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**Reference:**

Chys Michael, Demeestere Kristof, Ingabire Ange Sabine, Dries Jan, Van Langenhove Herman, Van Hulle Stijn W.H..- Enhanced treatment of secondary municipal wastewater effluent: comparing (biological) filtration and ozonation in view of micropollutant removal, unselective effluent toxicity, and the potential for real-time control  
Water science and technology - ISSN 0273-1223 - 76:1(2017), p. 236-246  
Full text (Publisher's DOI): <http://dx.doi.org/doi:10.2166/WST.2017.207>  
To cite this reference: <http://hdl.handle.net/10067/1419560151162165141>

Enhanced treatment of secondary municipal wastewater effluent: comparing (biological) filtration and ozonation in view of micropollutant removal, unselective effluent toxicity, and the potential for real-time control

**Short title:** Performance and online control of ozonation and (bio)filtration

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## ABSTRACT

Ozonation and three (biological) filtration techniques (trickling filtration (TF), slow sand filtration (SSF) and biological activated carbon filtration (BAC)) have been evaluated in different combinations as tertiary treatment for municipal wastewater effluent. The removal of 18 multi-class pharmaceuticals, as model trace organic contaminants (TrOCs), has been studied. (Biological) activated carbon filtration could reduce the amount of TrOCs significantly (> 99%) but is cost-intensive for full-scale applications. Filtration techniques mainly depending on biodegradation mechanisms (TF and SSF) are found to be inefficient for TrOCs removal as a stand alone technique. Ozonation resulted in 90% removal of the total amount of quantified TrOCs, but a post-ozonation step is needed to cope with an increased unselective toxicity. SSF following ozonation showed to be the only technique able to reduce the unselective toxicity to the same level as before ozonation. In view of process control, innovative correlation models developed for the monitoring and control of TrOC removal during ozonation, are verified for their applicability during ozonation in combination with TF, SSF or BAC. Particularly for the poorly ozone reactive TrOCs, statistically significant models were obtained that correlate TrOC removal and reduction in  $UVA_{254}$  as an online measured surrogate parameter.

Keywords: (biological) activated carbon; ozonation; pharmaceuticals; slow sand filtration; spectral measurements; trickling filter

## INTRODUCTION

Pending (European) legislation and the dedication to protect the aquatic ecosystem and drinking water resources are driving municipal wastewater treatment plants to upgrade their current treatment installations (Audenaert et al., 2014; Barbosa et al., 2016). Several tertiary treatment steps are being put forward of which ozonation and activated carbon (AC) are the most preferred (e.g. Hollender et al., 2009; Prasse et al., 2015; Reungoat et al., 2011). A Swiss study (Moser, 2008) emphasized that, in general, AC induces a higher cost compared to ozonation. The application of a tertiary ozonation step has been defined as one of the major solutions to reduce the discharge level of trace organic contaminants (TrOCs) in receiving water bodies (Eggen et al., 2014; Margot et al., 2013). Ozonation has shown very fast reactions in the presence of effluent organic matter (EfOM) with the removal of a broad range of TrOCs due to the generation of unselective hydroxyl radicals ( $\text{HO}\bullet$ ). Although most TrOCs are degraded by ozonation, oxidation products are formed not only due to reaction with TrOCs but mainly by reaction with the bulk organic matter or other constituents present in the water matrix. Ozonation is consequently been associated with the potential of by-product formation depending on the ozone dose and water matrix composition. Both bromate and N-nitrosodimethylamine (NDMA) formation, defined as potentially carcinogenic and harmful, have been associated with the ozonation of EfOM when exceeding effluent specific ozone dosage threshold values (Von Gunten, 2003; Zimmermann et al., 2011). Most by-products, originating from the reaction of ozone with different chemical moieties, have a higher biodegradability compared to their parent compounds. Consequently, a polishing step following ozonation is favorable as an additional barrier to prevent the discharge of potential toxic products. With the adaption of the Swiss water protection act in March 2014, ozonation was put forward together with powdered activated carbon to reduce the discharge of TrOCs, either followed by a polishing step (e.g. sand filtration) to eliminate bioavailable oxidation products (Eggen et al., 2014). Lim et al. (2016) stressed the potential for biological filtration processes to cope with NDMA formation as an alternative for the more energy intensive UV photolysis.

Mostly the use of (powder or granular) activated carbon (AC) or the combination of ozonation and slow sand filtration (SSF) is investigated, while the use of different other types and combinations of biological filtration steps is scarcely examined. Therefore, three different

(biological) filtration techniques are put forward in the current study of which their main principle is clearly different: trickling filtration (TF), slow sand filtration (SSF) and biological activated carbon filtration (BAC). Both SSF and BAC are filtration types in which the filter material is fully submerged resulting in anoxic or anaerobic conditions (lower in the filter bed) for the on-going biological processes. BAC has the additional benefit of adsorbing components present in the effluent on active sites of the carbon surface. Potential adsorption onto filter sand of a SSF can be seen as negligible compared to BAC. TF is studied as a potential alternative. To the best of the authors knowledge, TF has never been applied as a polishing technique for ozonation. TF is a relatively simple and highly reliable technique that produces effluent of consistent quality. In contrary to SSF or BAC, the TF contains non-submerged bed material (mostly small rocks or plastics) on which a biological slime can develop (Tchobanoglous et al., 2003), which is exposed to the air making oxygen more easily diffusing through the filter bed. Reungoat et al. (2011) could identify the oxygen concentration in the effluent as a limiting factor, even more than the EBCT (empty-bed contact time), for the performance of biological filters. Combining non-submerged with a part of submerged material, both aerobic and anaerobic organisms can develop, leading to a broader spectrum of organisms available to enhance the degradation of components present in secondary effluent.

A possible barrier for the implementation of these additional treatment techniques is the operators concern about monitoring and controlling the performance. Several monitoring and control strategies, mostly uniformly applicable, have been developed to optimize the ozone dosage to reduce operational costs but still reaching the desired removal of TrOCs. One of the most recent correlation models has been developed by Chys et al. (submitted) based on  $UVA_{254}$  measurements to control the ozone dose during ozonation of secondary effluents from municipal WWTPs, applied for the abatement of TrOCs. A generic framework is presented relating different surrogates and on-going chemical kinetics to construct correlations for any compound with known apparent second order reaction rate constants towards ozone ( $k_{O_3}$ ) and  $HO\bullet$  ( $k_{HO\bullet}$ ). Mainly, two different reaction phases are defined for which a separate linear correlation is obtained. Although this framework has been developed for a single ozonation step, it has not been investigated yet if these correlations models are more widely applicable also taking into account additional treatment steps following the ozonation. Studies relating  $UVA_{254}$  and AC adsorption are already available (Altmann et al., 2016; Zietzschmann et al., 2014). Considering

potential synergistic effects between ozonation and a post-treatment, an even more optimal ozone dosing can be pursued.

Given the discussion above, an optimal tertiary treatment is needed that is aiming for a high TrOC removal and a decrease of the unselective toxicity. In this study, biological filtration techniques are investigated with different governing main mechanisms (i.e. adsorption, aerobic, anoxic and/or anaerobic conditions). The intrinsic value of these filtration techniques is investigated in comparison with ozonation, as stand-alone tertiary treatment. The applicability of correlations models presented by Chys et al. (submitted) for ozonation in combination with TF, SSF or BAC is statistically investigated, keeping in mind the different reactivity of the studied TrOCs with ozone. As such (follow-up of) TrOC removal by the combination of ozonation and suitable (biological) post-treatment (i.e. polishing) techniques is investigated.

## MATERIALS AND METHODS

### **Experimental procedures**

Secondary effluent of the municipal WWTP in Harelbeke, Belgium (116,100 I.E., Aquafin NV) was weekly collected after conventional sludge treatment within a period of two months. A graphical representation of the complete lab-scale set-up is given in Figure 1. All sampled effluent was first fed to a rapid sand filter with a height of 0.60 m and a diameter of 0.065 m, containing sand with a grain size of 0.4 to 0.8 mm to remove any larger particles (e.g. sludge). A filtration rate of  $5.4 \text{ m h}^{-1}$  (or  $300 \text{ mL min}^{-1}$ ) was maintained.

In the next step, half of the effluent was ozonated in a reactor containing 11 L of effluent operated in semi-batch mode with a constant flow of an ozone/oxygen-gas mixture through a porous diffusion plate. An Anseros ozone generator was used (COM-AD-02) while the oxygen flow rate was set at  $600 \text{ mL min}^{-1}$ . On average,  $4.2 \pm 0.6 \text{ mg O}_3$  per liter of effluent was added which is considered as a commonly applied ozone dosage for the removal of TrOCs in pilot- and full-scale applications (Audenaert et al., 2014). Both the inlet and outlet gaseous ozone concentrations were monitored by means of a UV-based gas analyzer (GM-OEM, Anseros) and logged every second using a Cole-Parmer DAQ module (model No. FN-18200-00). Additional

details about the ozonation set-up and associated mass balance calculations are given by Audenaert et al. (2013) and Chys et al. (2015).

Three different post-treatment techniques using biological and physical-chemical filtration were applied to both ozonated and non-ozonated effluent. Six columns contained two replicates of each technique, being a trickling filter using lava stones (TF), a slow sand filter (SSF), and a (biological) activated carbon filter (BAC). Details about the different design characteristics are given in Table 1 and Figure 1. In literature, a wide range of flow rates (from 0.5 to  $\pm 50$  bed volumes per day (BVs day<sup>-1</sup>)) is used although it has been indicated that the fastest removal of dissolved organic carbon (DOC, i.e. a surrogate for the organic matter) occurs on the top of the columns (Reungoat et al., 2011; Tchobanoglous et al., 2003). Escolà Casas and Bester (2015) obtained high elimination of some TrOCs (e.g. 41% diclofenac, 94% propranolol, 85% iomeprol) in a SSF with a low flow rate ( $\pm 1$  BV day<sup>-1</sup>). Consequently, flow rates were chosen during experimentation to allow for sufficient residence time but also at a level that makes the experimental procedure practically feasible. At start-up, all columns were filled with the respective materials at the given heights. The water level within the trickling filter was significantly kept below the level of the filling material as this ensured having both aerobic and anoxic zones. All columns were fed from the top and were inoculated with 50 mL of supernatant of sludge (i.e. after 30 minutes settling), obtained from the municipal WWTP, before starting the experiments. Both ozonated and non-ozonated effluent, placed in two separate containers and weekly refilled, were fed to one of the two replicates of each post-treatment technique. During the experimental period, after initial start-up, the complete set-up was running for 6 consecutive weeks before sampling and measuring TrOCs and toxicity to allow for a certain adjustment period. Effluent was used without spiking of any TrOCs. Additional samples were taken biweekly for COD and nutrient analysis and weekly for BOD<sub>5</sub>. The follow-up of pH, conductivity and UV-VIS absorbance was done at least three times a week.

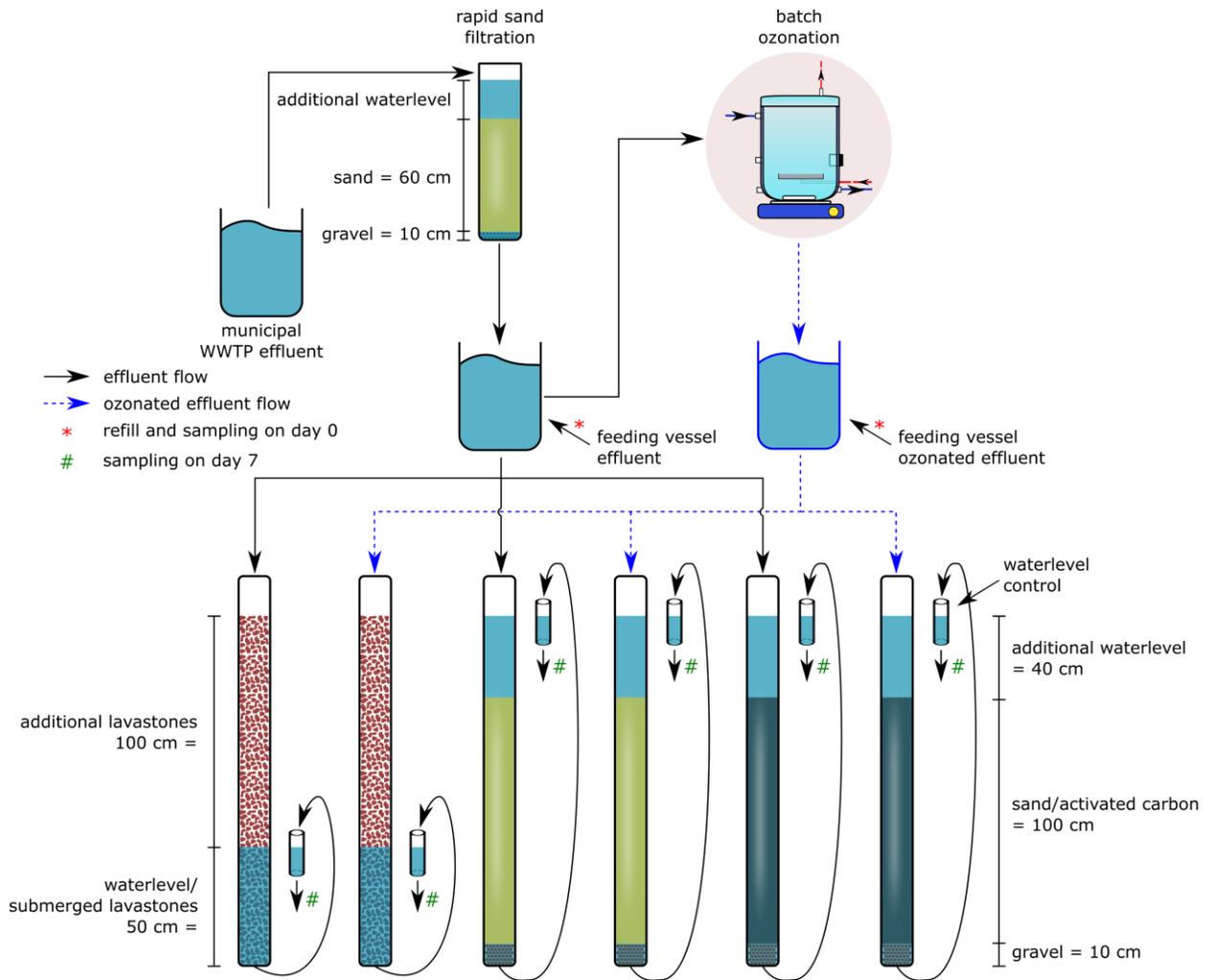


Figure 1: Schematic view of the experimental lab-scale set-up with, in chronological order: the sampled municipal WWTP effluent, rapid sand filtration, ozonation of effluent, and the different post-treatment columns (from left to right: trickling filter, slow sand filtration and (biological) activated carbon filtration; each in double of which the left one is fed with effluent and the right one with ozonated effluent). The \* and # are respectively indicating the time of sampling for TrOCs and toxicity analysis at day 0 and day 7.

Table 1: Design parameters of the three different post-treatment techniques and their set-up

Design parameter	Trickling filter TF	Slow sand filter SSF	(Biological) granular activated carbon filter BAC
Filter material	Lava stones	Fine sand	Granular activated carbon (Organosorb 10 <sup>®</sup> , Desotec, Belgium)
Filter material diameter (mm)	8 - 18	0.4 - 0.8	0.4 - 1.7
Supporting bottom material	n.a.	Gravel	Gravel
Supporting bottom material diameter (mm)	n.a.	1.7 – 2.5	1.7 – 2.5
Bed Volume, BV (L)	0.17 <sup>a</sup> 0.52 <sup>b</sup>	0.35	0.35
Flow rate (BV d <sup>-1</sup> )	5.1 <sup>a</sup> 1.7 <sup>b</sup>	2.5	7.1

<sup>a</sup> only considering the volume of submerged filter material

<sup>b</sup> considering the total volume of submerged and non-submerged filter material

n.a. = not applicable

### Analytical methods

Nitrate (NO<sub>3</sub><sup>-</sup>-N), ammonium (NH<sub>4</sub><sup>+</sup>-N), total nitrogen (TN), ortho-phosphate (oPO<sub>4</sub><sup>3-</sup>-P) and COD were determined spectrophotometric using Hach-Lange cuvettes, Hach powder pillows, and a DR2800 spectrophotometer (Hach, Belgium). Conductivity (EC) and pH were registered by a multi-meter (HQ30D, Hach, Belgium). BOD<sub>5</sub> was analyzed according to standard methods using Winkler bottles (Eaton et al., 2005). UV-Visible (UV-VIS) absorption data were obtained using a Shimadzu UV-1601 spectrophotometer. Spectra were taken between 200 and 800 nm with 0.5 nm increments using 1 cm quartz-cuvettes. Specific wavelengths were chosen for further analysis according to their broad use and relevance. The notation of the absorption coefficient (m<sup>-1</sup>) is given as UVA<sub>i</sub> with *i* related to the wavelength, e.g. 254 nm (UVA<sub>254</sub>).

Samples for TrOC analyses were stored in brown glass bottles at -20 °C in the dark, prior to analysis (within less than 3 weeks). Before storage, samples were filtrated using a glass microfiber filter (1.0 µm, class GF/B, Whatmann). Furthermore, Na<sub>2</sub>EDTA (1 g L<sup>-1</sup>) was added and samples were acidified to a pH of 3 with formic acid (LC-MS grade). After storage, samples were brought back to a pH of 7.0 ± 0.1 with 5 M NaOH and 10% formic acid, followed by filtration through a nylon filter (0.45 µm, Whatmann). TrOCs were then isolated and concentrated with solid-phase extraction (SPE) using Oasis HLB 6cc cartridges by loading 100 mL of each sample onto the cartridge after conditioning with 6 mL of HPLC-grade methanol and 6 mL of HPLC-grade water. Analyses were performed on the extract after washing with 6 mL HPLC-grade water, elution with 5 mL of HPLC-grade methanol and reconstitution in 1 mL MeOH:H<sub>2</sub>O (10:90) containing 0.1% (v/v) formic acid and 0.1 g L<sup>-1</sup> Na<sub>2</sub>EDTA.2H<sub>2</sub>O. The instrumental analyses were performed by injecting 10 µL in an UHPLC-HRMS benchtop Q-Exactive™ Orbitrap (Thermo-Fisher Scientific, USA) equipped with a reversed phase column, a heated electrospray ionization (HESI-II) source (working in positive ionization mode) and operated in full scan (150-500 m/z). More details on the analytical methodology is provided by Vergeynst et al. (2017).

Toxicity was measured using the BioTox kit (Aboatox Oy, Finland). This kit uses freeze-dried naturally bioluminescent marine bacteria *Vibrio fischeri* (Dries et al., 2014, 2013). Bioanalytical assays for the follow-up of unselective toxicity determining the reduction in luminescence of the *Vibrio fischeri* is widely applied in municipal wastewater effluent and ozonation studies (Macova et al., 2010). The test protocol involved combining 500 µL of test samples (with adjusted salinity of 2% sodium chloride) with 500 µL of reconstituted bacteria. After a contact time of 30 min at 15°C, the decrease of light intensity was measured with a portable tube luminometer (Berthold Technologies Junior LB 9509). The inhibitory effect is compared to a negative control (2% sodium chloride) to give the percentage growth (i.e. light) inhibition. Chromate was used to perform a positive control on the used protocol. More details on the usage of the BioTox kit is given in Dries et al. (2014).

## Correlation model for process control and data analysis

As a control strategy, the relationship between  $\Delta\text{UVA}_{254}$  and  $\Delta\text{TrOC}$  as proposed by several authors (Bahr et al., 2007; Chys et al., submitted; Dickenson et al., 2009; Gerrity et al., 2012; Pisarenko et al., 2015; Wittmer et al., 2015) was evaluated for both ozonation as a stand-alone treatment and for its combination with TF, SSF or BAC. In particular, the correlations experimentally constructed by Chys et al. (submitted) (see Appendix) for 9 model TrOCs with an ozone reactivity ranging from fast ( $k_{O_3} > 5 \times 10^4 \text{ M}^{-1} \text{ s}^{-1}$ ) to slow ( $k_{O_3} < 10 \text{ M}^{-1} \text{ s}^{-1}$ ) are investigated: diclofenac, trimethoprim, levofloxacin ( $k_{O_3} > 5 \times 10^4 \text{ M}^{-1} \text{ s}^{-1}$ ), amitriptyline, ciprofloxacin, venlafaxine ( $5 \times 10^4 \text{ M}^{-1} \text{ s}^{-1} > k_{O_3} > 10 \text{ M}^{-1} \text{ s}^{-1}$ ), amantadine, flumequine and metronidazole ( $k_{O_3} < 10 \text{ M}^{-1} \text{ s}^{-1}$ ). The same 9 TrOCs were under investigation within the current study.

Although this correlation model has been constructed for ozonation of municipal effluent, its applicability when also incorporating an additional post-treatment is of interest but not investigated yet. Therefore, the  $\Delta\text{UVA}_{254}$  determined by measurements before and after the entire tertiary treatment (ozone whether or not in combination with TF, SSF or BAC) is used to predict the TrOCs removal. The correspondence between measured, of which TrOC levels could be quantified before and after treatment, and predicted data is evaluated using (i) an unpaired t-test of which the null-hypothesis (difference is not significant) is rejected by  $p < 0.05$  and (ii) the Theil's inequality coefficient (TIC) of which a value below 0.3 is commonly seen as an indicator for a good agreement (Audenaert et al., 2010).

## RESULTS AND DISCUSSION

### Intercomparison of tertiary treatment techniques: ozonation versus TF, SSF and BAC

#### *Physical-chemical water characteristics*

During the experimental period, every week, fresh effluent was collected and supplied to the post-treatment techniques. Daily averages of the effluent flow rate and temperature (at the municipal WWTP, geoloket.VMM.be) showed an opposite behaviour (Figure 2). While the

effluent flow rate decreases from 97 to 46 m<sup>3</sup> day<sup>-1</sup> in the 6-weeks period, most probably due to a decrease of rain events, the effluent temperature slightly increases (from 9 to 12 °C). This phenomenon is likely due to a seasonal change as sampling was done in the transition from winter to spring (February – March). Parallel to these variations, conductivity (EC; from 825 to 1242 μS cm<sup>-1</sup>) and total nitrogen (TN; from 3.21 to 13.4 mg N L<sup>-1</sup>) indicate a lower dilution of the wastewater (e.g. less rain events) entering the WWTP. It is assumed that meteorological changes can have a significant influence on the biological processes within the WWTP. Consequently, a lower removal during this biological treatment step is temporarily expected (especially related to TN) resulting into higher values of the secondary treated effluent characteristics. Nevertheless, UVA<sub>254</sub> (13.0 – 16.5 m<sup>-1</sup>) and COD (15.5 – 18.6 mg O<sub>2</sub> L<sup>-1</sup>) remained more or less constant within the considered timeframe.

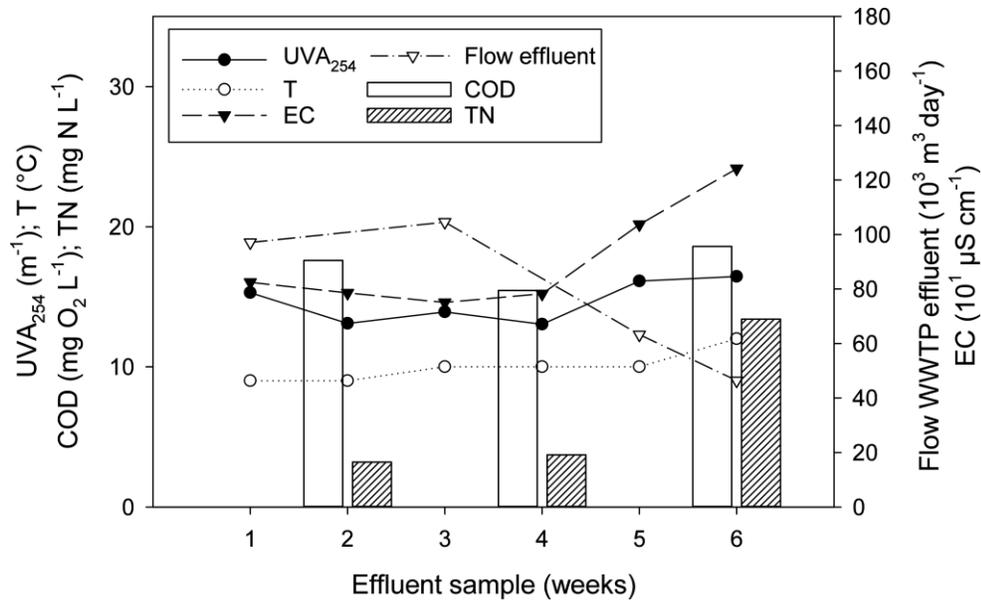


Figure 2: Municipal WWTP effluent characteristics before SSF, TF, BAC or ozone treatment during the 6 weeks of experimentation. The effluent flow rate and temperature are a daily average and was obtained through the Flanders Environment Agency ([www.VMM.be](http://www.VMM.be)).

The effect of different tertiary treatment techniques on these physical-chemical water characteristics is given in Figure 3. TF or SSF treatment do not induce a statistically significant change on the COD, BOD<sub>5</sub> and UVA<sub>254</sub> level of the effluent (Figure 3a), which are all surrogates related to the organic matter content. BAC treatment yields high removal efficiencies for COD ( $\geq 67\%$ ), BOD<sub>5</sub> ( $\geq 53\%$ ) and UVA<sub>254</sub> ( $\geq 93\%$ ) for all collected samples. Fresh granular activated carbon has been used at the start-up of the BAC experiments which makes that the total load of organics on the activated carbon has most likely not exceeded its maximum capacity. Ozonation resulted over all weeks of operation in an average reduction of  $42 \pm 5\%$  UVA<sub>254</sub> and only minor, non significant, variations in COD (decrease) and BOD (increase, due to the formation of smaller and more biodegradable oxidation products).

Considering the effect of the different treatments on NO<sub>3</sub><sup>-</sup>-N, oPO<sub>4</sub><sup>3-</sup>-P and TN, only some polishing and minor changes are noticed (Figure 3b). According to a t-test, oPO<sub>4</sub><sup>3-</sup>-P was significantly ( $p$ -value  $< 0.05$ ) removed during SSF and BAC (on average 22 and 16% respectively) but not by TF or ozonation (on average 14 and 9% respectively). Total nitrogen and NO<sub>3</sub><sup>-</sup>-N did not show any statistically significant alterations during TF, SSF, BAC or ozonation. Nevertheless, a remarkable increase of NO<sub>3</sub><sup>-</sup>-N after ozonation can be seen. As known, the reaction of ozone in the presence of NO<sub>2</sub><sup>-</sup>-N or nitrogen containing organic moieties might lead to an increase of NO<sub>3</sub><sup>-</sup>-N as a final oxidation product. Ammonium was only present at very low concentrations in the effluent (max. 0.03 mg NH<sub>4</sub><sup>+</sup>-N L<sup>-1</sup>) and, therefore, is not taken into further consideration.

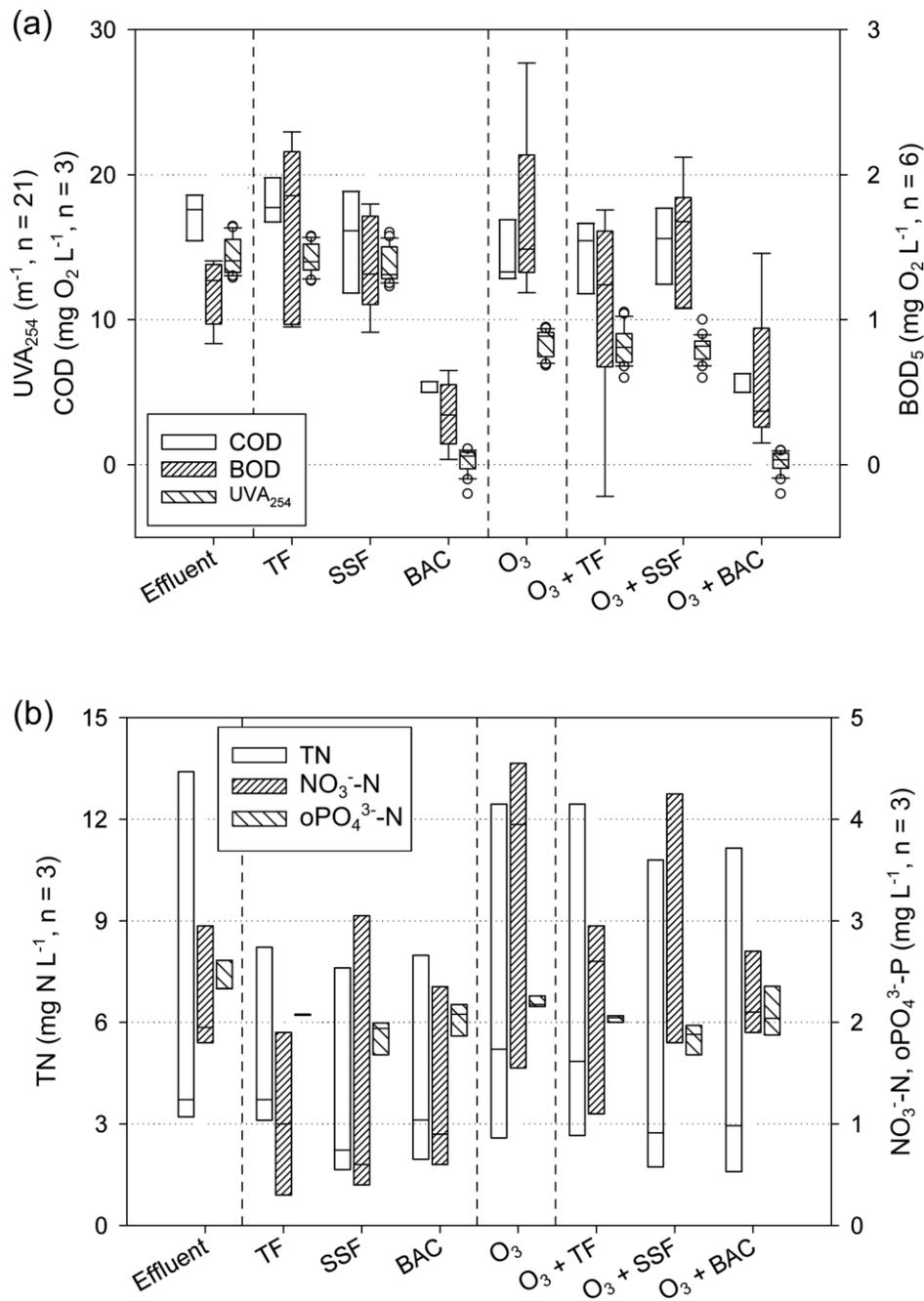


Figure 3: Physical-chemical water characteristics before and after (combined) treatment: (a) UVA<sub>254</sub> (m<sup>-1</sup>), COD and BOD<sub>5</sub> (mg O<sub>2</sub> L<sup>-1</sup>) and (b) nutrients TN, NO<sub>3</sub><sup>-</sup>-N (mg N L<sup>-1</sup>) and oPO<sub>4</sub><sup>3-</sup>-P (mg P L<sup>-1</sup>). The number of samples of each characteristic is indicated on the left or right y-axis.

## *Pharmaceuticals*

The WWTP effluent was analysed for a total of 35 pharmaceuticals of which 18 components could be quantified within a range of 2 to 506 ng L<sup>-1</sup> (Table 2). Large differences are noticed among the studied tertiary treatment techniques. No removal is obtained for 10 and 9 TrOCs by TF and SSF treatment, respectively, and the removal of most other TrOCs is rather similar and limited (< 59%) with both techniques. Ciprofloxacin (> 87 versus 70 %), levofloxacin (83% versus no removal) and metronidazole (76 versus 21%), however, are clearly better removed by SSF. Although these TrOCs are not easily biodegraded (i.e. they are still present after active sludge treatment), the bacteria present in the slow sand filter might start to adapt to the specific conditions (i.e. limited nutrients, presence of TrOCs). Ciprofloxacin has been shown to be recalcitrant for biodegradation in aqueous systems (Girardi et al., 2011) although some degradation has been reported in soil (Girardi et al., 2011) and in a biofilter (Liao et al., 2016). Most likely, the removal of ciprofloxacin, levofloxacin and metronidazole is a result of both enhanced biodegradation and sorption. Based on the log  $K_{ow}$  of these TrOCs (respectively 2.3, 0.35 and -0.1), a low tendency for sorption can be expected; although levofloxacin has been found to adsorb on granular media as e.g. sand (Dong et al., 2016). Yang et al. (2011) observed an averaged removal of 80 and 71% for ciprofloxacin and levofloxacin, respectively, during biological treatment. Sorption onto sludge flocs, as these TrOCs contain charged chemical groups, was seen to be significant compared to biodegradation as the log  $K_d$  (representative for the sorption of components on sludge) for ciprofloxacin is reported to be 4.3. Levofloxacin is more polar but no log  $K_d$  value is found in literature. Nevertheless, it is assumed by Yang et al. (2011) that the high  $K_d$  values for other fluoroquinolone antibiotics such as norfloxacin, trovafloxacin, and gemifloxacin suggest that levofloxacin is also strongly adsorbed. Filtration by BAC yields significant higher removal percentages for all 18 TrOCs. All are removed above 80% or even to concentrations below the detection limit. This clearly indicates the technical applicability of BAC filtration for a wide range of TrOCs. It can be assumed that, although inoculation of bacteria occurred before start-up of the filtration columns, adsorption will be the main removal mechanism as TrOC removal is clearly better compared to TF and SSF, and fresh AC was used at start-up.

Table 2: Removal (%) of TrOCs after different (combined) treatments of WWTP effluent

TrOCs	Effluent ng . L <sup>-1</sup>	TF %	SSF %	BAC %	O <sub>3</sub> %	O <sub>3</sub> + TF %	O <sub>3</sub> + SSF %	O <sub>3</sub> + BAC %
Alprazolam	3	n.r.	n.r.	bdl	42	34	29	bdl
Amantadine	45	n.r.	n.r.	98	59	59	56	98
Amitriptyline	35	51	46	94	96	52	65	94
Carbamazepine	487	n.r.	n.r.	bdl	bdl	bdl	bdl	bdl
Ciprofloxacin	71	70	bdl	bdl	59	bdl	bdl	bdl
Diazepam	2	18	n.r.	bdl	64	35	38	68
Diclofenac	506	n.r.	n.r.	bdl	bdl	bdl	bdl	bdl
Flumequine	5	15	10	bdl	17	n.r.	13	15
Indomethacin	48	bdl	bdl	bdl	bdl	bdl	bdl	bdl
Levofloxacin	30	n.r.	83	bdl	80	78	83	bdl
Metronidazole	24	21	76	82	56	46	76	57
Nalidixic acid	5	n.r.	15	bdl	n.r.	n.r.	n.r.	bdl
Nevirapine	8	n.r.	n.r.	bdl	bdl	bdl	bdl	bdl
Paracetamol	132	59	51	bdl	30	68	bdl	53
Sulfamethoxazole	24	n.r.	n.r.	bdl	95	82	92	bdl
Tetracycline	50	25	32	bdl	bdl	bdl	bdl	bdl
Trimethoprim	74	n.r.	n.r.	85	87	12	81	76
Venlafaxine	367	n.r.	n.r.	98	97	96	97	89

n.r. = removal efficiency < 10%; bdl = concentration after treatment is below detection limit

The performance of ozonation towards TrOCs removal is clearly better than that of TF and SSF, but not as good as that of BAC. For 10 pharmaceuticals, removal efficiencies were higher than 80% (or the compound was not detected anymore in the ozonated effluent). Only nalidixic acid showed to be fully recalcitrant towards ozonation, although the concentration was already close to the detection limit (DL = 2 ng L<sup>-1</sup>, see Vergeynst et al. (2017)). For the other TrOCs, removal efficiencies in the range of 17 to 64% are obtained. It should be noted that the measured TrOCs have a wide variety in ozone reactivity, as exemplified by their apparent secondary reaction rate constant with ozone,  $k_{O_3}$ .

Figure 4 shows the total quantified TrOC concentrations before and after tertiary effluent treatment. Whereas TF and SSF do not lead to a reduction in the summed TrOCs concentration, ozonation and BAC treatment enable a decrease of more than 90% and 99%, respectively. This

complies the target, i.e. removal of at least 80% of a set of indicator TrOCs during the full treatment train, as recently proposed by the Swiss regulator (Audenaert et al., 2014).

### *Toxicity*

Considering unselective toxicity (Figure 4), the tertiary treatment techniques are showing some differing results compared to TrOC removal. To start, it should be mentioned that the inhibition of the secondary effluent on the luminescent *Vibrio fischeri* of the BioTox kit was already negative (i.e. a lower toxicity) compared to the control solution (2% sodium chloride). It is likely to consider that the effluent contains more nutrients than the control solution (made in demineralised water) which probably favours the growth rate of the *Vibrio fischeri*. For further comparison of the inhibition after tertiary treatment, this phenomenon is non-essential as all results can be compared to the toxicity of the WWTP effluent. Although rather high deviations are noticed for most replicated measurements (see error bars in Figure 4), being inherent to the measuring protocol (Dries et al., 2014; Macova et al., 2010), interesting trends can be observed. Compared to the WWTP effluent, toxicity (procentual bioluminescence inhibition values) increases by a value of 9 and 7 % after ozonation and TF. SSF and BAC treatment do not show an important effect regarding the measured toxicity (i.e. < 3% increase or decrease). Especially for ozonation, an increase of the BOD<sub>5</sub>/COD ratio (from 0.07 to 0.16, Figure 4) indicates changes in the water matrix with the formation of smaller and more biodegradable moieties, which have been associated to an increased toxicity. The formation of possibly toxic by-products through reactions of ozone with bulk organic matter has already been discussed extensively in literature (see e.g. Knopp et al., 2016 and Reungoat et al., 2011). The minor increase of toxicity after TF is most likely associated with the slight decrease in available nutrients (mainly TN and NO<sub>3</sub><sup>-</sup>-N, Figure 3b) and thus hampering the *Vibrio fischeri* growth as a result of the biological activity within the filter. During BAC filtration, the significant decrease of TrOCs and other organics (as indicated by COD and UVA<sub>254</sub> measurements) may be compensated by a reduction in nutrients, resulting in similar toxicity values before and after BAC.

All in all, only little differences in toxicity are noticed for the different (bio)filtration techniques. Based on Figure 4, BAC shows high TrOC removals and a decreased BOD<sub>5</sub>/COD ratio but no

effect on toxicity. Ozonation clearly shows to remove TrOCs but also increases the toxicity level and BOD<sub>5</sub>/COD ratio which requires an additional post-treatment. TF and SSF seem inefficient as stand-alone techniques considering their limited effect on TrOCs and BOD<sub>5</sub>/COD.

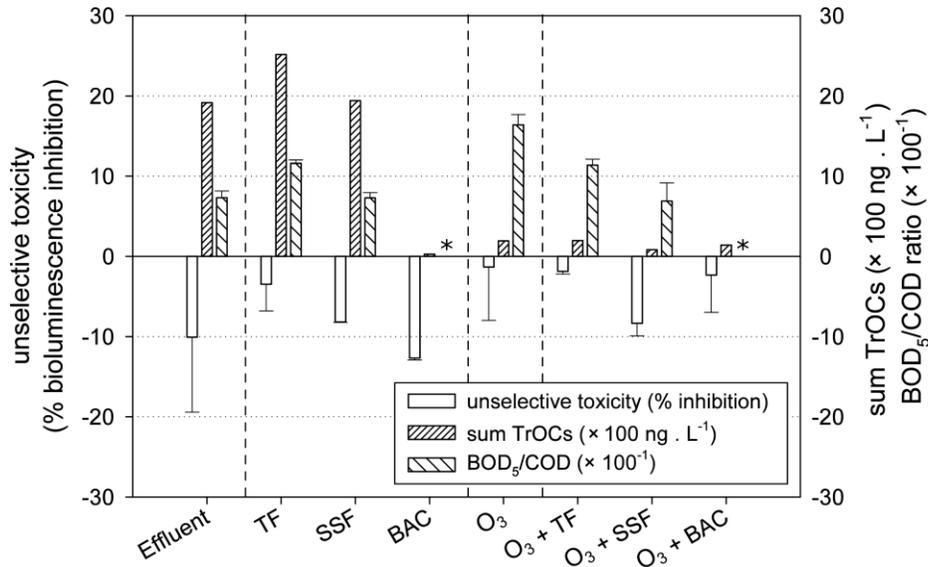


Figure 4: Toxicity, sum of quantified TrOCs, and biodegradability in the secondary treated WWTP effluent and after different (combinations of) post-treatments. The negative values for toxicity represent a lower percentage of inhibition than the control sample (i.e. 2% sodium chloride). The BOD<sub>5</sub>/COD ratio after BAC and ozonation + BAC could not be determined as the COD after treatment was below the detection limit (indicated with \*).

### Combination of ozonation and (bio)filtration

Among the three different post-treatment techniques, only BAC could improve the removal of BOD<sub>5</sub>, COD and UVA<sub>254</sub> compared to the levels obtained with a preceding ozonation (Figure 3a). This in agreement with previous results as also here TF and SSF are not able to result in a significant added removal of these organic surrogate parameters. In contrast, the latter two techniques could reduce the oPO<sub>4</sub><sup>3-</sup>-P level, measured after ozonation, by an additional 7 – 15 %, up to levels similar as obtained with TF and SSF without preceding ozonation. Total nitrogen

and  $\text{NO}_3^-$ -N showed some minor decreases although not statistically significant when adding TF, SSF or BAC as post-ozonation techniques. Although not investigated in detail, the combination of ozonation and BAC might increase the time before break-through.

Regarding TrOCs, the added value of a post-ozonation treatment technique is noticed only for the SSF. Figure 4 shows that the total amount of quantified TrOCs decreases from  $192 \text{ ng L}^{-1}$  (after ozonation) to  $82 \text{ ng L}^{-1}$  (after ozonation + SSF), showing the potential of SSF as an effective polishing step for the ozonated effluent. Considering the individual components in Table 2, the most pronounced improvement is obtained for ciprofloxacin (> 87% removal), metronidazole (76% removal) and paracetamol (> 80% removal), being TrOCs that could also be largely removed by stand-alone SSF (respectively > 87, 76 and 51% removal).

For both TF and BAC, the total concentration of the measured TrOCs could not be further reduced when applying these techniques as post-ozonation treatment. It can even be noticed that BAC as a stand-alone technique yields higher TrOCs removal compared to the combined ozonation + BAC treatment. This might be due to the fact that oxidative treatment during ozonation increases the polarity and hydrophilicity of the TrOCs which might result in less favourable adsorption on the active sites of the activated carbon surface. Schoutteten et al. (2016) concluded that when targeting mixtures of TrOCs with ozonation, a trade-off has to be made towards the overall reactivity and behavior of different TrOCs (products) when combined with AC. Although the parent TrOC will keep its original adsorption behavior, reaction products of ozonation were shown to be less adsorbed by AC depending on the transformations for specific TrOCs (e.g. atrazine, carbamazepine, dinoseb).

The increased toxicity of the municipal WWTP effluent after ozonation was lowered by all three post-treatment techniques (Figure 4), although the effect of TF and BAC following ozonation is only minor. However, when applying SSF after ozonation, the toxicity is reduced again to the level measured in the secondary effluent. Next to that, the biodegradability ( $\text{BOD}_5/\text{COD}$ ) of the treated water decreased to that of the WWTP effluent, supporting the hypothesis that the increased toxicity of the effluent after ozonation has been induced by changes in the matrix composition that also increased the biodegradability, in agreement with what has been previously described in literature (Knopp et al., 2016; Reungoat et al., 2011).

Overall, ozonation in combination with SSF or single BAC filtration are the treatment techniques giving the best technical performance regarding both TrOC removal and toxicity. Economical considerations might be determining in the choice to be made. Moser (2008) estimated the cost depending on the WWTP size for ozonation and sand filtration in the range of 4.8 to 36.7 and 5.9 to 32.2 CHF i.e.<sup>-1</sup> y<sup>-1</sup>. AC costs were higher, between 21.5 and 95 CHF i.e.<sup>-1</sup> y<sup>-1</sup>, mainly because of the replacement of exhausted activated carbon (Moser, 2008; Reungoat et al., 2011). Without replenishment of exhausted carbon, the biological filter will logically exhibit a behavior similar to more inert materials such as e.g. the slow sand filter. Using BAC as a polishing post-ozonation technique clearly becomes too expensive, as also Prasse et al. (2015) recently reported. Ozonation, followed by SSF to cope with a potential increase in toxicity and as final polishing step, is thus the preferred treatment chain to reduce TrOCs levels in secondary WWTP effluent.

### **Applicability of surrogate measurements for online control of TrOCs removal during combined tertiary treatment**

The measured TrOC removal of nine selected pharmaceuticals with a large range in 2<sup>nd</sup> order reaction rate constants ( $k_{O_3}$  ranging from  $< 1$  to  $10^6 \text{ M}^{-1} \text{ s}^{-1}$ ) is compared with the predicted TrOC removal, based on the  $\Delta\text{UVA}_{254} - \Delta\text{TrOC}$  correlations models developed by Chys et al. (submitted). More information is also given in Appendix.

Compared to ozonation, where a good agreement between measured and predicted values was exemplified by both a t-test ( $p > 0.05$ ) and a TIC value of 0.15, a lower predicting power was obtained when considering the data obtained through combined treatments. TIC values of 0.38 ( $\text{O}_3 + \text{TF}$ ;  $p = 0.026$ ), 0.22 ( $\text{O}_3 + \text{SSF}$ ;  $p = 0.047$ ) and 0.23 ( $\text{O}_3 + \text{BAC}$ ;  $p = 0.076$ ) were calculated. Although the t-test and TIC value are indicating a better correspondence for ozonation + SSF than for ozonation + TF, the correlation model can only be used as an indicator. Ozonation + BAC resulted in very high removal efficiencies, as previously described, for both the selected TrOCs and  $\text{UVA}_{254}$ , which resulted in a 100% predicted removal for all compounds. This makes it hard to draw strong conclusions about the applicability of the correlation model for this treatment chain because of the limited measuring range.

Overall, for most TrOCs having a  $k_{O_3} > 10 \text{ M}^{-1} \text{ s}^{-1}$  a removal of 100% was predicted by ozonation only at a  $\Delta\text{UVA}_{254}$  of 39%. Especially the slowly reacting TrOCs (and therefore less removed) are of interest for future regulation. For less ozone reactive TrOCs, the model predicts removal efficiencies of 70% (amantadine and flumequine) and 55% (metronidazole) for ozone only. When considering only these last three instead of nine TrOCs for ozone wether or not in combination with TF, SSF or BAC, the correspondence between predicted and measured removal is statistically significant. The predictive power of the models could not be established considering the TIC values. TIC (and p-)values of 0.28 ( $\text{O}_3$ ;  $p = 0.26$ ), 0.53 ( $\text{O}_3 + \text{TF}$ ;  $p = 0.19$ ), 0.36 ( $\text{O}_3 + \text{SSF}$ ;  $p = 0.18$ ) and 0.33 ( $\text{O}_3 + \text{BAC}$ ;  $p = 0.21$ ) were calculated. This means that, although the correlation models have been developed for ozonation only, the same models can statistically be used to give an indication for the removal of slowly reacting TrOCs considering the complete treatment train, combining ozonation with TF, SSF or BAC.

## CONCLUSION

Filtration techniques solely depending on any kind of biodegradation mechanisms (aerobic, anoxic, anaerobic) are inefficient for the removal of TrOCs in the secondary effluent of municipal wastewater treatment plants. In contrast, activated carbon filtration supported by slight biological activity can reduce the TrOCs levels by more than 99% but the replacement of the exhausted carbon makes this technique expensive for full-scale applications. A good alternative showed to be a treatment train consisting of ozonation, reducing the total TrOCs concentration by more than 90%, followed by slow sand filtration as a final polishing also reducing toxicity to the same level as before ozonation.

In terms of monitoring and control of TrOC removal, innovative correlation models based on the online measurement of changes in  $\text{UVA}_{254}$  were applicable during ozonation. Although the predictive power decreased when TF, SSF or BAC were added as a post-ozonation technique, the same models can give a good indication of the TrOC removal in secondary WWTP effluent particularly for the most relevant, poorly reactive TrOCs.

## ACKNOWLEDGEMENTS

We acknowledge the financial support (AUGE/11/016) from the Hercules Foundation (Flemish Government) for the UHPLC-Q-Exactive<sup>TM</sup> equipment used for the TrOCs analysis. Ghent University is acknowledged for the PhD grant of Michael Chys and for funding the automated SPE equipment (01B07512). This project was initiated within the LED H2O project. The LED H2O belongs to the LED network ([www.lednetwerk.be](http://www.lednetwerk.be)) and is financially supported by the Flemish Knowledge Center Water (Vlakwa vzw). The authors would also like to thank the staff of Aquafin NV, Belgium, for their help during sampling.

## APPENDIX. EQUATIONS FOR THE USED CORRELATION MODEL DEVELOPED BY CHYS ET AL. (SUBMITTED)

A generic framework relating UVA<sub>254</sub> as a surrogate measurement and on-going main ozone reactions is established by Chys et al. (submitted). The removal patterns of TrOCs having different reactivity towards ozone showed, in relation to  $\Delta\text{UVA}_{254}$ , an ‘insect wing’ shaped control zone. Two different reaction phases are defined, each of them described by a linear correlation function separated by an inflection point at 19%  $\Delta\text{UVA}_{254}$ . To allow on-line process control, the removal of each TrOC can be estimated using Eq. 1 ( $\Delta\text{UVA}_{254} \leq$  inflection point) and 2 ( $\Delta\text{UVA}_{254} \geq$  inflection point). The slopes of the correlation curves for the nine TrOCs that were selected to develop the models are given in Table SI 1.

$$\Delta\text{TrOC}_{0 \rightarrow \text{inflection}} = \text{slope}_{\text{phase1}} \times \Delta\text{UVA}_{254} \quad \text{Eq. 1}$$

$$\Delta\text{TrOC}_{\text{inflection} \rightarrow \dots} = \text{slope}_{\text{phase1}} \times \text{inflection} + \text{slope}_{\text{phase2}} \times (\Delta\text{UVA}_{254} - \text{inflection}) \quad \text{Eq. 2}$$

Table SI 1: Slopes of the correlations between the removal of nine selected TrOCs and  $\Delta\text{UVA}_{254}$  ranked according their apparent second order rate constant with ozone ( $k_{O_3}$ )

TrOC	$k_{O_3, pH 7}$ ( $\text{M}^{-1} \text{s}^{-1}$ ) <sup>a</sup>	slope <sub>phase1</sub>	slope <sub>phase2</sub>
Amantadine	n.a.	0.84	1.77
Metronidazole	< 1	0.92	2.21
Flumequine	n.a.	0.99	2.96
Amitriptyline	$2.5 \times 10^3$	3.30	2.72
Venlafaxine	$8.5 \times 10^3$	1.80	3.79
Ciprofloxacin	$1.9 \times 10^4$	3.58	2.65
Levofloxacin	$6 \times 10^4$	4.40	2.38
Trimethoprim	$2.7 \times 10^5$	4.24	1.95
Diclofenac	$1 \times 10^6$	4.46	2.45

n.a. = not available in literature but ranked according to current and previous observations

<sup>a</sup> see Chys et al. (submitted) and references therein for the values according to  $k_{O_3}$

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