Influence of Wastewater Particles on Ozone Degradation of Trace Organic Contaminants

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S *Supporting Information*

ABSTRACT: In this Article, we demonstrate the influence of effluent particles (in the range of <50 μm) on ozone degradation of trace organic contaminants (TrOCs) and effluent-quality parameters. Secondary effluent was filtered through different pore-size filters and ozonated at various ozone doses. Degradation of both ozone-reactive and ozone-refractory contaminants improved following ozonation of effluent filtered with smaller pore size filters, indicating that particles in this range may adversely affect ozonation. The inhibitory effect of particles was attributed to their reaction with ozone, reducing available ozone and HO$^{\bullet}$ radicals. In addition, increasing filtration level decreased the effluent's (instantaneous) ozone demand and increased removal of effluent UV absorbance (UVA$_{254}$),

further establishing that ozone reacts with effluent particles, in competition with dissolved matter. Moreover, ozone was shown to react with particles even during the first seconds of the process, suggesting a high rate of some ozone–particle reactions, comparable to ozone reaction with highly reactive dissolved organic matter moieties. Particle image analysis revealed that particle formation/aggregation and particle disintegration occurs simultaneously during wastewater (WW) ozonation. Our study implies that particles could affect the efficiency of WW ozonation, by increasing the effluent's ozone demand and decreasing contaminant degradation.
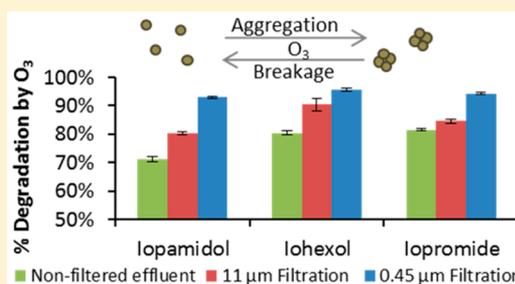
INTRODUCTION

Ozone efficiently degrades many trace organic contaminants (TrOCs) in wastewater (WW), and it is increasingly being used to remove these compounds from municipal and industrial WW effluent.[1−6] The extent of TrOC removal is typically determined by the applied ozone dose, the (second-order) reaction-rate constant of ozone with the target contaminant ($k_{O_3,TrOC}$, M^{-1} s^{-1}), and WW composition.[5,7,8] Among WW constituents, dissolved organic matter (DOM) and nitrite (which readily react with ozone) are considered the main influential parameters.[9,10] On the other hand, the influence of particulate matter in the WW is less clear.

Particles in water sources may be classified into various groups, such as living versus nonliving, nanosized versus submicron- to micron-sized, mineral versus organic and dispersed as individual entities or associated in flocs. The interactions of water and WW particles with ozone have been investigated primarily with respect to the influence of preozonation on particle-removal processes[11−13] and the impact of particles on ozone disinfection treatment.[14] For example, ozone is assumed to desorb organic matter from particle surfaces, reducing the electrostatic-stabilizing effect of organic matter and improving particle aggregation.[11] Ozone improved subsequent particle settling in kaolin/humic synthetic water, by breaking up large porous flocs (decreasing floc size), and increasing their density (higher fractal dimension).[15] In addition, ozone was shown to form particles through DOM polymerization.[16] With respect to disinfection, particles can protect embedded microbes, as ozone penetration into particles is limited.[17] Dietrich et al.[14] suggested that ozone inactivation of microbes associated with particles (>6 μm) will take place only at high ozone dose because of slow intraparticle ozone diffusion, and the preferential reaction of ozone with DOM.

The main factors affecting ozone–particle interactions are applied ozone dose,[18] water composition,[19] and particle characteristics as size and adsorbed organic matter. Studies have shown that ozone can destabilize and aggregate smaller particles into larger ones, while breaking down large particles into smaller ones.[20] With continual formation and continuous breakdown, aggregation and removal of particles, it is difficult to predict the net effect of ozone on the particle-size

Table 1. Summary of the Analyzed Trace Organic Contaminants

compound	class	molecular formula	CAS No.	k_{O_3} $(M^{-1} s^{-1})^{7,38}$
sulfamethoxazole	antibiotic	$C_{10}H_{11}N_3O_3S$	723-46-6	2.5×10^6
diclofenac	anti-inflammatory	$C_{14}H_{10}Cl_2NNaO_2$	15307-79-6	1×10^6
carbamazepine	antiepileptic	$C_{15}H_{12}N_2O$	298-46-4	3×10^5
iohexol		$C_{19}H_{26}I_3N_3O_9$	66108-95-0	1.4
iopromide	contrast media	$C_{18}H_{24}I_3N_3O_8$	73334-07-3	0.8
iopamidol		$C_{17}H_{22}I_3N_3O_8$	60166-93-0	1.4

distribution (PSD).[21] Li et al.[15] reported that ozonation of kaolin/humic synthetic water at a dose of 0.63 mg L^{-1} had no effect on PSD, whereas higher doses (>2.64 mg L^{-1}) shifted the distribution curve from smaller- to larger-sized particles (main peak shifted from ~4 μm to ~6 μm).

These studies demonstrate the potential interactions between ozone and water/WW particles. However, very little, information is currently available on the relevance of these interactions to ozone treatment of TrOCs in WW effluent. Huber et al.[2] showed that changes in WW total suspended solids (TSS) only marginally affect ozone degradation of TrOCs; however, particles were not directly measured and no experimental data were provided on the influence of particle size.

The goal of the present study was to examine the influence of particle concentration and size distribution on ozone degradation of TrOCs during WW application, as well as the influence of particles during ozonation on changes in different effluent-quality parameters (e.g., UV absorbance at 254 nm). In addition, the study examines the counter-effect of ozone on WW particles of different sizes, and evaluates the dominant interactions.

■ MATERIAL AND METHODS

Standards and Reagents. Six TrOCs were selected for this study, based on their reaction rate with ozone: fast-reacting ($k_{O_3} > 10^4$ M^{-1} s^{-1}) and slow-reacting ($k_{O_3} < 10$ M^{-1} s^{-1}) compounds (Table 1). All standards (purity >99%) were obtained from Sigma-Aldrich, with the exception of iopromide and iopamidol (Holland-Moran, Israel), and they were all used as received. Stock solutions were prepared with deionized (DI) water (Direct-Q3 UV system, Millipore). LC-grade methanol and water were purchased from Bio-Lab (Jerusalem, Israel).

Experimental Procedures. To determine the influence of different particle sizes on ozone degradation of TrOCs, secondary WW effluent from the Shafdan WW treatment plant (Tel Aviv, Israel) was first filtered through different pore sizes (11-, 6-, and 2.5-μm cellulose filters (Whatman), and 1.2-μm glass filters (Whatman) and 0.45-μm PVDF filters, (Millipore)). Particle analysis showed that approximately 80% of the particles above the pore size were removed by filtration. The presence of particles in the filtrate larger than the filter pore-size may occur because of particle with needle-like or plate-like shapes that can pass through a pore size less than its nominal parameter[22] or PSD measurement method via image analysis which may present two different particles as one floc when drawn simultaneously.[23] The commonly used distinction between dissolved, colloidal and suspended solids is <1 nm, 1 nm to 1 μm, and >1 μm, respectively. For operational reasons, however, particles are often considered as solids retained by a 0.45 μm membrane filtration;[24] this approach was adopted in this study. The filtered effluent samples were spiked with the examined TrOCs at initial concentrations of 100 μg L^{-1} (each

compound), before being subjected to ozonation. Concentration of dissolved organic carbon (DOC) and pH of the raw effluent were 10.3 ($\pm$0.2) mg L^{-1} and 7.8 ($\pm$0.1), respectively, and remained unchanged during filtration and ozonation.

The spiked effluent was treated with ozone, at doses of 0.17, 0.69, and 0.93 mg O$_3$ mg DOC^{-1}, in the range of WW applications.[25] In addition, ozone depletion in the first milliseconds (from 4 ms to several seconds) was evaluated using an ozone quench-flow reactor (QFM-400, Bio-Logic, USA). In this system, three syringes, driven by independent motors, introduce ozone stock (prepared separately), effluent and DI water at different ratios into a mixing chamber. The reacting mixture then passes through a single delay line, used as a contact chamber to control reaction time. The reaction is stopped by injecting an indigo solution with a fourth syringe to quench any residual oxidants, and the final solution is flushed through an exit line to a collection device.

For the high ozone doses (0.69 and 0.93 mg O$_3$ mg DOC^{-1}), experiments were carried out in a 0.5-L fully mixed-batch reactor, by adding concentrated stock solutions of ozone to the filtered effluent. To ensure more efficient mixing for the lowest ozone dose of 0.17 mg O$_3$ mg DOC^{-1}, the QFM was used without adding indigo as a quencher. Ozone stock solution (~40 mg L^{-1}) was prepared in chilled DI water, using an oxygen-fed ozone generator (up to 4 g h^{-1}, BMT 802N, Germany). After ozone completely reacted with the effluent (dissolved ozone <0.01 mg L^{-1}), the samples were analyzed for TrOC concentration, effluent-quality parameters and PSD. Experiments (i.e., filtration, ozonation, TrOC analysis) were performed in triplicate, using effluent grab samples taken during the period October 2012–June 2013.

Analytical Methods. Ozone concentration in the gas stream was measured by an ozone gas analyzer (BMT 963, Germany). Dissolved ozone was measured by the indigo method (APHA, method 4500B). TrOCs were detected by HPLC (Agilent 1100 series; ACE-RP phenyl column 2.1 mm × 250 mm) coupled with a mass spectrometer (Q-Tof MS, Waters Premier). The HPLC flow rate was 0.5 mL min^{-1} and the injected volume was 100 μL. The mobile phase consisted of water (A) and methanol (B), adjusted to pH 3 with formic acid. The eluent gradient started with 10% eluent B for 1 min, followed by a 4 min linear gradient to 90% B, a 5 min isocratic elution at 90% B, and a 2 min linear gradient back to 10% B, maintained for 4 min for equilibration. The Q-Tof MS was operated in positive mode, with limit of quantification (LOQ) of 0.1 μg L^{-1}.

Total organic carbon (TOC) and DOC were measured using a TOC analyzer (Torch, Teledyne Tekmar, USA), following APHA method 5310B. Light absorbance of the effluent at 254 nm (UVA$_{254}$) was measured in a UV–Vis spectrophotometer (Varian, Cary 100 BIO, Victoria, Australia) after filtration at 0.45 μm. Filtered biological oxygen demand (BOD$_f$) was analyzed (with indigenous seed from the WW facility)

Table 2. Particle-Size Distribution (PSD) in Shafdan Nonfiltered Secondary Effluent from October 2012–June 2013

	ECD (μm)	percent from total particle concentration (last column)							
		2–3	3–5	5–10	10–15	15–30	30–50	50+	total (no./mL)
winter	26 Dec. 2012	54.1	22.5	16.7	4.3	2.0	0.4	0.1	52,279
	17 Jan. 2013	57.8	21.3	13.9	5.1	1.6	0.2	0.1	46,558
	24 Jan. 2013	51.0	17.8	17.6	10.1	3.1	0.5	0.1	58,372
	12 Feb.2013	36.8	12.4	42.7	6.1	2.0	0.0	0.0	33,915
	6 Mar 2013	46.2	19.8	17.5	8.3	6.9	1.1	0.2	61,011
	average								50,427
summer	15 Oct. 2012	57.7	20.6	15.2	3.9	2.1	0.4	0.1	37,346
	5 Nov. 2012	66.0	11.8	16.3	3.4	2.2	0.2	0.1	29,926
	29 Nov.2012	56.2	12.7	20.2	5.7	4.2	0.9	0.2	34,356
	2 June 2013	44.7	16.0	29.3	7.6	2.1	0.3	0.0	11,702
	3 June 2013	42.8	16.1	31.1	7.1	2.5	0.5	0.0	12,912
	average								25,249

according to standard method SM5210B (LOQ = 1 mg L^{-1}). TSS and (filtered) chemical oxygen demand (COD$_f$) were measured using 1.2-μm and 0.45-μm filters, according to methods 2540D (LOQ = 0.2 mg L^{-1}) and 5220B (LOQ = 5 mg L^{-1}), respectively.[26]

Particle Analysis. Effluent particles were analyzed by Micro Flow Imaging technology (DPA 4100, Protein Simple Inc., Canada). This apparatus employs a digital camera with an illumination and magnification system to capture in situ images of suspended particles in a flowing sample. A detailed description of this analysis is published elsewhere.[27] In brief, a fluid sample is drawn through a flow cell, illuminated with a light-emitting diode at 470 nm wavelength, and the magnified image is captured by digital camera. This image was automatically analyzed to determine the particles' equivalent circular diameter (ECD), which represents the diameter of a sphere that occupies the same two-dimensional surface area as the particle. Analysis was conducted on particles of between ∼2 and 400 μm.

■ RESULTS AND DISCUSSION

Particle-Size Distribution (PSD) in Secondary Waste-water Effluent. Particles in WW effluent are typically quantified using bulk parameters such as turbidity and TSS, which do not provide information on specific particle characteristics (e.g., size and shape).[23] To determine the particles' size and size distribution in the Shafdan secondary effluent, a dynamic image analysis was applied. Table 2 presents the PSD for nonfiltered effluent samples, taken during the months of October 2012–June 2013.

The shape of the PSD curve was similar for both winter (December 2012–March 2013) and summer (October to November 2012, and June 2013) samples, with more than 99% of the particles smaller than 50 μm, and the highest fraction at ECD = 2–3 μm. Particles smaller than ∼2 μm were below the detection limit of the analytical instrument and could not be quantified. In general, particle count was higher in the winter than in summer, for all ECD ranges (with some minor exceptions). This trend is probably due to inhibition of the biological treatment by the cold weather (average winter temperature = 14 ± 2 °C; average summer temperature = 24 ± 4 °C), resulting in low sludge-settling efficiency.[28] The exceptionally low particle count during the month of February is likely the result of WW dilution because of an unusually high volume of rain during this month. On the basis of the PSD analysis, the study focused on particles smaller than 50 μm.

Influence of Particles on Ozone Degradation of TrOCs. Ozone degradation of the target TrOCs was determined for WW effluent filtered through different pore sizes, using ozone doses of 0.17, 0.69, and 0.93 mg O$_3$ mg DOC^{-1}. Sorption of the examined TrOCs to the suspended solids during the ozone experiments was considered negligible, as previously shown by others.[2,29]

Degradation of carbamazepine, diclofenac and sulfamethoxazole (fast-reacting compounds) in different pore-size-filtered effluents is presented in Figure 1, for the low ozone dose of
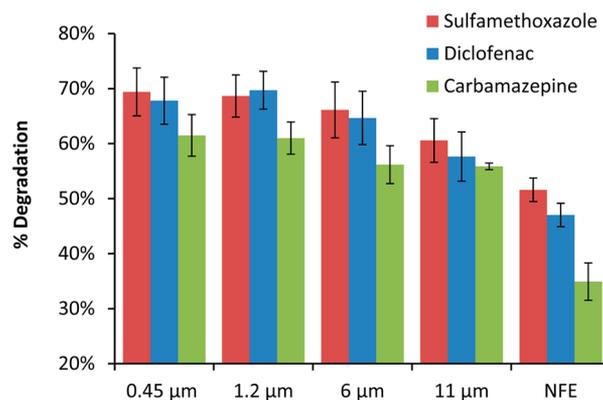

Figure 1. Ozone degradation of the fast-reacting trace organic contaminants (TrOCs) in different pore-size filtered effluents. Experiments were conducted in the quench-flow system, at 0.17 mg O$_3$ mg DOC^{-1}. NFE: Nonfiltered effluent. Error bars indicate standard deviations based on triplicate measurements.

0.17 mg O$_3$ mg DOC^{-1} (using a quench-flow reactor). Data for the slow-reacting TrOCs are not presented, as these compounds were ozone-resistant and only marginally degraded (<10%). In the nonfiltered effluent, carbamazepine, diclofenac and sulfamethoxazole were degraded by 35%, 47%, and 52%, respectively, values that are typical for effluent ozonation of fast-reacting compounds.[25]

A general trend could be seen between the level of effluent filtration and the mean TrOC degradation. For example, sulfamethoxazole was eliminated by 52%, 61%, 66%, 68%, and 69% for the nonfiltered, 11-μm, 6-μm, 1.2-μm, and 0.45-μm filtered effluents, respectively. In other words, increasing the level of filtration (i.e., smaller pore size) decreased the amount of particles in the effluent (and shifted the PSD toward smaller particles), resulting in improved degradation of the TrOCs.

Two possible mechanisms are potentially responsible for this phenomenon: (i) protection of the TrOCs by particles from ozone attack (possibly through sorption) and (ii) reaction of particles with the applied ozone, in competition with DOM (thus, lowering ozone exposure and inhibiting TrOC degradation). Zimmermann et al.[25] observed an overprediction of TrOCs oxidation in a full-scale ozone system treating secondary WW effluent with a model, coupling reactor hydraulics and ozone chemistry. They attributed this overprediction to contaminants' protection from ozone attack by their interaction with colloids (<1 μm), not accounted for in the model. Huber et al.[2] showed that the addition of 15 mg L^{-1} TSS of activated sludge to secondary effluent only marginally influenced ozone oxidation of fast-reacting TrOCs; however, the estimated size of the added sludge flocs was relatively large (ECD $\geq$ 50 μm). The presence of smaller particles on the other hand (size not specified) resulted in a significant inhibition of TrOCs oxidation, likely due to particle reaction with ozone.

Degradation results for the high ozone doses (i.e., 0.69 and 0.93 mg O$_3$ mg DOC^{-1}) are presented in Figure 2. Data for
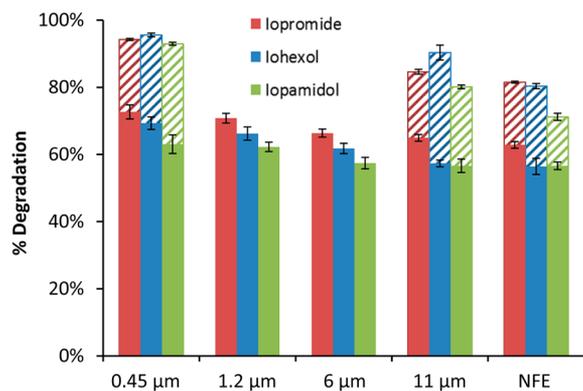

Figure 2. Ozone degradation of the slow-reacting trace organic contaminants (TrOCs) in different pore-size filtered effluents. Experiments were conducted in the batch system, at ozone doses of 0.69 (solid fill) and 0.93 (dashed fill) mg O$_3$ mg DOC^{-1}. NFE: Nonfiltered effluent. For technical reasons, experiments were not carried out at 0.93 mg O$_3$ mg DOC^{-1} using 6- and 1.2-μm filters. Error bars indicate standard deviations based on triplicate measurements.

carbamazepine, diclofenac and sulfamethoxazole are not shown, as these compounds were all removed below the detection limit of the analytical method at 0.69 mg O$_3$ mg DOC^{-1}. Previous studies have shown complete elimination of these compounds from WW effluent at an ozone dose of 0.47 mg O$_3$ mg DOC.[4]

The slow-reacting compounds (i.e., iopromide, iohexol, and iopamidol) were degraded by up to 63% (0.69 mg O$_3$ mg DOC^{-1}) and 82% (0.93 mg O$_3$ mg DOC^{-1}) in the nonfiltered effluent, because of their reaction with hydroxyl (HO$^\bullet$) radicals, generated principally by ozone's reaction with DOM.[30] Similar to the results obtained for the low ozone dose, increasing the level of effluent filtration improved the degradation of TrOCs. For example, at 0.69 mg O$_3$ mg DOC^{-1}, iopromide was eliminated by 63%, 65%, 66%, 71%, and 73% for the nonfiltered, 11-, 6-, 1.2-, and 0.45-μm filtered effluents, respectively. While the compound's degradation at 0.93 mg O$_3$ mg DOC^{-1} reached 71%, 80%, and 93% (for the nonfiltered, 11- and 0.45-μm filtered effluents). For technical reasons, experiments were not carried out at 0.93 mg O$_3$ mg DOC^{-1} using 6-μm and 1.2-μm filters. Since sorption of iodinated contrast agents to particles is unlikely because of their

hydrophilic nature,[31,32] we can safely assume that the inhibitory effect of particles on the oxidation of these compounds is due to particles reaction with ozone. This reaction likely generates HO$^\bullet$ at lower yield than ozone reaction with DOM, decreasing the ozone and HO$^\bullet$ exposure.

As a note, the differences between the degradation rates of the TrOCs (presented in Figures 1 and 2) in the nonfiltered and filtered effluent were statistically significant for all pore-size filters (p-value <0.05). However, the differences between adjacent filtrations were not always significant. To strengthen the hypothesis of the inhibitory effect and mechanism of particles on TrOC oxidation (i.e., ozone consumption by particles), we further examined the influence of particles on ozone consumption and the changes in effluent-quality parameters (during ozonation).

Influence of Particles on Ozone Consumption and Effluent-Quality Parameters. Ozone consumption was measured in the batch system during the first 20 s of ozonation (instantaneous ozone demand, IOD[33]), and illustrated in Figure 3 for effluent at different filtration levels (0.93 mg of
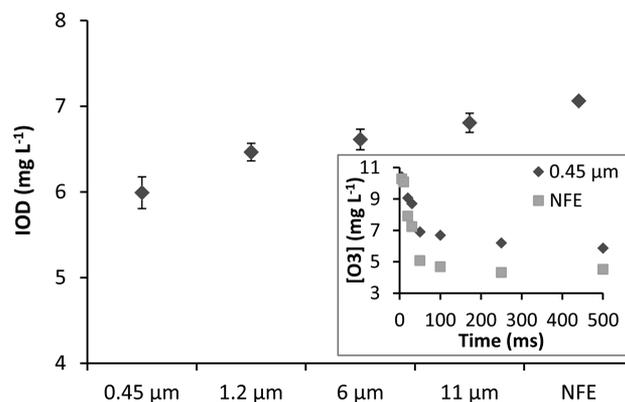

Figure 3. Instantaneous ozone demand (IOD) of different pore-size filtered effluents, during batch experiments at 0.93 mg O$_3$ mg DOC^{-1}. The inset presents O$_3$ depletion in a quench-flow system experiment during the first 500 ms for 0.45 μm filtered and nonfiltered effluent (NFE).

O$_3$ mg DOC^{-1}). In addition, ozone-consumption rate was monitored in the quench-flow reactor during the first 500 ms (Figure 3, inset). Clearly, increasing the level of filtration decreased the effluent IOD, and therefore fewer particles resulted in lower consumption of ozone in the first 20 s. A similar trend was observed using the quench-flow system, with less ozone depletion in the first 500 ms of the process for 0.45-μm filtered effluent, compared to the nonfiltered effluent. These data support the hypothesis that particles (in the range of 0.45 μm−50 μm) influence effluent ozonation through their reaction with applied ozone, in competition with DOM. Moreover, in the first few seconds of the process ozone typically reacts with highly reactive DOM moieties (e.g., amino- and phenolic groups).[30] Therefore, we can assume that at least some ozone−particle reactions occur at an extremely high rate (possibly ozone reactions with reactive moieties situated in the outer layers of the particles surface), in the upper range of the ozone reaction rates with DOM.

Removal of the effluent UV absorbance (UVA$_{254}$) during ozonation was directly correlated to the level of effluent filtration, with highest removal in the 0.45-μm filtered sample (Figure 4, for 0.93 mg O$_3$ mg DOC^{-1}). Removal of UVA$_{254}$ is
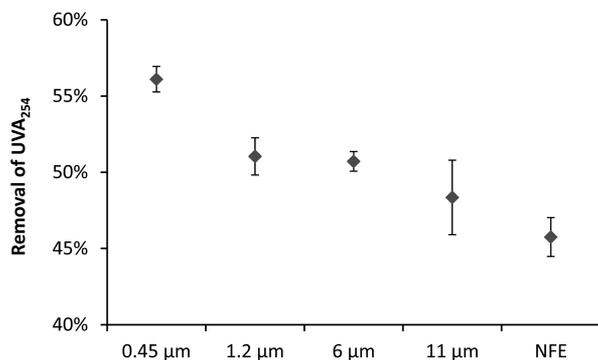
Figure 4. Ozone removal of UVA_{254} (at 0.93 mg O_3 mg DOC^{-1}) in different pore-size filtered effluents.

indicative of ozone reaction with conjugated systems in the DOM.[5] Thus, with fewer particles in the effluent (following filtration), more ozone is available for reaction with DOM, resulting in increased removal of UVA_{254}.

The changes in the effluent's BOD_f, COD_f, and TSS during ozonation are presented in Table 3, for nonfiltered and 1.2-μm

Table 3. Changes in Effluent-Quality Parameters Following Ozonation (0.69 mg O_3 mg DOC^{-1}) in Nonfiltered (NFE) and 1.2-μm Filtered Samples[a]

	O_3 treatment (mg L^{-1})	BOD_f (mg L^{-1})	COD_f (mg L^{-1})	TSS (mg L^{-1})
NFE	before ozone	3.0	32	3.3
	after ozone	6.1	32	3.5
1.2-μm filtration	before ozone	1.5	29	<0.2
	after ozone	4.5	26	1.4

[a]Standard errors were less than 15% and 5% for BOD_f and COD_f, respectively ($n = 3$).

filtered effluent samples (using 0.69 mg O_3 mg DOC^{-1}). For both samples, BOD_f concentration increased following ozonation (by ~3 mg of O_2 L^{-1}), due to the transformation of large organic molecules into smaller (biodegradable) ones.[6,34,35] The unexpected similar increase in BOD_f for the filtered and nonfiltered effluents is likely the result of the low sensitivity of the measurement method, especially at the low BOD range. TSS and COD_f remained relatively unchanged for the nonfiltered effluent while an increase in TSS and a decrease in COD_f were observed in the filtered effluent. The increase in TSS in the filtered sample may indicate the formation of particles (and TSS) by ozone-induced polymerization/floccu-lation of DOM.[11,16] This phenomenon was not seen in the nonfiltered effluent, probably due to equilibrium between the formation and disintegration of particles by ozone. The decrease in COD_f by ozone in the filtered effluent, as opposed to the unchanged COD_f level in the nonfiltered effluent, demonstrates once again the simultaneous reaction of ozone with particles and DOM (thus with less particles, more ozone reacts with DOM).

The results for ozone consumption and effluent-quality parameters, together with the data obtained for TrOCs oxidation, provide a strong indication of ozone's reaction with effluent particles (in the range of 0.45 μm < ECD < 50 μm), and its significance to ozone treatment. Huber et al.[2] used the film theory to estimate ozone consumption by sludge particles that were spiked to secondary effluent. Their model showed that for an ozone dose of 1 mg L^{-1}, TSS of 20 mg L^{-1},

and estimated particle size of 50 μm, only 0.4% of applied ozone was consumed by the particles. Changing the particle size in the model to 25 μm did not significantly increase ozone consumption by the particles.

In our case, the examined particles were in the range of ECD < 50 μm, with the vast majority smaller than 10 μm (~89%; Table 2). Since ozone consumption by particles is proportional to their surface area,[36] a portion of ozone higher than 0.4% will be consumed by particles in the present study. Moreover, some indications for significant ozone consumption by small effluent particles (<50 μm) were provided by Huber et al.,[2] showing that fine particles (much smaller than the sludge particles) occurring unintentionally in the effluent, highly inhibited ozonation of TrOCs. Our results extend the data provided by Huber et al.[2] to the lower range of particle size (0.45 μm < ECD < 50 μm), demonstrating the significance of these particles to WW ozonation.

Ozone Impact on PSD. Characteristic samples of non-filtered secondary effluent (for winter and summer) were analyzed for changes in PSD following ozonation at 0.93 mg of O_3 mg DOC^{-1} (Figure 5). Quantitative presentation of the
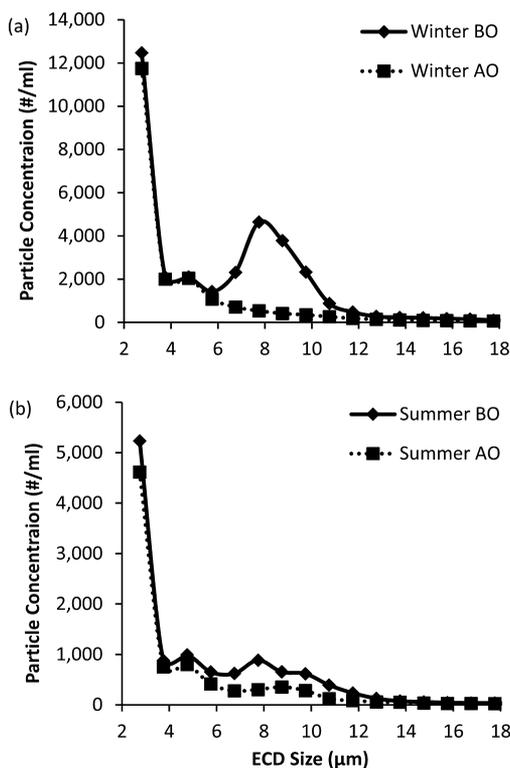

Figure 5. Particle-Size Distribution (PSD) in nonfiltered effluent samples taken during: (a) winter (February 12th, 2013) and (b) summer (June sixth, 2013) before ozonation (BO) and after ozonation (AO) at a dose of 0.93 mg O_3 mg DOC^{-1}.

particle-size distribution can be found in Supporting Information (Table S1). Blank experiments showed that dilution (by addition of ozone stock solution) did not affect the PSD (Figure S1 in Supporting Information). In general, the concentration of particles decreased following ozonation for all ECDs in both samples. This trend was most pronounced for particles with ECDs of 5−15 μm (up to 79% decrease), suggesting that these particles are highly reactive to ozone.
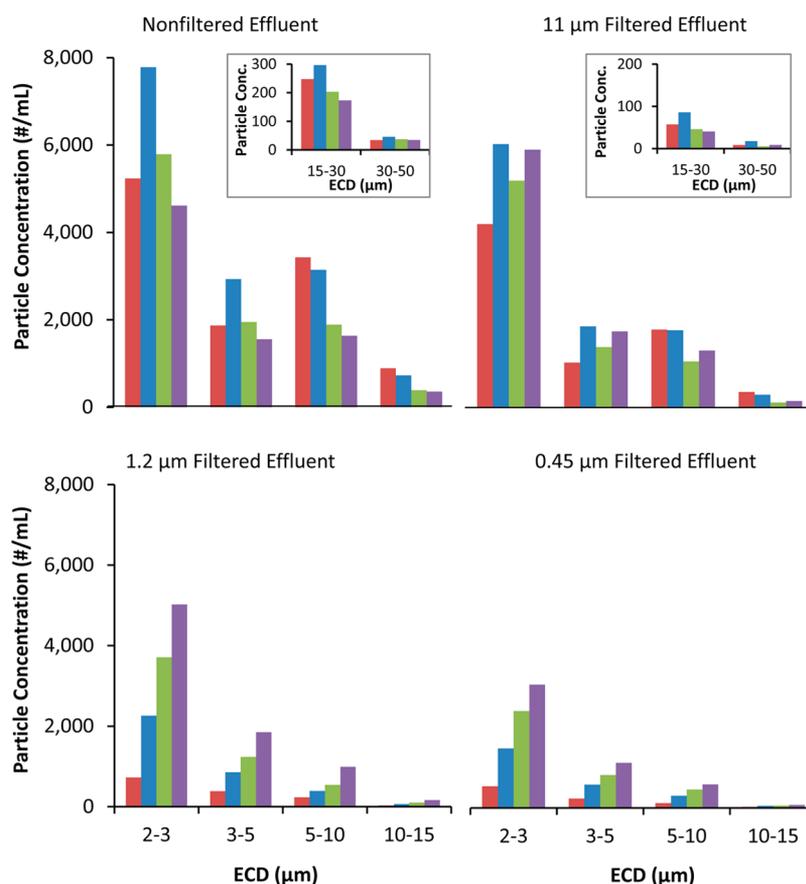
Figure 6. Particle-Size Distribution (PSD) analysis in different pore-size filtered effluents: nonfiltered, 11, 1.2, and 0.45 μm. Colored columns represent different ozone doses: before ozonation (red) and after ozonation with 0.17 (blue), 0.69 (green), and 0.93 (purple) mg O_3 mg DOC^{-1}. The inset is a magnification of particles in the range 15–50 μm (particles in this range were not detected at 1.2 and 0.45 μm filtration). The presented data was an average of two repetitions with differences of less than 10%.

Unexpectedly, a relatively small change was recorded for small-sized particles (i.e., ECD 2–3 μm), despite their relatively high specific surface area. This discrepancy can be explained by the different simultaneous processes, resulting in particle population balance. Specifically, (i) the formation of 2–3 μm particles from the breakdown of larger particles and the flocculation/aggregation of small particles/DOM, and (ii) the disintegration of 2–3 μm particles by ozone. Duguet et al.[16] showed that ozonation of industrial WW may transform DOM into insoluble compounds through phenol polymerization; Zho et al.[12] found that ozone can break large effluent particles into smaller ones.

To isolate the different ozone−particle interactions, we extended the PSD measurements to effluent samples filtered at 11, 1.2, and 0.45 μm (in addition to the nonfiltered samples), and ozonated with 0.17, 0.69, and 0.93 mg O_3 mg DOC^{-1}. Several trends were observed (Figure 6): (i) in the 0.45-μm and 1.2-μm filtered effluents, concentration of particles in the range of 2−15 μm increased with increasing ozone dose up to 0.93 mg O_3 mg DOC^{-1} (larger particles were not detected); (ii) in the nonfiltered and 11-μm filtered effluents, concentrations of small (2−5 μm) and large (15−50 μm) particles increased at low ozone dose (0.17 mg O_3 mg DOC^{-1}), while concentration of 5−15 μm particles remained relatively unchanged. Further increasing ozone dose up to 0.93 mg O_3 mg DOC^{-1} generally decreased the concentration of particles over the entire examined range (in the nonfiltered and 11-μm filtered effluents).

These results establish that both particle formation and breakage act concurrently during WW ozonation, with the dominant process generally shifting from the former to the latter with increasing ozone dose. Specifically, at low ozone dose, the dominant process is the formation (or growth) of particles, as demonstrated by the increase in particle concentrations in almost all cases. The relatively unchanged concentration of 5−15 μm particles in the nonfiltered and 11-μm filtered samples could be due to particle population balance. Applying a high ozone dose on the other hand (up to 0.93 mg O_3 mg DOC^{-1}) enhanced particle disintegration, as shown by the decrease in concentration of all-sized particles, in the nonfiltered and 11-μm filtered samples. Particle disintegration was not observed in the 1.2-μm and 0.45-μm filtered samples, since they were mostly removed by the filter.

Previous studies have confirmed the observed effect of ozone dose on PSD. Paode et al.[37] showed that ozonation of California State surface water with up to 0.4 mg O_3 mg DOC^{-1} increased the average diameter of supramicron particles (>2 μm) from ∼6.7 to ∼7.2 μm, implying that particle growth is an important process. Further increasing ozone dose up to 1.6 mg O_3 mg DOC^{-1} decreased the average particle diameter to ∼6.5 μm, likely because of particle disintegration. Others have demonstrated the same phenomenon in secondary wastewater effluent;[12] the growth of particles at the relatively low ozone dose of 0.55 mg O_3 mg TSS^{-1} (i.e., decreasing the fraction of 7−200 μm and increasing the fraction of 200−700 μm) and the disintegration of particles at 4.91 mg O_3 mg TSS^{-1} (decreasing

fraction of 7−200 μm particles and increasing fraction of 0.9−20 μm). A possible explanation for these trends might be that at low doses, ozone reacts solely with organic matter adsorbed onto the particle surfaces, reducing the particles' negative charge and lowering their stability (enhancing aggregation), whereas at high doses, ozone may also disrupt, and disperse colloidal aggregates.[37]

Ozone-particle interactions were also observed during large-scale ozone treatment, analyzing samples from an ongoing pilot system during winter 2014 (treating secondary effluent at the Shafdan WWTP, Tel Aviv, Israel). The pilot included coagulation/flocculation (polyaluminum chloride, PACl), followed by media filtration and ozonation (0.9−1.0 mg O_3 mg DOC^{-1}). A detailed description of the pilot is given in Supporting Information (Text S1, Figure S2).

As expected, particle concentration decreased after coagulation/flocculation and filtration for all ECDs (Table 4). On the

Table 4. Particle-Size Distribution in the Pilot System (Winter 2014)

ECD (μm)	secondary effluent	after filtration	after ozonation
2−3	37,324	10,334	5,856
3−5	13,833	3,681	3,785
5−10	8,895	1,556	1,440
10−15	2,390	206	281
15−30	1,057	35	63
30−50	102	1	5
50+	19	0	0

other hand, samples taken after ozonation showed a decrease in the concentration of small particles (most noticeable for 2−3 μm) and an increase in the larger-sized ones (10−50 μm) (Table 4). These trends were repeatedly observed during several monitoring campaigns (an example for samples taken during summer period is presented in Table S2 in Supporting Information). As previously noted, this behavior implies simultaneous formation and breakage of particles by ozone. Note that residual PACl after filtration was marginal (<0.06 mg L^{-1} as Al), excluding its involvement in particle growth during ozonation. Although direct comparison of the pilot results to the lab-scale data may be misleading (for example, due to different ozone injection systems), they nevertheless provide additional indications for ozone-particle interactions in large-scale systems. These interactions can potentially affect the efficiency of WW ozonation, and should not be overlooked. Moreover, our results suggest that the commonly used ozone/DOC ratio[34] may under-predict the ozone dose required for TrOCs degradation (especially in nonfiltered effluent), and the use of ozone/TOC ratio might be more appropriate.

■ ASSOCIATED CONTENT

ⓢ Supporting Information
Quantitative presentation and dilution effect on PSD, a detailed description of the pilot setup and, PSD data from the pilot system measured during summer 2014. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes
The authors declare no competing financial interest.

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