



# A hybrid process of biofiltration of secondary effluent followed by ozonation and short soil aquifer treatment for water reuse



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## ABSTRACT

The Shafdan reclamation project facility (Tel Aviv, Israel) practices soil aquifer treatment (SAT) of secondary effluent with hydraulic retention times (HRTs) of a few months to a year for unrestricted agricultural irrigation. During the SAT, the high oxygen demand ( $>40 \text{ mg L}^{-1}$ ) of the infiltrated effluent causes anoxic conditions and mobilization of dissolved manganese from the soil. An additional emerging problem is the occurrence of persistent trace organic compounds (TrOCs) in reclaimed water that should be removed prior to reuse. An innovative hybrid process based on biofiltration, ozonation and short SAT with  $\sim 22 \text{ d}$  HRT is proposed for treatment of the Shafdan secondary effluent to overcome limitations of the existing system and to reduce the SAT's physical footprint. Besides efficient removal of particulate matter to minimize clogging, coagulation/flocculation and filtration ( $5\text{--}6 \text{ m h}^{-1}$ ) operated with the addition of hydrogen peroxide as an oxygen source efficiently removed dissolved organic carbon (DOC, to 17–22%), ammonium and nitrite. This resulted in reduced effluent oxygen demand during infiltration and oxidant (ozone) demand during ozonation by  $23 \text{ mg L}^{-1}$  and  $1.5 \text{ mg L}^{-1}$ , respectively. Ozonation ( $1.0\text{--}1.2 \text{ mg O}_3 \text{ mg DOC}^{-1}$ ) efficiently reduced concentrations of persistent TrOCs and supplied sufficient dissolved oxygen ( $>30 \text{ mg L}^{-1}$ ) for fully oxic operation of the short SAT with negligible  $\text{Mn}^{2+}$  mobilization ( $<50 \text{ }\mu\text{g L}^{-1}$ ). Overall, the examined hybrid process provided DOC reduction of 88% to a value of  $1.2 \text{ mg L}^{-1}$ , similar to conventional SAT, while improving the removal of TrOCs and efficiently preventing manganese dissolution.

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## 1. Introduction

The Dan region reclamation project (Shafdan) is the major reclamation–reuse project in Israel, producing up to 130 million  $\text{m}^3$  of water for unrestricted agricultural irrigation annually (Cikurel et al., 2012). The treatment includes a primary clarification and conventional secondary (activated sludge) treatment. Further improvement of effluent quality prior to reuse is achieved by tertiary soil aquifer treatment (SAT).

During conventional (long) SAT, secondary effluent is infiltrated into the soil by surface spreading and reclaimed through wells (250–1600 m away from the recharge area) after a hydraulic

retention time (HRT) of 6–12 mo in the aquifer. This cost-effective technology, which is mostly used in arid and semiarid regions, results in efficient removal of many wastewater contaminants based on the combined effect of biological and physicochemical processes (Amy and Drewes, 2007). At Shafdan,  $\sim 80\%$  removal of dissolved organic carbon (DOC) has been observed (Icekson-Tal et al., 2013), which is high in comparison to other SAT systems worldwide, likely due to the Israeli climate conditions and long HRTs that enable effective biodegradation of organic matter.

A major problem for Shafdan is increasing hydraulic load accompanied by the strongly required HRT for DOC removal. A tendency toward maximum reuse along with growing amounts of secondary effluent and lack of land for spreading are resulting in extremely high hydraulic loading rates on the presently available infiltration fields. These conditions enhance the organic and ammonium load since Shafdan secondary effluent is characterized

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by relatively high levels of DOC and ammonium (10–12 and 4–6 mg L<sup>-1</sup>, respectively) (Icekson-Tal et al., 2013). Hence, the present infiltration fields are gradually becoming clogged and SAT efficiency is decreasing. Another concern is trace organic compounds (TrOCs) such as pharmaceutical residues, which partially persist during conventional wastewater treatment and can be detected in receiving surface waters worldwide (Kolpin et al., 2002). Although many of these TrOCs are efficiently removed in SAT systems by sorption and/or biodegradation, some polar and nonbiodegradable compounds persist and can be detected in reclaimed water (Kinney et al., 2006). The use of reclaimed water for irrigation is thus an important route for the introduction of TrOCs into the environment (Chefetz et al., 2008).

Another common problem with the conventional SAT at Shafdan is the presence of dissolved manganese (Mn<sup>2+</sup>) in the reclaimed water due to anoxic conditions in the subsurface. During infiltration, high levels of ammonium and DOC result in the rapid consumption of dissolved oxygen (DO) by aerobic biodegradation processes (Lance, 1972). Once the DO has been consumed, microorganisms utilize alternate electron acceptors, commonly nitrate (NO<sub>3</sub><sup>-</sup>) and manganese and ferric oxides, which are present in the soil (e.g. Curtis, 2003). The low solubility of oxygen in secondary effluent at the typically high temperatures in Israel compounds this problem, facilitating Mn<sup>2+</sup> mobilization from the soil. In the distribution system of the reclaimed water, manganese oxide precipitates, resulting in clogging of the farmers' irrigation systems (Goren, 2008).

Several pilot- and full-scale studies on alternatives to conventional SAT by multi-stage tertiary treatments based on ozonation with subsequent (bio)filtration were conducted and presented in the literature. Ozonation followed by soil columns to simulate the SAT process (Schumacher et al., 2004; Tiwari et al., 2014), quick biological sand filtration (Hollender et al., 2009) or biological activated carbon (BAC) treatment (Gerrity et al., 2011; Reungoat et al., 2012) demonstrated improved biodegradation of DOC and elimination of ozonation byproducts and TrOCs.

This research focused on the combination of biofiltration prior and following ozonation. We propose an alternative treatment consisting of biologically active dual-media filtration (termed bio-filter), ozonation and SAT with a short HRT of ~22 d to reduce the physical footprint of the existing SAT, eliminate residual TrOCs and minimize Mn<sup>2+</sup> mobilization. Filtration is operated with the addition of hydrogen peroxide for oxygen supply to remove particles as well as DOC, ammonium and nitrite, in order to reduce oxygen and ozone demand in subsequent treatment steps. Besides its major objective to remove TrOCs, ozonation is applied to supply oxygen for the enhancement of redox conditions during SAT. Post-ozonation natural biofiltration is achieved by the short SAT, as 1–2 m upper unsaturated layer simulates a biofilter while the saturated layer is an adsorption media. However, to the best of our knowledge, this is the first time such an integrative multistage treatment has been tested on a pilot-scale.

## 2. Materials and methods

### 2.1. Experimental pilot setup

The Shafdan pilot center constructed a study site with the hybrid ozonation–short SAT pilot system, which included a biologically active high-rate filtration unit (aimed to remove ammonium, nitrite and particles), an ozonation unit and the short SAT facility (Fig. 1, described in details in sections 2.1.1–2.1.3). The pilot plant was fed by treated wastewater from the secondary clarifier output. The operation was conducted in two infiltration modes: 4-mo infiltration of biofiltered effluent (*mode 1*, i.e. blank experiment) and 5-mo

infiltration of biofiltered–ozonated effluent (*mode 2*). During operation of the designed pilot system, 15 grab-sampling campaigns (in each unit of the pilot) were conducted from March 2013 to January 2014.

#### 2.1.1. Biofiltration unit

The biofiltration unit was fed continuously with 5–6 m<sup>3</sup> h<sup>-1</sup> 500- $\mu$ m-filtered secondary effluent from the Shafdan wastewater treatment plant (WWTP). The unit included coagulation/flocculation, which was carried out by injecting polyaluminum chloride (18% Al<sub>2</sub>O<sub>3</sub>) diluted with water in-line by peristaltic pump to achieve a final concentration of 1.27–1.88 mg L<sup>-1</sup> as aluminum in a 1.3-m<sup>3</sup> flocculator tank with 5 min HRT. Following flocculation, 30–35 mg L<sup>-1</sup> hydrogen peroxide was added to the filter influent to provide oxygen for microbial processes (catalase enzyme converts peroxide to oxygen inside the filter). Hydrogen peroxide was chosen as an oxygen source due to the high efficiency in supplying readily available oxygen throughout the biofilter volume with minor losses.

High-rate biofiltration was operated in a modified active dual-media filter (0.57-m diameter tank) with 5–6 m h<sup>-1</sup> filtration velocity (5 min HRT) and a backwash cycle of 12 h. Periodic backwashing included combined air/water followed by water backwashing and adjusted to avoid clogging of the filter concurrently with maintaining a steady and active biomass, as observed by the stable performance with low effluent turbidity. The filter consisted of 1 m of multilayer media: a 10-cm basalt (0.6–1.2 mm particle size range) support layer, a 30-cm basalt layer (0.3–0.6 mm), and a top 60-cm layer of anthracite (0.8–1.5 mm). No chlorine was used during the backwash to maintain bioactivity in the filter. The microbial community of the biomass is indigenous therefore not artificially inoculated, and developed over time by feeding the biofilter with secondary effluent wastewater.

#### 2.1.2. Ozonation unit

The outlet of the effluent biofiltration unit flowed into an ozonation system. The ozonation unit (100 g h<sup>-1</sup>, OCS GSO 30, Xylem Services GmbH, Germany) was operated in continuous mode with an ozone consumption of 10 mg L<sup>-1</sup> (1.0–1.2 mg O<sub>3</sub> mg DOC<sup>-1</sup>). Ozone was produced from pure oxygen (15 L min<sup>-1</sup>) and introduced by venturi injection into the effluent stream (~4.3–5 m<sup>3</sup> h<sup>-1</sup>). A 500-L reaction tank provided a HRT of 6–7 min. In-gas and off-gas ozone was measured using an ozone gas analyzer (BMT 963, Germany) to set up a complete mass balance. The system included monitoring of pH/ORP (oxidation–reduction potential) and dissolved ozone (Hefer systems and controls, Israel). The ozonated effluent flowed into a 10-m<sup>3</sup> reservoir before infiltration to ensure complete ozone depletion. At the final stage, the oxygen-rich treated effluents from the ozonation pilot unit were further infiltrated into the short SAT facility.

#### 2.1.3. Short SAT facility

The pretreated effluent was infiltrated through a recharge borehole (RBH) (Fig. 2), which was constructed in 2006 for the RECLAIM pilot project (Cikurel et al., 2012). The RBH is a cylindrical tube (2.5 m depth, 10 m<sup>2</sup> surface area) drilled into the unsaturated zone of local sands and calcareous sandstone. An observation well (OW) was drilled to a depth of 27.5 m at a distance of 7.3 m downstream of the RBH, to assess the performance and resulting water quality at the end of the suggested process.

In the current pilot system, a 12-h infiltration/12-h drying regime was applied (intermittent infiltration). The HRT of recharged pretreated secondary effluent during the short SAT infiltration was determined using a bromide salt tracer at a concentration of 60 mg L<sup>-1</sup> recharged into the RBH. The concentration

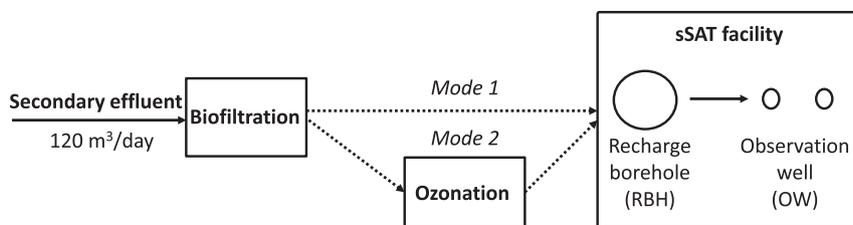


Fig. 1. Flow sheet of the pilot system at Shafdan, Israel, including operation in two modes: *mode 1* without or *mode 2* with ozone treatment.

of bromide was measured periodically in the OW and a typical breakthrough curve was determined. The breakthrough point (the point at which the concentration is about half of its initial value) occurred in the OW at ~22 d.

## 2.2. Chemicals and standards

The TrOCs monitored in this study were selected based on their rate of reaction with molecular ozone ( $k_{O_3}$ ) and their relevance for SAT systems. TrOCs can be categorized into three groups: rapidly ( $k_{O_3} > 10^4 \text{ M}^{-1} \text{ s}^{-1}$ ), moderately ( $10 \text{ M}^{-1} \text{ s}^{-1} < k_{O_3} < 10^4 \text{ M}^{-1} \text{ s}^{-1}$ ) and slowly ( $k_{O_3} < 10 \text{ M}^{-1} \text{ s}^{-1}$ ) reacting compounds (Hollender et al., 2009; Hübner et al., 2013). All standards (purity > 99%) were obtained from Sigma–Aldrich (with the exception of iopromide, provided by Holland–Moran, Israel), and used as purchased. 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). TrOC classes and rate constants for the reaction with ozone and hydroxyl radicals ( $k_{OH}$ ) are summarized in Table 1.

## 2.3. Analytical methods

### 2.3.1. TrOC sample extraction and analysis

To detect the presence of TrOCs at low concentrations in a pilot-scale application (without spiking) following ozonation and infiltration, samples were preconcentrated by solid-phase extraction (SPE), using 500-mg 6-mL Oasis-HLB cartridges connected to a 12-port SPE manifold and vacuum pump. The SPE cartridges were conditioned with 10 mL methanol and 10 mL DI water. After loading the samples, the cartridges were dried under a 5/9 nitrogen stream for 10 min. The analytes were eluted with 6 mL methanol, collected in 10-mL glass tubes and dried to zero under a nitrogen stream. Finally, the extracts were reconstituted with 1 mL HPLC-grade water (with 10% v/v methanol) at pH 3 and transferred to HPLC vials.

The target compounds were detected and quantified by HPLC (Agilent 1100 series; ACE-RP phenyl column 2.1 mm × 250 mm) equipped with a UV-diode array detector and a mass spectrometer (Q-TOF MS, Waters Premier). The column temperature was 40 °C, the flow rate was 0.5 mL min<sup>-1</sup> and the injected volume was 100 μL. The HPLC mobile phase consisted of water (A) and methanol (B), adjusted to pH 3 by the addition of formic acid. The mobile phase 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 prior to the next run. The flow from the HPLC passed through a split connector with effluent introduced into the MS interface at 60 μL min<sup>-1</sup>. The Q-TOF MS was operated in positive mode, with a limit of quantification (LOQ) of 0.01–0.1 μg L<sup>-1</sup>.

The accuracy of the TrOC measurements was validated for a wide set of samples (>50%) from all sampling points using an established HPLC–MS/MS with isotope standards at TU Berlin (Zietzschmann et al., 2014); 12% differentiation (maximum deviation of 10%) was observed between the two analyses for all TrOCs analyzed.

### 2.3.2. Analysis of wastewater–quality parameters

Total organic carbon (TOC) in the wastewater was measured using a TOC analyzer (Torch, Teledyne Tekmar, OH). To measure DOC, samples were filtered at 0.45 μm (APHA, method 5310B). The UV absorbance (UVA) of the effluent at 254 nm was measured following 0.45 μm filtration in a UV–visible spectrophotometer (Varian, Cary 100 BIO, Victoria, Australia). Wastewater parameters were analyzed using standard methods (APHA, 2005); Nitrite, nitrate and ammonium were determined according to standard methods 4500B, 4110B and 4500D, respectively. Soluble Mn<sup>2+</sup> concentration was determined by standard methods 3120B and 3030F. DO concentration was measured using the Winkler method (4500-O). Bromate concentration was measured using ion chromatograph by standard method 4110D.

## 3. Results and discussion

### 3.1. Biofiltration

The major objectives of filtration as a pretreatment for short SAT (*mode 1*) were to reduce clogging by wastewater particles and to minimize oxygen demand during infiltration by removing organic matter and ammonium. During operation in *mode 2* (as a pretreatment for ozonation), the additional requirement was to remove nitrite and particles to decrease ozone demand. Results from the turbidity analysis showed constant particle removal by >90%.

Fig. 3 shows the profile of the nitrogen compound concentrations analyzed at the different sampling points. Secondary effluents contained average concentrations of  $3.1 \pm 1.1 \text{ mg L}^{-1}$  ammonium ( $\text{NH}_4^+-\text{N}$ ),  $0.5 \pm 0.2 \text{ mg L}^{-1}$  nitrite ( $\text{NO}_2^--\text{N}$ ) and  $0.4 \pm 0.1 \text{ mg L}^{-1}$  nitrate ( $\text{NO}_3^--\text{N}$ ), indicating the incomplete nitrification process in the Shafdan secondary treatment. Results from both modes showed

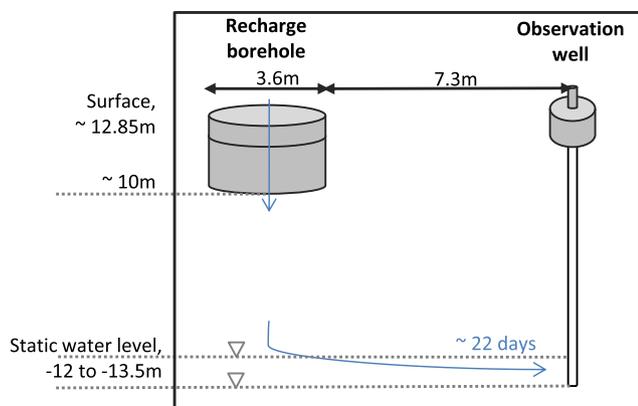


Fig. 2. Recharged effluent flow path through short SAT facility (unsaturated zone).

**Table 1**  
Class, chemical characteristics and rate constants at pH 7 for reaction of the selected TrOCs.

Name	Class	Rate constants		References
		$k_{O_3}$ [ $M^{-1}s^{-1}$ ]	$k_{OH}$ [ $10^9 M^{-1}s^{-1}$ ]	
Iopromide (IOP)	Contrast media	0.8	3.3	(Huber et al., 2003)
Primidone (PRI)	Anti-epileptic	1	6.7	(Real et al., 2009)
Acesulfame (ACS)	Sweetener	88	4.55	(Kaiser et al., 2013)
Bezafibrate (BZF)	Lipid regulator	590	7.4	(Huber et al., 2003)
Metoprolol (MTP)	$\beta$ -blocker	$2 \cdot 10^3$	7.3	(Benner et al., 2008)
Venlafaxine (VLX)	Anti-depressant	$3.3 \cdot 10^4$	8.8	(Lester et al., 2013; Wols et al., 2013)
Carbamazepine (CBZ)	Anti-epileptic	$3 \cdot 10^5$	8.8	(Huber et al., 2003)
Diclofenac (DCF)	Anti-inflammatory	$1 \cdot 10^6$	7.5	(Huber et al., 2003)
Sulfamethoxazole (SMX)	Antibiotic	$2.5 \cdot 10^6$	5.5	(Huber et al., 2003)

complete nitrification in the biofilter, with efficient removal of  $NH_4^+$  and  $NO_2^-$  approximating 0.12 and 0.05  $mg L^{-1}$  as N, respectively. The percentage removal during operation in *mode 2* was higher (97% and 93%) than in *mode 1* (95% and 88%) due to higher initial concentration for  $NH_4^+$  and  $NO_2^-$ , respectively. In addition, 17–22% of the average DOC concentration in Shafdan secondary effluent of  $10.2 \pm 1.6 mg L^{-1}$  was removed (Fig. 4). Average DO concentrations of  $\sim 5.5 mg L^{-1}$  in the biofilter effluent (Table 2) indicated fully oxic conditions throughout the filter. Although DO concentration fluctuated due to variations in effluent quality, it consistently exceeded 2–3  $mg L^{-1}$ , which is commonly suggested as the threshold value for denitrification or anaerobic bioactivity (Kremen et al., 2005).

These results demonstrate the benefits of the tested biofilter operation for the overall treatment scheme. Aside from the positive aspects of particle removal in preventing clogging in the short SAT and reducing ozone demand (Zucker et al., 2014), the efficient removal of ammonium, nitrite and DOC strongly reduced oxygen demand for biological processes in the short SAT, by approximately 23  $mg L^{-1}$  (calculated with 4.6  $mg O_2$  per  $mg NH_4-N$ , 1.1  $mg O_2$  per  $mg NO_2-N$  and 2.6  $mg O_2$  per  $mg DOC$ ). In addition, nitrite removal reduced ozone demand by approximately 1.5  $mg L^{-1}$  (calculated with 3.4  $mg O_3$  per  $mg NO_2-N$ ). In these experiments, oxic filtration was established by the addition of hydrogen peroxide. In future experiments, however, the use of ozonation off-gas as the oxygen supply will be examined as a cost-effective alternative to peroxide addition.

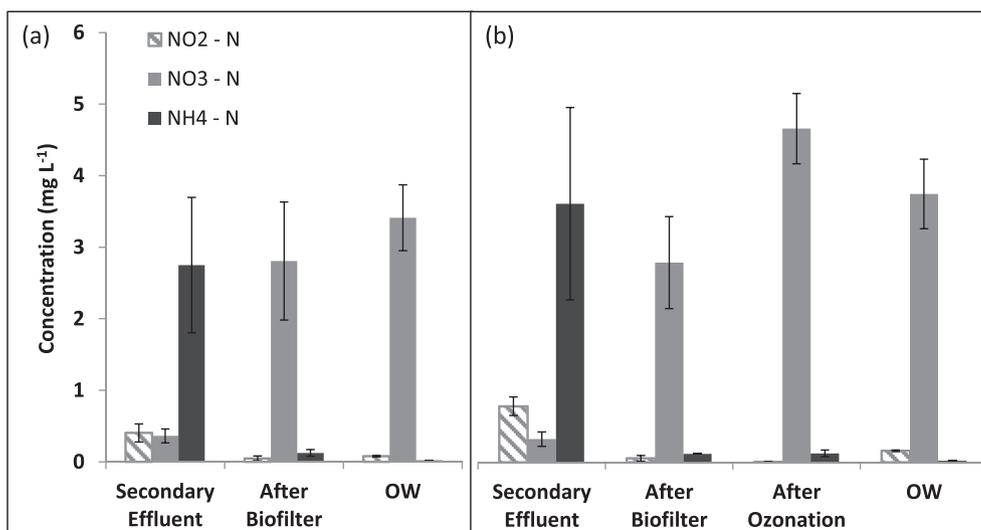
Fig. 5 summarizes the TrOC concentrations observed during the hybrid process. The typical concentrations of the analyzed TrOCs in

the Shafdan secondary effluents ranged from 0.17  $\mu g L^{-1}$  for MTP to 15.24 and 50.6  $\mu g L^{-1}$  for IOP and ACS, respectively. Extremely high concentrations of ACS, up to 46  $\mu g L^{-1}$ , have been observed in secondary effluent in Switzerland (Buerge et al., 2009). Concentrations fluctuated between campaigns (six repetitions for each data point), probably due to weather or operational conditions, varying input loads or even the sampling or analysis protocols.

As expected, biofiltration did not significantly reduce the concentrations of most TrOCs. Only ACS and IOP were removed by approximately 60% and 30%, respectively. Although no differentiation was made between sorption and biodegradation, based on the physicochemical properties and literature data, the elimination of these compounds can be attributed to biodegradation (Buerge et al., 2011; Ternes et al., 2007). Whereas rapid degradation of IOP has been previously described (Batt et al., 2006), the high degradation of ACS in the biofilter was in contrast to most of the reports from the literature (Scheurer et al., 2010). Possible explanations for this rapid degradation are the comparably high initial concentration of ACS (inducing the growth of ACS degraders) or a microbial population composition that differed from that in the activated sludge in the filter (e.g. nitrifying bacteria).

### 3.2. Ozonation

During the 4-mo operation, ozonation was conducted at a constant ozone consumption of 1.0–1.2  $mg O_3 mg DOC^{-1}$ . Ozonation increased  $NO_3-N$  concentration (Fig. 3b), which could not be explained by oxidation of  $NO_2^-$  and ammonium residues. The



**Fig. 3.** Nitrogen compound concentrations at the different sampling points in (a) *mode 1* and (b) *mode 2*.

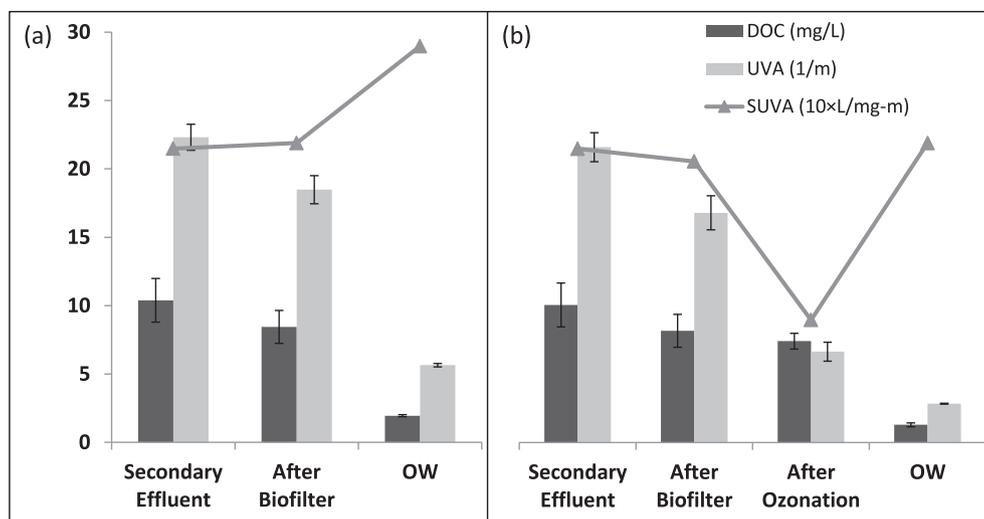


Fig. 4. Organic matter-related parameters at the different sampling points in (a) mode 1 and (b) mode 2.

increase might be partially attributed to oxidation of organic nitrogen (measured as  $1.17 \pm 0.57 \text{ mg L}^{-1}$ ).

Limited DOC removal (~10%, Fig. 4b) by ozone is in line with the literature for similar ozone dosages (e.g., Bahr et al., 2007). In contrast, efficient reduction of UVA (60%) to  $6.7 \text{ m}^{-1}$  was observed due to selective attack of the conjugated systems in DOC. It should be noted that for large-scale ozonation units, the monitoring of UVA is mentioned as an easily managed control parameter that provides a good indication of oxidation performance (Bahr et al., 2007).

Specific UV absorbance (SUVA) was determined as the ratio between UVA and initial DOC concentration (Fig. 4). Trends in SUVA, as an index of aromaticity, could be detected along the different pilot stages; similar values of SUVA were obtained following biofiltration, whereas lower values were seen following ozonation, indicating removal of the aromatic components.

Removal of TrOCs by ozonation strongly depended on their rate constants with ozone (Table 1). Observed removal rates were in line with literature data (Bahr et al., 2007; Hollender et al., 2009; Hübner et al., 2012). The fast-reacting compounds DCF, SMX, CBZ and VLX were efficiently removed. Previous studies have indicated complete removal of these compounds at the much lower ozone consumption of  $0.4\text{--}0.6 \text{ mg O}_3 \text{ mg DOC}^{-1}$  (Hollender et al., 2009). The relatively low removal rate of VLX (93%) was not expected, as higher removal of 99% has been reported following ozonation at  $0.6 \text{ mg O}_3 \text{ mg DOC}^{-1}$  (Hollender et al., 2009). However, VLX concentration following ozonation was always close to the LOQ.

Incomplete removal was observed for the moderately reacting compounds ACS (61%) and MTP (78%), with better removal of MTP due to its higher rate constant with ozone. The low initial concentrations of PRI and BZF were removed to below LOQ, accounting for reductions of >65% and >79%, respectively (calculated with LOQ/2 as residual concentration). Concentrations of the ozone-resistant compounds IOP and PRI decreased by 52% and >65%, respectively, confirming the high efficiency of OH-radical formation during the ozonation of secondary effluent (Hübner et al., 2013).

### 3.3. Short SAT

The short SAT pilot system was set up as part of the RECLAIM project in 2006 to test options for improving water quality and infiltration rates by pretreatment of secondary effluent. Under RECLAIM, it was operated for 3 y (2006–2008) with 500- $\mu\text{m}$  wire-mesh prefiltration, UV disinfection and ultrafiltration (UF) before infiltration in the RBH system. The UF significantly improved the infiltration velocity ( $10 \text{ m d}^{-1}$ ) in comparison to conventional SAT ( $1\text{--}2 \text{ m d}^{-1}$ ), and removed nitrogen compounds as well as DOC prior to infiltration (Cikurel et al., 2012). The dissolution of  $\text{Mn}^{2+}$ , however, was still problematic (Table 2).

Similar results were obtained from infiltration of the biofiltered effluent (mode 1, Table 2). Both treatment systems exhibited efficient removal of DOC and UVA to levels of  $\sim 2 \text{ mg L}^{-1}$  and  $5.6 \text{ m}^{-1}$ , respectively. Although the removal of ammonium and the decrease in DOC by the biofilter resulted in an actual reduction of  $23 \text{ mg L}^{-1}$

Table 2

Summary of water-quality parameters in different pilot operations (average values from at least six samples for each experiment).

	Sec. effluent		Effluent for recharge		Observation well			
	2006–2008	2011–2013	RECLAIM project 2006	Enhanced short SAT		RECLAIM project 2006	Enhanced short SAT	
				Mode 1	Mode 2		Mode 1	Mode 2
$\text{NO}_2^- \text{-N}$ ( $\text{mg L}^{-1}$ )	1.00	0.47	0.38	0.05	0.01	0.20	0.08	0.16
$\text{NO}_3^- \text{-N}$ ( $\text{mg L}^{-1}$ )	0.79	0.37	1.13	2.80	4.66	2.33	3.41	3.75
$\text{NH}_4^+ \text{-N}$ ( $\text{mg L}^{-1}$ )	1.61	3.13	0.82	0.12	0.12	0.07	<0.02	<0.02
DOC ( $\text{mg L}^{-1}$ )	10.2	10.2	7.4	8.2	7.4	2.5	2	1.2
UVA ( $\text{m}^{-1}$ )	21.1	22.0	18.0	18.5	6.7	4.5	5.6	2.8
CBZ ( $\mu\text{g L}^{-1}$ )	0.27	1.12	0.28	0.99	0.02	0.61	1.28	0.26
DO ( $\text{mg L}^{-1}$ )	2.2	3.5	2	5.5	33.1	1.3	1.6	3.5
$\text{Mn}^{2+}$ ( $\mu\text{g L}^{-1}$ )						109	98	32

DOC, dissolved organic carbon; UVA, UV absorbance; CBZ, carbamazepine; DO, dissolved oxygen.

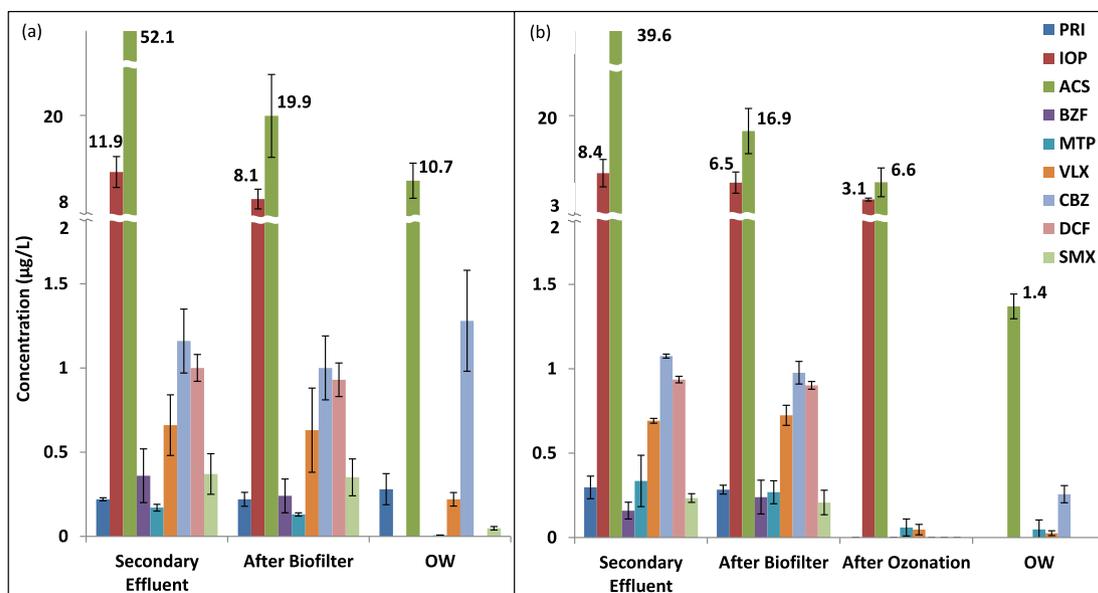


Fig. 5. TrOC concentrations at different sampling points during operation in (a) mode 1 and (b) mode 2.

in oxygen demand prior to the short SAT (compared to 11 mg L<sup>-1</sup> reduction in the RECLAIM project), no significant reduction of Mn<sup>2+</sup> dissolution was observed (Table 2). The parallel availability of NO<sub>3</sub><sup>-</sup> and dissolution of Mn<sup>2+</sup> indicated heterogeneous conditions in the subsurface. Such effects were also observed by Cikurel et al. (2012), who hypothesized that microbial processes in heterogeneous soil systems do not strictly follow predictable redox sequences. The occurrence of NO<sub>2</sub><sup>-</sup> in the OW confirmed this hypothesis as it indicated incomplete denitrification (or nitrification of organic nitrogen) under suboxic conditions. Analysis of nitrogen compounds before and after infiltration showed 18% removal of total nitrogen following infiltration. The hybrid process reclaimed water at the Shafdan stands for the limit for nitrogen compounds according to the California Code of Regulations (Title 22).

Pre-ozonation of secondary effluent may affect redox conditions directly by supplying pure oxygen to the water, and indirectly by oxidation of organic matter. The infiltration of ozonated water resulted in a significant increase in redox potential as observed by an increase in the DO level and a decrease in dissolved Mn<sup>2+</sup> in the OW (Table 2). However, nitrite concentrations in the OW (Table 2) indicated the persistence of suboxic zones in the soil. Although the Israeli water reuse standards allow 200 µg L<sup>-1</sup> dissolved Mn<sup>2+</sup> in treated effluents for unrestricted irrigation, 50 µg L<sup>-1</sup> is suggested as an upper limit for Mn<sup>2+</sup> due to operational clogging problems along the dripper distribution pipelines. Operation of the pilot in mode 2 meets this enforceable standard (<50 µg L<sup>-1</sup>) for recharged water with a HRT of 22 d.

Pretreatment with ozone resulted in an additional decrease in DOC level and UVA in reclaimed water to 1.2 mg L<sup>-1</sup> and 2.8 m<sup>-1</sup>, respectively (total reduction of 87% for the complete treatment), as can be seen in Fig. 4b. SUVA increased after short SAT in both modes, reflecting preferential removal of nonaromatic (non-humic) components (Amy and Drewes, 2007). The increased biodegradability of dissolved organic matter following ozonation is well known (Hübner et al., 2012; Lee et al., 2013). Results from this study confirmed that the combination of ozonation and SAT provides a good way to benefit from this effect. A significant reduction in DOC following a treatment combining ozonation and sand columns was also demonstrated by Schumacher et al. (2004).

Bromate was formed as a by-product following ozonation in

concentration of approximately 50 µg L<sup>-1</sup> as a result of high bromide concentrations in Israel (approx. 0.6 mg L<sup>-1</sup> in Shafdan effluent) and relatively high applied ozone dosages. Although bromate removal was not observed in slow and aerobic filtration (Hübner et al., 2012; Zimmermann et al., 2011), bromate concentration following short SAT was below 5 µg L<sup>-1</sup>. Bromate reduction can be attributed to biological process in anoxic zones where bromate reacted as an electron acceptor (Kirisits et al., 2001). Hence, bromate reduction during infiltration may indicate again on the persistence of suboxic zones in the soil. So far, the final bromate concentration is below the drinking water standard (10 µg L<sup>-1</sup>) and a proposed ecotoxicological threshold value of 3 mg L<sup>-1</sup> (Hutchinson et al., 1997) but establishment of oxic conditions throughout the aquifer will probably necessitate measures for bromate minimization, e. g. reduction of ozone dosages.

The elimination of TrOCs by passage through the soil can be attributed to either sorption or biodegradation (Hiscock and Grischek, 2002). Therefore, the sorption properties of the TrOCs to soil and the types of mineral and organic sorbents are essential for assessing their potential to leach into the groundwater and be transported in aquifers and surface water (e.g. Arye et al., 2011).

Following the infiltration of biofiltered effluent (mode 1, Fig. 5a), a further decrease in TrOC concentrations was observed in the OW (22 d HRT). The compounds IOP, BZF and DCF were removed to below LOQ, which is in line with results from other bank filtration and artificial recharge sites (Grünheid et al., 2005; Ternes et al., 2007). High persistence of CBZ in biological water treatment and aquifer recharge systems is well established, and it has been proposed as a marker for anthropogenic influences (e.g. Arye et al., 2011). Under strong reducing conditions, however, CBZ removal might occur (Wiese et al., 2011). PRI has also been described as highly persistent in groundwater recharge systems (Drewes et al., 2003).

Significant but incomplete removal was observed for ACS, SMX and VLX. Slow degradation of SMX in oxic and anoxic soil systems is well known (Baumgarten et al., 2011) and its occurrence in reclaimed water has also been reported for the conventional SAT at Shafdan (Cikurel et al., 2010). ACS concentration decreased significantly in the short SAT (~50%). Despite its high persistence in biological systems, biologically mediated ACS degradation in soil

has been demonstrated (Buerge et al., 2011) and rationalized by the presence of a suitable microbial community and long HRTs (Reif et al., 2008). VLX has not been found to decrease considerably in other tertiary treatment processes (deep bed filtration), and has been detected in aquifers and rivers in Israel (Gasser et al., 2012).

The TrOCs remaining after infiltration in *mode 2* were ACS, MTP, VLX, and CBZ. Their concentrations in the OW were decreased by 79–88% by the addition of ozonation treatment prior to infiltration (*mode 2* versus *mode 1*). Monitoring the degradation of TrOCs by short SAT in *mode 2* was limited to a few compounds since most TrOCs were efficiently removed by the ozone before infiltration. Pre-ozonation might affect biodegradation of TrOCs during aquifer recharge by (i) reducing the initial compound concentration before infiltration, (ii) changing the amount and composition of biodegradable organic matter as a primary substrate for co-metabolic TrOC degradation, and (iii) increasing redox conditions in the subsurface. However, increased removal following infiltration in *mode 2* was only observed for ACS (80% compared to 46% in *mode 1*). Due to removal of VLX and MTP to concentrations close to LOQ (combined effect of ozonation and short SAT), evaluating the effect of ozonation on removal efficiency was not possible.

During ozonation, complete mineralization is not anticipated and transformation of organic compounds usually occurs. The removal of these products in short SAT was not addressed in this study, but recent studies revealed an increased biodegradability of most major products from ozone reactions with the olefinic compounds CBZ (Hübner et al., 2014) and ACS (Scheurer et al., 2012) in biological post-treatment. In addition, results from a literature study indicate that products persistence in biological processes is related to the ozone-reactive sites within the compound (Hübner et al., 2015). Enhanced removal efficiencies can be expected for olefins and aromatic compounds, whereas ozonation has probably a minor effect on biomineralization of amines (e.g. MTP, VLX).

Surprisingly high concentrations of CBZ were observed in the OW, indicating an increase during infiltration. One possible reason for this is mixing with native groundwater present in the OW prior to the arrival of the pretreated effluents. However, mixing effects could not be proven by bromide salt tracer test. Previous studies have reported retardation of CBZ by sorption to soil organic matter (Arye et al., 2011; Chefetz et al., 2008). Although measured concentrations of CBZ were stable at  $0.26 \pm 0.05 \mu\text{g L}^{-1}$  for 11 w, incomplete elution is expected due to slow desorption of CBZ from the soil after years of adsorption.

#### 3.4. Comparison with conventional SAT at Shafdan

The subsurface infiltration of pretreated effluent was tested as an alternative to conventional SAT as operated at the Shafdan WWTP to provide high-quality reclaimed water for unrestricted agricultural irrigation in the south of Israel. Conventional SAT at Shafdan effectively removes effluent DOC by 80%. Our results showed that the combination of biologically active flocculation/filtration, ozonation and short SAT can provide similar water quality in terms of bulk organic carbon and nitrogen compounds with a HRT of 22 d. Together with the higher infiltration rates ( $10\text{--}12 \text{ m d}^{-1}$  versus  $1\text{--}2 \text{ m d}^{-1}$  in the same infiltration area) resulting from reduced clogging, the proposed treatment combination can significantly reduce land use for infiltration and reclamation of effluent. In addition, pretreatment effectively reduced oxygen demand during infiltration, thereby helping to prevent manganese oxide dissolution, which is currently a serious problem for irrigation (Goren, 2008). The ozonation further provided an effective barrier for persistent TrOCs, i.e. CBZ and SMX, which are not efficiently removed during SAT and can be detected at concentrations of up to  $1.38 \mu\text{g L}^{-1}$  (Gasser et al., 2011) and  $0.36 \mu\text{g L}^{-1}$

(Cikurel et al., 2010) in reclaimed water, respectively. The occurrence of these compounds in reclaimed water for irrigation are of concern for human health, since they can be taken up by food crops (Chefetz et al., 2008).

Given these benefits and the fact that ozonation also provides an additional barrier to pathogens (e.g. Paraskeva and Graham, 2002), the proposed combination of filtration, ozonation and short SAT can also be considered for indirect potable reuse purposes. However, to evaluate the potential to include the proposed treatment in potable reuse schemes, a more detailed monitoring and assessment of human pathogens and quality assurance are needed in future studies.

#### 4. Conclusions

Incomplete nitrification during secondary treatment at the Shafdan WWTP as well as high effluent DOC result in a high oxygen demand of  $>40 \text{ mg L}^{-1}$  during tertiary treatment by SAT. Under the resultant anoxic conditions in the soil, dissolution of manganese oxides and the presence of  $\text{Mn}^{2+}$  in the reclaimed water lead to clogging during reuse application for irrigation. In this study, we succeeded to reduce oxygen demand and supply of additional DO during infiltration with the proposed pretreatment of biofiltration and ozonation. The proposed technology, based on a multistage post-treatment of Shafdan secondary effluent, demonstrated synergistic effects of the hybrid system components, which might improve the quality of the reclaimed water in multiple ways: improved effluent quality during biofiltration in terms of nitrite and particle removal, and enhanced performance of the ozonation stage via higher removal of TrOCs due to less consumption of ozone by nitrite and particles (Zucker et al., 2014). In addition, reducing DOC and ammonium during biofiltration significantly decreases the oxygen demand by  $> 20 \text{ mg L}^{-1}$  for additional aerobic processes occurring during infiltration. Furthermore, ozonation allows efficient TrOC removal, an increase in organic matter biodegradability and sufficient DO to establish and maintain oxic conditions throughout the SAT system. Finally, the combination of biofiltration and ozonation allows shortening the SAT HRT, along with decreased manganese oxide dissolution, elimination of TrOCs and improved DOC removal in the final produced water.

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