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Occurrence of emerging pollutants in urban wastewater and their removal through biological treatment followed by ozonation

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Abstract

This work reports a systematic survey of over seventy individual pollutants in a Sewage Treatment Plant (STP) receiving urban wastewater. The compounds include mainly pharmaceuticals and personal care products, as well as some metabolites. The quantification in the ng/L range was performed by Liquid Chromatography-QTRAP-Mass Spectrometry and Gas Chromatography coupled to Mass Spectrometry. The results showed that paraxanthine, caffeine and acetaminophen were the main individual pollutants usually found in concentrations over 20 ppb. N-formyl-4-amino-antipiryne and galaxolide were also detected in the ppb level. A group of compounds including the beta-blockers atenolol, metoprolol and propanolol; the lipid regulators bezafibrate and fenofibric acid; the antibiotics erythromycin, sulfamethoxazole and trimethoprim, the antiinflammatories diclofenac, indomethacin, ketoprofen and mefenamic acid, the antiepileptic carbamazepine and the antiacid omeprazole exhibited removal efficiencies below 20% in the STP treatment. Ozonation with doses lower than 90 μM allowed the removal of many individual pollutants including some of those more refractory to biological treatment. A kinetic model allowed the determination of second order kinetic constants for the ozonation of bezafibrate, cotinine, diuron and metronidazole. The results show that the hydroxyl radical reaction was the major pathway for the oxidative transformation of these compounds.

Keywords: Emerging pollutants; pharmaceuticals; personal care products; wastewater treatment; ozonation.

1. Introduction

The presence of a wide variety of pharmaceutical and personal care products (PPCP) in water and wastewater has been frequently reported after the findings of Ternes (1998) and Daughton and Ternes (1999). These compounds are a source of concern because they are used and released in large quantities and their physical and chemical properties contribute to their widespread distribution into the environment. The presence of small concentration of PPCP has been associated to chronic toxicity, endocrine disruption and the development of pathogen resistance. The consequences are particularly worrying in aquatic organisms as they are subjected to multigenerational exposure (Halling-Sørensen et al., 1998). The presence of micropollutants also endangers the reuse of treated wastewater, a generally proposed solution to achieve a sustainable water cycle management (Muñoz et al., 2009). PPCP represent a rising part of the trace organic micropollutants found in urban and domestic wastewaters that reach sewage treatment plants (STP), either metabolised or not (Castiglioni et al., 2006). Many of these substances escape to conventional activated sludge wastewater treatments allowing them to reach surface water streams and distribute in the environment (Tauxe-Wuersch et al., 2005).

The need for treatment technologies that can provide safe treated effluents led to the proposals for upgrading STP and to implement new competing technologies for biological degradation of organic matter like membrane bioreactor (Radjenovic et al., 2008). In addition to these strategies, effective tertiary treatment technologies are also needed in order to ensure a safe use for reclaimed wastewater. The available technologies include oxidation processes alone or combined with nanofiltration or reverse osmosis (Ernst and Jekel, 1999). Many oxidation processes have been described for the removal of organic compounds in wastewater. Ozone-based and Advanced Oxidation Processes (AOP) using hydrogen peroxide or radiation have been repeatedly proposed for this task (Gogate and Pandit, 2004a; Ikehata et al., 2006). Proper combinations of AOP can also be considered in order to treat the more refractory pollutants. Fenton and Fenton-based systems, heterogeneous photocatalysis, and ultraviolet or ozone-based oxidation processes have been described (Gogate and Pandit, 2004b, Comninellis et al., 2008). The choice of the most suitable technology or combination lies on the quality required for the reclaimed water.

Ozone has been largely used as oxidant in drinking water treatment and repeatedly proposed to remove organics in wastewater treatment (Raknes, 2005, Beltrán, 2004). The ozone molecule can react with many organic compounds, particularly those unsaturated or containing aromatic rings or heteroatoms also being able to decompose in water to form hydroxyl radicals. In a previous work (Rosal et al., 2008a) we studied the ozonation of wastewater from the secondary clarifier of urban and domestic STP by using ozone (pH ~ 8) and ozone-hydrogen peroxide (O_3/H_2O_2). The presence of hydrogen

peroxide improved the mineralization of dissolved carbon from 15% to over 90% after one hour, from which most part took place during the first five minutes. The disappearance of a selected group of over thirty pharmaceuticals revealed removal efficiencies were over >99% for most compounds after five minutes on stream, with slightly better results in the absence of hydrogen peroxide. This result is consistent with the fact that many PPCP directly react with ozone with large second order kinetic constants (Huber et al., 2003).

The objective of this research was to verify the occurrence and fate of 84 pollutants of different classes, mainly PPCP traced during wastewater treatment in a conventional urban STP. These include pharmaceuticals (analgesics, antidepressants, antiinflammatories, antibiotics, antiepileptics, beta-blockers and lipid regulators among others), personal care products (sunscreen agents, synthetic musks), stimulants (caffeine, nicotine) and some metabolites (clofibric acid, cotinine, several metabolites of dipyrone). The effectiveness of the STP process for the removal of these compounds has been assessed in a monitoring program undertaken in Alcalá de Henares (Madrid) during a one-year period with samples taken before and after a biological activated sludge with nutrient removal process. The research was also trying to identify the impact of ozone exposure on individual pollutants encountered in the secondary effluent. The doses of ozone required for a given degree of removal of the most representative individual pollutants has been assessed. For certain pollutants, the determination of second order kinetic constants for the ozonation reaction in a real wastewater matrix was also performed.

2. Experimental

2.1. Materials and plant description

Wastewater samples were taken every month over a one year period from the input and output of the secondary clarifier of a STP located in Alcalá de Henares (Madrid). This plant treats a mixture of domestic and industrial wastewater from some facilities located near the city with a nominal capacity of 3000 m^3/h of raw wastewater. The Council Directive 91/271/EEC concerning urban wastewater treatment established strict limits for the wastewater discharged to sensitive areas particularly by plants serving an equivalent population of 10000 or more. In the period prior to the sampling campaign, the need to adapt STP to the new conditions forced, the implementation of a biological nutrient removal process aimed to the elimination of phosphorous and nitrogen. The biological treatment worked under a traditional A2O multistage configuration with nitrification-denitrification and enhanced phosphorus removal by phosphorus-accumulating microorganisms. The treatment takes place in three zones: anaerobic, anoxic and oxic. The nitrate produced in the oxic zone is recycled, with mixed liquor to the anoxic zone where denitrification takes place. The return sludge from the settler is recycled to the anaerobic zone where the influent and sludge are mixed under anaerobic conditions. All samples were immediately processed or stored in a refrigerator (< 4ºC) inside glass bottles. The main characterization parameters of wastewater before and after the biological treatment of the STP are shown in Table 1.

Table 1. Wastewater characterization parameters for influents and effluents from Alcalá STP. Standard deviations in parenthesis.

pH	7.54 (0.24)	7.63 (0.17)
TSS (mg/L)	67.8 (40.9)	7.5 (9.3)
Turbidity (NTU)	65 (14)	5.3 (4.4)
Conductivity (μS/cm)	703 (139)	589 (131)
COD (mg/L)	269 (50)	59 (24)
BOD_5 (mg/L)	42 (17)	7.8 (3.7)
TOC (mg/L)	-	6.9 (1.4)
Total-P (mg/L)	4.8 (0.3)	0.82 (1.34)
N-NO_3 (mg/L)	0.50 (0.47)	3.7 (2.3)
N-NH_4 (mg/L)	14.7 (5.6)	8.5 (1.8)
Sulphate (mg/L)	100 (36)	107 (30)
Chloride (mg/L)	74.2 (24.0)	78.8 (21.4)
Sodium (mg/L)	60.2 (13.0)	60.3 (10.6)
Potassium (mg/L)	23.6 (15.1)	11.3 (1.5)
Magnesium (mg/L)	17.8 (3.7)	17.0 (2.4)
Calcium (mg/L)	45.3 (8.0)	37.5 (3.8)
Alkalinity (mg/L $CaCO_3$)	-	472(39)

2.2. Liquid Chromatography-QTRAP-Mass Spectrometry

Previous to LC-QTRAP-MS analysis, wastewater samples were preconcentrated by automated solid phase extraction (SPE) using Oasis HLB cartridges (Waters, 200 mg, 6 cc). The operational procedure, which mainly includes a preconditioning step with MeOH and deionized water (pH = 8); sample loading (200 mL of effluent wastewater and 400 mL of the treated samples at pH=8) and final elution with 2 x 4 ml of MeOH, has been described in detail elsewhere (Bueno et al., 2007). The final extracts were evaporated and reconstituted with 1 mL of MeOH:H_2O, 10:90 (v/v), filtered, and diluted 1:1 with MeOH:H_2O (10:90) before the analysis. Sample analysis was performed in a HPLC series 1100 (Agilent Technologies) coupled to a 3200 QTRAP MS/MS system (Applied Biosystems) using a turbo ionspray source in positive and negative modes. Separation was performed in a C-18 analytical column (ZORBAX SB, 250 mm; 3.0 mm I.D.; 5 mm). For the analysis in positive mode, the compounds were separated using acetonitrile (A) and water with 0.1% formic acid (B) at a flow rate of 0.2 mL/min. A linear gradient progressed from 10% A to 100% A in 40 min, and was maintained at 100% A for 10 min. In negative mode mobile phase composition was acetonitrile (A) and water (B) at a flow rate of 0.3 mL/min. LC gradient started with 30% A, was linearly increased to 100% A in 7 min, and was maintained at 100% A for 8 min. The volume of injection was of 20 μL in both modes.

2.3. Gas chromatography/Mass spectrometry (GC–MS)

For GC-MS analysis, sample aliquots of 500 mL (pH=3) were preconcentrated by liquid-liquid extraction (LLE) using n-hexane as extraction solvent (Gómez et al., 2009). The organic phase was evaporated at a final volume of 3 mL. A higher preconcentration factor was applied to the treated samples, for which an aliquot of 1 ml of the final extract was evaporated to 0.4 mL. GC–MS analyses were run on an Agilent 7890 series gas chromatograph (Agilent Technologies, Santa Clara, CA) interfaced to an Agilent 5975 mass-selective detector. Analytes were separated in an Agilent HP-5MSi capillary column (5% biphenyl/95% dimethylsiloxane), 15 m x 0.25 mm i.d., 0.25 μm film thickness. The inlet operating conditions were as follows: injection volume 10 μL; the temperature programme went from 79 ºC (0.25 min) to 300 ºC (2 min) at 710 ºC min^{-1}. The oven temperature programme was 70 ºC (1 min), to 150 ºC at 50 ºC min^{-1}, then to 200 ºC at 6 ºC min^{-1} and finally to 280 ºC at 16 ºC min^{-1}; it was kept at this temperature for 5 min. Electron impact (EI) mass spectra in full-scan mode were obtained at 70 eV; the monitoring was from *m/z* 50 to 400. The ion source and quadrupole analyzer temperatures were fixed at 230 ºC and 150 ºC, respectively.

2.4. Other analyses

The concentration of dissolved ozone was continuously measured using an amperometric Rosemount 499A OZ analyser whose signal was sent to a Rosemount 1055 SoluComp II Dual Input. The analyser was calibrated against the standard Indigo Colorimetric Method (SM 4500-O_3 B). The pH of the reaction mixture was determined by means of a CRISON electrode connected to a Eutech αlpha-pH100 feed-back control system whose final control element was a LC10AS Shimadzu pump delivering a solution of sodium hydroxide. The signals corresponding to the concentration of dissolved ozone, pH and temperature were recorded using an Agilent 34970 Data Acquisition Unit connected to a computer. Based on the dynamic response of the three measuring devices, the sampling period was set as 5 s. The determination of Total Organic Carbon (TOC) was performed using a Shimadzu TOC-VCSH analyzer equipped with ASI-V autosampler. Inorganic anions were determined by means of a Dionex DX120 Ion Chromatograph with conductivity detector and an IonPac AS9-HC 4x250mm analytical column + ASRS-Ultra suppressor using 9.0 mM Na_2CO_3 with a flow of 1.0 mL/min as eluent. Inorganic cations were determined by an IonPac CS512A 4 x 250 mm cation exchange analytical column with Dionex CSRS Ultra II suppressor and 20 mM metasulphonic acid as eluent. Total suspended solids were determined by the American Public Health Association (APHA) Method 2540 D, "Total Suspended Solids Dried at 103–105°C". The determination of COD and BOD followed APHA Methods 5220 C and 5210 B respectively. The Standard Method SM 4500-P E was used for the determination of ortho-phosphate. Nitrates were determined according to ISO 7890/1 and ammonia nitrogen by means of SM 4500-NH_3 D. Total alkalinity was measured by titration.

2.5. Ozonation

The ozonation runs were carried out in a 5-L glass jacketed reactor operating in semi-batch mode. A temperature of 25ºC, chosen to be close to average ambient temperature, was kept using a Huber Polystat cc2 and monitored throughout the runs by means of a Pt100 Resistance Temperature Detector (RTD). Ozone was produced by a corona discharge ozonator (Ozomatic, 119 SWO100) fed by an AirSep AS-12 PSA oxygen generation unit. The gas containing about 9.7 g/Nm^3 ozone was bubbled by means of a porous glass disk with a gas flow of 0.36 Nm^3/h. The reaction vessel was agitated with a Teflon four-blade impeller at 1000 rpm. The mass transfer coefficient was determined in transient runs with pure water with a value of $k_La = 0.010 \pm 0.005$ s^{-1}. Additional details on the experimental set-up and procedure are given elsewhere (Rosal et al., 2008a, 2008b). Throughout the runs, certain samples were withdrawn for analysis at prescribed intervals. Residual ozone was removed by bubbling nitrogen in order to prevent oxidation reactions to continue. For the desorption conditions used, residual ozone fell down below 10 % in less than 20 s. During the ozonation reactions a moderate increase of pH took place that can be attributed to the stripping of CO_2 from solution. In conditions that favour the generation of hydroxyl radicals, this effect is not observed, and pH tend to decrease during ozonation due to the accumulation of carboxylic acids. The choice of a pH higher than that of the raw wastewater not only favours hydroxyl radical mediated reactions but allowed to keep an almost constant pH value of 8.5 ± 0.1 by using the feed-back control procedure described above.

3. Results and discussion

3.1. Occurrence

The pollutants analyzed were mainly PPCP and their metabolites together with some agrochemicals. A list of the 72 anthropogenic emerging pollutants detected in at least one wastewater sample from the influent to the biological treatment is detailed in the Appendix together with the analytical method applied, the molecular formula and the octanol-water partition coefficient, when available. The limit of quantification for the biological effluent (LOQ), for most compounds in the tens of ng/L, is also shown in the Appendix that also lists the compounds checked but not detected with their limits of detection (LOD). Several pesticides like chlorfenvinphos and the herbicide isoproturon were never detected, as expected considering the urban origin of wastewater. Atrazine, however, was found in all samples with an average concentration at the inlet of the biological treatment of 109 ng/L. Diuron was encountered in two samples and simazine in three with maximum concentrations of 196 and 32 ng/L, respectively. Some

drugs like paroxetine, the antibiotic cefotaxime and the antiinflammatory fenoprofen were not detected in any of the analyzed samples. A similar negative result was reported for paroxetine by Terzić et al. (2008), whereas the occurrence of fenoprofen was reported in concentrations as high as 0.759 μg/L in Canadian wastewater facilities (Metcalfe et al., 2004).

The detailed data for the concentrations of the most significant individual pollutants are shown in Table 2. It includes maximum and minimum values of those compounds encountered over their quantification limit in at least 4 samples in the influent of the biological treatment. The compounds excluded for not complying with this criterion comprise, among other, carbamazepine-10,11-epoxide that was detected in 2 samples with a maximum concentration of 63 ng/L, sotalol, detected three times in the influent with concentrations in the 25-30 ng/L range or celestolide with a maximum influent concentration of 30 ng/L. In addition, fenofibrate was encountered in one sample with 101 ng/L, whereas its human metabolite, fenofibric acid has been detected in all samples at concentrations as high as 117 ng/L. Table 2 also excludes some compounds not systematically analyzed during the sampling campaign due to improvements in the analytical procedure. Certain compounds such as terbutaline or simazine have been encountered in several samples, but these data have not been considered statistically significant because they were found at concentrations so close to the LOQ that removal efficiency in STP could not be properly assessed and, therefore, they were not included in Table 2. Among them, diazepam was detected in half of the samples with a maximum concentration of 8 ng/L in the influent and 5 ng/L in the effluent, the average in both cases being near 3 ng/L (that equals LOQ). Also, mepivicaine was found in 7 samples with an average concentration of 8 ng/L in the influent and 7 ng/L in the effluent and maximum concentration in the influent of 14 ng/L.

Paraxanthine, caffeine and acetaminophen were the individual pollutants usually found in higher concentration, with averages near 20 ppb in the influent. N-formyl-4-amino-antipiryne (4-FAA) and galaxolide also exhibited averages in the μg/L level. The fact that caffeine is the dominant micropollutant in STP is not new. Caffeine has been detected in many surface streams and STP effluents in concentration as high as 230 μg/L (Ternes et al., 2001, Heberer et al., 2002). Recently, Wilcox et al. (2009) also report caffeine, paraxanthine and acetaminophen as the most frequently detected compounds, in the influent of conventional septic systems. Muñoz et al. (2009) found several substances at μg/L level, with the highest concentrations corresponding to caffeine, acetaminophen, atenolol, and paraxanthine, that exceeded 40 μg/L each. In this work, atenolol was part of the group of compounds found with averages over the ppb limit that included ciprofloxacin, hydrochlorthiazide, ibuprofen, N-acetyl-4-amino-antipiryne (4-AAA), naproxen, nicotine, and ofloxacin.

The occurrence of dipyrone (metamizol) residues in STP effluents has been less frequently assessed, but Feldmann et al., (2008) have recently reported concentrations up to 7 μg l^{-1} in influents and effluents of STP in Berlin. These dipyrone residues have been attributed to effluents originated in hospitals more than to private households. Nicotine was found in concentrations as high as 12 μg/L in the influent and 148 ng/L in the effluent. Cotinine, its major urinary metabolite, was detected in the biological effluent with a concentration of 100 ng/L. These values agree with those published by Buerge et al. (2008) who found approximately 1-10 μg/L cotinine in untreated wastewater, and 0.01-0.6 μg/L in the treated effluent, corresponding to elimination efficiencies of over 90%.

Concerning the less polar compounds, the UV filters 3-(4-methylbenzylidene) camphor, octocrylene and ethylhexyl methoxycinnamate were detected with maximum concentrations in the effluent of the STP of 55 ng/L, 114 ng/L and 234 ng/L, respectively. Other works reported higher mean for the secondary effluent or a STP of 70 ng/L and < 10 ng/L for 3-(4-methylbenzylidene) camphor and octocrylene, respectively (Kupper et al., 2006). Celestolide, a synthetic musk was detected in low concentrations with a maximum of 30 ng/L in the influent. Several other compounds, not checked in the influent, were detected in the treated wastewater. It is the case of famotidine with concentration over 1 μg/L or the antiacid lansoprazole, 337 ng/L. Minor constituents include loratadine, 29 ng/L, musk xylene, 52 ng/L or the antibiotic norfloxacin, with 38 ng/L.

3.2. Removal in STP

As indicated before, Table 2 shows the pK_a values for those compounds for which data were considered sufficient and statistically significant. The table also shows the maximum and minimum values for concentration together with the average for influent and effluent to the biological treatment sequence. The removal efficiency for every individual compound was determined from average concentrations calculated excluding samples whose concentrations fell below LOQ. It is well known that during wastewater treatment in STP, PPCP as well as their metabolites partition into the solid phase or remain dissolved depending on their hydrophobicity. The hydrophobicity of a neutral compound can be expressed as its octanol-water partition coefficient, K_{ow}, but in the case of compounds that can exist in ionized form, the acid-base equilibrium must also be taken into account. The pH-dependent or apparent octanol-water distribution coefficient, D_{ow}, that considers both the dissociation constant of acidic of basic solutes, pK_a, and the current pH of wastewater can be derived from the Herderson-Hasselbalch equations (Scheytt et al., 2005). For acidic compounds, that are dissociated at the pH of wastewater, the equation yields:

$$D_{ow} = \frac{K_{ow}}{1 + 10^{pH - pK_a}} \qquad [1]$$

Table 2. Concentrations of pollutants in the influent and effluent of the studied STP calculated for compounds detected over LOQ in at least four influent samples along the monitoring programme. Averages and removal efficiencies have been calculated excluding concentrations below LOQ.

		Influent (ng/L)			Effluent (ng/L)			Removal Efficiency (%)
Compound	**pKa[a]**	**Maximum**	**Minimum**	**Average**	**Maximum**	**Minimum**	**Average**	
4-amino-antipyrine (4-AA)	4.3	3325	262	1517	2253	127	676	55.4
4-methylaminoantipyrine (4-MAA)	4.3	1894	314	880	1098	34	291	66.9
Acetaminophen	9.4	37458	1571	23202	< LOQ	< LOQ	< LOQ	100
Antipyrine	1.4	72	< LOQ	40	58	< LOQ	27	32.8
Atenolol	9.6	2432	660	1197	2438	517	1025	14.4
Bezafibrate	3.3	361	48	141	280	33	128	9.1
Benzophenone-3	7.6	904	< LOQ	393	121	< LOQ	86	78.2
Caffeine	10.4	65625	5010	22849	1589	< LOQ	1176	94.9
Carbamazepine	13.9	173	106	129	173	69	117	9.5
Ciprofloxacin	8.9	13625	160	5524	5692	< LOQ	2378	57.0
Clofibric acid	3.2	127	< LOQ	26	91	< LOQ	12	54.2
Codeine	8.2	2087	150	521	319	< LOQ	160	69.3
Diclofenac	4.2	561	< LOQ	232	431	6	220	5.0
Diuron	NA	196	30	109	81	2	42	61.5
Erythromycin	8.9	2310	< LOQ	346	760	< LOQ	331	4.3
Fenofibric acid	2.9	117	< LOQ	79	129	< LOQ	78	1.3
Fluoxethine	10.1	1827	< LOQ	585	929	34	223	61.9
Furosemide	3.9	1051	< LOQ	413	666	< LOQ	166	59.8
Galaxolide	-	24971	< LOQ	10022	2766	< LOQ	1225	87.8
Gemfibrozil	4.7	17055	415	3525	5233	3	845	76.0
Hydrochlorothiazide	7.9	10018	617	2514	1702	679	1176	53.2
Ibuprofen	4.9	4113	< LOQ	2687	653	< LOQ	135	95.0
Indomethacine	4.5	113	< LOQ	42	59	20	37	11.1
Ketoprofen	4.5	801	< LOQ	441	539	277	392	11.2
Ketorolac	3.5	2793	< LOQ	407	607	< LOQ	228	43.9
Mefenamic Acid	4.2	220	101	141	163	87	138	1.8
Metoprolol	9.6	52	< LOQ	20	38	< LOQ	19	6.5
Metronidazole	2.4	165	44	90	127	< LOQ	55	38.7
N-acetyl-4-amino-antipiryne (4-AAA)	4.6	22200	1760	8333	6745	< LOQ	4489	46.1
Naproxen	4.2	5228	1196	2363	2208	359	923	60.9
N-formyl-4-amino-antipiryne (4-FAA)	5.0	71000	1005	17579	27444	< LOQ	5593	68.2
Nicotine	8.0	11671	< LOQ	4368	158	< LOQ	81	98.7
Ofloxacin	7.9	5286	848	2275	1651	< LOQ	816	64.1
Omeprazole	7.1	2134	57	365	922	< LOQ	334	8.5
Paraxanthine	8.5	98500	4547	26722	1796	< LOQ	836	96.9
Propanolol	9.4	61	12	36	57	< LOQ	36	1.0
Ranitidine	1.9	1466	< LOQ	524	942	< LOQ	360	31.2
Sulfamethoxazole	5.7	530	162	279	370	104	231	17.3
Tonalide	-	1932	< LOQ	952	315	< LOQ	146	84.7
Triclosan	7.8	2417	< LOQ	860	512	< LOQ	219	74.5
Trimethoprim	6.8	197	78	104	148	< LOQ	99	5.1

[a] Muñoz et al., 2008

In the case of basic drugs, the apparent partition coefficient can be expressed using the pK_a for the corresponding conjugate acid:

$$D_{ow} = \frac{K_{ow}}{1 + 10^{pK_a - pH}} \qquad [2]$$

Codeine or fluoxethine are among compounds that are substantially dissociated at ambient pH, whose average was 7.61 ± 0.39, with boundaries representing the 95% confidence interval. For neutral substances, $D_{ow} = K_{ow}$.

There is experimental evidence that the removal of organic pollutants in STP is largely controlled by sorption process with solid-water distribution coefficients being a function of the octanol water distribution coefficient D_{ow} (Carballa et al., 2088). The removal

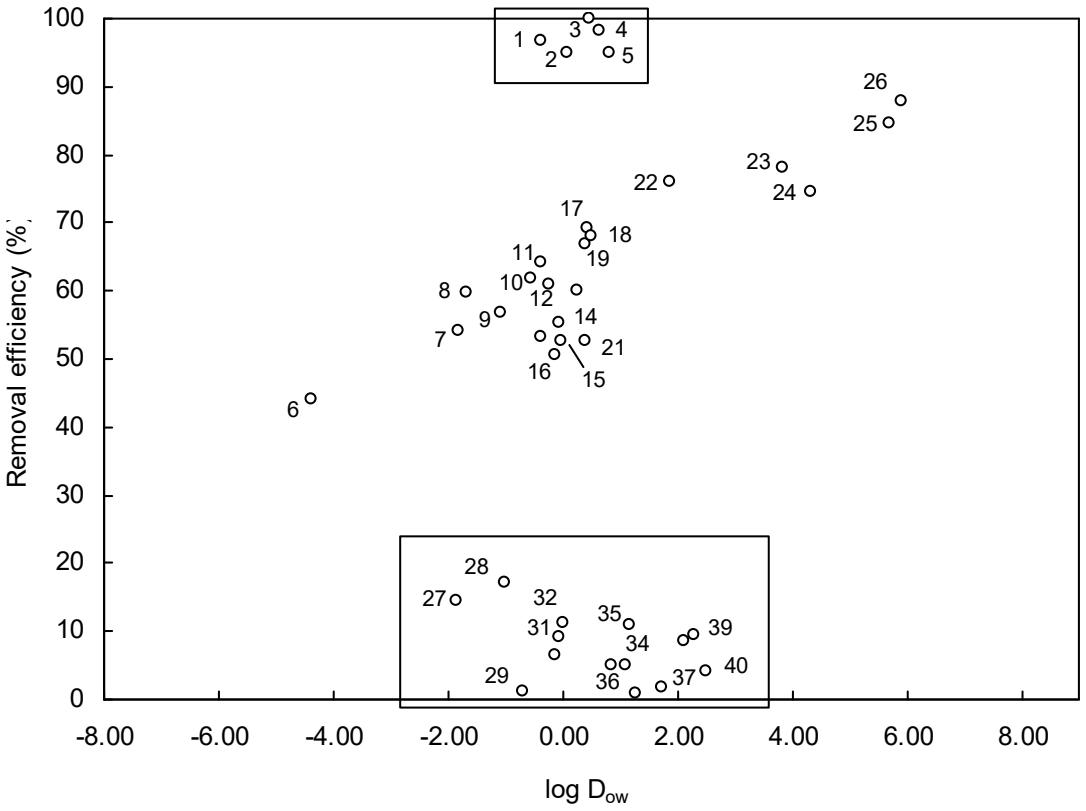

Figure 1. Removal efficiency during conventional activated sludge treatment: (1) paraxanthine, (2) caffeine, (3) acetaminophen, (4) nicotine, (5) ibuprofen, (6) ketorolac, (7) clofibric acid, (8) furosemide, (9) ciprofloxacin, (10) fluoxethine, (11) ofloxacin, (12) naproxen, (13) hydrochlorothiazide, (14) 4-amino-antipyrine, (15) metronidazole, (16) N-acetyl-4-amino-antipiryne, (17) codeine, (18) N-formyl-4-amino-antipiryne, (19) 4-methylaminoantipyrine, (20) ranitidine, (21) antipyrine, (22) gemfibrozil, (23) benzophenone-3, (24) triclosan, (25) tonalide, (26) galaxolide, (27) atenolol, (28) sulfamethoxazole, (29) fenofibric acid, (30) metoprolol, (31) bezafibrate, (32) ketoprofen, (33) trimethoprim, (34) Diclofenac, (35) indomethacine, (36) propanolol, (37) mefenamic acid, (38) omeprazole, (39) carbamazepine, (40) erythromycin.

efficiency obtained in this work for the compounds indicated in Table 2 has been related to D_{ow} and the results represented in Fig. 1. For a significant group of compounds, ranging from ketorolac (44 %) to galaxolide (88%), a clear relationship is observed between removal efficiency and D_{ow}. A group of five compounds were almost completely removed in the STP even they present relatively low D_{ow} values. They are the metabolite of caffeine paraxanthine, caffeine itself, acetaminophen (paracetamol), ibuprofen and nicotine, compounds otherwise usually found in high concentrations in raw urban wastewater (Table 2). A similar result was reported by Muñoz et al., (2008) who reported concentrations of caffeine, acetaminophen, atenolol, and paraxanthine that exceeded 40 μg/L each but a substantial removal in an activated sludge STP (90 %, >99 %, 43 %, and 67 %, respectively). Joss et al. (2005) reported removal efficiencies for ibuprofen beyond its quantification limit (> 90 %) and also coincident are data corresponding to naproxen (50-80 %).

This work also identified 14 compounds with removal efficiencies fell below 20 % but exhibiting intermediate D_{ow} values ($-2 < D_{ow} < 2.5$). They have been marked by the lower square in Fig. 1 and are the beta-blockers atenolol, metoprolol and propanolol; the lipid regulator bezafibrate and the metabolite of fenofibrate fenofibric acid; the antibiotics erythromycin, sulfamethoxazole and trimethoprim; the antiinflammatories diclofenac, indomethacin, ketoprofen and mefenamic acid; the antiepileptic carbamazepine and the antiacid omeprazole. Joss et al. (2005) reported no significant removal of sulfamethoxazole and carbamazepine and partial elimination of diclofenac, results generally coincident with this work. For musk fragrances, galaxolide and tonalide, Joss et al. (2005) reported, however, removal efficiencies somewhat lower (>50 %) than those found in this work (~85 %). Carballa et al. (2004) also reported overall removal efficiencies of the ranging between 70 % and 90% for fragrances in coincidence with this work and generally higher for antiinflammatories (40-60 %) and sulfamethoxazole. In a further work, Carballa et al. (2007) indicated different removal efficiencies for several PPCP during the anaerobic digestion of sewage sludge with high efficiencies for naproxen or sulfamethoxazole. In general, a high variability can be expected as a consequence of different pollutant

concentrations, changes in the processes of the STP as well as operational conditions (Liu et al., 2008).

3.3. Removal by ozonation

The ozonation of a dissolved organic compound may take place by direct reaction with ozone molecule and also through the action of secondary oxidants produced from ozone in aqueous medium. Among them, the strongest oxidant is hydroxyl radical, generally associated with the oxidation of the more refractory substances. A mass balance to a given compound in solution yields the following expression:

$$-\frac{d\,C_i}{d\,t} = k_{O_3}\,C_i\,C_{O_3} + k_{HO\bullet}\,C_i\,C_{HO\bullet} \qquad [3]$$

Elovitz and von Gunten (1999) introduced a parameter R_{ct} defined as the relationship between the concentrations of ozone and hydroxyl radical at any moment. Based on the observation that R_{ct} can be considered constant at least though certain periods of the ozonation runs, the concentration of the two main oxidants involved in ozonation reactions can be related so that Eq. 3 can be solved without experimental determination of $C_{HO\bullet}$:

$$ln\frac{C_i}{C_{io}} = k_{O_3}\int_0^t C_{O_3}dt + k_{HO\bullet}\int_0^t C_{HO\bullet}dt = \left(k_{O_3} + R_{ct}k_{HO\bullet}\right)\int_0^t C_{O_3}dt = k_R\int_0^t C_{O_3}dt \qquad [4]$$

The kinetic parameter k_R would behave as second order kinetic constant provided R_{ct} is constant throughout the sampling period. As shown below, this work shows that R_{ct} is constant during ozonation at least for the samples taken after ozone appeared in solution. The preceding findings also lie on the assumption of slow kinetic regime. The kinetics of a heterogeneous gas-liquid semicontinuous process is determined by the relative rates of absorption and chemical reaction and is characterized by Hatta number. It represents the maximum rate of chemical reaction relative to the maximum rate of mass transfer, yielding, for a second order reaction, the following expression:

$$Ha = \frac{\sqrt{k_{O_3}\,C_{i,o}\,D_{O_3}}}{k_L} \qquad [5]$$

In the case of wastewater treatment, ozone reacts with many compounds in a complex parallel reaction system so that $k_{O_3}C_{i,o}$ can be substituted by $\sum_i k_{O_3}C_{i,o}$. As raw wastewater contains a number of compounds whose second order direct reaction constants with ozone are very large (Huber et al., 2003) mass transfer is likely to limit the ozonation rate during the first reaction minutes. Once ozone appears in solution, the following inequality holds:

$$k_L a\left(C^*_{O_3} - C_{O_3}\right) > \sum_i k_{O_3}\,C_{i,o}\,C_{O_3} \qquad [6]$$

Therefore an upper limit can be obtained for *Ha* as follows:

$$Ha < \frac{\sqrt{k_L a\left(\frac{C^*_{O_3}}{C_{O_3}} - 1\right)D_{O_3}}}{k_L} \qquad [7]$$

where D_{O_3} is the diffusivity of ozone in water (1.77 x 10^{-9} m^2 s^{-1}). The equilibrium concentration of ozone $C^*_{O_3}$ was calculated from Henry's law using the correlation of Rischbieter et al. (2000) from the concentration in the gas phase that was 9.4 g/Nm^3. The value of the mass transfer coefficient, k_L = 5.5 x 10^{-5} m s^{-1}, was calculated by using the correlation of Calderbank and Moo-Young (1961). At the beginning of the run, there was no ozone in solution and *Ha* is supposed to reach high values. After about three minutes, the concentration of ozone that increased during runs approaching equilibrium was over 2 x 10^{-3} mM. This, considering that $C^*_{O_3} = 0.05\ mM$, ensures *Ha* < 0.3 and, therefore, the kinetic regime was slow and for the sample taken at 4 min and those taken thereafter.

Second order kinetic constants could be obtained as indicated before for bezafibrate, cotinine, diuron, ketoprofen and metronidazole. The logarithmic concentration decay is represented against the integral ozone dose in Fig. 2 in which, the experimental points represent data from samples taken at 4, 6, 10 and 15 min, the first being considered the initial concentration, C_{io}. The comparison with literature data shows that the transformation of ozone-resistant micropollutants takes place primarily via indirect radical oxidation inhibited by the wastewater matrix. The values reported in the literature for the second order direct and indirect rate constants are: bezafibrate, k_{O3} = 590 M^{-1} s^{-1} and $k_{HO\bullet}$ = 7.40 x 10^9 M^{-1} s^{-1} in Huber et al. (2005); ketoprofen, k_{O3} = 0.4 M^{-1} s^{-1} and $k_{HO\bullet}$ = 8.40 x 10^9 M^{-1} s^{-1} in Real et al. (2009), diuron, k_{O3} = 16.5 M^{-1} s^{-1} and $k_{HO\bullet}$ = 4.6 x 10^9 M^{-1} s^{-1} in Benitez et al. (2007) and k_{O3} = 14.7 M^{-1} s^{-1} and $k_{HO\bullet}$ = 6.6 x 10^9 M^{-1} s^{-1} in de Laat et al. (1996); metronidazole, k_{O3} = < 350 M^{-1} s^{-1} in Sánchez-Polo et al. (2008) and $k_{HO\bullet}$ = 1.98 x 10^9 M^{-1} s^{-1} in Johnson and Mehrvar (2008). No data have been published for cotinine. The ozonation of bezafibrate was also studied by Dantas et al. (2007) who reported a direct kinetic constant k_{O3} = 4.24 x 10^3 ± 0.66 x 10^3 $M^{-1}s^{-1}$ for pH 7 and k_R = 1.0 x 10^4 ± 1.07 x 10^3 $M^{-1}s^{-1}$ for pH 8. The reported direct rate constant for ketoprofen is particularly low and allows to calculate R_{ct} by dividing the value of k_R obtained in this work by $k_{HO\bullet}$ reported by Real et al. (2009). The value found, R_{ct} = 3.62 x 10^{-7}, is very close to those that could be derived using Eq. 4 for bezafibrate and diuron. The partial contribution of the direct ozone and radical pathways can be calculated for a given organic compound as follows:

$$f_{OH} = \frac{k_{HO\bullet}\, C_{HO\bullet}\, C_i}{k_{HO\bullet}\, C_{HO\bullet}\, C_i + k_{O_3}\, C_i} = \frac{k_{HO\bullet}\, R_{ct}}{k_{HO\bullet}\, R_{ct} + k_{O_3}} \quad [8]$$

Using literature constants, the fraction degraded by hydroxyl radicals were 0.819 for bezafibrate, 0.996 for diuron, 1.000 for ketoprofen and > 0.887 for metronidazole. The contribution of direct ozone reaction is obviously low because the five compounds studied are relatively refractory to ozonation. By means of Eq. 8 and taking into account that $k_R = k_{O_3} + k_{HO\bullet}\, R_{ct}$, the second order rate constants, k_R, can be derived from literature data with the following results: metronidazole 1.07×10^3 $M^{-1}\ s^{-1}$, bezafibrate 3.27×10^9 $M^{-1}\ s^{-1}$ and diuron 2.41×10^3 $M^{-1}\ s^{-1}$ (Benitez at al., 2007). The two last are in good agreement with experimental values. In the case of metronidazole, the low value obtained for R_{ct} suggests that $k_{HO\bullet}$ could have been underestimated.

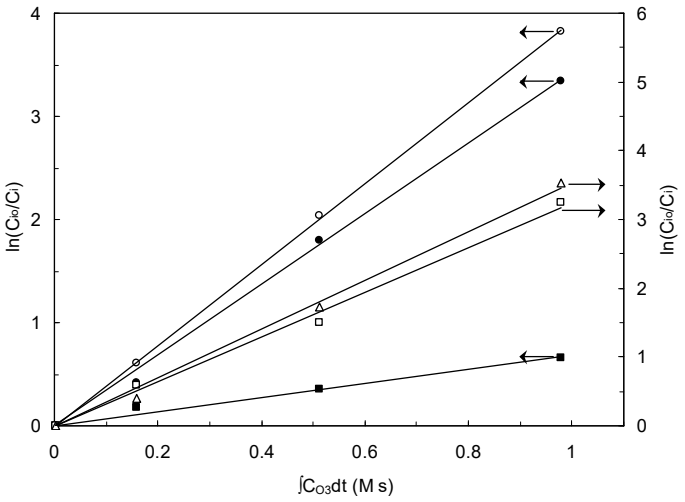

Figure 2. Logarithmic decay of the concentration of diuron (○), metronidazole (●), ketoprofen (Δ) bezafibrate (□) and cotinine (■) as a function of the integral ozone exposure. (Two y-axes have been used for clarity.)

The efficiency of ozonation for the removal of the main micropollutants whose concentration in biologically treated wastewater was > 10 ng/L is indicated in Table 3. The table shows the evolution of the concentration for samples taken during ozonation up to a reaction time of 15 min and the amount of ozone required for a given degree of removal. Only concentrations above LOQ are shown. These LOQ apply for ozonated samples and are lower than those reported in the Appendix for untreated samples. They could be reached, because of the higher preconcentration factor applied to the ozonated samples (see experimental section) and the reduction in the matrix effects observed in these cleaner extracts. The amount of ozone transferred to the liquid at a certain reaction time, *TOD*, was determined, from the integration of the ozone absorption rate equation:

$$TOD(t) = k_L a \left(C^*_{O_3}\, t - \int_0^t C_{O_3}\, dt \right) \quad [9]$$

For the experimental conditions used in this work C_{O_3} was always less than 10% of $C^*_{O_3}$ and, therefore, *TOD(t)* was essentially linear with time. The last right column of Table 3 shows the dose of ozone required for the complete removal (no detection) of a given compound or to achieve certain removal efficiency in cases where ozonation was unable to get complete oxidation in less than 15 min corresponding to a dose of ozone of 0.34 mmol/L of wastewater. It is to be noted that a change in the pH of wastewater modifies the ozone doses required for a given effect. A pH increase causes a higher hydroxyl radical exposure increasing R_{ct} and leading, for a similar integral radical exposure, to lower ozone doses. Also, it is important to point out that a change of pH may affect the direct ozonation rates of dissociating compounds. In our case, raising pH from that of raw wastewater to 8.5, at which the ozonation took place, could affect the ozonation rate of some proton-accepting compounds whose $pK_a \sim 8$, particularly benzophenone-3, hydrochlorthiazide, nicotine, ofloxacin and triclosan.

A group of 15 compounds rapidly disappear during the first 120 s on stream, with ozone doses < 50 μM. These include codeine, diclofenac, indomethacin or naproxen, whose disappearance during the first minutes of ozonation has already been reported in a former work whose target was the mineralization of dissolved organics (Rosal et al., 2008a). Antipyrine, erythromycin, ketorolac, norfloxacin, propanolol, ranitidine, and trimethoprim became completely removed for doses < 90 μM. Carbamazepine, ciprofloxacin, citalopram hydrobromide, hydrochlorothiazide, metoprolol, omeprazole, venlafaxine and the two metabolites of metamizol, (4-AAA and 4-FAA), required < 130 μM of ozone to disappear. Higher ozone doses area necessary to remove atenolol, lansoprazole, loratadine, primidone, sulfamethoxazole and diuron. Another group of four personal care products were completely refractory to ozone, not being removed at all after 15 min of reaction. These were the UV filters 3-(4-methylbenzylidene) camphor and ethylkexyl methoxycinnamate together with the sunscreen agent benzophenone-3 and the aromatic nitro musk xylene. Finally, certain compounds were removed in different extents using an ozone dose of 340 μM. From ketoprofen, metronidazole or ofloxacin, with removal efficiencies over 95% to the musk ketone and the UV filter octocrylene, with 38% and 20% removal respectively. It is interesting to point out than some compounds like diclofenac, indomethacin or the beta-blockers atenolol, metoprolol and propanolol, which are poorly removed in the activated sludge conventional treatment, exhibit large ozonation rates that allow their removal from wastewater using moderate ozone doses. It is interesting to note that during the first part of the reaction there is no ozone in solution and therefore the concepts of homogeneous kinetics can not be applied. During this period, the reaction must take place at the interface and the rate of reaction depends on the surface

Table 3. Removal of pollutants contained in wastewater during ozonation. The ozone doses are those required to reach concentrations below the limit of quantification (LOQ*) in treated samples.

Ozonation time (min)	LOQ*	0	2	4	6	10	15	Ozone doses for remotion	k_R (M^{-1} s^{-1})
3-(4-methylbenzylidene) camphor	39	55	50	65	39	72	54	Not removed	
4-Aminoantipyrine	19	58	-	-	-	-	-	< 50 μM	
4-methylaminoantipyrne (4-MAA)	2	389	-	-	-	-	-	< 50 μM	
Antipyrine	8	30	16	-	-	-	-	< 90 μM	
Atenolol	3	911	655	265	24	-	-	< 220 μM	
Azithromycin	12	235	-	-	-	-	-	< 50 μM	
Benzophenone-3	33	123	89	100	102	119	119	Not removed	
Bezafibrate	4	115	72	67	37	15	4	Still detected at 340 μM	3260 ± 780
Carbamazepine	1	106	17	2	-	-	-	< 130 μM	
Carbamazepine epoxide	9	32	23	19	13	-	-	< 220 μM	
Ciprofloxacin	5	522	334	28	-	-	-	< 130 μM	
Citalopram hydrobromide	2	60	31	4	-	-	-	< 130 μM	
Clarithromycin	5	39	-	-	-	-	-	< 50 μM	
Codeine	5	378	-	-	-	-	-	< 50 μM	
Cotinine	12	100	61	54	48	38	28	28% remained for 340 μM	680 ± 29
Diclofenac	1	433	-	-	-	-	-	< 50 μM	
Diuron	1	100	60	46	25	6	1	Still detected at 340 μM	3890 ± 200
Erythromycin	10	72	16	-	-	-	-	< 90 μM	
Ethylkexyl methoxycinnamate	15	234	274	322	231	214	204	Not removed	
Famotidine	14	1045	-	-	-	-	-	< 50 μM	
Fluoxethine	2	17	-	-	-	-	-	< 50 μM	
Furosemide	82	840	-	-	-	-	-	< 50 μM	
Galaxolide	23	1486	749	552	178	196	173	83% for 340 μM	
Gemfibrozil	1	332	50	18	19	15	15	95% for 340 μM	
Hydrochlorothiazide	1	707	461	199	-	-	-	< 130 μM	
Indomethacin	2	37	-	-	-	-	-	< 50 μM	
Ketoprofen	2	162	156	102	68	18	3	Still detected at 340 μM	3040 ± 770
Ketorolac	2	533	165	-	-	-	-	< 90 μM	
Lansoprazole	9	337	162	84	32	-	-	< 220 μM	
Lincomycin	3	12	-	-	-	-	-	< 50 μM	
Loratadine	1	29	18	7	2	-	-	< 220 μM	
Mefenamic acid	2	59	-	-	-	-	-	< 50 μM	
Metoprolol	3	27	17	5	-	-	-	< 130 μM	
Metronidazole	3	113	73	85	56	14	3	Still detected at 340 μM	3100 ± 780
Musk xylene	3	89	92	95	89	98	91	Not removed	
Musk ketone	36	123	125	140	95	105	76	38% for 340 μM	
N-acetyl-4-aminoantipyrine (4-AAA)	50	8605	2419	101	-	-	-	< 130 μM	
Naproxen	12	109	-	-	-	-	-	< 50 μM	
N-formyl-4-aminoanttipyrine (4-FAA)	17	1776	471	21	-	-	-	< 130 μM	
Nicotine	4	81	12	10	13	10	14	Still detected at 340 μM	
Norfloxacin	8	38	56	-	-	-	-	< 90 μM	
Octocrylene	16	114	115	113	81	95	91	20% for 340 μM	
Ofloxacin	3	3594	276	18	11	9	10	Still detected at 340 μM	
Omeprazole	3	1015	231	7	-	-	-	< 130 μM	
Primidone	5	80	86	65	40	-	-	< 220 μM	
Propanolol	2	32	7	-	-	-	-	< 50 μM	

Propyphenazone	2	23	-	-	-	-	-	< 90 μM	
Ranitidine	2	111	3	-	-	-	-	< 90 μM	
Sulfamethoxazole	8	95	39	19	15	-	-	< 220 μM	
Sulfapyridine	12	50	-	-	-	-	-	< 50 μM	
Tonalide	19	188	131	130	53	67	53	72% for 340 μM	
Triclosan	52	246	55	72	79	70	53	Still detected at 340 μM	
Trimethoprim	2	73	7	-	-	-	-	< 90 μM	
Venlafaxine	6	179	127	21	-	-	-	< 130 μM	

* LOQ calculated in ozonated samples.

concentration, that is related to the polarity of the compound. This may explain why diclofenac and sulfamethoxazole, with similar direct ozonation constants (Huber et al. 2005) behave in a rather different way, the later being detected during a much longer period. The apparent octanol-water partition coefficient (see Appendix and Table 2) is, at pH 8.5, tow orders of magnitude larger diclofenac (0.21) than for sulfamethoxazole (-1.91). A certain insight into the efficiency of the ozonation process can be reached by considering the global removal of micropollutants as a function of ozone doses. Our data showed that the removal of micropollutants reached 86% for a dose of ozone of 90 μM. For higher doses, the efficiency of removal considerably decreased with very limited gains over 130 μM. In fact, an additional ozone dose of 200 μM results in less than 1% removal of the compounds studied in this work.

4. Conclusions

This research showed the regular presence of over seventy anthropogenic individual pollutants, some of which are encountered in relatively high amounts. In raw sewage, 25 compounds were detected in the μg/L range, 15 of which exceeded this level in yearly averages. Acetaminophen (paracetamol) and caffeine were persistently detected over 1 ppb in untreated wastewater. Galaxolide was also encountered in high concentration, but its occurrence showed a significant variability. Two metabolites, paraxanthine from caffeine and 4-FAA from metamizol were also found in high amounts in almost all samples. Other metabolites detected were 4-AA and 4-MAA from dipyrone, fenofibric acid from fenofibrate and 4-AAA also from metamizol. These findings stress the need for exploring not only the pattern PPCP, but also their metabolic or photodegradation intermediates

The efficiency of removal of PPCPs in STP was roughly dependent on its hydrophobicity expressed as apparent octanol-water distribution coefficient, D_{ow}, a parameter that takes into account the octanol-water partition coefficient, K_{ow}, as well as the dissociation constant of acidic or basic compounds. For most compounds, the removal efficiency during biological treatment increased with hydrophobicity as expected considering the higher sorption of non-polar compounds on sludge. Certain compounds showed important deviations with a group of relatively polar substances formed by paraxanthine, caffeine, acetaminophen, ibuprofen and nicotine that were almost completely removed during biological treatment. Another group formed by 14 compounds exhibited removal efficiencies below 20%, even their octanol-water distribution coefficient was not particularly low. They are all important pharmaceuticals prescribed and delivered to sewage in high amounts and include the beta-blockers atenolol, metoprolol and propanolol; the lipid regulator bezafibrate, fenofibric acid; the antibiotics erythromycin, sulfamethoxazole and trimethoprim; the antiinflammatories diclofenac, indomethacin, ketoprofen and mefenamic acid; the antiepileptic carbamazepine and the antiacid omeprazole.

An ozonation treatment yielded high removal efficiencies of most individual pollutants detected in treated wastewater. The kinetic analysis of the part of the run that takes place in the slow kinetic regime, allowed the determination of second order kinetic constants for the ozonation of bezafibrate, cotinine, diuron, ketoprofen and metronidazole in its wastewater matrix. This work shows that R_{ct}, a concept developed for drinking water, can be applied for the ozonation of wastewater as it was constant at least for the samples taken after ozone appeared in solution. The ratio of the concentrations of ozone and hydroxyl radical, R_{ct}, during this period was 3.62×10^{-7} and the fraction degraded by hydroxyl radicals was in the 0.819-1.000 range for the aforementioned compounds. Even when most compounds disappear for doses lower than 340 μM, and most for less than 90 μM, some pollutants, essentially personal care products were not significantly removed during ozonation. These were the UV filters 3-(4-methylbenzylidene) camphor and Ethylkexyl methoxycinnamate, the sunscreen agent Benzophenone-3 and the aromatic nitro musk xylene. On the other hand, certain polar compounds like diclofenac, indomethacin or the beta-blockers atenolol, metoprolol and propanolol, which are poorly removed in the activated sludge conventional treatment, exhibit large ozonation rates and can be removed from treated wastewater using moderate ozone doses.

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Notation

C_i concentration of a given organic compound (M)

$C_{HO\bullet}$ concentration of hydroxyl radical (M)

C_{O_3} concentration of dissolved ozone (M)

$C^*_{O_3}$ equilibrium concentration of dissolved ozone (M)

D_{O_3} diffusivity of ozone in water, $m^2\ s^{-1}$

D_{ow} apparent octanol-water partition coefficient (dimensionless)

f_{OH} fraction of a given compound degraded by hydroxyl radicals

Ha Hatta number, defined in Eq. 5 (dimensionless)

k_L liquid-phase individual mass transfer coefficient, $m\ s^{-1}$

k_{O_3} second order ozone-based rate constant for a direct ozonation reaction ($M^{-1}\ s^{-1}$)

$k_{HO\bullet}$ second order rate constant for a reaction with hydroxyl radical ($M^{-1}\ s^{-1}$)

k_R second order rate constant for the ozonation of a given compound ($M^{-1}\ s^{-1}$)

k_La volumetric mass transfer coefficient (s^{-1})

K_{ow} octanol-water partition coefficient for neutral species (dimensionless)

TOD dose of ozone transferred to the liquid (M)

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Supplementary Information

Occurrence of emerging pollutants in urban wastewater and their removal through biological treatment followed by ozonation

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Contents

1. Detected PPCP, method of analysis and limit of quantification (LOQ).

Name	Application	Method	LOQ (ng/L)	logKow[a]	CAS	Formula
3-(4-methylbenzylidene)camphor	UV filter	GC	99	3.04	464-49-3	$C_{10}H_{16}O$
4-aminoantipyrine (4-AA)	Metabolite of dipyrone	LC+	38	-0.07[b]	83-07-8	$C_{11}H_{13}N_3O$
4-methylaminoantipyrine (4-MAA)	Metabolite of dipyrone	LC+	5	0.39[b]	519-98-2	$C_{12}H_{15}N_3O$
Acetaminophen (paracetamol)	Antiinflammatory	LC+	33	0.46	103-90-2	$C_8H_9NO_2$
Antipyrine	Analgesic	LC+	16	0.38	60-80-0	$C_{11}H_{12}N_2O$
Atenolol	Beta-blocker	LC+	6	0.16	29122-68-7	$C_{14}H_{22}N_2O_3$
Atrazine	Herbicide	LC+	5	2.61	1912-24-9	$C_8H_{14}ClN_5$
Azithromycin*	Antibiotic	LC+	46	0.90	83905-01-5	$C_{38}H_{72}N_2O_{12}$
Benzophenone-3	UV filter	GC	79	3.82	131-57-7	$C_{14}H_{12}O_3$
Bezafibrate	Lipid regulator	LC-	8	4.25	41859-67-0	$C_{19}H_{20}ClNO_4$
Caffeine	Secondary stimulant	LC+	15	0.07	58-08-2	$C_8H_{10}N_4O_2$
Carbamazepine	Antiepileptic	LC+	1	2.30	298-46-4	$C_{15}H_{12}N_2O$
Carbamazepine epoxide	Metabolite of carbamazepine	LC+	18	0.95[b]	36507-30-9	$C_{15}H_{10}N_2O_2$
Celestolide	Synthetic musk	GC	23	5.93[b]	13171-00-1	$C_{17}H_{24}O$
Ciprofloxacin	Antibiotic	LC+	10	-1.08	85721-33-1	$C_{17}H_{18}FN_3O_3$
Citalopram hydrobromide*	Antidepressant	LC+	3	3.94[b]	59729-32-7	$C_{20}H_{22}BrFN_2O$
Clarithromycin*	Antibiotic	LC+	7	3.16	81103-11-9	$C_{38}H_{69}NO_{13}$
Clofibric acid	Metabolite of several lipid regulators	LC-	6	2.57	882-09-7	$C_{10}H_{11}ClO_3$
Codeine	Analgesic	LC+	40	1.14	76-57-3	$C_{18}H_{21}NO_3$
Cotinine*	Metabolite of nicotine	LC+	10	-0.32	486-56-6	$C_{10}H_{12}N_2O$
Diazepan	Anxiolytic	LC+	3	2.82	439-14-5	$C_{16}H_{13}ClN_2O$
Diclofenac	Antiinflammatory	LC-	1	4.51[c]	15307-79-6	$C_{14}H_{10}Cl_2NO_2Na$
Diuron	Herbicide	LC-	0.7	2.78	330-54-1	$C_9H_{10}Cl_2N_2O$
Erythromycin	Antibiotic	LC+	99	2.54	114-07-8	$C_{37}H_{67}NO_{13}$
Ethylhexyl methoxycinnamate	UV filter	GC	33	5.80[b]	5466-77-3	$C_{18}H_{26}O_3$
Famotidine*	Antiulcer	LC+	27	-0.69	76824-35-6	$C_8H_{15}N_7O_2S_3$
Fenofibrate	Lipid regulator	LC+	4	5.19	49562-28-9	$C_{20}H_{21}ClO_4$
Fenofibric Acid	Metabolite of fenofibrate	LC+	8	4.00[b]	42017-89-0	$C_{17}H_{15}ClO_4$
Fluoxethine	Antidepressant	LC+	3	1.95	54910-89-3	$C_{15}H_{21}F_3N_2O_2$
Furosemide	Diuretic	LC-	160	2.03	54-31-9	$C_{12}H_{11}ClN_2O_5S$

Galaxolide	Synthetic musk	GC	56	5.90[d]	1222-05-5	$C_{18}H_{26}O$
Gemfibrozil	Lipid regulator	LC-	0.1	4.77[b]	25812-30-0	$C_{15}H_{22}O_3$
Hydrochlorothiazide	Antihypertensive	LC-	2	-0.20	58-93-5	$C_7H_8ClN_3O_4S_2$
Ibuprofen	Antiinflammatory	LC-	4	3.50	15687-27-1	$C_{13}H_{18}O_2$
Indomethacin	Antiinflammatory	LC+	4	4.27	53-86-1	$C_{19}H_{16}ClNO_4$
Ketoprofen	Antiinflammatory	LC+	105	3.12	22071-15-4	$C_{16}H_{14}O_3$
Ketorolac	Antiinflammatory	LC+	3	-0.27[e]	74103-06-3	$C_{19}H_{24}N_2O_6$
Lansoprazole*	Antiacid	LC+	52	3.68[b]	103577-45-3	$C_{16}H_{14}F_3N_3O_2S$
Lincomycin*	Antibiotic	LC+	0.9	0.29[b]	859-18-7	$C_{18}H_{34}N_2O_6S$
Loratadine*	Antihistamine	LC+	0.9	5.66[b]	79794-75-5	$C_{22}H_{23}ClN_2O_2$
Mefenamic acid	Antiinflammatory	LC+	3	5.12	61-68-7	$C_{15}H_{15}NO_2$
Mepivacaine	Anesthetic	LC+	2	1.95	96-88-8	$C_{15}H_{22}N_2O$
Metoprolol	Beta-blocker	LC+	14	1.88	37350-58-6	$C_{15}H_{25}NO_3$
Metronidazole	Antibiotic	LC+	17	-0.02	69198-10-3	$C_6H_9N_3O_3$
Musk ketone*	Synthetic musk	GC	69	4.31[b]	81-14-1	$C_{14}H_{18}N_2O_5$
Musk xylene*	Synthetic musk	GC	3	4.90[d]	81-15-2	$C_{12}H_{15}N_3O_6$
N-acetyl-4-amino-antipiryne (4-AAA)	Metabolite of metamizol	LC+	100	-0.13[b]	83-15-8	$C_{13}H_{15}O_2N_3$
Naproxen	Antiinflammatory	LC+	24	3.18	22204-53-1	$C_{14}H_{14}O_3$
N-formyl-4-amino-antipiryne (4-FAA)	Metabolite of metamizol	LC+	33	0.50[b]	1672-58-8	$C_{12}H_{13}O_2N_3$
Nicotine	Secondary stimulant	LC+	72	1.17	54-11-5	$C_{10}H_{14}N_2$
Norfloxacin*	Antibiotic	LC+	56	-1.03	70458-96-7	$C_{16}H_{18}FN_3O_3$
Octocrylene	UV filter	GC	36	6.90[d]	80135-31-5	$C_{24}H_{27}NO_2$
Ofloxacin	Antibiotic	LC+	33	-0.39	82419-36-1	$C_{18}H_{20}FN_3O_4$
Omeprazole	Antiacid	LC+	6	2.23	73590-58-6	$C_{17}H_{19}N_3O_3S$
Paraxanthine	Metabolite of caffeine	LC+	55	-0.39[b]	611-59-6	$C_7H_8N_4O_2$
Pravastatin*	Anticholesterol	LC-	81	-0.71[b]	81131-70-6	$C_{23}H_{36}O_7$
Primidone*	Antiepileptic	LC+	53	0.73[b]	125-33-7	$C_{12}H_{14}N_2O_2$
Propanolol	Beta-blocker	LC+	4	3.09	526-66-6	$C_{16}H_{21}NO_2$
Propyphenazone*	Analgesic	LC+	5	1.94	479-92-5	$C_{14}H_{18}N_2O$
Ranitidine	Acid reducer	LC+	153	0.27	66357-35-5	$C_{13}H_{22}N_4O_3S$
Salbutamol	Bronchodilator	LC+	4	-0.90	18559-94-9	$C_{13}H_{21}NO_3$
Salicylic Acid*	Metabolite of acetylsalicylic acid	LC-	18	2.26	69-72-7	$C_7H_6O_3$
Simazine	Pesticide	LC+	8	2.18	122-34-9	$C_7H_{12}ClN_5$

Sotalol	Antiarrhythmic	LC+	12	0.24	3930-20-9	$C_{12}H_{20}N_2O_3S$
Sulfamethoxazole	Antibiotic	LC+	15	0.89	723-46-6	$C_{10}H_{11}N_3O_3S$
Sulfapyridine*	Bactericide	LC+	24	0.35	000144-83-2	$C_{11}H_{11}N_3O_2S$
Terbutaline	Bronchodilator	LC+	3	-1.07	23031-25-6	$C_{12}H_{19}NO_3$
Tonalide	Synthetic musk	GC	53	5.70[d]	1506-02-1	$C_{18}H_{26}O$
Traseolide	Synthetic musk	GC	59	8.10[d]	68140-48-7	$C_{18}H_{26}O$
Triclosan	Antiseptic	GC	145	4.53	3380-34-5	$C_{12}H_7Cl_3O_2$
Trimethoprim	Antibiotic	LC+	29	0.91	738-70-5	$C_{14}H_{18}N_4O_3$
Venlafaxine*	Antidepressant	LC+	14	0.87	93413-69-5	$C_{17}H_{27}NO_2$

[a] Unless otherwise indicated, values obtained from the experimental database LOGKOW Databank, Sangster Research Laboratories, Montréal, Canada (http://logkow.cisti.nrc.ca/logkow/)
[b] Value estimated with the KOWWIN program included in EPI Suite (Meyland and Howard, 1995).
[c] Tixier et al., 2003.
[d] Kameda et al., 2007.
[e] Zhu, et al., 2002.
* Compounds analyzed only in the biologically treated effluent and in a part of the samples.

2. Compounds not detected in any sample, method of analysis and limit of detection (LOD).

Name	Application	Method	LOD (ng/L)	CAS	Formula
4-dimethylaminoantipyrine (4-DAA)	Antipyretic	LC+	2	58-15-1	$C_{13}H_{17}N_3O$
Alfa-endosulfan	Pesticide	GC	68	958-98-8	$C_9H_6Cl_6O_3S$
Beta-endosulfan	Pesticide	GC	32	33213-65-9	$C_9H_6Cl_6O_3S$
Cefotaxime	Antibiotic	LC+	17	63527-52-6	$C_{16}H_{17}N_5O_7S_2$
Chlorfenvinphos	Pesticide	LC+	2	470-90-6	$C_{12}H_{14}Cl_3O_4P$
Chlorpyriphos-methyl	Pesticide	LC+	7	5598-13-0	$C_7H_7Cl_3NO_3PS$
Clorophene	Antiseptic	LC-	0.5	120-32-1	$C_{13}H_{11}ClO$
Fenoprofen	Antiinflammatory	LC-	1	34597-40-5	$C_{15}H_{14}O_3$
Isoproturon	Herbicide	LC+	13	34123-59-6	$C_{12}H_{18}N_2O$
Methylprednisolone 6-alpha sodium succinate	Antiinflammatory	LC+	10	2375-03-3	$C_{26}H_{33}O_8Na$
Paroxetine	Antidepressant	LC+	4	61869-08-7	$C_{19}H_{20}FNO_3$
Phantolide	Synthetic musk	GC	17	15323-35-0	$C_{17}H_{24}O$

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