in the influent of the pilot plant and of 0.288 mg/L after ozonation, with a confidence interval of ± 0.010 mg/L from the cuvette test [100]) but was partially removed through the GAC filter (mean concentration of 0.232 mg/L after the GAC filter). PO_4–P increased by up to 67% after ozonation and by over 400% after GAC filtration, compared to the concentration in the secondary clarifiers' effluent, but the average concentration of total P remained continuously higher than PO_4–P in the pilot plant (mean concentration of PO_4–P of 0.125 mg/L in the influent, of 0.171 mg/L after ozonation, and of 0.204 mg/L after the GAC filter). Algae formed in the tank 3 (see Figure 1) during the experimentation period, where samples were collected. This may explain the decrease in total phosphorus, despite the increase in PO4–P concentration. This increase may, however, be due to a release of biomass. However, the correlations between the dissolved and undissolved fractions of phosphorus during the entire removal process are currently unknown.

The concentration of inorganic nitrogen (sum of NO_2–N, NO_3–N, and NH_4–N) increased throughout the entire process, and its composition changed. While there was no clear pattern regarding changes in ammonium concentrations through ozonation, nitrite decreased, and nitrate was formed during this treatment step. The elimination of nitrite depends on the ozone dose: the higher the ozone dose, the higher the elimination of nitrite during ozonation. The investigations indicated that at lower ozone doses (0.1–0.2 mg_{O3}/mg_{DOC}), only a portion of the nitrite is converted into nitrate (removal 13–50%). At higher ozone doses, around 0.5 mg_{O3}/mg_{DOC}, the NO_2–N concentration in the effluent of the ozonation was below the LOQ, resulting in nearly 100% elimination. The nitrate concentration increased during ozonation and GAC filter treatment, exceeding what could be explained by the decrease in nitrite. It is presumed that other nitrogen compounds, such as organic nitrogen or ammonium, were also converted into nitrate during ozonation and GAC filtration. Averaged over all experiments, the mean NO_3–N concentration increases from 3.13 mg/L in the influent of the ozonation to 5.07 mg/L in the GAC filter effluent. The maximum NO_3–N concentration measured in the GAC filter effluent was 7.96 mg/L, with 5.58 mg/L in the influent of the ozonation on the same sampling day. Average concentrations, along with minimum and maximum concentrations, can be found in Table S5 in the Supplementary Document.

4. Discussion

4.1. Selection of Organic Micropollutants

For the regular analysis, a selection of the OMP from the screening was made for the regular analysis (short list). One limitation of our method is that it relies on literature results in order to be able to carry it out at all, e.g., for the calculation of the residual concentrations after the individual process stages. No eliminations for ozone were found in the literature for 18 substances out of 50 and none for the GAC filter for 4 substances. For the rating of ecotoxicity, no values are available for 17 substances. Overall, at least one value was missing for 22 substances. Therefore, the procedure could not be carried out completely for these substances, and they were excluded from the selection process as the aim was to have comparable results. However, 9 of these 22 substances were already eliminated in the first step ((a) 2/3 of data points < LOQ) due to their rare occurrence.

As a result, our short list is quite similar to the various national lists mentioned. The KomS List B (Germany) [69] differs from ours by only 5 substances (KomS List B includes Ibuprofen and Irbesartan; our short list includes 10,11-dihydro-10,11-dihydroxycarbamazepine, Clarithromycin, and Diuron). In comparison to the Swiss list [81] and EU list [4], our short list differs by 9 substances (Swiss and EU list includes irbesartan; our short list includes 10,11-dihydro-10,11-dihydroxycarbamazepine, Diatrizoic acid, Diuron, Iohexol, Iomeprol, Iopamidol, Iopromide, and Sulfamethoxazole). Nevertheless, by selectively excluding and including other substances, we ensured that of 224 individual micropollutant analyses in 14 secondary clarifiers' effluent samples, 206 analyzed concentrations were above the limit of quantification. This enables a reliable calculation of the elimination of the individual substances during the individual process stages ozonation and GAC.

4.2. Removal During Ozonation

4.2.1. Organic Micropollutants

The approach of predicting OMPs removal with the help of data from the literature worked well for ozonation. The obtained eliminations were compared with those from the literature, where comparable ozone doses (0.2 and 0.5 mg_{O3}/mg_{DOC}) were used (Tables 6 and 7). The eliminations for most of the micropollutants were within the expected range from the literature or slightly lower. Differences in the test setup or wastewater matrix could result in varying ozone consumption.

Table 6. Comparison of the elimination through ozonation with literature data from two WWTPs in Switzerland [62] and Germany [49] for a specific ozone dose from around 0.2 mg_{O3}/mg_{DOC}. n.d.: no data.

	Experiment	**Literature**		
Specific Ozone Dose [mg_{O3}/mg_{DOC}] (Number of Samples)	**0.2 (*n* = 6)**	**0.21 (*n* = 3)**	**0.26 (*n* = 2)**	**0.24 (*n* = 9)**
	Elimination ± Standard Deviation	**Full-Scale WWTP Furt-Bülach [62]**		**Semi-Technical Scale WWTP Detmold [49]**
Benzotriazole	15.4 ± 6.8%	23%	24%	22%
4-Methylbenzotriazole	14.6 ± 4.2%	27%	26%	n.d.
5-Methylbenzotriazole	6.3 ± 41.4%	27%	26%	n.d.
Carbamazepine	76.3 ± 13.3%	60%	67%	87%
DCBZ	16.6 ± 9.5%	n.d.	n.d.	n.d.
Candesartan	23.8 ± 6.6%	n.d.	n.d.	n.d.
Diclofenac	79.9 ± 2.6%	67%	71%	93%
Hydrochlorothiazid	19.2 ± 8.5%	27%	32%	n.d.
Metoprolol	21.9 ± 4.8%	25%	27%	34%
Sulfamethoxazole	36.6 ± 6.1%	n.d.	n.d.	43%

Table 6. *Cont.*

	Experiment	Literature		
Specific Ozone Dose [mg_{O3}/mg_{DOC}] (Number of Samples)	**0.2 (*n* = 6)**	**0.21 (*n* = 3)**	**0.26 (*n* = 2)**	**0.24 (*n* = 9)**
	Elimination ± Standard Deviation	**Full-Scale WWTP Furt-Bülach [62]**		**Semi-Technical Scale WWTP Detmold [49]**
Diatrizoic acid	−2.8 ± 10.8%	n.d.	n.d.	−4%
Iohexol	13.1 ± 3.3%	n.d.	n.d.	n.d.
Iomeprol	9.5 ± 11.8%	n.d.	n.d.	n.d.
Iopamidol	−0.7 ± 16.8%	n.d.	n.d.	n.d.
Iopromid	7.1 ± 18.6%	n.d.	n.d.	n.d.

Table 7. A comparison of the elimination through ozonation with the literature data from a project report [64] and two papers [31,83] for a specific ozone dose from around 0.5 mg_{O3}/mg_{DOC}. n.d.: no data.

	Experiment	Literature		
Ozon Dose [mg_{O3}/mg_{DOC}] (Number of Samples)	**0.5 = 3.75 mg_{O3}/L (*n* = 4)**	**0.6 (*n* = 17–20)**	**0.54 (*n* = 3)**	**3.5–5.4 mg_{O3}/L (*n* = 3–6)**
	Elimination ± Standard Deviation	**Full-Scale WWTP Weißenburg [64]**	**Full-Scale WWTP Neugut [31]**	**Laboratory Experiment with 5 Swedish WWTP Effluents [83]**
Benzotriazole	63.7 ± 8.2%	37.9 ± 21.6%	74 ± 3%	n.d.
4-Methylbenzotriazole	74.9 ± 10.9%	n.d.	n.d.	n.d.
5-Methylbenzotriazole	73.2 ± 9.6%	n.d.	n.d.	n.d.
Carbamazepine	98.4 ± 0.5%	45.1 ± 23.8%	>98 ± 1%	86 ± 18%
DCBZ	57.5 ± 5.0%	n.d.	n.d.	n.d.
Candesartan	69.1 ± 11.0%	89.1 ± 11.1%	82 ± 3%	n.d.
Diclofenac	99.5 ± 0.1%	87.8 ± 18.0%	100 ± 1%	77 ± 22%
Hydrochlorothiazid	86.6 ± 11.0%	58.6 ± 30.6%	>98 ± 2%	n.d.
Metoprolol	78.9 ± 11.3%	48.6 ± 25.6%	94 ± 3%	57 ± 24%
Sulfamethoxazole	87.2 ± 11.25%	n.d.	>97 ± 1%	73 ± 17%
Diatrizoic acid	14.1 ± 6.3%	n.d.	n.d.	n.d.
Iohexol	34.0 ± 9.0%	n.d.	n.d.	n.d.
Iomeprol	34.3 ± 4.6%	n.d.	n.d.	n.d.
Iopamidol	27.2 ± 11.6%	n.d.	n.d.	n.d.
Iopromid	25.9 ± 7.4%	n.d.	43%	n.d.

4.2.2. By-Products Generated from Ozonation (Bromate, NDMA) and Transformation Product from Diclofenac

During ozonation, Bromate formation was minimal at low ozone doses < 0.25 mg_{O3}/mg_{DOC}, which was expected. At low ozone doses, ozone's lifetime is very short, and it first oxidizes OMPs rich in electrons (like Phenols and Carbamazepine) [101]. Then, Bromate formation increases steadily with ozone dose > 0.25 mg_{O3}/mg_{DOC}, but it also depends on wastewater matrix and experimental design [24,26,101,102]. In the two experiments with a higher ozone dose (around 0.5 mg_{O3}/mg_{DOC}), Bromate formed once with a very low yield of

2.1% (µg/L BrO_3-/µg/L Br-), with Bromide with relative high concentrations (150 and 160 µg/L). Similar Bromate yields (around 3%) were also observed at the ARA Neugut in Switzerland, with a Bromide concentration up to 150 µg/L and an ozone dose around 0.55 mg_{O3}/mg_{DOC} [31]. Soltermann et al. [24] also reported that Bromate yields did not exceed 3% with ozone dose between 0.4 and 0.6 mg_{O3}/mg_{DOC} and bromide concentration from 40 to 700 µg/L in several Swiss wastewaters. The results for Bromate largely correspond with observation in the literature. The experiments confirmed that with a bromide concentration up to around 150 ug/L and maintaining an ozone dose < 0.5 mg_{O3}/mg_{DOC}, bromate formation remains low [81] and should stay below the limit concentration of 10 µg/L for the European Union's drinking water quality standard [103]. Soltermann et al. (2017) investigated two alternatives to reducing the ozone dose to prevent bromate formation [25]. The first one is the identification of major bromide sources from the influent of the WWTP. It involves extensive sampling efforts, but it can help in significantly lowering bromide concentration. The second one is the addition of hydrogen peroxide (H_2O_2), which can react with an intermediate of bromate and partially prevent its formation. It showed potential in mitigating bromate formation; however, the required concentration of H_2O_2 is relatively high (>5 mg/L), and its residual must be removed through biological post-treatment. However, Merle et al. (2017) [104] developed a novel process (MEMBRO$_3$X), enhancing the ozone-based advanced-oxidation process (AOP) O_3/H_2O_2 with a membrane. This resulted in lower bromate formation compared to the AOP O_3/H_2O_2 alone in experiments with groundwater and could potentially be applied with wastewater. Schachler et al. (2019) [102] researched experimental designs that also helped prevent Bromate formation. A multi-stage ozone input was operated at the WWTP Neugut in Switzerland, where ozone input was divided in two chambers. Hence, ozone concentration in contact with wastewater was reduced, leading to decreased Bromate formation.

NDMA formation during ozonation increases with higher ozone dose but in smaller concentrations (<40 ng/L), which are still below the WHO guideline value of 100 ng/L for drinking water [105]. This is similar to other ozonation plants, such as the ARA Neugut in Switzerland [31], where NDMA concentration remained below 30 ng/L with an ozone dose of around 0.5 mg_{O3}/mg_{DOC}. Although N,N-dimethylsulfamide (DMS) has been identified as a typical educt product from NDMA [22] in which the presence of bromide enhances the NDMA formation during ozonation [76], DMS was detected in only one of the seven samples, and its concentration in this single sample did not change during ozonation. NDMA can be formed from multiple other precursors. For example, [106] reported that N,N-dimethylhydrazine, unsymmetrical dimethylhydrazine (UDMH), or daminozide (MDZ) are substances that can also lead to high NDMA formation yield. Those educts could be measured in the wastewater stream for further research. To prevent NDMA formation during ozonation, Song et al. (2022) [106] recommended ozone-based advanced-oxidation processes (AOPs), such as O_3/H_2O_2, UV/O_3, and O_3/peroxymonosulfate (PMS). Song et al. suggests that the membrane used to prevent bromate formation [104] could also be used to control NDMA formation.

The transformations product 2,6-Dichloroaniline from Diclofenac formed at ozone doses of 0.45 mg_{O3}/mg_{DOC} in relatively small concentrations (<0.07 µg/L). Concentrations tested in experiments of [77,78] were significantly higher (a minimum of 1 mg/L), in which acute toxicity was reported. No other literature data were found about the toxicity of 2,6-dichloroaniline at lower concentrations, so no conclusion ca be drawn regarding its effects.

The results of this study clearly demonstrate that using low ozone doses (<0.4 mg_{O3}/mg_{DOC}) prevents the formation of bromate and other undesired by-products, like NDMA or 2,6-dicloroaniline.

4.2.3. C, N, and P Parameters

The calculated change in DOC concentrations in the ozonation varied between −6% and 30% with a tendency to decrease. A connection to the weather condition was observed. DOC elimination in dry weather samples was approximately 25–30% at low ozone doses $< 0.25\ mg_{O3}/mg_{DOC}$, while at higher ozone doses, around $0.5\ mg_{O3}/mg_{DOC}$, the elimination was almost around 0%. In rainy weather, DOC elimination was nearly 0% across all ozone doses (see Figure 6). This may be due to a higher content of particles in the water during wet weather conditions. According to the literature, DOC decreases in filtered water during the ozonation, while elimination in unfiltered water is variable due to the conversion of solid carbons to dissolved ones [29,51]. An explanation for the higher elimination during dry weather may be a lower particle content in the secondary clarifiers' effluent (TSS not measured).

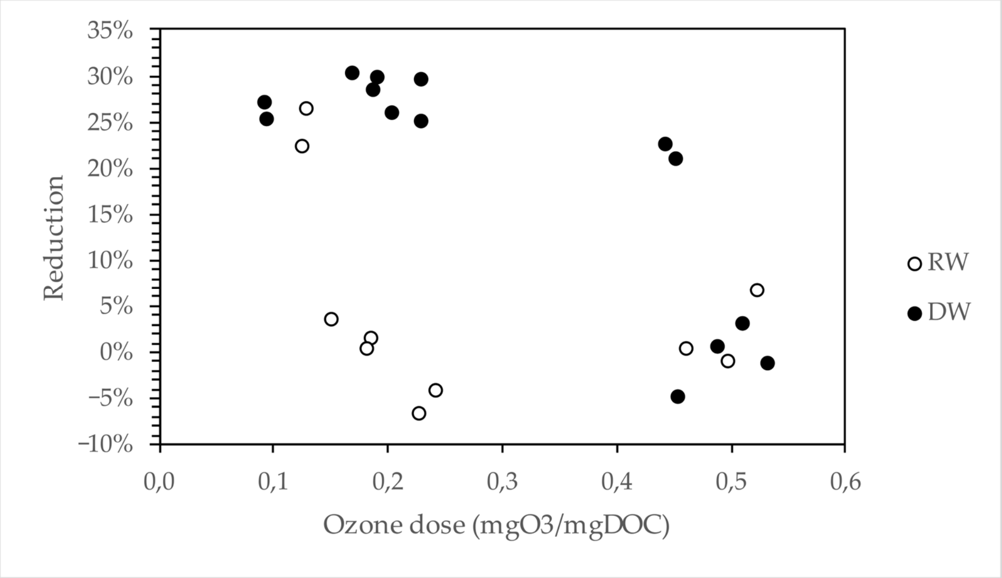

Figure 6. Elimination of dissolved organic carbon (DOC) depending on the ozone dose and weather condition. DW = dry weather; RW = rainy weather.

Nitrite reacts quickly with the ozone in the water and can significantly contribute to ozone consumption. In some publications, for waters with high nitrite levels, the ozone consumption of the nitrite is subtracted when calculating the specific ozone dose [29,31,45]. For this, it is assumed that nitrite is completely transformed during the ozonation process which we observed only at the higher ozone dose of $0.5\ mg_{O3}/mg_{DOC}$. In our investigations, nitrite concentrations ranged from 0.08 to 0.35 mg NO_2-N/L (mean concentration 0.20 ± 0.08 mg NO_2–N/L) in the influent of the ozone reactor. At the low ozone doses of 0.1 or 0.2 $mg_{O3}/mg_{DOC,\ however,}$ it was only reduced by 32% and 51%, respectively, as a mean elimination during ozonation. At an ozone dose of $0.5\ mg_{O3}/mg_{DOC}$, nitrite was reduced mostly below or near the LOQ, resulting in around 90% elimination. Ozone consumption by nitrite was calculated with the stoichiometric value of 3,43 $mg_{O3}/mg_{NO2\text{-}N}$. As Table 8 shows, absolute ozone consumption of nitrite increases as ozone dosage increases, but relative consumption decreases from 35% to 12% as the ozone dose increases. The theoretical consumption of ozone for total oxidation of nitrate was not reached. Kohlgrüber et al. (2022) also reported that not all nitrites were reduced at ozone doses of 0.33–0.52 mg_{O3}/mg_{DOC}, and a maximum of 8% of the ozone applied was consumed by nitrite [65].

Table 8. Ozone consumption of nitrite for three ozone doses in the secondary clarifiers' effluent. Mean concentrations of NO_2–N in each experimental phase are given for secondary effluent and for the oxidized concentration in ozonation. Comparison of measured ozone consumption by nitrite with theoretical consumption if whole NO_2–N was oxidized.

Specific Ozone Dose mg_{O3}/mg_{DOC} (mg_{O3}/L)	**NO_2–N in Secondary Clarifiers' Effluent mg/L**	**Oxidized NO_2–N in Ozonation mg/L**	**Ozone Consumed for Oxidation of Nitrite mg_{O3}/L (%)**	**Theoretical Ozone Demand for Oxidation of Total NO_3–N mg_{O3}/L**
0.1 (0.79)	0.27	0.08	0.28 (35.2)	0.91
0.2 (1.46)	0.22	0.11	0.36 (24.7)	0.75
0.5 (3.75)	0.133	0.126	0.43 (11.5)	0.46

The ozonation had little impact on the phosphorus parameters. A slight increase in the concentration of total phosphorus was observed. Since an increase in the total phosphorus content cannot be explained by the ozonation itself, it is suspected that some phosphorus compounds become more analyzable after ozonation. Multhaup et al. (2023) [107] also observed an increase in total P due to an ozonation with an ozone dose of 1.54 mg_{O3}/mg_{DOC}, which can be explained by an increase in particulate P compounds [107]. There may be an issue with conventional P analysis where not all P fractions are accurately detected in the total phosphorous value. This issue warrants further investigation in the future.

It is very likely that the P removal requirements for municipal wastewater treatment plants will become stricter, necessitating lower P concentrations in the effluents will be required. Therefore, the conversion of other P compounds into PO_4–P in the ozonation is to be considered positive as PO_4–P can be easily removed with precipitant in post-treatment.

4.3. Removal Through the Combination of Ozonation and GAC Filter

4.3.1. Organic Micropollutants

During treatment in the GAC filter, the relatively fresh filter bed eliminated most of the OMPs to below the LOQ, which does not align with the literature data in Table 3. The period of use (ca. 6000 treated-bed volumes) was too short to achieve a breakthrough. The eliminations previously researched for substance selection did not match the results obtained in the experiment. They represented average values from the respective experimental periods in the literature and accordingly included the lower eliminations near or after breakthrough that has not been reached in the experiment. Nevertheless, the literature research was useful to classify and select the substances according to their adsorbability on GAC.

During ozonation, most substances are poorly eliminated due to the low ozone dosages, but post-treatment in the GAC filter reduces micropollutants concentrations to mostly below the LOQ. In the range of 4000 to 6000 BV, the high elimination efficiency of the ozone and GAC combination could also be achieved by GAC alone (compare own results and literature in Tables 9 and 10), but with the pre-treatment with ozone, a longer service life of the filter bed can be reached (compare with literature in Tables 11 and 12). The extended service life could not be verified due to the very short loading time of less than 6000 BV.

Table 9. Elimination of the combination ozone and GAC filtration. Comparison of experimental data with literature (project reports [49,63,64]) for the period of 4000–6000 bed volumes.

	Experiment	**Literature**		
Specific Ozone Dose [mg_{O3}/mg_{DOC}] (Number of Samples)	**0.1–0.5** (*n* = 7)	**0.6** (*n* = 15)	**0.35–0.92** (*n* = 3)	**0.34** (*n* = 1)
Empty Bed Contact Time EBCT [min]	**27–33**	**15–45**	**14.5 ± 3**	**25**
	Elimination ± Standard Deviation	**Full-Scale WWTP Weißenburg [64]**	**Full-Scale WWTP Neugut [63]**	**Semi-Technical Scale WWTP Detmold [49]**
Benzotriazole	99.8 ± 0.05%	97.8%	98%	97%
4-Methylbenzotriazole	99.4 ± 0.17%			
5-Methylbenzotriazole	99.3 ± 0.12%			
Carbamazepine	98.6 ± 0.49%	92.7%		95%
DCBZ	99.1 ± 0.50%			
Candesartan	99.2 ± 0.56%	57.3%	93%	
Diclofenac	99.6 ± 0.31%	95.2%	91%	99%
Hydrochlorothiazid	99.5 ± 0.24%	93.9%	94%	
Metoprolol	99.7 ± 0.18%	94.4%	94%	99%
Sulfamethoxazole	98.0 ± 0.79%			90%
Diatrizoic acid	73.1 ± 7.43%			
Iohexol	97.1 ± 1.04%			
Iomeprol	97.9 ± 0.94%			
Iopamidol	98.1 ± 0.76%			
Iopromid	66.3 ± 42.83%			

Table 10. Comparison of the elimination of the combination (experimental data) with elimination of GAC filter as stand-alone (literature data from project reports [49,58,63,65]) in the period of 4000–6000 bed volumes.

	Experiment	**Literature**			
Specific Ozone Dose [mg_{O3}/mg_{DOC}] (Number of Samples)	**0.1–0.5** (*n* = 7)	**0** (*n* = 2)	**0** (*n* = 3)	**0** (*n* = 3)	**0** (*n* = 5)
Empty Bed Contact Time EBCT [min]	**27–33**	**15**	**14**	**25**	**30**
	Elimination ± Standard Deviation	**Pilot-Scale WWTP Köln-Rodenkirchen [65]**	**Full-Scale WWTP Neugut [63]**	**Semi-Technical Scale WWTP Detmold [49]**	**Pilot-Scale WWTP Wien [58]**
Benzotriazole	99.8 ± 0.05%		99%	99%	
4-Methylbenzotriazole	99.4 ± 0.17%				82.8%
5-Methylbenzotriazole	99.3 ± 0.12%	99%			
Carbamazepine	98.6 ± 0.49%	99%		95%	
DCBZ	99.1 ± 0.50%	95%			76.6%
Candesartan	99.2 ± 0.56%		76%		

Table 10. *Cont.*

	Experiment	**Literature**			
Specific Ozone Dose [mg_{O3}/mg_{DOC}] (Number of Samples)	**0.1–0.5 (n = 7)**	**0 (n = 2)**	**0 (n = 3)**	**0 (n = 3)**	**0 (n = 5)**
Empty Bed Contact Time EBCT [min]	**27–33**	**15**	**14**	**25**	**30**
	Elimination ± Standard Deviation	**Pilot-Scale WWTP Köln-Rodenkirchen [65]**	**Full-Scale WWTP Neugut [63]**	**Semi-Technical Scale WWTP Detmold [49]**	**Pilot-Scale WWTP Wien [58]**
Diclofenac	99.6 ± 0.31%		95%	94%	
Hydrochlorothiazid	99.5 ± 0.24%		97%		57.0%
Metoprolol	99.7 ± 0.18%		98%	99%	
Sulfamethoxazole	98.0 ± 0.79%	99%		90%	76.5%
Diatrizoic acid	73.1 ± 7.43%			60%	43.6%
Iohexol	97.1 ± 1.04%				desorption
Iomeprol	97.9 ± 0.94%				
Iopamidol	98.1 ± 0.76%				
Iopromid	66.3 ± 42.83%				

Table 11. Treated-bed volumes until reaching an elimination <80% for the first time. Ozonation followed by GAC filtration in own experiments and literature from project reports [49,63,86].

	Experiment	**Literature**		
Specific Ozone Dose [mg_{O3}/mg_{DOC}]	**0.1–0.5**	**0.6–0.8**	**0.35–0.92**	**0.34**
Empty Bed Contact Time EBCT [min]	**27–33**	**15–45**	**14.5 ± 3**	**25**
	Elimination ± Standard Deviation	**Full-Scale Weißenburg [86]**	**Full-Scale Neugut [63]**	**Semi-Technical Scale WWTP Detmold [49]**
Benzotriazole	>6000	>32,000	20,000	25,000
4-Methylbenzotriazole	>6000	>32,000		
5-Methylbenzotriazole	>6000	>32,000		
Carbamazepine	>6000	>32,000		34,500
DCBZ	>6000			
Candesartan	>6000		10,000	
Diclofenac	>6000	>32,000	20,000	>40,000
Hydrochlorothiazid	>6000	>32,000	16,500	
Metoprolol	>6000	>32,000	23,500	19,000
Sulfamethoxazole	>6000	>32,000		14,000
Diatrizoic acid	4400			4000
Iohexol	>6000			
Iomeprol	>6000			
Iopamidol	>6000			
Iopromid	>6000			

Table 12. Treated-bed volumes until reaching an elimination < 80% for the first time. GAC filtration as stand-alone from literature from project reports [49,58,63] and a paper [59].

	Experiment	**Literature**			
Specific Ozone Dose [mg_{O3}/mg_{DOC}]	**0.1–0.5**	**0**	**0**	**0**	**0**
Empty Bed Contact Time EBCT [min]	**27–33**	**14**	**25**	**30**	**14**
	Elimination ± Standard Deviation	**Full-Scale WWTP Neugut [63]**	**Semi-Technical Scale WWTP Detmold [49]**	**Pilot-Scale WWTP Wien [58]**	**Pilot-Scale WWTP Berlin [59]**
Benzotriazole	>6000	21,000	16,000		10,500
4-Methylbenzotriazole	>6000			2300	13,300
5-Methylbenzotriazole	>6000				13,300
Carbamazepine	>6000		16,000		3100
DCBZ	>6000			6900	
Candesartan	>6000	5500			
Diclofenac	>6000	12,000	11,500		8100
Hydrochlorothiazid	>6000	12,000		1900	
Metoprolol	>6000	21,000	16,000		13,300
Sulfamethoxazole	>6000		9000	2000	3400
Diatrizoic acid	4400		5000	1400	1700
Iohexol	>6000			1700	
Iomeprol	>6000				3600
Iopamidol	>6000				
Iopromid	>6000				3600

All substances, except Diatrizoic acid, did not experience breakthroughs during the experimental period, as expected from the literature. The reduced elimination of Diatrizoic acid at about 3000 BV and an elimination of less than 80% after 4400 BV corresponds very well with findings in the literature (breakthrough after pre-treatment with ozone in the literature: 3150 BV [48,49], 2500–3000 BV [58]) and is comparable to or better than in GAC filtration alone (breakthrough GAC as stand-alone: 5000 [49], 1400 [58], 1700 [59]). A pre-treatment with ozone also seems to have positive impact on the breakthrough of other X-ray contrast media such as Iohexol, Iomeprol, and Iopromid as their elimination did not fall below 80% during the 6000 BV experimental period. Schoutteten et al. (2016) [108] confirmed that oxidizing the X-ray contrast media Diatrizoic acid before adsorption onto activated carbon improves its adsorption. However, if its elimination is targeted, a catalytic reduction prior to adsorption could be more effective in achieving higher removal efficiencies [108].

4.3.2. By-Products Generated from Ozonation and Transformation Product from Diclofenac

As expected from the literature [74], almost no bromate was removed from the GAC filter. However, as mentioned in Section 4.2.2, its concentration after ozonation (3.3 µg/L) and after GAC (2.9 µg/L) remained below the limit of drinking-water standard (10 µg/L) [103].

One advantage of combining ozonation and GAC filter is that transformation products formed in ozonation are partially removed in the GAC step. This was demonstrated for the by-product NDMA and transformation product 2,6-dichloroaniline, which were detected in higher concentrations after ozonation compared to before ozonation in some sample series, particularly at higher ozone doses. After GAC treatment, the concentrations were again significantly lower or below LOQ, as expected based on the findings of [27]. No correlation was found between the residence time (EBCT) in the filter (27 to 40 min) and the decrease in the concentrations of the transformation products. Further investigations could be conducted on the OMPs resorption in backwashing water, which was not analyzed in this study.

4.3.3. Microplastics

The removal of microplastics particles occurs primarily in the GAC filter. However, compared to Benstöm et al. (2014) [40] with a setup of GAC filter only, higher removal rates of solid particles (5–1000 µm) exceeding 92%, compared to 81–87%, were observed with the combined system of ozonation and GAC filtration. This improvement is likely attributed to the prior reduction in surface charge on particles due to ozonation. Additionally, the removal rates of MPs in this study (92–99%) are similar to those reported by Kim and Park [97], where an electro-coagulation step preceded GAC filtration. This suggests that a pretreatment step, such as ozonation, can enhance removal efficiency in GAC filters.

The smaller MP size fraction (5–50 µm) was rarely detected both before and after the combined removal. This may be related to a limitation in the sampling method where 30–100% of this size fraction can be captured depending on the flow rate into the SBs. However, using the same flow rates in the two SBs theoretically mitigates this limitation, ensuring that the removal of this size fraction remains relevant. Further investigation is needed to better understand the removal mechanism of smaller MP particles (<50 µm), particularly in terms of adsorption versus filtration, within the combined ozonation and GAC filter step. This would help to optimize removal processes when smaller MPs are more abundant and ensure efficient regulation of operational parameters at the plant (e.g., ozone doses).

The additional removal of MPs at treatment plants using this method adds remarkable value beyond the primary objective of removing OMPs. With an average MP removal rate of approximately 96% from secondary clarifiers' effluent to the combined ozone/GAC System and a suggested annual MP emission of around 0.94 g/(ca.*a) from the effluent of the secondary clarifiers' effluent [109], the annual emission could be reduced to about 0.042 g/(ca.*a).

4.3.4. C, N, and P Parameters

The concentrations of carbon parameters in the wastewater were further reduced by the post-treatment with GAC. During the experimental period of around 6000 BV, a slight decrease in elimination was observed for carbon parameters, for example, from approximately 70% to 50% for DOC. The impact of the contact time (EBCT) and the ozone dose in pre-treatment on elimination cannot be assessed with certainty. Differences may be attributed to both parameters or the decreasing adsorption capacity of the filter bed over time (see Figure 7).

A good correlation between OMPs and SAC_{254} was observed for ozonation ($R^2 = 0.92$), while the overall eliminations in the combination of ozonation and GAC did not correlate well ($R^2 = 0.33$) (Figure 8). The correlation has already been described in the literature for ozonation (for example [52,53,55]), granular activated carbon [56], and the combination of ozone and activated carbon as well [29,30].

Nitrite and ammonium are converted to nitrate during ozonation and GAC filtration, indicating aerobic conditions in the GAC filter. The in- and decreases are in a similar range to those described in the literature for a similar pilot plant [48,49]. The overall increase in inorganic nitrogen compounds can be attributed to a decrease in organic ones that were not measured in this experiment but described in the literature [110].

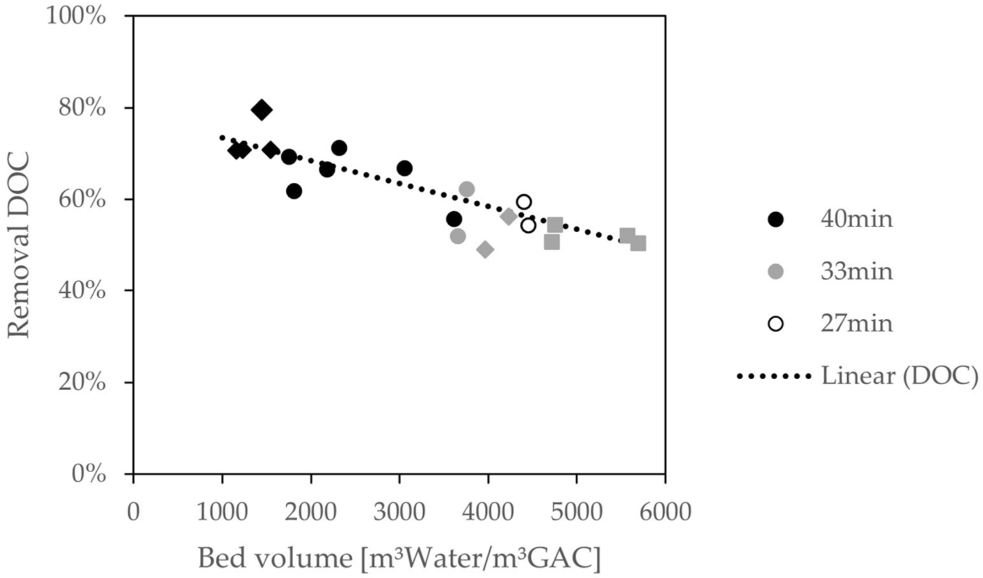

Figure 7. Breakthrough curve of DOC in the combination ozonation and GAC filtration over time. Results of the pilot plant with varying specific ozone doses (0.1–0.5 mg_{O3}/mg_{DOC}) and EBCT between 27 and 40 min. Rhombus = 0.5 mg_{O3}/mg_{DOC}; circle = 0.2 mg_{O3}/mg_{DOC}; square = 0.1 mg_{O3}/mg_{DOC}.

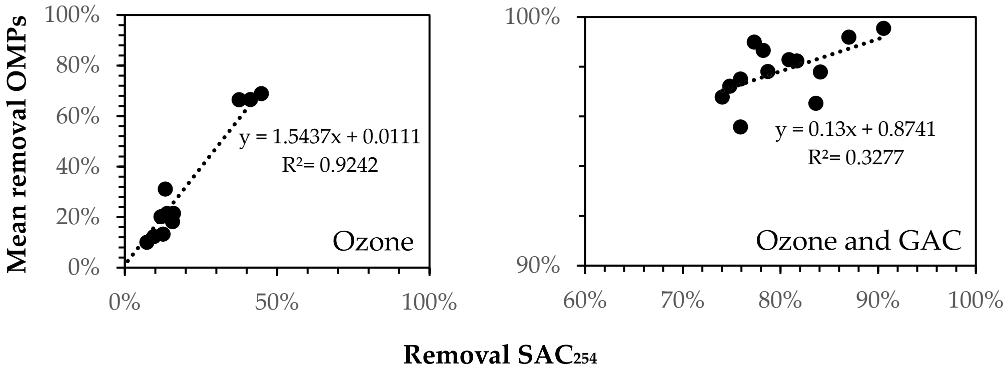

Figure 8. Correlation of arithmetic mean of all measured organic micropollutants (OMPs) and the removal of Spectral Absorption Coefficient at 254 nm (SAC_{254}) through ozonation and ozonation and GAC in combination.

In GAC filtration, total P is removed, and PO_4–P is further formed. These findings do not correspond to the results of Multhaup et al. (2023) [107], who also investigated GAC filtration with and without an ozonation with 1.54 mg_{O3}/mg_{DOC}. They observed a minimal reduction in the total P concentration for the combination of ozone and GAC, and in contrast to GAC as a stand-alone, the particulate fraction was higher. PO_4–P was present in similar concentrations after ozonation and GAC filter as before the treatment [107]. To our knowledge, changes in phosphorus compositions have not been described more often in the literature. Given the upcoming stricter requirements, synergetic effects of the micropollutants elimination on P and N compounds should be investigated further.

5. Conclusions

This study demonstrated the performance of combined ozonation and GAC filtration on the simultaneous elimination of a wide range of wastewater constituents for the first time. The effects of the treatment processes on OMP, MP, and on C, N, and P parameters could be evaluated from a WWTP effluent under different operating conditions at a pilot scale level.

A low ozone dose of 0.1–0.5 mg_{O3}/mg_{DOC} in combination with the GAC filter is an efficient way to prevent the formation of toxic oxidation by-products, such as bromate and NDMA, while achieving high removal levels of OMP (>80%). A higher elimination and a later breakthrough is achieved than with GAC filtration as a stand-alone even for substances that are difficult to eliminate, such as Diatrizoic acid. Further research with longer experiments (>6000 BV) is needed to determine when OMP would have a breakthrough in the GAC filter when using low ozone concentrations and when GAC must be reactivated. Then, an overview of the environmental impact associated with the combination of ozonation and GAC filtration could be provided by a life cycle assessment.

In addition, this study demonstrated the potential of integral sampling methods, specifically sampling boxes (SBs), for effective long-term monitoring of MP emissions in wastewater treatment processes. More importantly, the combination of ozonation and GAC filtration proved to be a highly effective treatment strategy, achieving a remarkable 97% reduction in MP from the secondary clarifiers' effluent. This led to a significant decrease in specific emissions, based on calculations in this study, from approximately 940 mg/(p.e.*a) to 42 mg/(p.e.*a).

Concentrations of the C parameters (DOC, COD, and SAC_{254}) decreased by at least 50% after the GAC filter regardless of the ozone dose was applied during the experiment. Regardless of the ozone dose administered, nitrite and ammonium concentrations decreased (both to a mean concentration of 0.02 mg/L and a maximum concentration of 0.18 and 0.11 mg/L, respectively) after the combined ozonation and GAC filter, while the nitrate concentration increased (to an average of about 5 mg/L and a maximal concentration up to 7.96 mg/L). Moreover, total P concentration decreased after the pilot plant (mean concentration of 0.23 mg/L and a maximum concentration of 0.44 mg/L). P concentrations are still below the future limit given specified by the adopted text of the EU Urban Wastewater Treatment Directive, in which WWTP effluent shall maintain a maximum concentration of P_{tot} of 0.5 mg/L for WWTP $\geq$ 150,000 population equivalent. The combination of ozonation and GAC filter yields positive results for several parameters. This approach is particularly significant for addressing future requirements concerning to harmful substances, such as OMP, ammonium, nitrite, and P, which can benefit water bodies. However, the results also indicate that inorganic nitrogen is only converted and not removed. For this reason, the upstream stage of the OMP treatment step must already eliminate N below the 8 mg/L required for effluents from WWTP $\geq$ 150,000 population equivalent to ensure compliance with the nitrogen effluent value even when combined ozonation and GAC is used.

Supplementary Materials: The following supporting information can be downloaded at: https://www.mdpi.com/article/10.3390/environments11110241/s1, Figure S1: The GAC filter as a vertical column outside of the ozonation plant; Figure S2: Stainless-steel sedimentation box for Microplastic sampling; Figure S3: Particle size distribution of MP of the two sampling cycles; Figure S4: Removal of total solids and change in particle size distribution after the two sampling cycles. High TS loads (about 300 mg) were detected in the SB2 after cycle 2 due to release of GAC particles into SB2, which were visually observed (black carbon particles); Figure S5: Breakthrough curves of the GAC filter with all operation parameters; Figure S6: Bubbles in ozone reactor with diameter of the ozone reactor for size comparison. Table S1: Average concentration with minimum and maximal concentrations of organic micropollutants analyzed for the 6 screenings performed during the year 2020; Table S2: Concentration of pesticides analyzed during campaign measurement in 2012 and 2013; Table S3: Analytical methods of ozone by-products and transformation products. LOQ: Limit of Quantification; Table S4: Average concentrations with minimum and maximal concentrations of indicators substances in the effluent of secondary clarifier of the WWTP, after ozonation and after GAC filter during the pilot plot operation; Table S5. Average concentrations with minimum and maximal concentrations of C, N, and P parameters in the effluent of secondary clarifier of the WWTP, after ozonation and after GAC filter during the pilot plot operation.

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