

Treatment of micropollutants in municipal wastewater: Ozone or powdered activated carbon?

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Highlights

- Micropollutants are efficiently removed by both ozone and powdered activated carbon
- Specific substances were removed more efficiently by ozone
- Powdered activated carbon effectively removed a wider range of pollutants
- Both treatments significantly reduced the toxicity of WWTP effluent
- Both treatments are feasible for use in municipal WWTPs

Abstract

Many organic micropollutants present in wastewater, such as pharmaceuticals and pesticides, are poorly removed in conventional wastewater treatment plants (WWTPs). To reduce the release of these substances into the aquatic environment, advanced wastewater treatments are necessary. In this context, two large-scale pilot advanced treatments were tested in parallel over more than one year at the municipal WWTP of Lausanne, Switzerland. The treatments were: i) oxidation by ozone followed by sand filtration (SF) and ii) powdered activated carbon (PAC) adsorption followed by either ultrafiltration (UF) or sand filtration. More than 70 potentially problematic substances (pharmaceuticals, pesticides, endocrine disruptors, drugs metabolites and other common chemicals) were regularly measured at different stages of treatment. Additionally, several ecotoxicological tests such as the yeast estrogen screen, a combined algae bioassay and a fish early life stage test were performed to evaluate effluent toxicity. Both treatments significantly improved the effluent quality. Micropollutants were removed on average over 80% compared with raw wastewater, with an average ozone dose of $5.7 \text{ mg O}_3 \text{ l}^{-1}$ or a PAC dose between 10 and 20 mg l^{-1} . Depending on the chemical properties of the substances (presence of electron-rich moieties, charge and hydrophobicity), either ozone or PAC performed better. Both advanced treatments led to a clear reduction in toxicity of the effluents, with PAC-UF performing slightly better overall. As both treatments had, on average, relatively similar efficiency, further criteria relevant to their implementation were considered, including local constraints (e.g., safety, sludge disposal, disinfection), operational feasibility and cost. For sensitive receiving waters (drinking water resources or recreational waters), the PAC-UF treatment, despite its current higher cost, was considered to be the most suitable option, enabling good removal of most micropollutants and macropollutants without forming problematic by-products, the strongest decrease in toxicity and a total disinfection of the effluent.

Keywords: *Organic Micropollutant, Pharmaceutical, Wastewater Treatment, Ozone, Powdered Activated Carbon, Effluent Toxicity*

1. Introduction

About 3000 pharmaceutical compounds and more than 300 pesticides and biocides are commercially available in Switzerland (OPBio, 2005; OPPh, 2010; Swissmedic, 2012). They can enter urban sewer systems via human excretion in urine and faeces, by improper disposal, or through leaching of pesticides and biocides from urban areas during rain events. In conventional wastewater treatment plants (WWTPs), many of these hydrophilic organic compounds are poorly removed (Choubert et al., 2011; Deblonde et al., 2011), and are thus characterized by a relatively constant input at low concentrations (ng l^{-1} to $\mu\text{g l}^{-1}$) into the aquatic environment. As most of these substances are designed to be biologically active, they can affect sensitive aquatic organisms even at very low concentrations (Santos et al., 2010), hence the name “micropollutant”. For instance, endocrine effects on fish and mussel populations such as intersex, reproductive disruption or feminization of males have been observed in rivers downstream of municipal WWTP outfalls (Alan et al., 2008; Gagné et al., 2011; Tetreault et al., 2011; Tyler and Jobling, 2008; Vethaak et al., 2005; Woodling et al., 2006). These effects were attributed to the release of endocrine-active chemicals such as the synthetic estrogen 17α -ethinylestradiol (found in contraceptive pills), natural estrogens estrone and 17β -estradiol or nonylphenol. Furthermore, as lakes and rivers are used in many places for drinking water supply, pharmaceuticals and pesticides can therefore be found in tap water at very low concentrations, even after drinking water treatment (Huerta-Fontela et al., 2011; Mompelat et al., 2009; Stackelberg et al., 2007). Acute human health effects are not expected (Webb et al., 2003), but effects of long term exposure are unknown and, therefore, the release of these compounds into the environment should be avoided.

Effluents of WWTPs are the main source of pharmaceuticals in the aquatic environment (Bartelt-Hunt et al., 2009; da Silva et al., 2011). Since it is unrealistic to limit the consumption of pharmaceuticals, additional steps during wastewater treatment are one of the

best options to reduce the release of these compounds into surface waters. Currently, two main technologies with a potential for large-scale application in terms of efficiency, costs and energy requirements have been identified (Abegglen and Siegrist, 2012; Joss et al., 2008): oxidation of micropollutants with ozone or adsorption onto activated carbon.

Through the strong oxidative properties of ozone and of the hydroxyl radicals produced spontaneously in its decomposition, ozonation was found to degrade efficiently most micropollutants present in treated wastewater with a dose of 3-8 mg O₃ l⁻¹ (Hollender et al., 2009; Lee et al., 2012; Nakada et al., 2007; Reungoat et al., 2012; Reungoat et al., 2010; Rosal et al., 2010). A potential disadvantage of this process is the formation of unknown reactive by-products due to partial oxidation of the compounds and reaction with matrix components (von Gunten, 2003a). For example, undesirable toxic oxidation by-products such as nitrosamines N-Nitrosodimethylamine (NDMA), bromate or formaldehyde can be formed (Hollender et al., 2009; Richardson, 2003; Wert et al., 2007), potentially increasing the toxicity compared to non-ozonated wastewater (Petala et al., 2006; Petala et al., 2008; Stalter et al., 2010a; Stalter et al., 2010b). These oxidation products are usually more easily biodegradable and can be partially removed during biological post-filtration (Hollender et al., 2009; Richardson et al., 1999; Stalter et al., 2010a; Stalter et al., 2010b).

Activated carbon allows removal of a broad spectrum of micropollutants via adsorption to its high specific surface area and is thus widely used in drinking water treatment (Snyder et al., 2007; Westerhoff et al., 2005). As organic matter present in wastewater effluent can compete for adsorption sites, larger amounts of activated carbon are required. The efficiency of granular activated carbon (GAC) filtration to remove micropollutants has been studied in some WWTPs, showing a mitigated efficiency depending on the compound and the frequency of GAC regeneration/replacement (Grover et al., 2011; Nguyen et al., 2012; Reungoat et al., 2012; Reungoat et al., 2010; Snyder et al., 2007). Powdered activated carbon

(PAC) adsorption, with a dosage of 10-20 mg l⁻¹, has been proposed as a more efficient alternative compared to GAC treatment (Boehler et al., 2012; Metzger et al., 2005; Nowotny et al., 2007; Serrano et al., 2011). However, to date, very few large scale studies evaluating the efficiency of micropollutants removal via PAC treatment in municipal wastewater have been reported.

In order to find a feasible and efficient solution for the removal of pharmaceuticals and pesticides in wastewater, a global pilot study was conducted at the municipal WWTP of Lausanne, Switzerland. The goals were to evaluate and compare the efficiency of ozonation and PAC adsorption (i) to remove a broad range of micropollutants in WWTP effluents, and (ii) to reduce ecological impacts of the effluent. Finally, we aimed to determine the feasibility of these advanced treatments at the WWTP scale in terms of operation, energy consumption and costs.

2. Materials and methods

2.1 Lausanne wastewater treatment plant

The municipal WWTP of Lausanne, Switzerland, is the largest in the Lake Geneva watershed and treats on average 95,000 m³ d⁻¹ of wastewater representing a population equivalent (PE) of 220,000 individuals. The sewer system is only partially separated, collecting a significant amount of urban runoff during rain events. The watershed includes a major hospital and several clinics, which are a potential source of specific pharmaceuticals. The wastewater treatment consists of pre-treatments (grit removal and screening at 1 cm), primary clarifiers, biological activated sludge treatment (AS, sludge age of 2 d) without nitrification, or, for 5% of the flow, a moving bed bioreactor (MBBR) with partial to complete nitrification (< 1 mg N-NH₄ l⁻¹). In both treatments, phosphorus is removed by precipitation with iron chloride. Treated wastewater (WWTP effluent) is then discharged in Lake Geneva, which is the main

drinking water reservoir for more than 600,000 inhabitants (www.cipel.org, last accessed 7 May 2013).

Table 1 near here

2.1.1 Ozonation pilot plant

The pilot plant for ozonation was designed to treat a maximum flow rate of 100 l s^{-1} (13,000 PE) and consisted of a plug flow reactor (volume of 129 m^3) separated into four chambers (nine compartments) in series (Figure 1a) to assure optimal hydraulic conditions and a minimal reaction time of 20 min. Characteristics of the feed water (effluent of the conventional WWTP) are presented in Table 1. Ozone-containing gas (2-14% w/w) was continuously produced by an ozone generator (Effizon SMO 600 from ITT Wedeco, Wallisellen, Switzerland) fed with pure oxygen. 60% of the gas was injected counter currently into the 1st or 2nd chamber depending of the water flow rate and 40% in the 3rd chamber. The reaction time in the reactor ranged between 20 and 60 min. The ozone dosage was automatically adjusted to the water quality (oxidative demand) by varying the gas flow to maintain a constant residual concentration of dissolved ozone (around $0.1 \text{ mg O}_3 \text{ l}^{-1}$), measured with an online sensor (AMI codes II, from Swan, Hinwill, Switzerland), and confirmed with a second probe (AquaTector from Mesin, Winterthur, Switzerland) at the outlet of the 3rd chamber. Corresponding initial ozone doses varied between 2 and $13 \text{ mg O}_3 \text{ l}^{-1}$, with on average $5.7 \text{ mg O}_3 \text{ l}^{-1}$. Ozone concentrations in the feed and off gas were continuously measured with BMT 964 probes (Berlin, Germany). The transfer efficiency of ozone into the dissolved phase was between 70 to over 90% depending on the gas flow. In this paper, the ozone dose refers to the amount of gaseous ozone injected and not to the ozone dissolved into the water. The remaining gaseous ozone was catalytically converted to oxygen before its release into the atmosphere. The effluent of the ozone reactor was then filtered

through a rapid sand filter (flux of 8 m h^{-1} , characteristics described in the next section) with biological activity to remove reactive oxidation products.

Figure 1 near here

2.1.2 Powdered activated carbon treatment pilot plant

The pilot plant for PAC treatment was designed to treat WWTP effluent, in parallel to the ozonation, at a maximum flow of $10\text{-}15 \text{ l s}^{-1}$ (ca. 1700 PE). Based on bench-scale batch adsorption tests on five different PACs (Omlin and Chesaux, 2010), two PACs were selected for the pilot study to assess if the treatment efficiency was influenced by the type of PAC: Norit SAE SUPERTM (Norit Activated Carbon, The Netherlands), with grain size d_{50} of $15 \mu\text{m}$, specific surface area of $1150 \text{ m}^2 \text{ g}^{-1}$, pH of point of zero charge $\text{pH}_{\text{PZC}} > 7.3$, and ash content of 12%; and SORBOPORTM MV-125 (Enviro Link SA, Switzerland) with grain size $d_{80} < 45 \mu\text{m}$, specific surface area of $1100 \text{ m}^2 \text{ g}^{-1}$, pH_{PZC} of 9-11, and ash content $< 6\%$. Norit SAE SUPER and SORBOPOR MV-125 were used during the first and the second half of the study respectively with ultrafiltration separation. The installation was composed of a well-mixed contact reactor of 30 m^3 where PAC slurry ($3\text{-}5 \text{ g l}^{-1}$) was added continuously in proportion to the wastewater flow to reach a final dosage of $10 \text{ to } 20 \text{ mg PAC l}^{-1}$. A coagulant (FeCl_3 at $4\text{-}15 \text{ mg l}^{-1}$) was added to improve the subsequent separation of the PAC. Treated water was then filtrated in low transmembrane-pressure ($0.1\text{-}0.3 \text{ bar}$) cross-flow hollow fibres ultrafiltration (UF) membranes (Norit AirLiftTM, in PVDF, molecular weight cut-off of $100\text{-}300 \text{ kDa}$, total filtration surface of 660 m^2) to remove the PAC (Figure 1b). The tangential filtration process allowed increasing the concentration (up to $1\text{-}2 \text{ g PAC l}^{-1}$) and the residence time of the PAC in the system. Every four hours, the system was partially drained (volume removed proportional to the PAC dose) to maintain a constant PAC concentration in the reactor and to remove excess old PAC, which was then incinerated with the sewage sludge

from the conventional treatment. The hydraulic residence time in the contact reactor varied between 40 and 170 min, depending on the flow rate. The corresponding solid (PAC) residence time was between 2 and 17 d in order to reach adsorption equilibrium. UF membranes were backwashed every 10 min for 10 s, and chemical cleaning with citric acid and sodium hypochlorite was performed every month to avoid fast clogging of the membranes. The PAC separation was also studied over a 5-month period with a pilot sand filter (SF) without concentration and recirculation of the PAC (with the PAC SORBOPOR MV-125). The filter, also used after ozonation, consisted of 1.2 m of expanded shale (grain size 1.6-2.4 mm), and 60 cm of quartz sand (grain size 0.7-1.2 mm), with a filtration flux of 8-16 m h⁻¹ and one backwash per day. Supplementary information concerning the operation of the ozonation and PAC-UF pilot plants can be found in Margot et al. (2011).

2.2 Sampling campaigns

The pilot systems were operated continuously for more than one year. To monitor long term efficiency and to optimize the treatments, 25 sampling campaigns of one day (2-3 per month) and four seasonal campaigns of one week were performed between June 2009 and October 2010. During the campaigns, 24-h to 72-h composite samples (taken time proportional every 15 min) were collected with refrigerated automatic samplers (ISCO 6712 FR, Teledyne, USA, and WS 316, Watersam, Germany) at 5 locations: 1. Influent of the WWTP after grit removal and screening (Influent), 2. Effluent of the biological activated sludge treatment (only the first seasonal campaign) or effluent of the biological MBBR with nitrification (BIO), 3. Effluent of the ozone reactor (OZ), 4. Effluent of the sand filter following the ozonation (SF), and 5. Effluent of the PAC with ultrafiltration (PAC-UF) or with sand filter (PAC-SF) treatment (the last seven one-day campaigns). Composite samples were stored at 4°C and transferred in less than 12 h (or 24 h for the bioassays) to the laboratories performing analyses.

2.3 Chemicals and reagents

High purity micropollutants, deuterated standards and reagents used for micropollutant analysis have been listed previously (Morasch et al., 2010).

2.4 Analyses of micropollutants

Upon arrival in the laboratory, samples were immediately acidified to pH 2.5 with 5 N HCl and filtered at 0.7 μm through glass fibre filters (type GF/F, Whatman). Analysis of 58 hydrophilic micropollutants (36 pharmaceuticals, 13 biocides and pesticides, 2 corrosion inhibitors and 7 endocrine compounds, Table S1, Supporting information (SI)), identified in Switzerland as priority micropollutants (Morasch et al., 2010; Perazzolo et al., 2010), were conducted on the filtrate by solid phase extraction (SPE) followed by ultra-performance liquid chromatography coupled to tandem quadrupole mass spectrometer (UPLC-MS/MS). The analytical method, described in Morasch et al. (2010), was developed and validated for wastewater matrix (further details can be found in the SI). Uncertainties of the micropollutant analyses, including recovery and repeatability uncertainties, were compound- and concentration-dependent with a decreased reproducibility close to the limit of detection (LOD). For the large majority of the compounds, the relative standard deviation was $< 30\%$ (Bonvin et al., 2011). Compounds detected with this method are presented in Table 2 (analytical method A) with their respective LODs.

Chemical properties of these 58 micropollutants are reported in Table S1, SI. Hydrophobicity was expressed by the $\log D_{\text{ow}}$ at pH 7, a corrected form of the octanol-water partition coefficient ($\log K_{\text{ow}}$) determined for non-ionic substances, to account for the molecule dissociation or protonation at pH 7 (de Ridder et al., 2010). The $\log D_{\text{ow}}$ values were calculated from the corresponding pK_{a} values following Schwarzenbach et al. (2003). For neutral molecules, $\log D_{\text{ow}} = \log K_{\text{ow}}$, for ionic compounds, $\log D_{\text{ow}} < \log K_{\text{ow}}$.

During two seasonal campaigns, a broader range of 120 micropollutants, including human pharmaceutical metabolites, were analysed on filtered 7-d composite samples (glass fibre filter APFD09050, Millipore) following Hollender et al. (2009) and Kern et al. (2009). The method consists of SPE, with the same cartridges as for method A, followed by LC-MS/MS with an XBridge C-18 column (Waters) and Linear Trap Quadrupole orbitrap mass spectrometer with electrospray ionization (Thermo Fisher Scientific Corporation, USA). Compounds detected with this method are presented in Table 2 (analytical method B) with their respective LODs.

Analyses of the endocrine disrupting compounds 17β -estradiol (E2) and 17α -ethinylestradiol (EE2) (analytical method C in Table 2) were done on filtered 7-d composite samples during two seasonal campaigns by solid phase extraction (LiChrolut® EN-RP18 cartridge, Merck, Germany) followed by LC-MS/MS detection (API 4000 LC-MS/MS, Applied Biosystems, USA). The method used is described in Table S2 and S3, SI.

In case when the effluent concentration was below the LOD of the compound, the removal rate was calculated as a minimum value using the LOD as effluent concentration. These minimum removal rates were not integrated into the global removal average unless they were above 80%, in order not to bias the results.

2.5 Bioassays

In this pilot study, a broad range of bioassays was performed, showing that most acute toxicity bioassays were not sensitive enough to detect the effects of low micropollutant concentrations in wastewater. An overview on these bioassays can be found in Kienle et al. (2011). Two kinds of assays were therefore selected based on their sensitivity: i) bioassays on enriched samples and ii) chronic toxicity tests in the whole effluent. These two approaches can be seen as complementary for evaluating the effects of the effluents: the first mentioned

assays are very sensitive and focus on the effects produced by specific pollutants, while the second assays evaluate the long-term toxicity of the effluent, including the effect of very polar compounds not well extracted during the enrichment process, such as ozonation by-products (Stalter et al., 2011). For the first approach, two bioassays were performed on enriched samples: the *Yeast Estrogen Screen* (YES) to evaluate the estrogenicity (Routledge and Sumpter, 1996) and the *Combined Algae Assay* to evaluate the global toxicity and the presence of photosynthesis inhibitors (Escher et al., 2008b). For the second approach, a fish early life stage test (FELST, OECD, 1992b) with rainbow trout was performed by exposing the fish for 67 d to the effluent from the different treatments under flow-through conditions.

2.5.1 *Sample enrichment (YES and combined algae assay)*

The sample enrichment was done by solid phase extraction (SPE), which allows for increased pollutant concentrations in the extracts and thereby enables a better detection in the bioassays. It also limits the impact of the matrix components and metals, which are partially separated during the extraction (Macova et al., 2010). 7-d composite samples were enriched using SPE as described in Escher et al. (2008b) and as presented in Table S2, SI. Briefly, 200 ml (influent samples) or 500 ml (all others) were enriched 200 and 500 times respectively using LiChrolut® EN-RP18 cartridges (Merck, Germany), and then stored in 1 ml of a solvent mixture (~50% ethanol, ~50% acetone and methanol) at -20°C until analysis.

2.5.2 *Yeast Estrogen Screen (YES)*

The yeast estrogen screen with the recombinant yeast *Saccharomyces cerevisiae* was performed according to Routledge and Sumpter (1996) in 96-well microtitre plates as described in the SI. The estrogenic activity in the wastewater samples was assessed relative to a reference substance (17β-estradiol, a potent estrogen) and expressed as 17β-estradiol equivalent concentrations (EEQ). Both, the reference substance and the wastewater samples,

were tested in triplicates in a 1:2 dilution series. The highest tested concentration of 17 β -estradiol was 1.25×10^{-9} M (340 ng l⁻¹, in ethanol) and the maximum enrichment factors of the wastewater samples were 5 for the WWTP influent and 50 for all additional treatment steps. Ethanol served as solvent control (50 μ l/well, 8 wells/plate).

2.5.3 Combined Algae Assay

The combined algae assay on the green algae *Pseudokirchneriella subcapitata* was conducted as described by Escher et al. (2008a) and in the SI. Photosynthesis inhibition was measured by means of effective quantum yield (after 2 h of exposure) and algae growth by means of absorbance at 685 nm (after 24 h of exposure). The herbicide diuron served as the reference substance and ethanol as the solvent control (50 μ l/well, 8 wells/plate). Both, the reference substance and the wastewater samples, were tested in triplicates in a 1:2 dilution series, with the highest concentration of diuron being 3×10^{-7} M (69.9 μ g l⁻¹, in ethanol) and maximum enrichment factors of the wastewater samples of 20 (WWTP influent) and 83.3 (all additional treatment steps). The toxicity of the wastewater samples was expressed as diuron-equivalent concentrations (DEQs) for the endpoint “inhibition of Photosystem II” and toxic equivalent concentrations (TEQs, virtual baseline toxicant) for growth inhibition (Escher et al., 2008a).

Comparison of the measured photosynthesis inhibition with the concentration of photosynthesis inhibitors was based on the concept of concentration addition for substances with similar mode of action according to Chèvre et al. (2006). The concentrations of the four most abundant photosynthesis inhibitors included in the analytical list, the herbicides atrazine, diuron and isoproturon, and the algicide terbutryn were converted to diuron-equivalents based on their relative potency (HC50-EC50: hazardous concentration affecting 50% of the species with 50% effect, Chèvre et al., 2006) and then summed up. One μ g l⁻¹ of

atrazine, diuron, isoproturon and terbutryn corresponds to 0.084, 1, 0.559 and 0.881 $\mu\text{g l}^{-1}$ DEQs respectively.

2.5.4 *Fish early life stage test with rainbow trout (Oncorhynchus mykiss)*

This test was performed according to OECD guideline 210 (OECD, 1992b). Details of the methodology are described by Stalter et al. (2010b) (further information can be found in the SI). In brief, freshly fertilized eggs (< 1 h, 40 eggs per replicate) of rainbow trout were exposed to the test waters in 8-l stainless steel vessels in a flow-through system.

Reconstituted water (OECD guideline 203, OECD, 1992a) served as the control medium. In total, four controls and three replicate treatments for each wastewater were assessed. During the test period several endpoints were determined daily, namely: hatching, mortality, swim up, malformations and abnormal behaviour. After the end of the test fish were humanely killed with an overdose of MS222 (tricaine methanesulfonate, Sigma–Aldrich, St. Louis, USA). Afterwards, individual fish were blotted dry and fresh weight and length were measured. Plasma vitellogenin concentration was determined in whole body homogenates of 20 fish per control and wastewater as described by Holbech et al. (2006) using a vitellogenin ELISA test kit for rainbow trout (Biosense, Bergen, Norway) in a 1:20 dilution.

The significance of the difference in the response between the treatments was assessed with the Tukey's test for single-step multiple comparison. Significant differences are reported for p values < 0.05. All calculations were performed using R (R Foundation for Statistical Computing, Vienna, Austria).

2.6 **Laboratory-scale batch adsorption experiment**

The influence of wastewater dissolved organic carbon (DOC) concentration on PAC removal efficiency was assessed in laboratory-scale batch adsorption experiments. Adsorption tests

were conducted in triplicates on 24-h composite wastewater samples collected at the Lausanne WWTP after either simple coagulation-precipitation treatment (DOC of 17 mg l⁻¹), activated sludge treatment without nitrification (DOC of 11 mg l⁻¹), or moving-bed bioreactor treatment with full nitrification (three composite samples with DOC of 5, 7 and 8 mg l⁻¹). PAC (10 mg of SORBOPORTM MV-125, Enviro Link SA, Switzerland) was added to one litre of the different types of wastewater and agitated at 140 rpm during 24 h in the dark at 20°C. Analyses of initial and final sample concentrations, after filtration at 0.45 µm, of carbamazepine, diclofenac, benzotriazole, mecoprop and iopamidol were done by SPE followed by UPLC-MS/MS as described above. DOC was analysed by catalytic combustion oxidation method (Shimadzu TNM1 device).

2.7 Other analyses

Standard wastewater quality parameters (TSS, DOC, COD, BOD₅, NH₄, NO₃, NO₂, P_{total}, and P_{soluble}) were regularly analysed on 24 h-composite samples by standard methods recommended in Switzerland (DFI, 1983). Temperature, pH and conductivity were continuously analysed on-line with E+H measurement systems (Endress+Hauser, Switzerland). Indicator bacteria (*Escherichia coli*, intestinal enterococci and total viable bacteria) and coliphages (F-specific (RNA) and somatic phages) were analysed by standard plate count methods. Bromide and bromate were analysed by High Performance Ion Chromatography (HPIC) with a post column-reaction, with UV-detection for bromate and suppressed conductivity detection for bromide.

3. Results and discussion

3.1 Micropollutant concentrations in WWTP influent and effluent

3.1.1 Raw wastewater

Most of the micropollutants analysed were detected in the raw wastewater, with 70 compounds quantified in at least one sample (Table 2). The highest average concentrations of pharmaceuticals were observed for the analgesics paracetamol ($51 \mu\text{g l}^{-1}$) and ibuprofen ($4.1 \mu\text{g l}^{-1}$), the iodinated contrast media family (3.3 to $21 \mu\text{g l}^{-1}$), the antidiabetic metformin ($> 10 \mu\text{g l}^{-1}$) and the antihypertensive irbesartan ($4.7 \mu\text{g l}^{-1}$). High concentrations ($> 5 \mu\text{g l}^{-1}$) were also detected in raw wastewater for food components (aspartame and caffeine), corrosion inhibitors (benzotriazole and methylbenzotriazole) and an industrial additive (benzothiazole). On average, 25 compounds reached an influent concentration $> 1 \mu\text{g l}^{-1}$. A similar range of concentrations was observed in other Swiss municipal wastewater (Hollender et al., 2009), with the exception of the contrast media. In the present study, these showed higher concentrations probably due to the presence of many hospitals and clinics in the watershed.

High variations of the influent daily average concentration of the same compound were observed between the different campaigns. A factor > 4 in the 10-90 percentile range of the concentrations was observed for half of the compounds due, inter alia, to variations of the consumption of these compounds (Coutu et al., 2013). These variations highlight the importance of long term sampling campaigns, lasting at least one year, to cover the different consumption habits of the respective substances. During rain events, no noticeable different variations of the influent concentration could be detected compared to the background variability despite dilution by runoff water. Only the pesticides isoproturon, carbendazim and terbutryn showed a significant concentration increase during wet weather ($p\text{-value} < 0.05$ for the correlation with the dilution factor, Figure S1, SI), presumably due to the leaching of facades and runoff of pesticides used in gardens in the urban area (Burkhardt et al., 2007; Coutu et al., 2012).

3.1.2 Biological treatment

As presented in Table 2, most of the micropollutants were not well removed in the conventional biological wastewater treatment. Average removals of less than 50 % were found for 50 (i.e., 71 %) of the 70 compounds detected, with 16 having an average concentration in the effluent above $1 \mu\text{g l}^{-1}$, and 52 a concentration above 100 ng l^{-1} . Only the analgesic paracetamol was completely eliminated in all the campaigns. The most persistent micropollutants (less than 10% removal on average) were the pharmaceuticals carbamazepine, clindamycin, diclofenac, gabapentin and metoprolol, the pesticides carbendazim and diuron, and most of the pharmaceutical metabolites. All these compounds have been reported as persistent in many studies (Kupper et al., 2006; Oulton et al., 2010; Singer et al., 2010; Verlicchi et al., 2012). Some compounds such as the antibiotic clindamycin, the beta blocker metoprolol and most of the pharmaceutical metabolites were found at higher concentrations (in the dissolved phase) in the effluent of the biological treatment than in the influent. Similar observations in other studies were attributed to (i) release during the treatment of compounds trapped in faeces particles (Göbel et al., 2007), (ii) biological cleavage in the treatment of pharmaceutical conjugates (human metabolites) producing again the parent compound (Onesios et al., 2009), (iii) formation of bacterial metabolites during the biological treatment or (iv) analytical uncertainties.

Large variations of the removal rate in the biological treatment were observed among the different campaigns (Table 2 and Figure S2a, SI). For 24 of the 42 regularly studied micropollutants, these removal efficiency variations could be explained in part by the different levels of nitrification reached in the biological treatment. Indeed, significant positive correlations were observed between the removal of those compounds and the degree of nitrification of ammonium (Table S4, SI), with especially strong correlations ($r > 0.8$) for 11 substances and medium correlations ($0.6 < r < 0.8$) for 7 others (Figure S3, SI). Less than 30% removal in a non-nitrifying sludge compared with more than 60% elimination in a

treatment with complete nitrification was observed for instance for atenolol, bezafibrate, bisphenol A, gemfibrozil, methylbenzotriazole or metronidazole (Figure S3, SI and Margot and Magnet, 2011). Similar observations were reported for some of these substances by Clara et al. (2005). The higher micropollutant removal observed at high nitrification levels is presumably due to the longer hydraulic residence time in the reactor, leading to a higher time available for biodegradation processes, as well as to the presence of a more diverse microbial population with different metabolisms and a higher activity of nitrifying bacteria. These bacteria have the ability to degrade many micropollutants, probably by cometabolic oxidation by the ammonium monooxygenase enzyme (Fernandez-Fontaina et al., 2012). But, even for the most efficient biological treatment with complete nitrification ($< 1 \text{ mg N-NH}_4 \text{ l}^{-1}$), less than 50% removal was observed for 21 out of 43 compounds, with an average removal of only 50%. These results confirm the need for advanced treatments.

Table 2 near here

3.2 Removal of micropollutants with advanced treatments

Both advanced treatments were able to reduce the micropollutant concentrations in the effluent significantly (Table 2). The number of micropollutants with an average concentration above $1 \mu\text{g l}^{-1}$ in the effluent of the advanced treatments was reduced from 16 in the biologically treated wastewater to nine after ozonation and to seven after PAC-UF.

Substances with concentrations $> 1 \mu\text{g l}^{-1}$ after both treatments were the contrast media iohexol, iomeprol, iopamidol and iopromide, the pharmaceuticals gabapentin and metformin and the sweetener aspartame, and after ozonation additionally the chemicals benzotriazole and benzothiazole. The number of micropollutants with an average concentration above 100 ng l^{-1} was reduced from 52 (out of 70) in the biologically treated wastewater to 30 after both advanced treatments.

3.2.1 Ozonation

The removal percentages during the ozonation of the 40 micropollutants routinely analysed are presented in Table 2 (method A) and Figure S2b, SI.

Substances with high ozone reactivity

Twelve substances were eliminated to over 90% even with the lowest ozone dose (2.3 mg O₃ l⁻¹, eq. 0.3 g O₃ g⁻¹ DOC), including 4 antibiotics (trimethoprim, clindamycin, sulfamethoxazole and clarithromycin), 2 beta-blockers (sotalol and propranolol), 2 anti-inflammatory drugs (mefenamic acid and diclofenac), carbamazepine, gemfibrozil, estrone and bisphenol A. All these compounds contain electron-rich moieties such as phenols, anilines, olefins or amines (except gemfibrozil with a benzene derivate), which are known to have high ozone reactivity (second-order rate constant $k_{O_3} > 10^4 \text{ M}^{-1} \text{ s}^{-1}$) (Lee and von Gunten, 2012). The removal of substances with lower reactivity was more dependent on the operational conditions, such as the ozone dose (from 2.3 to 9.1 mg O₃ l⁻¹) and the wastewater quality (presence of ozone and hydroxyl radical scavengers or competitors, pH, etc.), leading to higher variations in the transformation rate between the different sampling campaigns.

The macrolide azithromycin showed lower removals (average of 74%) than expected based on its reported high ozone reactivity ($k_{O_3} 6 \times 10^6 \text{ M}^{-1} \text{ s}^{-1}$) (Lee and von Gunten, 2012). One potential explanation is the possible sorption (up to 15% in WWTP effluent) of this substance to colloid particles (1 nm to 1 μm, considered as being part of the aqueous phase) (Maskaoui et al., 2007; Worms et al., 2010), which could protect it against ozone attack (Zimmermann et al., 2011). Potential short-circuiting of a small water fraction through the reactor, which could reduce the exposure to ozone, may also explain the incomplete removal of very reactive substances such as azithromycin, diclofenac or carbamazepine.

Substances with low ozone but high OH radical reactivity

Ibuprofen, ketoprofen, metronidazole, primidone, mecoprop and benzotriazole, which have low reactivity with ozone ($k_{O_3} < 350 \text{ M}^{-1} \text{ s}^{-1}$, Beltrán et al., 1994; Real et al., 2009; Rosal et al., 2010; Zimmermann et al., 2011) showed moderate average removals (around 60%), mainly due to reaction with the strong and unselective oxidant OH hydroxyl radical originating from reaction of ozone with the organic wastewater matrix (Huber et al., 2003; Rosal et al., 2010). As the OH radical formation in wastewater is mainly due to the reaction of ozone with specific moieties of the effluent organic matter (EfOM), variation in the composition of EfOM, for instance by addition of coagulant, can lead to different amounts of OH radical formed per unit of ozone (Gonzales et al., 2012; Wert et al., 2011). Moreover, OH radical exposure varies with the concentration of HO \cdot scavengers (such as carbonate) and pH (Buffle et al., 2006). Reactions of micropollutants with OH radicals are thus more affected by the quality of the wastewater than direct ozone oxidation (Wert et al., 2011), which could explain the high removal variation observed for compounds with low ozone reactivity.

Substances with low ozone and low OH radical reactivity

Under the applied ozone doses (average $5.7 \text{ mg O}_3 \text{ l}^{-1}$ or $0.8 \text{ g O}_3 \text{ g}^{-1} \text{ DOC}$), only low removals (average of 34 to 43%) of the iodinated contrast media iohexol, iopromide, iomeprol, and iopamidol were obtained, with particularly low elimination (16%) of diatrizoic and iothalamic acids. Diatrizoate, the anionic form of diatrizoic acid, is one of the most ozone-resistant pharmaceuticals, having, as other contrast media, very low ozone reactivity, but also a low OH radical reactivity (Huber et al., 2005; Real et al., 2009). Low removals of atrazine (34%), gabapentin (38%), irgarol (32%) and propiconazole (32%) were also observed. Atrazine is reported to have low reactivity with ozone and OH radicals (Acero et al., 2000). Poor oxidation of gabapentin was also obtained in other studies (Reungoat et al.,

2010). Low removals of the pesticides irgarol and propiconazole during ozonation were also observed by Bundschuh et al. (2011), but for irgarol, higher removals were reported by Hollender et al. (2009). Irgarol is expected to have low ozone reactivity due to its triazine ring, which is very resistant to oxidation (Chen et al., 2008). The very low concentration of this substance in WWTP effluent (2 to 17 ng l⁻¹), close to the limit of quantification, leads however to high analytical uncertainties and could be the cause of the divergences observed. Resistance to ozonation is particularly of concern for the contrast media and gabapentin due to their high concentration in wastewater (above 1 µg l⁻¹) and their persistence even for efficient biological treatment.

Removal efficiency with higher ozone doses

A higher ozone dose, 17.6 mg O₃ l⁻¹, equivalent to 2.6 g O₃ g⁻¹ DOC, was tested during one campaign (data not illustrated). At this dosage, much better removal of the recalcitrant micropollutants was found, with 88% gabapentin elimination, 66% atrazine, and 84, 82 and 81%, respectively, of iopamidol, iohexol and iomeprol. Higher doses lead however to higher costs and a higher risk of forming bromate, a toxic by-product (see below “*Formation of toxic oxidation by-products*”), and therefore were not further tested.

Removal of other micropollutants and human drugs metabolites measured in a screening campaign

Table 2 presents also the removal of 23 other micropollutants (analytical method B), which were analysed only once on a 7-d composite sample (with 6 mg O₃ l⁻¹). Half of them were removed at a rate of over 70%. One can notice however the lower efficiency (< 51% removal) of ozone for the antihypertensive irbesartan, the anticonvulsant levetiracetam, the anxiolytic oxazepam and the insect repellent DEET. These substances contain amide functions that exhibit low reactivity with ozone (Lee and von Gunten, 2012). The human

pharmaceutical metabolites, which are mainly hydroxylated, hydrolysed or conjugated forms of the parent compound (Ikehata et al., 2006), were mostly not as well removed as the parent compound. This is especially the case for the 10,11-dihydro-10,11-dihydroxy carbamazepine and N-acetyl sulfamethoxazole, with an elimination of only 50% compared to > 90% for carbamazepine and sulfamethoxazole. The lower ozone reactivity of the metabolites can be explained by the protective effect of the hydroxyl or acetyl group on the reactive moiety, which changes the electron density and thus slows down the reaction (Huber et al., 2005).

Influence of the pH on the oxidation process

Reactivity of a substrate with ozone is strongly influenced (up to 4 orders of magnitude) by the protonation of the reactive amine or phenol (Lee and von Gunten, 2012). Dissociated moieties have a higher electron density and thus are more reactive towards ozone (Lee and von Gunten, 2012). Due to their two pKa values close to the pH of wastewater (Table S1, SI), the reactivity of fluoroquinolone antibiotics is particularly susceptible to pH variations. The variations of pH measured in the wastewater, from 6.3 to 8, can thus increase the reactivity of ciprofloxacin, norfloxacin and ofloxacin by 1 or 2 orders of magnitude (Dodd et al., 2006), explaining partially the high variation in the removal rates of these compounds during the different campaigns. This assumption is supported by the significant positive correlations observed between the pH and the removal rate of these three compounds (Figure S4, SI).

Relation between ozone dose and micropollutant removal rate

Effluent organic matter containing electron-rich organic moieties and nitrite react rapidly with ozone, contributing to the ozone demand with 0.2-0.6 mg O₃ mg⁻¹ C and 3.4 mg O₃ mg⁻¹ N-NO₂ respectively (Wert et al., 2011; Wert et al., 2009). Thus, in order to have enough residual ozone for the oxidation of micropollutants and to assure a sufficient and relatively constant ozone exposure, the ozone dosage was regulated to maintain a constant ozone

residual concentration near the end of the reactor. During the campaigns, the dosage varied from 2.3 to 9.1 mg O₃ l⁻¹ depending mainly on the DOC (0.38 g O₃ g⁻¹ C) and NO₂ (3.4 g O₃ g⁻¹ N) concentrations (Figure S5, SI), but also due to the residence time of the water in the reactor and the choice of the chamber in which ozone was injected. No clear relation between ozone dose (in mg O₃ l⁻¹) and micropollutant transformation rate was evident. However, when the ozone dose was normalized by the concentration of scavenger equivalent, a weighted sum of DOC and NO₂ concentrations (3.4 [N-NO₂] + 0.38 [DOC]), higher doses (in g O₃ g⁻¹ scavenger equivalent) tended to lead to higher removal rates for most micropollutants (Figure S6, SI). An average ozone dose of 5.7 mg O₃ l⁻¹, corresponding to 1.6 g O₃ g⁻¹ scavenger equivalent or around 0.85 g O₃ g⁻¹ DOC in case of 0.3 mg N-NO₂ l⁻¹, was sufficient to achieve an average reduction of 80% of the 65 studied micropollutants in the WWTP (compared with raw wastewater).

Effect of the sand filter on micropollutant removal

The sand filter following the ozonation had only a limited effect on micropollutant removal, with a slight improvement in the average removal of 36 compounds from 73.2% for ozone alone to 75.8% for ozone combined with the sand filter. Higher removals (> 10%) were observed mainly for compounds that were well eliminated in an efficient biological treatment, such as ibuprofen, metronidazole and ciprofloxacin, and for two pesticides carbendazim and propiconazole, possibly due to sorption on the biofilm (Figure S7, SI).

Formation of toxic oxidation by-products

Formation of toxic oxidation by-products can occur during ozonation of wastewater, such as carcinogenic bromate, nitrosamines or formaldehyde (Wert et al., 2007; Zimmermann et al., 2011). High concentrations of bromide (350 µg l⁻¹) measured in a 7-d composite sample in the wastewater suggested that excessive bromate formation could occur during ozonation

(von Gunten, 2003b). The concentration of bromate was below the detection limit ($1 \mu\text{g l}^{-1}$) in the effluents of the biological treatment and PAC-UF. After ozonation ($6 \text{ mg O}_3 \text{ l}^{-1}$, equal to $0.8 \text{ g O}_3 \text{ g}^{-1} \text{ DOC}$) and sand filtration, the bromate concentration increased to 3.7 and $5.1 \mu\text{g l}^{-1}$ respectively. These concentrations remained however below the Swiss drinking water standard of $10 \mu\text{g l}^{-1}$ (OSEC, 1995) and far below the proposed ecotoxicologically relevant concentration of 3 mg l^{-1} (Hutchinson et al., 1997). The formation of bromate was dependent on the ozone dose applied, exceeding the drinking water standard for an ozone dose above $1.4 \text{ mg O}_3 \text{ mg}^{-1} \text{ DOC}$ ($7 \text{ mg O}_3 \text{ l}^{-1}$, with $70 \mu\text{g l}^{-1}$ bromide), as shown in a laboratory scale experiment (Figure S8, SI). Unlike nitrosamines that can be partially removed in a sand filter (Hollender et al., 2009), the bromate concentration was not reduced during the sand filtration, and therefore a high ozone dose should be avoided to ensure low bromate concentrations in the effluent.

3.2.2 *Powdered activated carbon treatment*

The removal percentage during the PAC-UF treatment of the 40 micropollutants routinely analysed is presented in Table 2 (method A) and Figure S2c, SI. High variations in the removal rate, especially for compounds with lower PAC affinity, were observed among the different campaigns. Indeed, to optimize the treatment the PAC dose was increased from 10 to 20 mg l^{-1} during the study. Moreover, the DOC concentration in the feed water was not constant, leading to variable competition for the adsorption sites between EfOM and micropollutants. As the type of PAC (Norit SAE SUPER and SORBOPOR MV-125) did not significantly influence the removal rate compared to other variables, results are presented for both PAC types together.

Substances with high PAC affinity

Seven substances were removed at a rate of more than 90% in almost all the campaigns, including the beta-blockers propranolol and metoprolol, as well as methylbenzotriazole, trimethoprim, mefenamic acid, estrone and carbendazim. In 50% of the campaigns, over 90% of the following compounds were removed as well: clarithromycin, carbamazepine, benzotriazole, ofloxacin, norfloxacin and atenolol. These 13 micropollutants have a very good affinity for PAC, with high elimination rates even with 10 mg PAC l⁻¹. Apart from the hydrophobic mefenamic acid, all those compounds were either positively charged (five substances) or neutral (seven substances) at the pH of the wastewater, covering a broad range of hydrophobicity (log D_{ow} from -1.3 to 3.7).

Substances with medium PAC affinity

A second group of 15 substances (from metronidazole to azithromycin on Figure S2c, SI) had, on average, between 70 and 90% removal, including six neutral and six negatively charged compounds. The medium PAC affinity for diclofenac and gemfibrozil was reported elsewhere (Snyder et al., 2007; Westerhoff et al., 2005), but better removal of ibuprofen was observed in our case, either due to different PAC characteristics or to biodegradation phenomena in the reactor.

Substances with variable or low PAC affinity

The 12 remaining substances (from sulfamethoxazole to diatrizoic acid on Figure S2c, SI), composed of neutral or negatively charged compounds (including all the hydrophilic contrast media), showed poor or very variable affinity for PAC with an average removal between 11 and 66%. The high removal variation observed for sulfamethoxazole, ciprofloxacin, mecoprop, primidone and the contrast media were partly due to the different PAC doses applied, with increasing removal when the dose increased from 10 to 20 mg l⁻¹. High variations (< 20% to > 60% removal) occurred also within the same PAC dose (mainly at 10

mg l⁻¹), which could not be explained by the different parameters monitored (water quality and operational parameters such as residence time, PAC concentration, PAC type, etc.).

These high variations may be due to different EfOM content and composition, as discussed below.

The anionic contrast media diatrizoic and iohalamic acids and the anticonvulsant gabapentin showed less than 20% removal by PAC-UF. The low PAC affinity of these hydrophilic (log D_{ow} of -1.2 to -0.4) and charged substances were reported by Reungoat et al. (2010) and Boehler et al. (2012). Low adsorption of gabapentin could be caused by the absence of an aromatic ring (de Ridder et al., 2010). The variable elimination of irgarol (0% to > 60%), despite its hydrophobicity (log D_{ow} of 4), is probably due to its very low concentration in the feed water, leading to high uncertainties in estimates of the removal rate.

Removal efficiency with higher PAC dose

A higher PAC dose of 60 mg l⁻¹ was tested during one campaign, leading to more than 90% removal of substances with a low PAC affinity (e.g., sulfamethoxazole, mecoprop, primidone and the contrast media iohexol, iomeprol and iopromide). Even this high dose was unable to remove gabapentin satisfactorily (56% removal, data not illustrated). Higher doses of PAC lead however to higher costs and larger amounts of sludge produced.

Removal of other micropollutants and human drug metabolites measured in a screening campaign

Table 2 shows the removal of 24 other micropollutants (analytical method B), which were analysed once on a 7-d composite sample (12 mg PAC l⁻¹). About half of them were removed at a rate of over 70%. We observe, however, a lower efficiency (< 60% removal) for most of the human pharmaceutical metabolites. Indeed, pharmaceutical compounds are usually

transformed in the liver or kidney to more polar and hydrophilic metabolites in order to be readily excreted in the urine or bile (Ikehata et al., 2006). For instance, the metabolite 10,11-dihydro-10,11-dihydroxycarbamazepine has a log K_{ow} of 0.13 compared to 2.45 for the parent compound carbamazepine (Miao et al., 2005). Therefore, due to the low hydrophobicity of human metabolites, a lower PAC affinity is expected. The low removal of the UV filter oxybenzone and the antidepressant venlafaxine is not explained, however, given the good PAC affinity for those substances reported in the literature (Reungoat et al., 2012; Snyder et al., 2007).

Possible influence of effluent organic matter on removal efficiency

The adsorption process in complex matrix is not yet fully understood and can be influenced by many parameters, the main one being the competitive effect of the EfOM, either by direct competition for the adsorption sites or by pore blockage/constriction (Delgado et al., 2012). EfOM characteristics, mainly the concentration of low molecular weight and hydrophobic molecules, determine the competitiveness of the organic matter (de Ridder et al., 2011; Newcombe et al., 1997). Variation in the concentration and composition of the EfOM, due to different treatments of the wastewater (biodegradation, chemical coagulation, etc.) can thus lead to different micropollutant removal rates at the same PAC dose. This issue was investigated with laboratory batch adsorption experiments. Five micropollutants in Lausanne wastewater treated to different levels (coagulation/precipitation, biological treatment without nitrification or with full nitrification) were examined. A strong influence of the feed water DOC (from 5 to 17 mg l⁻¹) on the substance removal with PAC was observed for all the compounds (Figure S9, SI), confirming the high competitive effect of EfOM for the adsorption sites. The highest PAC efficiency was observed in the effluent of the biological treatment with full nitrification (DOC of 5 mg l⁻¹), significantly higher than in wastewater coming from a treatment without nitrification (DOC of 11 mg l⁻¹). Wastewater treated only

with coagulation/precipitation (DOC of 17 mg l^{-1}) led to a strong reduction of the PAC adsorption capacity, probably due to the persistence of smaller biodegradable molecules. Thus, different degrees of secondary treatment can lead to variable adsorption rates. Consequently, the PAC dose necessary to achieve an average overall micropollutant removal above 80% (whole treatment) in wastewater with a DOC of 5 to 10 mg l^{-1} , was variable: 10 mg l^{-1} was sometimes sufficient but in most cases 20 mg l^{-1} was required. These minimum doses were noted in other studies as well (Boehler et al., 2012; Nowotny et al., 2007).

Role of electrostatic and hydrophobic interaction in the adsorption process

Electrostatic and hydrophobic interactions seem to play an important role in the adsorption process. As presented in Figure 2, on average more than 80% (most more than 90%) of all the positively charged molecules were removed, independently of their hydrophobicity. Only the large molecule azithromycin, diprotonated at pH 7, was eliminated to a lower extent despite its higher hydrophobicity, possibly by size exclusion in the micropores of the PAC (Ji et al., 2010). The removal of the negatively charged and neutral substances was more dependent of their hydrophobicity, the most hydrophilic compounds being eliminated to a lesser extent. For the same $\log D_{ow}$, neutral and especially negatively charged compounds were on average less adsorbed than those that were positively charged.

Figure 2 near here

The two PACs studied have a point of zero charge $\text{pH}_{PZC} > 7.3$, thus the fresh PAC is expected to be neutral or slightly positively charged at the pH tested. However, in wastewater, the adsorption of EfOM, negatively charged at neutral pH, leads to a decrease in the PAC pH_{PZC} due to the EfOM coverage, resulting from a net negative surface charge on the loaded PAC (Newcombe, 1994; Yu et al., 2012). As both EfOM and micropollutant adsorption occurred simultaneously, electrostatic attraction between the cationic compounds

and the negatively charged surface of the loaded PAC are expected, even for hydrophilic substances. Conversely, charge repulsion should occur for the anionic substances. These electrostatic repulsions can be offset by hydrophobic partitioning (expulsion in the solute-water system) at high $\log D_{ow}$. Thus, in wastewater, hydrophobic interaction is expected to be more significant for negatively charged and neutral compounds than for positively charged substances, as observed in our results. This assumption was tested in batch tests by de Ridder et al. (2011) where very similar behaviour was observed, confirming that both $\log D_{ow}$ and charge interaction have a significant influence on micropollutant adsorption in wastewater. But, for neutral or negatively charged substances, $\log D_{ow}$ was not by itself sufficient to explain the observed removals. Although hydrophobic partitioning has been reported as the dominant mechanism leading to PAC adsorption for compounds with $\log D_{ow} > 3.7$, other adsorption mechanisms such as hydrogen bond formation and pi-pi interaction between micropollutants and the PAC surface have been reported to be more prominent as $\log D_{ow}$ decreases (de Ridder et al., 2010). Thus, for hydrophilic compounds with the same $\log D_{ow}$, very different PAC affinities can be expected depending of the characteristics of the molecules.

Separation of PAC with ultra- or sand filtration – Influence on micropollutant removal

As observed in other studies (Snyder et al., 2007; Yoon et al., 2007), the influence of ultrafiltration on the removal of hydrophilic micropollutants ($\log K_{ow} < 2.8$) is expected to be negligible due to the relatively high molecular weight cut-off of the membrane (100-300 kDa) compared to the molecular mass of micropollutants (< 1 kDa). For more hydrophobic compounds, significant adsorption on the membranes can occur (Yoon et al., 2007), but at a much lower level than on PAC. Therefore, PAC adsorption is considered to be by far the main removal process in the PAC-UF system. To check this assumption and to evaluate another (cheaper) separation system, a sand filter was used instead of the UF membrane

during seven campaigns. Good PAC retention (> 90%) was observed with less than 1-3 mg TSS l⁻¹ in the effluent. Similar micropollutant removal rates were measured with both separation systems (UF and sand filter), on average around 80%, indicating that the PAC, and not the ultrafiltration, was responsible for micropollutant removal.

3.3 Ecotoxicological evaluation

In addition to chemical analysis, the results of bioassays provided information on potential effects of the mixture of compounds. Both advanced treatments were able to reduce significantly the toxicity of the biological treatment effluent, both in bioassays with algae on enriched samples and in a chronic test on fish with continuous exposure to the raw effluent.

Figure 3 near here

3.3.1 Combined algae assay on enriched samples

3.3.1.1 Photosynthesis inhibition

As presented in Figure 3a, raw wastewater induced photosynthesis inhibition equivalent to 253 ± 92 ng l⁻¹ of diuron. This specific effect of substances acting on the photosystem II (Escher et al., 2008a) was not strongly reduced during the biological treatment ($14 \pm 37\%$, 228 ± 155 ng DEQ l⁻¹), suggesting low biodegradability of these compounds. However, both advanced treatments led to a clear decrease in this effect with $82 \pm 8\%$ removal (32 ± 9 ng DEQ l⁻¹) during ozonation and $87 \pm 11\%$ removal (18 ± 11 ng DEQ l⁻¹) during PAC-UF treatment. The residual toxicity was significantly lower ($p < 0.05$) after PAC-UF compared to OZ in campaigns 1 and 3 (no significant difference in campaign 2). Photosynthesis inhibition was not significantly reduced after the sand filter following ozonation (27 ± 5 ng DEQ l⁻¹), presumably due to the low biodegradability of those compounds. The overall removal in the WWTP was $87 \pm 4\%$ with ozonation followed by sand filtration and $92 \pm 9\%$ with PAC-UF

treatment, showing the ability of these two treatments to improve the quality of the WWTP effluent.

The herbicides atrazine, diuron and isoproturon, and the algicide terbutryn act as photosystem II inhibitors in plants and algae and can have a cumulative effect when present in a mixture (Brust et al., 2001; Knauert et al., 2010; Nyström et al., 2002). A clear relation (correlation $r = 0.909$, $p < 0.001$) between inhibition of the photosystem II and the concentration of relevant pesticides measured in the samples was observed (Figure 4). The sum of the relative potency of these four compounds, expressed as diuron equivalents, could explain, on average, 56% of the total inhibition observed. The other (unmeasured) compounds participating in the remaining photosynthesis inhibition are expected to be eliminated to the same extent as these four inhibitors. Indeed, a reduction of the concentrations of these inhibitors in advanced treatments led to a similar reduction of the photosynthesis inhibition. Similar effects were observed for ozonation in a previous study at the Regensdorf WWTP, Switzerland (Escher et al., 2009).

Figure 4 near here

3.3.1.2 Algae growth inhibition

A relatively high algae growth inhibition was observed in the raw wastewater (Figure 3b), with a non-specific toxicity of $26 \pm 7.3 \text{ mg l}^{-1}$ (baseline toxic equivalent concentration, Escher et al., 2008a). This was clearly reduced ($73 \pm 6\%$, $6.9 \pm 1 \text{ mg l}^{-1}$) during the biological treatment. This non-specific toxicity, contrary to the photosynthesis inhibition, can thus be partially attributed to biodegradable or adsorbable compounds that were removed in this treatment. The advanced treatments were able to reduce the residual toxicity (attributed to non-readily biodegradable micropollutants) by $75 \pm 7\%$ during ozonation ($1.67 \pm 0.45 \text{ mg l}^{-1}$) and $84 \pm 5\%$ during PAC-UF treatment ($1.07 \pm 0.17 \text{ mg l}^{-1}$). This toxicity was significantly

lower after PAC-UF compared to OZ in campaigns 2 and 3 (no significant difference in campaign 1). The sand filtration following ozonation was also able to reduce the growth inhibition from 10 to 46% (mean: $1.28 \pm 0.16 \text{ mg l}^{-1}$), the highest improvement being observed when the biological treatment was not effective, meaning that biodegradable toxic compounds remained in the ozone effluent. This resulted in a mean overall elimination (compared to WWTP influent) of $96 \pm 1\%$ with ozonation followed by sand filtration and $97 \pm 0.1\%$ with PAC-UF treatment. In a comparable study, Escher et al. (2009) detected a higher maximum reduction of non-specific toxicity during biological treatment (70 - 99.5%) at the Regensdorf WWTP and a subsequently lower removal efficiency during ozonation.

3.3.2 *Estrogenic activity on enriched samples*

High estrogenic activity was detected with the YES in raw wastewater (37-100 ng l^{-1} estradiol equivalents, EEQ), which was then strongly reduced ($88 \pm 10\%$) during the biological treatment (Figure 3c). The removal of estrogenic activity was dependent on the level of nitrification, from 75% without nitrification to 99% with full nitrification ($< 1 \text{ mg N-NH}_4 \text{ l}^{-1}$) (Figure S10, SI). The low estrogenicity level measured in the effluent of the biological treatment (0.7-8.3 ng l^{-1} EEQ) could, however, be sufficient to affect the fertility of sensitive fish species (Lahnsteiner et al., 2006), as shown also with the fish test (cf. §3.3.3). Estrogenic activity was further significantly diminished by $89 \pm 4\%$ during ozonation and $77 \pm 17\%$ with PAC-UF, which is similar to results obtained by Stalter et al. (2011) and Escher et al. (2009). This resulted in a mean overall elimination (compared to WWTP influent) of $99 \pm 1\%$ with both advanced treatments. The residual estrogenicity observed in the effluents, significantly lower after OZ (0.1-0.65 ng l^{-1} EEQ) than after PAC-UF (0.29-1.32 ng l^{-1} EEQ) in campaigns 1 and 2 (no significant difference in campaign 3), was in most cases below the environmental quality standard of 0.4 ng l^{-1} proposed for 17- β -estradiol (Kase et al., 2011). Therefore, advanced treatments or biological treatment with full nitrification are efficient means to

reduce the release of endocrine compounds, and thus to reduce the risk of feminization of fish and mussel populations. As the estrogenic activity was already very low after the ozonation, there was no improvement due to the sand filter. During one campaign an increase in estrogenicity was observed, presumably due to contamination of the new sand by estrogenic compounds. Indeed, an unexplained increase in bisphenol A concentration was measured after the sand filter for this case.

3.3.3 Fish early life stage toxicity

Both advanced treatments significantly decreased the toxicity of the WWTP effluent on the development of rainbow trout embryos for all endpoints measured: the overall survival of the fish, the hatching success, the swim up, the individual development (weight and size) and the induction of estrogenic effects.

Overall survival

The overall survival of the rainbow trout after 69 d of continuous exposure in the effluent of the biological treatment (BIO) was relatively low, with only $58 \pm 6.6\%$ survival (Figure 5a). The survival was significantly improved after the ozonation (OZ) ($85 \pm 6.6\%$ survival) and the PAC-UF treatment ($93 \pm 3.8\%$), reaching a level statistically similar to the control ($95 \pm 2\%$ survival). The subsequent sand filtration (SF) step did not improve the survival of the fish compared to the ozonation alone.

Hatching success

The hatching success of the fish reached $80 \pm 5\%$ in BIO effluent, which was significantly lower than in the control (100% success). Both advanced treatments improved the hatching success to a level statistically similar to the control, with $97 \pm 3.8\%$ for OZ, $98 \pm 2.9\%$ for SF and $100 \pm 0\%$ for PAC-UF. However, the hatching progress was on average delayed for 2 d

in OZ and SF effluents compared to PAC-UF or the control, and delayed for one week in the BIO effluent (Figure 6a). Delay in hatching after ozonation was also observed by Stalter et al. (2010b), and not notable in the sand filter effluent, as discussed below.

Swim-up

The swim-up, which is the developmental transition from larval stage to juvenile fish stage, appeared after 60 d in BIO effluent, delayed by 8 d compared to the control (Figure 6b). Both advanced treatments reduced the delay in the swim-up. The beginning of the swim-up appeared simultaneously in PAC-UF effluent and in the control, but was delayed by 3 d compared to the control in OZ and SF effluents. A notable delay in the swim-up was also observed after ozonation by Stalter et al. (2010b), possibly due, in their case, to the presence of toxic oxidation by-products. 28% of the fish died during the larvae stage in BIO effluent, with only $45 \pm 9\%$ of the larvae reaching the juvenile stage at the end of the test. This was much improved after the advanced treatments, with $93.3 \pm 3.8\%$ of the larvae in PAC-UF effluent, $88.2 \pm 10\%$ in OZ, and $85.5 \pm 10.4\%$ in SF that swam up, showing no significant difference with the control ($93.1 \pm 3.1\%$).

Weight and length of the fish

Weight and length of the fish at the end of the test was relatively low in BIO effluent and increased significantly after the advanced treatments. Those parameters were however still significantly lower in OZ and SF effluents compared to the control, while no difference was observed in PAC-UF effluent (Figure 5b and c). The fish were on average 6.7% longer and 22% heavier in PAC-UF effluent than in OZ or SF effluents, and 32% longer and twice as heavy as in BIO effluent. The sand filter did not improve growth of the fish compared to the ozonation alone.

Vitellogenin concentration

The vitellogenin (VTG) concentration in the juvenile fish was significantly higher in the BIO effluent ($63.1 \pm 33.2 \text{ ng ml}^{-1}$) compared to the fish in the control ($10.6 \pm 4.7 \text{ ng ml}^{-1}$) (Figure 5d). Similar VTG concentrations ($67.3 \pm 26.9 \text{ ng ml}^{-1}$) were found by Stalter et al. (2010b) in juvenile rainbow trout exposed to secondary effluent. VTG, an egg yolk precursor normally produced by mature female fish, can be used as a biomarker for exposure to exogenous estrogens for juvenile and male fish (Jobling et al., 2006; Thorpe et al., 2000). The increase of VTG content in juvenile fish in BIO effluent indicates the presence of environmentally-relevant concentrations of estrogenic compounds. This effect was not observed after both advanced treatments, the VTG content in the fish being on par with the control in PAC-UF ($10.2 \pm 5.8 \text{ ng ml}^{-1}$), OZ ($9.9 \pm 7.1 \text{ ng ml}^{-1}$) and SF effluent ($14.1 \pm 9.1 \text{ ng ml}^{-1}$). These results confirm the ability of ozonation and PAC-UF to eliminate the estrogenicity in wastewater, as presented in Figure 3c. The minor increase of VTG in the fish exposed to SF effluent compared to OZ effluent, also observed in the YES, is probably due to contamination of the new sand by endocrine active compounds.

Figure 5 near here

Toxicity of the biologically treated effluent and possible influence of nitrite and ammonia

As presented above, the effluent of the biological treatment impaired the survival and the development of rainbow trout, delaying their swim-up and their growth as expressed by lower biomass and body length. Besides the mortality observed (43%), a delay in the development can, for instance, increase the risk for predation in natural systems since larvae are unable to escape before the swim-up (Stalter et al., 2010b). Moreover, changes in VTG concentrations in fish can be an indicator for an effect on their reproduction system (Miller et al., 2007; Thorpe et al., 2007). Therefore, effluents from conventional WWTPs can have a significant

impact on salmonid fish in natural environments in the case of low dilution of the effluent. Besides the estrogenic substances and other micropollutants present in the effluent, macropollutants such as nitrite and ammonia or bacterial contamination could also affect the fish.

Rainbow trout are sensitive to nitrite (NO_2^-), with lower growth rates observed at $0.3 \text{ mg N-NO}_2^- \text{ l}^{-1}$ and 65% mortality at $0.91 \text{ mg N-NO}_2^- \text{ l}^{-1}$ (with $10 \text{ mg Cl}^- \text{ l}^{-1}$) (Kroupova et al., 2008). The toxicity can, however, be strongly inhibited by chloride ions (Lewis and Morris, 1986). The relatively high concentration of chloride in the investigated wastewater ($80\text{-}170 \text{ mg l}^{-1}$) could have therefore drastically reduced (up to a factor of 10) the toxic effect of nitrite. In the present study, NO_2^- concentrations varied between 0.04 and $0.55 \text{ mg N-NO}_2^- \text{ l}^{-1}$ in BIO and OZ effluents and around $0.22 \text{ mg N-NO}_2^- \text{ l}^{-1}$ in PAC-UF effluent. Those concentrations are very unlikely to have induced significant lethal and sub-lethal effects on the fish.

Embryos and larvae of rainbow trout are additionally very sensitive to ammonia (NH_3), the unionized form of ammonium NH_4^+ . Sub-lethal effects such as a decrease in the larvae weight were observed after 20 d of exposure at 0.006 to $0.18 \text{ mg N-NH}_3 \text{ l}^{-1}$ (Vosyliënė and Kazlauskienė, 2004) and a delay in development to the swim-up stage appeared at concentrations above $0.01 \text{ mg N-NH}_3 \text{ l}^{-1}$ (Brinkman et al., 2009). Lethal effects were reported for concentrations above 0.022 to $0.13 \text{ mg N-NH}_3 \text{ l}^{-1}$ (Brinkman et al., 2009; Solbé and Shurben, 1989). In the present study, the concentrations of unionized ammonia, calculated according to Armstrong et al. (2012), were relatively high in the BIO, OZ and SF effluents, varying between 0.02 and $0.06 \text{ mg N-NH}_3 \text{ l}^{-1}$ during the first 10 d, decreasing then below $0.01 \text{ mg N-NH}_3 \text{ l}^{-1}$ in all effluents until the end of the test. The NH_3 concentration in the PAC-UF effluent was always $< 0.01 \text{ mg N-NH}_3 \text{ l}^{-1}$ due to further nitrification in the reactor. Ammonia concentrations in BIO, OZ and SF effluents at the beginning of the test were therefore high enough to induce sub-lethal effects and even mortality. Ammonia could be

thus partly responsible for the lower weight and length of the fish exposed to OZ and SF effluents, as well as for their delay in reaching the swim-up stage. The clear impact on fish development and the high mortality observed in the BIO effluent is, however, not attributable to ammonia toxicity alone as much smaller impacts and mortality rates were observed with the same ammonia concentration in OZ effluent. Therefore, the toxicity observed in the BIO effluent can presumably be related to compounds oxidized during ozonation, such as pharmaceuticals and pesticides. This demonstrates that several compounds influencing rainbow trout development and survival in the BIO effluent were removed in the advanced treatment. Ozonation and activated carbon are therefore efficient techniques to reduce effects of micropollutants on fish.

Figure 6 near here

Ozonation influence on fish toxicity

Stalter et al. (2010b) reported that fish toxicity increased during the ozonation process, probably due to the formation of labile oxidative by-products such as toxic aldehydes or metabolites. These adverse effects were reduced after the sand filtration, probably due to biodegradation or spontaneous degradation of the reactive products. Unlike Stalter et al. (2010b), in our case ozonation clearly reduced the fish toxicity compared to the BIO effluent to a level close to the control. Moreover, the sand filter did not affect the residual toxicity of the OZ effluent. These contradictory results are likely due to different ozone reactor configurations and/or different water compositions. Indeed, the reactor used in Stalter et al. (2010b) contained 3 chambers with an HRT of only 3 to 15 min (Zimmermann et al., 2011), risking release of toxic reactive products or even residual ozone in the effluent. In our case, the fourth large contact chamber (Figure 1a) ensured complete reaction of ozone and reactive

products within the reactor, with an overall hydraulic residence time (HRT) of 20 to 60 min depending of the flow.

3.4 Costs and energy needs

The costs of the construction and the operation of the pilot plants are presented in Table 3 for an average micropollutant removal of 80% compared to raw wastewater. An average ozone dose around $5.7 \text{ mg O}_3 \text{ l}^{-1}$ and a PAC dose around 15 mg l^{-1} (between 10 and 20 mg l^{-1}) was needed to reach this level, remembering that the doses required varied according to the feed water quality. Although some substances were poorly eliminated with those doses, an average removal of 80%, as recommended by Swiss authorities, is a good compromise to reduce the load of micropollutants significantly while keeping the cost of the treatment in an acceptable range. Ozone-SF and PAC-SF had a similar cost (0.16 - 0.18 € m^{-3}) with a similar average removal rate. Compared to the average price and energy consumption of wastewater treatment in Switzerland (0.54 € m^{-3} , 0.33 kWh m^{-3}) (Abegglen and Siegrist, 2012), these two advanced treatments increased the costs and the electricity consumption by about 30%, which represents an annual increase of about 20 € per inhabitant. The PAC separation by ultrafiltration was not optimized, generating high electricity consumption and high costs because of the rapid clogging of the membrane. On-going tests on other more efficient ultrafiltration systems (12 months of operation) showed, however, that these prices could be reduced by a factor 4 to 5, reaching 0.16 - 0.25 € m^{-3} , with an electricity consumption of 0.1 - 0.2 kWh m^{-3} . If these costs can be maintained for long term operation, UF separation will become a very competitive alternative, enabling high effluent quality. The costs of these advanced treatments (ozone-SF or PAC-SF) for larger WWTPs could be reduced to less than 0.12 € m^{-3} due to the scale effect (Abegglen and Siegrist, 2012).

Table 3 near here

3.5 Comparison of the advanced technologies

3.5.1 Micropollutant removal

As presented in Table 2, ozone and activated carbon were both able to reduce of 80% or more the concentration of the majority of the micropollutants monitored. The average removal of the 40 substances routinely studied was very similar between ozone (71% with an average dose of 5.65 mg O₃ l⁻¹) and PAC-UF treatment (73% with an average dose of 13 mg PAC l⁻¹). However, for some compounds, different removal rates can be observed (Figure 7). For instance, PAC-UF gave on average better removal of compounds without specific reactive moieties such as atrazine, propiconazole, ibuprofen or benzotriazole. On the other hand, ozone gave better removal of hydrophilic or negatively charged compounds such as gabapentin, sulfamethoxazole or diclofenac.

Some micropollutants were resistant to both treatments, although they could be mostly removed with higher ozone and PAC doses. A more economically feasible alternative would be to avoid their release into the sewer system. For instance, collection of patient urine in separate containers within the 24 h after X-ray examinations, and treatment of this urine in a separate system (such as incineration) could avoid the release of persistent iodinated contrast media in wastewater (Heinzmann et al., 2008).

For the tested operation conditions and the micropollutants studied, ozone appeared to be more compound-specific than PAC. Many reactive compounds could be eliminated by more than 95% with the ozone dose applied but substances with low ozone reactivity were only partially removed. With PAC, fewer compounds were removed above 95% but also fewer substances were removed below 80%. Thus, for a same average removal of the 40 substances, PAC removed a broader range of compounds but to a lower degree than ozone. PAC efficiency was in general less predictable than for ozone, especially for compounds with

low PAC affinity where high variations in the removal rate were observed, probably due to variation of the wastewater composition (competition for the adsorption sites).

Removal mechanisms are different in ozone and PAC. At the ozone dose applied, no mineralization to CO₂ seemed to take place (cf. §3.5.3), meaning that micropollutants were presumably transformed to (unknown) oxidation products. The transformation products are expected to lose their biological activity (Dodd et al., 2009; Larcher et al., 2012), but higher toxicity of the metabolites has also been reported in some cases (Larcher et al., 2012; Luster-Teasley et al., 2002; Rosal et al., 2009). Unlike ozone, PAC physically removes the micropollutant from the water, which avoids the release of unknown transformation products.

Figure 7 near here

3.5.2 Toxicity removal

Ozone, with an average of 5.38 mg O₃ l⁻¹ (eq. 0.86 g O₃ g⁻¹ DOC), and activated carbon, with an average of 14 mg l⁻¹, were both able to reduce the toxicity of WWTP effluent significantly and with a relatively similar efficacy. PAC-UF was slightly more effective than ozone in reducing toxicity to algae (PAC: 84 % [79-88%], OZ: 75% [67-81%]), photosynthesis inhibition (PAC: 87% [77-99%], OZ: 82% [77-92%]) and fish development impact (PAC: similar to control, OZ: delay in the development). On the other hand, ozone was slightly better in reducing estrogenic activity (PAC: 77% [58-90%], OZ: 89% [85-92%]).

In other studies, increases in toxicity after ozonation compared to the feed water were observed, leading to mortality and delays in development of juvenile rainbow trout (Stalter et al., 2010b), reproduction inhibition of lumbriculus worms (Stalter et al., 2010a), mortality of zebra mussels (Stalter et al., 2010a) and growth inhibition of duckweed (Magdeburg et al., 2012). Increases of genotoxic and mutagenic potential after ozonation were also reported

(Petala et al., 2008; Stalter et al., 2010a). These effects were attributed to the formation of toxic oxidation by-products during ozonation, such as aldehydes, which could then be removed after sand filtration. Our study gave different results, with a clear decrease of the toxicity after ozonation in all bioassays. No genotoxicity or mutagenicity (Micronucleus, UmuC and Ames test) was detected in OZ effluents (Kienle et al., 2011) despite the formation of bromate. This could be attributed to the longer reaction time in our OZ reactor, promoting the degradation of labile intermediate products (Petala et al., 2006). Reduction of toxicity during ozonation was also observed by Misík et al. (2011), Reungoat et al. (2010) and Takanashi et al. (2002), confirming that ozonation, if carefully designed, is comparable to PAC-UF treatment to improve the effluent quality.

3.5.3 *General improvement of water quality*

Advanced treatments had a positive impact on macropollutants and bacterial contamination, as presented in Figures S11 and S12, SI. The PAC-UF treatment, working as a bioreactor with addition of coagulant, enabled a significant reduction of the residual DOC ($54 \pm 10\%$), phosphorus ($> 90\%$), NH_4 ($85 \pm 20\%$) and BOD_5 ($72 \pm 18\%$), and complete removal of TSS, intestinal bacteria and coliphages ($< 5 \text{ UFP ml}^{-1}$, indicator of human viruses). The PAC-SF treatment had similar removal efficiencies for COD, TOC, DOC and NH_4 , but was less effective in removing TSS and phosphorus, and afforded only very limited disinfection with no elimination of total viable bacteria, only 11% removal of *E. coli* and 79% removal of enterococci (data not illustrated). Effluent colour intensity was greatly reduced after PAC-SF and disappeared after PAC-UF. PAC alone had an influence only on DOC (20-35% removal) and colour removal. The biologically active filtration steps (UF or sand filter) were the main cause for improvement of general water quality, UF being more efficient than the sand filter.

Ozonation was able to disinfect the effluent partially, with removal of coliphage virus below the detection limit (5 UFP ml^{-1}) (> 95% removal) and a reduction over 97% in the concentration of fecal bacteria; this level being below the European standard for good bathing water quality (European Commission, 2006) (Figure S12, SI). Ozonation alone was able to reduce the colour of the effluent but not to reduce the concentration of macropollutants (Figure S11, SI), with little effect only on soluble phosphorus probably due to residual precipitation with FeCl_3 . The absence of DOC removal and the significant increase in BOD_5 ($49 \pm 54\%$) suggest that organic pollutants were not mineralized but transformed to more biodegradable compounds, which were then partially removed in the sand filter. The sand filter was responsible for most of the macropollutant removals, with $80 \pm 13\%$ of TSS, $79 \pm 10\%$ of P_{total} , $59 \pm 21\%$ of BOD_5 , $44 \pm 34\%$ NH_4 and $20 \pm 8\%$ of DOC.

Due to its nonspecific removal mechanism, PAC is able to eliminate other kinds of micropollutants not analysed here, such as dissolved heavy metals (Cr, Fe, Zn or Pb), which is not the case for ozone even with a sand filter (Martin Ruel et al., 2011; Renman et al., 2009).

3.5.4 Feasibility and implications for WWTP

Both advanced treatments proved to be technically feasible at large scale in the municipal WWTP, with reasonable and relatively similar costs ($0.16\text{-}0.18 \text{ € m}^3$) in case of PAC separation by sand filtration.

PAC with ultrafiltration separation was not economically competitive although this could change for this rapidly improving technology, especially considering the other beneficial effects of membranes on water quality (disinfection, total PAC and suspended solid retention). PAC separation by sand filtration showed a good retention of the suspended

solids, but release of low amounts of loaded PAC into the effluent cannot be excluded, thus membrane systems represent a safer alternative.

The spent PAC has to be eliminated. Incineration with the sewage sludge is a good solution assuring complete mineralization of organic pollutants. Recirculation of the spent PAC to the biological treatment before its elimination can additionally improve the global micropollutant removal efficiency without impacting the quality of the biological treatment (Boehler et al., 2012; Zwicklenpflug et al., 2010), improving by the way sludge dewaterability (Satyawali and Balakrishnan, 2009). Addition of 10 to 20 mg l⁻¹ of PAC increased the WWTP sewage sludge production (dry matter) by 5 to 10% respectively. For plants that dispose sewage sludge on agricultural land (stopped in Switzerland in 2006), separate treatment of the PAC is necessary, increasing the costs.

Unlike ozonation where the dose was regulated by the oxidative demand of the water, PAC addition was only regulated by the flow to maintain a constant dose. Short pollution variations (< 1 d) are expected to be buffered by the long residence time and the high concentration of PAC in the system. But, in case of longer pollution peaks, the treatment efficiency would likely be reduced. Regulation of the PAC dose by the amount of DOC in the feed water should be studied as DOC was shown to influence PAC efficiency.

Operation of the ozone reactor required staff training as well as specific safety measures due to the toxicity of ozone gas. As such, ozonation is not suitable for small WWTPs with non-permanent staff.

Optimization of these treatments in terms of energy and resource consumption remains.

Although they were able to reduce aquatic toxicity, their energy and resource consumption is still significant and should for example be balanced by energy efficiency measures on the WWTP and in the sewer system. In all cases, the application of the treatment should be

proportional to its benefit. Additional studies on the environmental impact of these advanced treatments taking into account their life cycle are thus necessary, with a special focus on the PAC due to its energy-intensive production (Larsen et al., 2010).

Given that the performance of these advanced treatments is relatively similar, selection of an optimal solution is nuanced. For a given WWTP the choice thus depends mainly on local conditions, involving consideration of multiple factors in a cost-benefit analysis.

4. Conclusions

- Of the 70 dissolved organic micropollutants detected in untreated wastewater, 50 were removed on average less than 50% in conventional treatment. Addition of a nitrification step significantly improved the removal of 24 substances.
- Both advanced treatments, ozonation and PAC-UF, reduced the concentration of the remaining compounds on average by more than 70%, with an average ozone dose of 5.65 mg O₃ l⁻¹ or an average PAC dose of 13 mg l⁻¹.
- For the studied operation conditions, ozone appeared to be more compound-specific than PAC. Ozone was more effective in removing almost completely certain compounds and PAC acted better on a broad spectrum of micropollutants. Removal rates of micropollutants with low ozone reactivity or PAC affinity were depending more directly on variations in the feed water quality.
- Ozone efficiency was strongly dependent on the presence of micropollutants with electron-rich moieties. PAC efficiency was improved for hydrophobic or positively charged compounds.
- Both advanced treatments significantly reduced the toxicity of WWTP effluent, with PAC-UF performing slightly better overall.

- Both treatments proved to be feasible at large scale and for long term operation in real WWTP conditions, with similar costs if sand filters were used for the PAC retention.
- For sensitive receiving waters, such as recreational waters or drinking water resources, the PAC-UF treatment seemed to be the most suitable technology, despite its current higher costs and energy consumption. Indeed, PAC-UF treatment led to a good removal of most micropollutants and macropollutants without forming problematic by-products, the strongest decrease in toxicity and a total disinfection of the effluent.

Supplementary data

Supporting information associated with this article can be found in the online version.

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Table 1. Characteristics of the effluent of the biological treatments (feed water for the advanced treatments). Average and standard deviation of 33 24-h composite samples taken after the biological treatment with low to complete nitrification depending on the campaigns.

Conventional parameters		
Total suspended solids (TSS)	[mg l ⁻¹]	14.8 (± 5.3)
Dissolved organic carbon (DOC)	[mg l ⁻¹]	7.3 (± 1.9)
Chemical oxygen demand (COD)	[mg l ⁻¹]	24.4 (± 12)
Biochemical oxygen demand (BOD ₅)	[mg l ⁻¹]	11.2 (± 10.2)
N-NH ₄	[mg l ⁻¹]	7.7 (± 7.7)
N-NO ₃	[mg l ⁻¹]	9.9 (± 5.6)
N-NO ₂	[mg l ⁻¹]	0.4 (± 0.3)
P _{total}	[mg l ⁻¹]	0.7 (± 0.6)
P _{soluble}	[mg l ⁻¹]	0.09 (± 0.08)
pH	[-]	7.2 (± 0.4)
Temperature	[°C]	17.1 (± 3.5)
Conductivity	[μS cm ⁻¹]	914 (± 96)

Table 2. Concentrations of 70 micropollutants in raw wastewater and after biological treatment (WWTP effluent), and removal rate obtained with the conventional (with low to complete nitrification) or the advanced treatments (in reference to the concentration in the effluent of the biological treatment) (ozone doses between 2.3 and 9 mg l⁻¹ (median 5.9 mg l⁻¹) and PAC doses between 10 and 20 mg l⁻¹ (median 12 mg l⁻¹)). Average with standard deviation of n analyses (24-h composite samples) conducted between June 2009 and October 2010. Compounds with analytical method A were regularly analysed to monitor the efficiency of the treatments. Data for compounds with analytical methods B and C correspond to one or two analyses of a 7-d composite sample taken for a larger screening campaign (with partial nitrification, 6 mg O₃ l⁻¹, or 12 mg PAC l⁻¹). Comparison with removal rates obtained in other studies in similar conditions is presented for the two advanced treatments.

Compound	Compound class	LOD (ng l ⁻¹)	Analytical method	Number of analysis (n)	Influent concentration (ng l ⁻¹)	(n)	Effluent concentration (ng l ⁻¹)	(n)	WWTP removal (%)	(n)	Ozone removal (%)	(n)	PAC-UF removal (%)
Pharmaceuticals													
Atenolol	Beta blocker	1.2	A	37	1274 (±436)	37	682 (±267)	37	42 (±27)	28	85 (±14) ^a	21	88 (±9) ^e
Azithromycin	Antibiotic	75.6	A	19	2272 (±1472)	19	935 (±333)	19	44 (±26)	12	74 (±10) ^d	8	76 (±8) ^c
Bezafibrate	Lipid regulator	1.5	A	37	953 (±262)	37	595 (±314)	37	38 (±26)	27	81 (±8) ^a	21	79 (±12) ^e
Carbamazepine	Anticonvulsant	0.1	A	37	482 (±586)	37	461 (±292)	37	7.6 (±18)	28	97 (±4) ^a	21	90 (±9) ^e
Ciprofloxacin	Antibiotic	36.5	A	19	2291 (±600)	19	779 (±372)	19	63 (±18)	12	53 (±29) ^{b8}	8	63 (±32) ^f
Clarithromycin	Antibiotic	0.4	A	37	709 (±418)	37	440 (±302)	37	37 (±26)	28	93 (±4) ^a	21	92 (±5) ^e
Clindamycin	Antibiotic	0.2	A	19	65 (±33)	19	115 (±69)	19	0 (±0)	12	99 (±1) ^a	8	82 (±13) ^c
Diatrizoic and iothalamic acid	Iodinated contrast medium	32.8	A	17	597 (±628)	19	370 (±366)	17	28 (±25)	12	16 (±16) ^{b2}	8	15 (±13) ^e
Diclofenac	Analgesic / Anti-inflammatory	1.2	A	37	1197 (±497)	37	1187 (±389)	37	9 (±14)	28	94 (±3) ^a	21	69 (±19) ^e
Eprosartan	Antihypertensive	20	B	2	1055 (±488)	1	880	1	37	1	98 ^c	1	65 ^c
Fluconazole	Antifungal	20	B	2	120 (±14)	1	110	1	15	1	27 ^d	1	> 64 ^c
Gabapentin	Anticonvulsant	1.8	A	37	3867 (±1339)	37	3692 (±1456)	37	9.2 (±12)	28	38 (±16) ^{b5}	21	11.8 (±11) ^f
Gemfibrozil	Lipid regulator	2.9	A	19	411 (±128)	19	265 (±159)	19	36 (±32)	12	94 (±5) ^{b11}	8	76 (±16) ^d
Ibuprofen	Analgesic / Anti-inflammatory	13.4	A	19	4101 (±2465)	19	952 (±759)	19	57 (±46)	11	63 (±12) ^{b11}	6	83 (±7) ^e
Iohexol	Iodinated contrast medium	2177.3	A	35	21275 (±6975)	34	15191 (±7294)	32	31 (±27)	26	38 (±16) ^a	19	57 (±25) ^e
Iomeprol	Iodinated contrast medium	306.9	A	35	14467 (±9657)	35	10534 (±6338)	35	25 (±24)	28	43 (±12) ^{b2}	20	54 (±21) ^c
Iopamidol	Iodinated contrast medium	145.4	A	30	3360 (±2574)	30	2535 (±1587)	30	21 (±20)	24	42 (±13) ^a	16	49 (±21) ^e
Iopromide	Iodinated contrast medium	2044.6	A	22	6408 (±2663)	23	4141 (±2086)	21	29 (±27)	15	34 (±19) ^a	11	47 (±30) ^c
Irbesartan	Antihypertensive	20	B	2	4700 (±4808)	1	1700	1	79	1	51 ^{b7}	1	98 ^c
Ketoprofen	Analgesic / Anti-inflammatory	6.0	A	19	1119 (±1328)	19	669 (±757)	19	32 (±21)	12	63 (±16) ^a	8	81 (±9) ^c
Levetiracetam	Anticonvulsant	10	B	2	2100 (±566)	1	330	1	87	1	18 ^a	1	> 97 ^c
Losartan	Antihypertensive	20	B	2	2405 (±2256)	1	510	1	87	1	> 96 ^{b7}	1	80 ^c
Mefenamic acid	Analgesic / Anti-inflammatory	2.6	A	19	946 (±455)	19	581 (±299)	19	33 (±29)	12	98 (±2) ^a	8	93 (±2) ^e
Metformin	Antidiabetic	< 1000	B	2	> 10000	1	> 4000	1	-	0	-	1	> 55 ^c
Metoprolol	Beta blocker	4.4	A	19	561 (±299)	19	653 (±400)	19	4.6 (±13)	12	88 (±8) ^a	8	95 (±4) ^f
Metronidazole	Antibiotic	21.0	A	19	1168 (±866)	19	567 (±497)	19	45 (±34)	12	64 (±12) ^{b6}	5	79 (±17) ^c
Morphine	Analgesic / Anti-inflammatory	20	B	1	270	1	190	1	30	1	> 90 ^c	1	> 90 ^c
Naproxen	Analgesic / Anti-inflammatory	9.4	A	37	697 (±249)	37	380 (±110)	37	41 (±23)	28	90 (±8) ^a	21	81 (±12) ^e
Norfloxacin	Antibiotic	1.9	A	19	334 (±167)	19	59 (±35)	19	76 (±19)	12	75 (±29) ^{b9}	8	82 (±21) ^c
Ofloxacin	Antibiotic	0.4	A	19	234 (±60)	19	84 (±36)	19	61 (±17)	12	85 (±20) ^c	8	83 (±24) ^c
Oxazepam	Anxiolytic	20	B	2	305 (±134)	1	350	1	13	1	9 ^d	1	69 ^c
Paracetamol	Analgesic / Anti-inflammatory	7.9	A	18	51438 (±31884)	18	< 7.9	19	100 (±0)	1	> 85 ^{b11}	0	-
Primidone	Anticonvulsant	0.7	A	37	114 (±39)	37	97 (±21)	37	16 (±15)	28	57 (±11) ^a	21	51 (±19) ^f
Propranolol	Beta blocker	0.3	A	19	127 (±37)	19	114 (±17)	19	13 (±17)	12	99 (±1) ^a	8	99 (±1) ^c
Ritonavir	Antiretroviral	20	B	2	110 (±14)	1	90	1	25	1	> 78 ^c	1	> 56 ^c
Simvastatin	Lipid regulator	29.7	A	14	736 (±503)	14	98 (±96)	14	77 (±23)	8	> 70 ^c	4	> 65 ^c
Sotalol	Beta blocker	0.5	A	37	337 (±175)	37	247 (±63)	37	23 (±20)	28	99 (±1) ^a	21	81 (±15) ^c

^a Similar removal (<10% difference) obtained with about 0.6 g O₃ g⁻¹DOC by Hollender et al. (2009). ^b Similar range of removal obtained in other studies (¹Temes et al. 2003, ²Huber et al. 2005, ³Ormad et al. 2008, ⁴Wert et al. 2009, ⁵Reungoat et al. 2010, ⁶Rosal et al. 2010, ⁷Huerta-Fontela et al. 2011, ⁸Yang et al. 2011, ⁹Senta et al. 2011, ¹⁰Bundschuh et al. 2011, ¹¹Sudhakaran et al. 2012). ^c Not reported in other studies. ^d Contradictory to other studies (>10% lower removal) (Hollender et al. 2009, Reungoat et al. 2010 and 2012). ^e Similar removal (<10% difference) obtained with 10 to 20 mg PAC l⁻¹ by Zwicklenpflug et al. 2010 (in Abegglen et al. 2012). ^f Similar range of removal obtained with granular activated carbon (GAC) filters (Reungoat et al. 2010 and 2012, Yang et al. 2011)

Compound	Compound class	LOD (ng l ⁻¹)	Analytical method	Number of analysis (n)	Influent concentration (ng l ⁻¹)	(n)	Effluent concentration (ng l ⁻¹)	(n)	WWTP removal (%)	(n)	Ozone removal (%)	(n)	PAC-UF removal (%)
Pharmaceuticals													
Sulfamethoxazole	Antibiotic	0.2	A	37	340 (±261)	37	171 (±127)	37	38 (±30)	25	93 (±7) ^a	20	64 (±25) ^c
Trimethoprim	Antibiotic	0.2	A	37	235 (±52)	37	158 (±73)	37	35 (±23)	28	99 (±2) ^a	21	94 (±4) ^f
Valsartan	Antihypertensive	5	B	2	2250 (±354)	1	2100	1	16	1	61 ^{b7}	1	65 ^c
Venlafaxine	Antidepressant	10	B	2	235 (±21)	1	150	1	40	1	75 ^d	1	46 ^d
Pharmaceutical metabolites													
10,11-dihydro-10,11-dihydroxy carbamazepine	Drug metabolite	10	B	2	975 (±106)	1	1000	1	0	1	47 ^{b10}	1	52 ^c
Atenolol acid	Drug metabolite	10	B	2	1550 (±212)	1	1700	1	0	1	72 ^d	1	> 99 ^c
Fenofibric acid	Drug metabolite	20	B	2	390 (±57)	1	490	1	0	1	57 ^{b1}	1	78 ^c
Formyl-4-aminoantipyrine	Drug metabolite	10	B	2	445 (±92)	1	700	1	0	1	> 99 ^{b6}	1	59 ^c
N,N-didesvenlafaxine	Drug metabolite	10	B	1	250	1	330	1	0	1	> 97 ^c	1	61 ^c
N-acetyl sulfamethoxazole	Drug metabolite	20	B	2	570 (±156)	1	50	1	93	1	50 ^{b2}	1	> 20 ^c
N-acetyl-4-aminoantipyrine	Drug metabolite	20	B	2	920 (±28)	1	1200	1	0	1	> 98 ^{b6}	1	34 ^c
Valsartan acid	Drug metabolite	10	B	2	125 (±21)	1	150	1	0	1	39 ^c	1	43 ^c
Endocrine disrupting compounds													
17α-Ethinylestradiol	Hormonal contraceptive	1.9	C	2	5.3 (±4.3)	1	< 1.9	1	> 18	0	-	1	-
17β-Estradiol	Hormone	0.5	C	2	14 (±1)	1	1.3	1	91	1	> 61 ^{b2}	1	> 61 ^c
Bisphenol A	Plastic component	48.9	A	18	834 (±460)	18	338 (±311)	18	50 (±36)	3	> 95 ^{b4}	3	> 83 ^c
Estriol	Hormone	97.5	A	12	306 (±140)	12	< 97.5	11	> 75 (±12)	0	-	0	-
Estrone	Hormone	15.6	A	12	134 (±87)	12	71 (±83)	12	58 (±31)	3	> 90 ^{b2}	3	> 92 ^c
Biocides - pesticides													
Atrazine	Herbicide	0.2	A	37	21 (±16)	37	14 (±8)	37	20 (±24)	28	34 (±13) ^a	21	74 (±17) ^c
Carbendazim	Fungicide	16.1	A	19	106 (±92)	19	132 (±79)	19	1.5 (±3.5)	12	79 (±17) ^c	5	> 93 ^c
Diuron	Herbicide	13.7	A	9	69 (±49)	9	70 (±41)	9	10 (±16)	7	73 (±16) ^a	3	> 82 ^f
Irgarol	Algicide	1.0	A	19	16 (±14)	19	7.5 (±6.2)	19	34 (±29)	10	32 (±21) ^d	5	0 to > 60 ^c
Isoproturon	Herbicide	16.9	A	16	62 (±67)	16	39 (±32)	16	27 (±22)	3	68 (±26) ^{b3}	2	75 (±12) ^c
Mecoprop	Herbicide	9.6	A	37	386 (±408)	37	245 (±239)	37	29 (±25)	28	60 (±22) ^a	21	48 (±27) ^c
Propiconazole	Fungicide	6.9	A	19	59 (±28)	19	40 (±17)	19	28 (±16)	12	32 (±14) ^c	7	66 (±15) ^c
Terbutryn	Algicide	0.1	A	37	38 (±21)	37	19 (±16)	37	49 (±25)	28	85 (±10) ^a	20	80 (±13) ^c
Other common chemicals													
Aspartame	Sweetener	< 100	B	2	> 10000	1	> 4000	1	-	0	-	1	-
Benzothiazole	Industrial additive	400	B	2	6500 (±566)	1	1400	1	80	1	7 ^d	1	> 71 ^c
Benzotriazole	Corrosion inhibitor	4.1	A	37	9224 (±3112)	37	6948 (±1846)	37	24 (±22)	28	64 (±14) ^a	21	90 (±7) ^e
Caffeine	Food component	< 50	B	2	> 10000	1	820	1	> 92	1	> 92 ^{b11}	1	65 ^f
Galaxolidone	Fragrance (HHCB) metabolite	40	B	2	335 (±177)	1	220	1	52	1	0 ^d	1	77 ^c
Methylbenzotriazole	Corrosion inhibitor	48.5	A	19	5720 (±2810)	19	4201 (±2488)	19	29 (±24)	12	80 (±15) ^a	8	96 (±2) ^e
N,N-diethyl-3-methylbenzamide (DEET)	Insect repellent	< 50	B	2	805 (±445)	1	290	1	74	1	48 ^{b8}	1	66 ^f
Oxybenzone	UV filter	20	B	2	425 (±290)	1	60	1	90	1	> 67 ^a	1	50 ^c

^a Similar removal (<10% difference) obtained with about 0.6 g O₃ g⁻¹ DOC by Hollender et al. (2009). ^b Similar range of removal obtained in other studies (¹Temes et al. 2003, ²Huber et al. 2005, ³Ormad et al. 2008, ⁴Wert et al. 2009, ⁵Reungoat et al. 2010, ⁶Rosal et al. 2010, ⁷Huerta-Fontela et al. 2011, ⁸Yang et al. 2011, ⁹Senta et al. 2011, ¹⁰Bundschuh et al. 2011, ¹¹Sudhakaran et al. 2012). ^c Not reported in other studies. ^d Contradictory to other studies (>10% lower removal) (Hollender et al. 2009, Reungoat et al. 2010 and 2012). ^e Similar removal (<10% difference) obtained with 10 to 20 mg PACl⁻¹ by Zwickenpflug et al. 2010 (in Abegglen et al. 2012). ^f Similar range of removal obtained with granular activated carbon (GAC) filters (Reungoat et al. 2010 and 2012, Yang et al. 2011)

Table 3. Costs and energy needs for construction and operation of the pilot plants. Costs are given excluding VAT, based on local (Swiss) prices in 2010 (0.17 € kWh⁻¹ of electricity, 0.25 € Nm⁻³ O₂, 2 € kg⁻¹ PAC, 66 € h⁻¹ staff costs) for an average removal of 80% of the 65 studied micropollutants (compared to raw wastewater). Investment costs are calculated with an interest rate of 4.5% y⁻¹, with amortization periods of 10, 20 and 30 y for, respectively, electromechanical, mechanical and structural equipment.

		Ozonation with sand filter	PAC with sand filter	PAC with ultrafiltration
Dosage		5.7 mg O ₃ l ⁻¹	15 mg PAC l ⁻¹	15 mg PAC l ⁻¹
Capacity (average flow)	[l s ⁻¹]	60	15	5
Electricity consumption	[kWh m ⁻³]	0.117	0.08	0.9
Operating costs	[€ m ³]	0.043	0.054	0.404
Investment costs	[€ m ³]	0.133	0.107	0.399
Total costs (excluding VAT)	[€ m³]	0.176	0.161	0.803

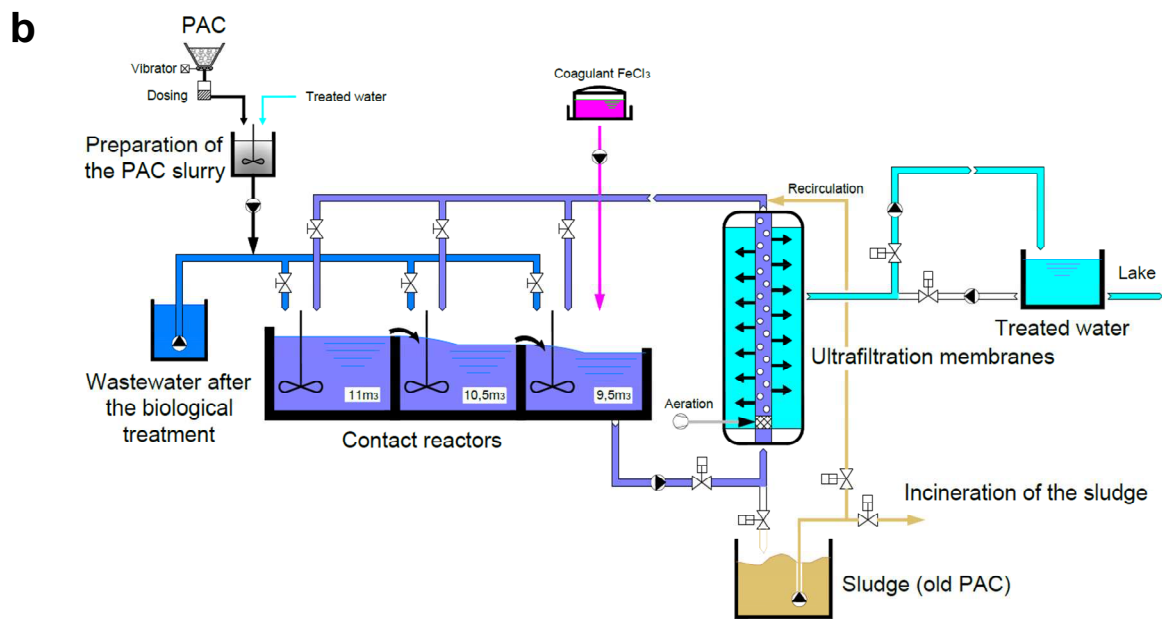
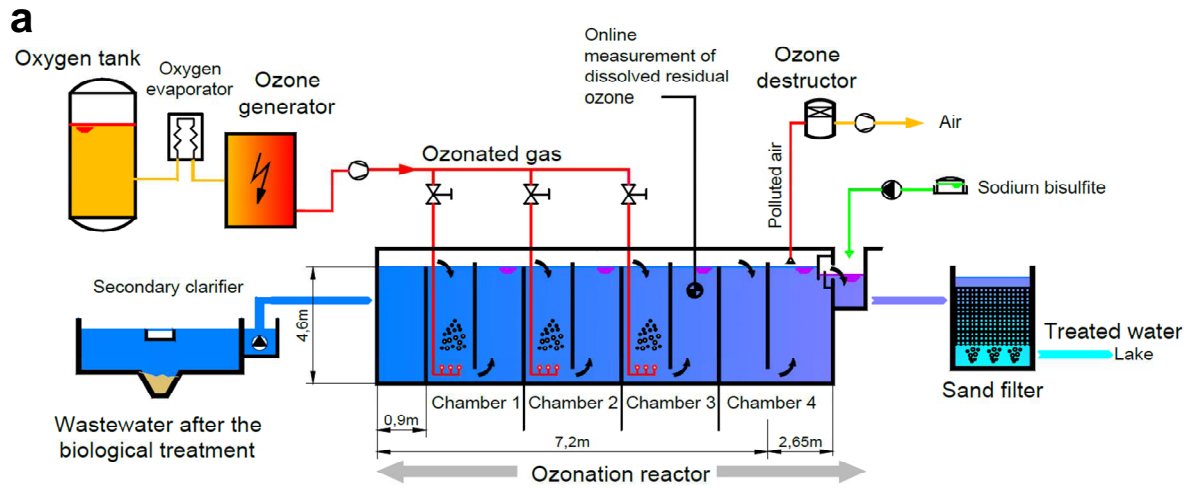


Figure 1. (a) Ozonation installation (b) Powdered activated carbon (PAC) installation with ultrafiltration separation (after Margot and Magnet, 2011)

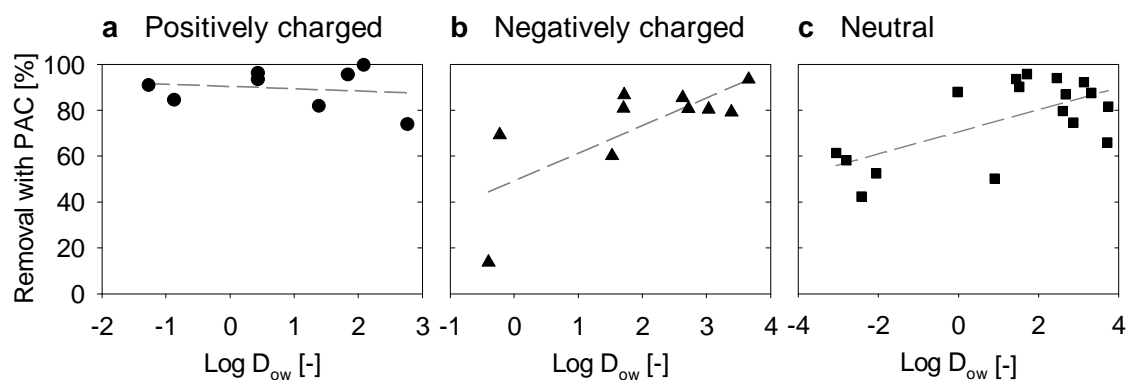


Figure 2. Removal of 35 micropollutants with PAC-UF treatment as a function of micropollutant hydrophobicity ($\log D_{ow}$) and charge at pH 7. **(a)** positively charged, **(b)** negatively charged, and **(c)** neutral. Median removal of eight 48-72 h composite samples. Correlation r between PAC removal and $\log D_{ow}$ not significant (p -value > 0.05) for positively charged compounds and zwitterions, and significant for negatively charged ($r = 0.743$, $p = 0.014$) and neutral compounds ($r = 0.648$, $p = 0.005$).

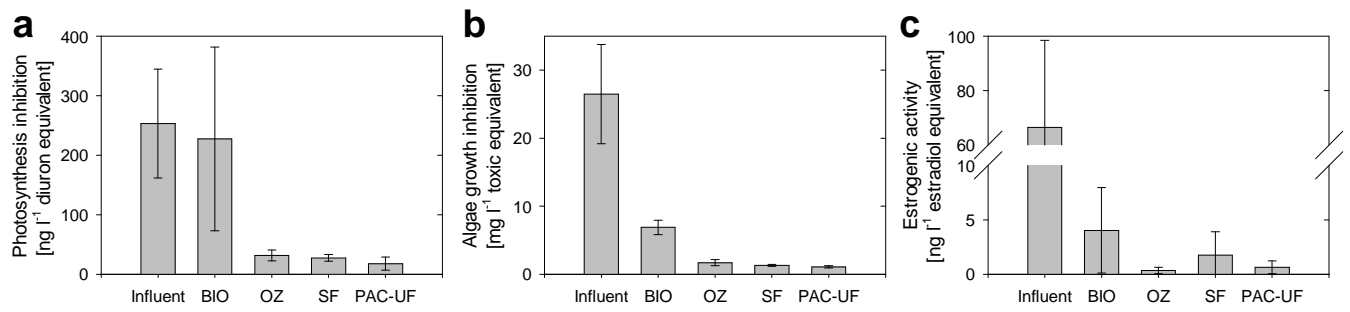


Figure 3. **(a)** Inhibition of photosynthetic activity (diuron-equivalent concentration) and **(b)** inhibition of growth (toxic-equivalent concentration) of the green algae *Pseudokirchneriella subcapitata*. **(c)** Estrogenic activity (YES, estradiol-equivalent concentration). Average results (\pm standard deviation) of three campaigns of one week in the raw wastewater (influent) and in the effluents of the biological treatment (BIO), the ozonation (OZ), the sand filter following the ozonation (SF) and the PAC-UF treatment. Ozone doses of 3.5, 6.0 and 6.7 mg O₃ l⁻¹ (eq. 0.76, 0.91, 0.92 g O₃ g⁻¹ DOC), and PAC doses of 10, 12 and 20 mg l⁻¹ for, respectively, campaigns 1, 2 and 3.

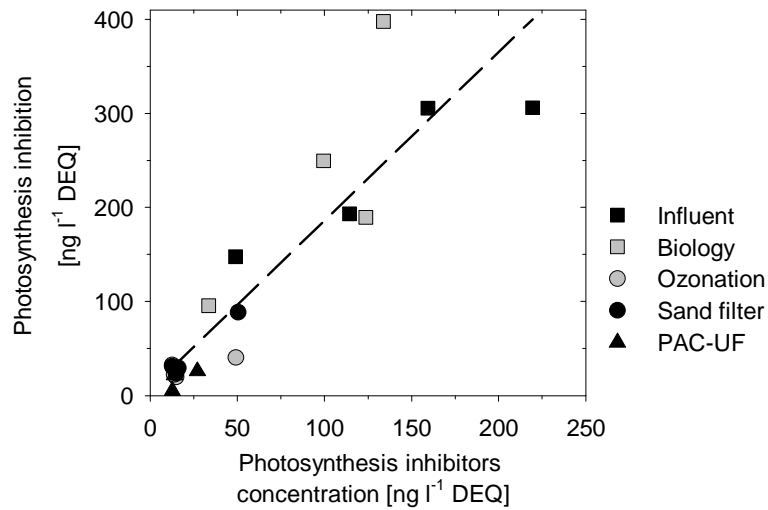


Figure 4. Comparison of the green algae photosynthesis inhibition (in diuron-concentration equivalent DEQ) with the sum of the wastewater concentrations of the four most abundant photosynthesis inhibitors included in the analytical list (atrazine, diuron, isoproturon, and terbutryn), converted to DEQ based on their relative potency. Results of 19 analyses on 7-d composite samples taken after the different treatments. Dashed line: linear regression.

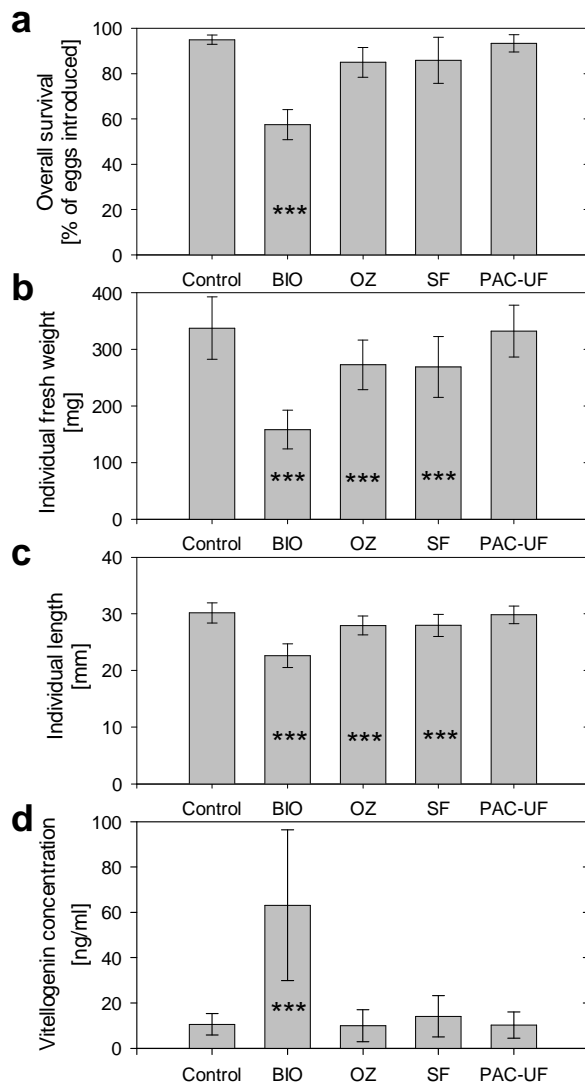


Figure 5. Results of the Fish Early Life Stage Test (FELST) with **(a)** the overall survival (average of three replicates per treatment), **(b)** the individual fresh weight (average of 69 to 152 fish per treatment), **(c)** the individual length (average of 69 to 152 fish per treatment) and **(d)** the vitellogenin concentration (average of 20 fish per treatment) of the fish larvae at the end of the test (after 69 d). Significant differences with the controls are represented by * (p value < 0.05), ** (p < 0.01), *** (p < 0.001). All the endpoints for the control, OZ, SF and PAC-UF were significantly different from the endpoints of BIO. Ozone dose: $4.7 \pm 1.5 \text{ mg O}_3 \text{ l}^{-1}$. PAC dose: $13.1 \pm 2.6 \text{ mg l}^{-1}$.

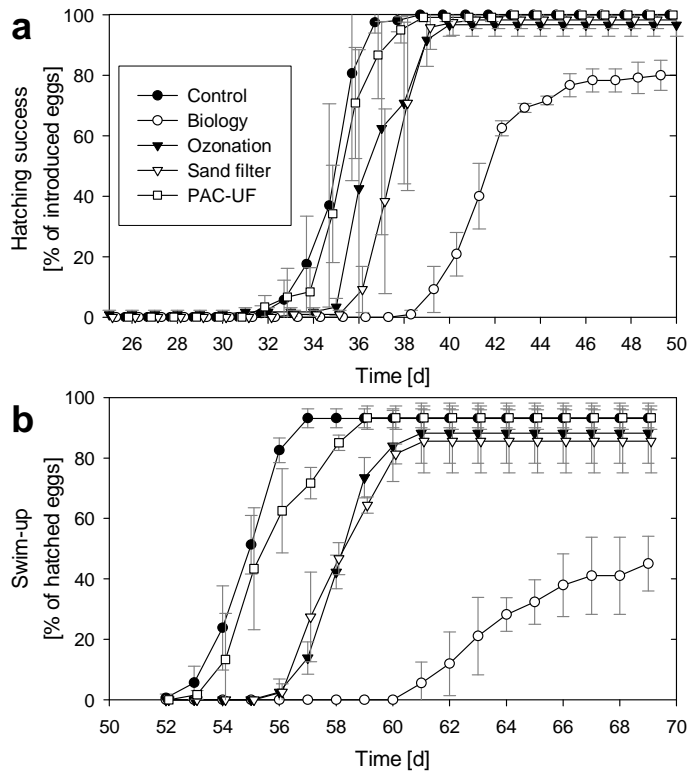


Figure 6. Hatching success **(a)** and swim-up **(b)** of the eggs and larvae of the rainbow trout in the effluent of the different treatments. Average and standard deviation of 3 replicates. Ozone dose: $4.7 \pm 1.5 \text{ mg O}_3 \text{ l}^{-1}$. PAC dose: $13.1 \pm 2.6 \text{ mg l}^{-1}$.

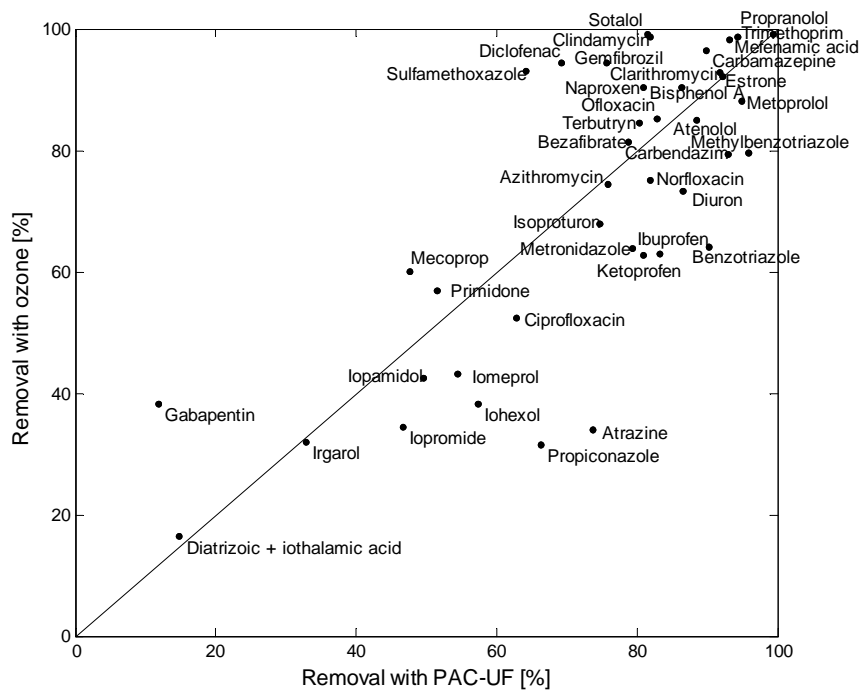


Figure 7. Comparison of the average removal of 40 micropollutants with PAC-UF treatment (dose of 10-20 mg PAC l⁻¹, median 12 mg l⁻¹), or ozonation (dose of 2.3-9.1 mg O₃ l⁻¹, median 5.9 mg O₃ l⁻¹ or 0.83 g O₃ g⁻¹ DOC) during one year of operation (3 to 28 analyses depending of the substance).