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Environmental Impact Statement

The increasing diversity of pharmaceuticals, personal care products, and pesticides entering urban waterways and wastewater treatment plants is causing concern because of potential downstream environmental impacts. Ideally, potentially harmful chemicals should be degraded to benign fragments as upstream as possible. However, it is often difficult to assess persistency in urban waterways. The majority of degradations studies are often conducted in "artificial" waters for standardized testing, and not real world urban- and wastewater. We therefore explored the degradation behavior of nine diverse contaminants in real world urban- and wastewater under varying conditions, at both ambient and cold temperatures, and compared them with laboratory tests. This study presents a more accurate picture of contaminant transformation processes in an urban-water environment.

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ARTICLE SUBMISSION

The degradation behaviour of nine diverse contaminants in urban surface water and wastewater prior to water treatment

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An increasing diversity of emerging contaminants are entering urban surface water and wastewater, posing unknown risks for the environment. One of the main contemporary challenges in ensuring water quality is to design efficient strategies for minimizing such risk. As a first step in such strategies, it is important to establish the fate and degradation behavior of contaminants prior to any engineered secondary water treatment. Such information is relevant for assessing treatment solutions by simple storage, or to assess the impacts of contaminant spreading in the absence of water treatment, such as during times of flooding or in areas of poor infrastructure. Therefore in this study we examined the degradation behavior of a broad array of water contaminants in actual urban surface water and wastewater, in the presence and absence of naturally occurring bacteria and at two temperatures. The chemicals included caffeine, sulfamethoxazole, carbamazepine, atrazine, 17ß-estradiol, ethinylestradiol, diclofenac, desethylatrazine and norethindrone. Little information on the degradation behavior of these pollutants in actual influent wastewater exist, nor in general in water for desethylatrazine (a transformation product of atrazine) and the synthetic hormone norethindrone. Investigations were done in aerobic conditions, in the absence of sunlight. The results suggest that all chemicals except estradiol are stable in urban surface water, and in waste water neither abiotic nor biological degradation in the absence of sunlight contribute significantly to the disappearance of desethylatrazine, atrazine, carbamazepine and diclofenac. Biological degradation in wastewater was effective at transforming norethindrone, 17ß-estradiol, ethinylestradiol, caffeine and sulfamethoxazole, with measured degradation rate constants *k* and half-lives ranging respectively from 0.0082-0.52 d^{-1} and 1.3-85 days. The obtained degradation data generally followed a pseudo-first-order-kinetic model. This information can be used to model degradation prior to water treatment.

Introduction

Increasing attention has been given to pesticides, pharmaceuticals and personal care products (PPCP) in surface and groundwater.[1] The diversity of these substances on the market has grown continuously and methods of their removal from municipal wastewater are being studied intensively.[2-4] Many PPCP and pesticides are generally found in urban surface waters, wastewater treatment plants (WWTP) as well as drinking waters in the ng L^{-1} to µg L^{-1} range.[3, 5-15] Though it is important to develop water treatment strategies for handling these diverse compounds, it is also important to understand their fate before - or in the absence of - water treatment. This is needed not only for assessing chemical fate in areas or situations with little water treatment (e.g. due to floods or pore infrastructure), but also to potentially better incorporate low-energy treatment options, such as by extending storage time in a primary settling tank.

The objective of this study was therefore to measure the degradation of a range of pesticides and PPCPs in urban surface waters and wastewater in the absence of secondary or tertiary treatment and calculate the contribution of biotic (biodegradation) and abiotic (hydrolysis and oxidation) processes to their disappearance in aquatic systems. Among the target compounds, we have chosen to focus on seven PPCPs: 17ß-estradiol (E2), ethinylestradiol (EE2), norethindrone (NOR), caffeine (CAF), carbamazepine (CBZ), sulfamethoxazole (SMX) and diclofenac (DCF); along with the pesticide atrazine (ATZ) and its main degradation metabolite, desethylatrazine (DEA). The target compounds are fairly mobile in water, represent a range of diverse structures and physico-chemical properties and are commonly emitted to wastewater.[16, 17] In the last few years, they have all been detected in the surface river waters of eastern Canada, including some rivers adjacent to WWTPs, implying that their removal during wastewater treatment is not optimal as reported by previous authors[2-4]: ATZ and DEA between 2.0 and 479 ng L^{-1},[15, 18, 19] E2, EE2, NOR and SMX at low ng L^{-1}

concentrations,[19, 20] CBZ between 0.2 and 80 ng L^{-1},[15, 18, 19, 21] CAF between 14 and 110 ng L^{-1} [18, 21] and DCF up to 50 ng L^{-1}.[2, 21-26] Studies reporting degradation rate half-lives and rate constants for these compounds have focused on activated sludge,[10, 27-30] and selected aquatic environments, such as muddy waters, river waters, marine waters or water-sediment systems (**Table 1**). This variety of environmental media has produced a wide range of kinetic data, making it difficult to understand the degradation behaviour of the nine target compounds in actual urban surface water or raw wastewater. More data are required given that water is probably the best natural transport vector for those compounds, which in sufficient concentrations can have clear effects on aquatic organisms, wild life and human health.[31]. Toxic effects on fresh water phytoplankton populations have been reported at ATZ concentrations of 1 µg L^{-1}.[22] E2, EE2 and NOR can behave as endocrine disruptors to fish species at low ng L^{-1} concentrations.[23-25] Chronic exposure to SMX is negatively impacting many plants, algae and invertebrates in aquatic environments, inhibiting their folic acid synthesis, an essential vitamin for the DNA and RNA synthesis.[26] Studies have reported that environmental concentrations of CBZ and DCF have limited acute toxicity on aquatic bacteria, algae, micro-crustaceans and fish but that chronic exposition can be hazardous.[2] The two compounds most unique to this study are desethylatrazine (a transformation product of atrazine) and norethindrone (a synthetic steroid that is less well studied than other hormones like E2 and EE2), in which scarce information could be found in the literature regarding their degradation. Regarding the other compounds, the photolysis degradation pathway in aqueous environments is currently better studied and documented[2, 6, 32-36] than other chemical and microbial degradation pathways. Therefore in this study we set out to quantify and understand the degradation behaviour of these compounds by comparing their persistency in typical urban river waters vs wastewater in absence of sunlight and prior to any secondary or tertiary water treatment. Abiotic degradation (excluding photo degradation) assessed in typical urban surface waters will give more insight about the contribution of abiotic degradation (natural hydrolysis and oxidation) once the target compounds are released into the environment through poor water treatment while abiotic and biological degradation measured in wastewaters will give useful information for the management of areas and situations with limited possibility for water treatment.

Table 1 Overview of literature values of degradation in comparable aqueous systems for the studied compounds

Compound	Studied system	System characteristics	$t_{1/2}$ (days)	Degradation % in (time)	Implied process
ATZ[32]	Water downstream of a sugar refinery	500 ml water : 12.5 g sediments, 10 ppm sugar, 22°C, aerobic	n.a.	100 (6w)	B
ATZ[32]	Sterile buffered water	pH 7	none	n.a.	H
ATZ[37]	Synthetic river water, pH 6.4 (aerobic)	ATZ 500 ppb, reactor operated in continuous mode	none	n.a.	B
ATZ[37]	Synthetic river water , pH 6.4 (anaerobic)		none	n.a.	B
ATZ[22]	Autoclaved estuarine and marine waters	n.a.	n.a.	persistent (128d)	C
ATZ[22]	Laboratory aqueous systems	pH 7.0, 5 mg/L fulvic acid	742	n.a.	H
DEA[38]	Potable water	n.a.	n.a.	persistent (10d)	G
DEA[39]	Groundwater microcosm under low O_2	DEA~20 µg/L, DO <3.0 mg/L	n.a.	persistent (45d)	G
DEA[40]	Aerobic aquifer	DEA~3 µg/L, DO~6.9 mg/L	n.a.	persistent (60d)	G
E2[41]	Digestion unit (mud)	aerobic, 21 °C	n.a.	88 (24h)	B
E2[41]	Digestion unit (mud)	anaerobic, 21 °C	7	n.a.	B
E2[41]	Bioreactor	21 °C	n.a.	92 (7h), 100 (49h)	B
E2[34]	Aerobic river water	20 °C	n.a.	100 (1.2d)	B
EE2[34]				17 (1.2d)	B
E2[42]	English river waters (water column)	Initialy aerobic (potentially ↓ of oxic conditions) 20 °C	2-3	n.a.	B
EE2[42]			4-6		B
E2/EE2[42]		sterile	none	persistent	H + O
E2[43]	Potable water	n.a.	n.a.	38.9 (10d)	G
EE2[43]				22.4 (10d)	G
E2[44]	Japanese river waters	15 °C (winter)/28 °C (summer)	n.a.	100 (7d)/100 (5d)	B
EE2[44]		15 °C (winter)/28 °C (summer)	>14/14	n.a.	B
E2/EE2[44]		sterile	none	persistent (5d)	H + O
CBZ[45]	Aquatic microcosm of 12,000 L	unspecified T(°C) and O_2	n.a.	not significant	H
CBZ[46]	Stream muddy water (3 water:1 sediment)	Oxic, pH 7.7, 1.4% C_{org}, 20 ˚C	328	n.a.	B
CBZ[47]	11 wastewaters from different treatments	bacterial beds aged 1-40 days, oxic and anoxic conditions	n.a.	not significant (treatment)	B
CBZ[48]	Estimation Program Interface	Aqueous systems, pH 7 at 25˚C	> 365	n.a.	H
CAF[45]	Aquatic microcosm of 12,000 L	unspecified T(°C) and O_2	n.a.	not significant	H
CAF[6]	Lake water	sterile (darkness) at 20°C	none	persistent	H + O
CAF[49]	WWTP primary inlet	BOD 67 mg/L, TSS 76 mg/L, pH 7, 19 °C	~1	≈100 (3d)	B
CAF[49]	WWTP outlet	BOD 3.6 mg/L, TSS 7.9 mg/L, pH 6.4, 19 °C	~5	≈100 (10d)	B
CAF[50]	Waters upstream of 2 WWTP	oxic, 23 °C	none	not significant	B
CAF[50]	Water downstream of a WWTP		n.a.	100 (46d)	B
CAF[48]	Estimation Program Interface	aqueous systems, pH 7 at 25˚C	30-500	n.a.	H
SMX[45]	Aquatic microcosm of 12,000 L	unspecified T(°C) and O_2	n.a.	not significant	H
SMX[49]	WWTP primary inlet	BOD 67 mg/L, TSS 76 mg/L, pH 7, 19 °C	~18.	90 (25d)	B
SMX[49]	WWTP outlet	BOD 3.6 mg/L, TSS 7.9 mg/L, pH 6.4, 19 °C	none	persistent (56d)	B
SMX[51]	Synthetic system (3 water: 1 sediment)	unspecified O_2, 25 °C	14	n.a.	B
SMX[36]	Natural waters	Sterile (initial O_2 of 7.8 mg/L, no air bubbling)	none	persistent	H
SMX[36]	Sediment slurry (4.7% C_{org})	sterile	none	persistent	H
SMX[36]		natural	10.1	n.a.	B
DCF[52]	Liquid phases of WWTP sludges	sterile (0.5 g TSS/L)	n.a.	persistent	H
		aerobic, pH 5.5-7.3, 20˚C (0.5 g TSS/L)	n.a.	persistent	B
DCF[53]	Aerobic synthetic wastewater	(10 mg activated sludge/L deionized water)	none	persistent (28d)	B
DCF[54]	Lake surface waters	darkness	none	persistent (37d)	H + B

[a] A more detailed table can be found in the ESI (Table S8)
[b] Classification symbols are h = hours, d = days, w = weeks, B = biodegradation, H = hydrolysis, O = oxidation, G = general degradation, P = photolysis and C = abiotic degradation

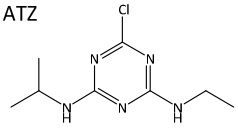
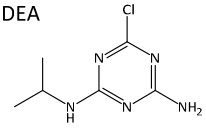
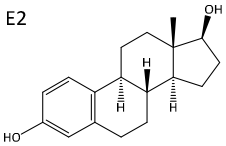
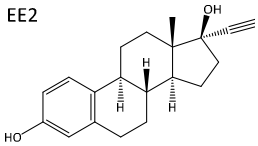
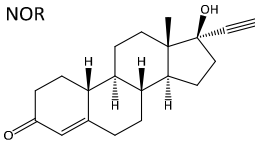
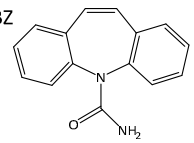
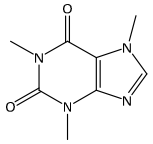
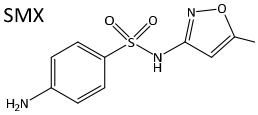
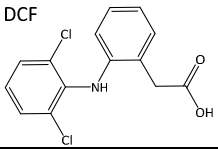
Experimental

A protocol based on published studies[34, 44, 55, 56] and the standardised OECD's 309 –Simulation Biodegradation Test[57] was created to achieve the objectives. A specific analytical technique developed earlier was used to quantify the degradation of the spiked chemicals over time in water.[58] This method uses a laser diode thermal desorption atmospheric pressure chemical ionization coupled to tandem mass spectrometry (LDTD-APCI-MS/MS).

Chemicals, reagent and stock solutions

The characteristics and the molecular structures of the nine selected analytes used for this study are listed in **Table 2**. These standards (purity ≥ 97.4%) were purchased from Sigma Aldrich (Oakville, ON, Canada).

Table 2 Studied compounds, their physical-chemical properties and the selected ions in LDTD-APCI(+)-MS/MS for the chemical analysis.

Compound name and structure	MW[a] [g mol^{-1}]	pKa	Water Solubility (X°C) [mg L^{-1}]	Log K_{ow}	Sampled WWTP sludge* average Log K_d[16]	Other sludge Log K_d (min-max)[16]	Henry's Law Constant at 25°C[59] [atm m^3 mol^{-1}]	MS/MS parameters: Precursor Ion [M+H]$^+$ (m/z)	MS/MS parameters: Product Ion (m/z)	MS/MS parameters: Internal standard used
ATZ 	215. 69	1.7[a]	34.7 (26)[60]	2.61[61]	0.95	0.7-2.1	2.36 x10^{-9}	216.12	131.9 173.9	[$^{13}C_3$]-ATZ
DEA 	187.63	1.65[62]	3200 (22)[63]	1.51[61]	-0.1	n.a.	1.53 x10^{-9}	188.1	103.9 145.9	[$^{13}C_3$]-ATZ
E2 	272.39	10.33[b]	3.6 (27)[64]	4.01[61]	2.0	1.2-2.9	3.64 x10^{-11}	255.18	133.1 159.1	[$^{13}C_6$]-E2
EE2 	296.41	10.33[b]	11.3 (27)[64]	3.67[61]	2.35	2.3-3.7	7.94 x10^{-12}	279.1	133.1 159.1	[$^{13}C_6$]-E2
NOR 	298.43	17.59[b]	7.04 (25)[64]	2.97[61]	1.7	n.a.	5.80 x10^{-10}	299.205	109.1 91.1	[$^{13}C_6$]-E2
CBZ 	236.28	13.9[d]	17.7[b]	2.45[a]	1	0.1-2.5	1.08 x10^{-10}	237.12	192.1 194.1	CBZ-d_{10}
CAF 	194.19	10.4[a]	21600 (25)[64]	0.07[61]	0.85	0.9-3.1	3.58 x10^{-11}	195.12	109.9 137.9	[$^{13}C_3$]-CAF
SMX 	253.28	5.7[d]	610 (37)[64]	0.89[61]	0.35	0.4-2.6	6.42 x10^{-13}	254.06	107.9 156.1	[$^{13}C_6$]-SMX
DCF 	296.16	4.15[a]	2.37 (25)[65]	4.51[66]	1.75	1.2-3.1	4.73 x10^{-12}	296.01	215.0 249.9	DCF-d_4

*These data are from the same water, [a]SRC PhysProp database http://www.syrres.com, [b]HSDB database http://toxnet.nlm.nih.gov/cgi-bin/sis/htmlgen?HSDB, [c]Drugbank database http://www.drugbank.ca/ and [d]EPA http://www.epa.gov/pesticides/science/efed/policy_guidance/team_authors/endangered_species_reregistration_workgroup/esa_reporting_fate.htm.

All isotopically-labelled compounds used as internal standards ([$^{13}C_3$]-ATZ, [$^{13}C_6$]-E2, CBZ-d_{10}, [$^{13}C_3$]-CAF and [$^{13}C_6$]-SMX) were purchased from Cambridge Isotope Laboratories, Inc. (Andover, MA, USA) except diclofenac (DCF-d_4, 99%, solid), which was obtained from CDN Isotopes (Pointe-Claire, PQ, Canada). Other chemicals used were of analytical grade and used without further purification: silver nitrate ($AgNO_3$), copper sulfate ($CuSO_4$) and methanol (MeOH) were obtained from

Fisher Scientific (Whitby, ON, Canada) and mercury chloride ($HgCl_2$) was obtained from BDH Chemicals (Montréal, PQ, Canada). Sodium hydroxide 1M (NaOH) was prepared by dissolution of the commercial compound in water. Formic acid was obtained from Sigma Aldrich (Oakville, ON, Canada). Ultrapure distilled-deionized water (dd-H_2O) was obtained by filtration on a Milli-Q apparatus (Millipore, USA).

Individual compound stock solutions were prepared in methanol at a concentration of 1000 mg L^{-1} and kept at -20°C in amber vials for a maximum of 6 months. Mixed 20 mg L^{-1} working solutions were prepared by diluting stock solutions in MeOH and kept for a maximum of 6 months. Individual stock solutions (1000 mg L^{-1}) of silver nitrate, copper sulfate and mercury chloride were prepared by dissolution of the appropriate compound in acidified dd-H_2O and stored in LDPE amber bottles at ambient temperature for the length of the project. Individual working solutions (10 mg L^{-1}) were prepared by dilution in dd-H_2O.

Urban river water and wastewater characterisation

Sample collection

The urban surface water was sampled from the urban/industrial stretches of the Milles-Iles River, entering the Ste-Rose drinking water treatment plant intake (Laval, QC) during March 2012. The wastewater samples were selected to be representative of wastewater that has undergone no or very limited treatment, and therefore we collected wastewater from municipal outflow of a primary sludge tank (PST) located in the vicinity of Quebec City, QC, and sampled twice; in February and June 2012. Water samples were collected in 4-L amber glass bottles previously washed and rinsed with ultrapure water and autoclaved at 121°C. Collected water was stored at 4˚C at most 2 hours after sample.

Urban river water and wastewater characteristics

Water characterisation were done within 48 hours after sample collection. Parameters were evaluated according to the test objectives. Solution pH was measured with a VWR SB20 pH-meter, bacterial count with an Olympus BX51 fluorescence microscope, and DOC & TOC with a Sievers 5310 TOC Laboratory Analyser. Hach methods 10205 & 10208 were used for NH_4 & N_{tot} as well as an Ultrospec 3100 pro UV-Vis spectrophotometer at 630 nm. Turbidity was measured with a Hach 2100N Series Laboratory Turbidimeter. TSS, COD, conductivity and alkalinity were respectively measured following APHA 2005 standard methods 2540D, 5220D, 2510B & 2310B. Finally, lipids were measured by repeated Soxhlet extraction with hexane and sugars by colorimetry.[67] Results are presented in **Table 3.**

Table 3 Characterisation of water samples

Water type tested	Initial water characteristics	
Urban river (surface) water	pH	7.42-7.46
	bacterial presence [nb L^{-1}]	negligible
	TOC [mg L^{-1}]	7.44
	Turbidity [NTU]	0.20-1.36
	Alkalinity [mg $CaCO_3$ L^{-1}]	33
Raw wastewater (primary settling tank outlet)	pH	7.41-7.52
	viable bacteria [nb L^{-1}]	7.12 x10^{10}
	total bacteria [nb L^{-1}]	9.41 x10^{10}
	DOC [mg L^{-1}]	14.2
	TOC [mg L^{-1}]	18.7
	NH_4-N [mg L^{-1}]	5-25
	COD [mg O_2 L^{-1}]	170-278
	TSS [mg L^{-1}]	90-127
	Lipids [mg L^{-1}]	0.05-0.16
	Carbohydrates [mg L^{-1}]	13-47
	Q (m^3 h^{-1})	8

Laboratory bench-scale degradation experiments

Procedures common to all experiments

Degradation experiments corresponded to the measurement of the target compound stability over time in oxic conditions. The length of the adaptation period, i.e. the lag phase, was also measured. Abiotic degradation was tested in urban river water and raw wastewater (in which microbial activity was inhibited) by waiting for spontaneous hydrolysis/oxidation with no chemical additives (other than biocide for the wastewater). Experiments were carried out in 30-mL large neck (untreated) amber vials provided by Fisher Scientific (Whitby, ON, Canada). All kinetic degradation assays were initiated within 48 hours after sample collection, run in duplicates and incubated in controlled temperature chambers, as specified in the summary of the experiments in **Table 4.**

Table 4 Assessed parameters of the degradation kinetic experiments.

Water type tested	Test duration [days]	Sterilization method	Water temp. [°C]	Degradation pathway evaluated
Urban river (surface) water	469	Filtration 0.45 µm	4 ± 0.5	abiotic degradation
			ambient (21 ± 2)	
Raw wastewater	72	Biocide Vs. No Sterilization (raw)[a]	4 ± 0.5	abiotic degradation[a] *vs* biological degradation
			21.5 ± 0.5	

[a] A series treated with biocides was tested in parallel where biological activity was inhibited with [Cu^{2+}] 9.5 mg L^{-1}, [Ag^{+}] 16 mg L^{-1}, [SMX] 10 mg L^{-1} and acidified with formic acid

Temperatures (Table 4) were selected based on average data for surface waters and WWTP in the Quebec City area and reflected seasonal variations. Maintenance of oxic conditions was achieved by bubbling air through each bottle 60 mins per day for the duration of the degradation assays. A correction factor was used to correct the quantified concentrations of the target compounds, to prevent them being biased to high due to long term water evaporation. Volatilization was not an issue for the studied compounds, due to their low Henry's law constant (**Table 2**), which warrants their classification as being non-volatile from water. More information about the maintenance of oxic conditions is available in the ESI.

All kinetic experiments were launched by spiking the compounds together into tested waters to a nominal concentration of 400 µg L^{-1} with a mix working stock solution in MeOH. This nominal concentration, which is higher than typically observed concentrations in such water samples,[3, 5-15, 68], was chosen to facilitate analytical quantification at multiple time-steps down to trace environmental levels, and to avoid time consuming solid-phase extraction procedures. If we assume the mechanism of degradation kinetics is consistent at all concentrations, starting from an elevated concentration should not influence the observed rate constant. Also, this avoided the concentration of the studied compounds already present in the studied waters from contributing to concentration measurements at the initial time steps. The proportion of MeOH in the tested waters was always between 1 and 2 %, which should not cause any bactericide or bacteriostatic effects.[69] Aliquots were then collected at specific time intervals from the water bottles and the studied compounds were analysed by LDTD-APCI-MS/MS. The first quantification of the degradation experiment was always done at least 5 hours after having spiked the compounds in the studied waters to ensure sorption equilibrium was obtained, based on a previous investigation on sorption kinetics for these compounds in water samples,[16] as described below.

Urban river water

Abiotic degradation of the target compounds

The investigations of the urban river water were carried out to estimate the abiotic degradation in urban river waters (**Table 4)**. For this, microbial activity was inhibited by filtration. Filtrations were done under suction with 0.45-µm nitrocellulose membrane manufactured by Millipore (Billerica, MA). Although this method may not have completely sterilized the studied system, it does increased the microbial lag time (the end of which would be evident in the experimental results if microbial degradation occurs quicker than abiotic degradation) and also avoids adding chemicals that may influence the degradation rate.

Raw wastewater

Abiotic degradation of the target compounds

Unlike in urban river waters, filtration was not considered an appropriate way to minimize microbial activity for the abiotic degradation experiments, as doing so was found to dramatically lower the TSS content and other properties; therefore, it was done through addition of biocides. Copper sulfate and silver nitrate were added to concentrations substantially higher than their typically recognized microbiological lethal thresholds[70, 71] **(Table 4).** The metals were used together because their combination is known to have synergic effects in inactivation of bacteria.[72] Wastewaters used here were acidified to pH ≈4.5 with formic acid to maintain the bioavailability of the biocide metals. This will have an effect on DOC values of some compounds since sorption is more important at neutral forms; SMX (pKa of 5.7) will be neutral at pH 4.5 and ionic at pH 7, DCF (pKa 4.15) will be a mixture of charged and ionic at pH 4.5). Thus, unlike the urban river experiments, the chemical composition of the water phase was slightly altered. Sodium azide, an effective biocide widely used in similar experiments[73] could not be used because of its capacity to chemically transform atrazine (ATZ).[74] Autoclaving, another widely used method,[56] was not chosen because three autoclaving cycles would have had to be realized within three days in order to properly sterilize such a complex aqueous system and it would likely have add a significant change on the chemical composition. Furthermore, the efficacy of autoclaving could not even be guaranteed given the importance of TSS presence.[75]

Biological degradation of the target compounds

A series of samples of raw wastewater was run in parallel with the series of wastewater with biocides (above). A comparison of the results of both series will give the impact of biodegradation, since both abiotic and biological degradation can contribute simultaneously to the disappearance of the target compounds. Only SMX, whose 50% minimum inhibitory concentrations against pathogenic bacteria in aquatic environments were reported[76] between 2 µg L^{-1} and 256 mg L^{-1}, was evaluated in a separate series of bottles to prevent its potential toxic effect.

The composition of the wastewater was the source of biomass to recreate real conditions. No nutrient solutions were used to maintain biological life inside the bottles. To ensure the microbial community was not substantially depleted over the course of the degradation experiments (e.g. due to lack of nutrients), viable bacterium in the wastewater was measured in a parallel set of vials. Initially, the parallel wastewater sample had 2.09 x 10^{10} viable bacterium. After 38 days, the wastewater incubated at 4˚C had 2.99 x 10^{9} viable bacterium and the wastewater incubated at 21.5˚C had 6.94 x 10^{9} viable bacterium. Thus, we conclude that the bacteria was not substantially depleted to alter the experiments. Further degradation, when observed, kept occurring after 90 days. Water samples were kept at ambient pH to recreate real-world conditions.

Sorption considerations

The possibility of sorption contributing to the disappearance of the target compounds was evaluated before launching the degradation experiments. The solid-water distribution coefficient (K_d, $L \cdot kg^{-1}$) quantifies the affinity for compounds to be sorbed to particles rather than be dissolved in the aqueous phase.[77] The K_d is defined as the ratio of contaminant concentration in the solid phase (C_s, µg $kg_{dw\ suspended\ sediment}^{-1}$) to the contaminant concentration in the aqueous phase (C_w, µg L^{-1}) in a system that has reached equilibrium.[78]

$$K_d = \frac{C_s}{C_w} \quad (1)$$

Morissette[16] measured the sorption of the 9 studied compounds in sludge systems coming from the wastewater used in the present study and reported minor sorption for the more polar contaminants (*i.e.* ATZ, DEA, CBZ, CAF and SMX, **Table 2**), while the others sorbed more significantly and reached equilibrium 5 minutes after spiking, when placed on an orbital shaker. The compound with the highest K_d value is EE2, which we previously measured to have a log K_d of 2.35 for sewage sludge, and which the highest literature values is 3.7. With the wastewater in this study having a TSS of 127 mg L^{-1}, this would imply that the percentage of EE2 sorbed to particles at equilibrium would be between 2.8% and 38.9%, respectively. However, considering that the highest TOC in our wastewater was , 0.0187 g_{OC} L^{-1}, which is significantly lower than Morissette et al's 23.8 g_{oc} L^{-1}, it is likely that the sorption of EE2 in our system is < 2.8% (as sorption to sediments generally decreases with decreasing OC content[79]). Thus sorption is not considered an issue in our experimental system. As a further step to ensure this, we set the initial time of the experiments as 5h after spiking (T_0=5h), as sorption kinetics are often most evident in the first hours, and degradation kinetics are typically observed on the scale of days to months.[16]

Analytical methods

Sample preparation

Aliquots of 500 µL were collected at specific time intervals from the water bottles of the bench-scale experiments and diluted into a 2 mL amber vial containing 100 µg L^{-1} of all six IS in 500 µL of MeOH. A small volume of this solution was spotted (3-5 µL depending on the water tested) into Lazwell 96-well metal plate cavities, which was left for 15 min in a forced air oven at 35°C to dry before quantification of the residual concentration. The proportion of MeOH and the volume spotted in the cavities were chosen after preliminary tests carried out to maximize sensitivity and minimize analytical variability.

Chemical Analysis

The compounds were analysed by LDTD-APCI(+)-MS/MS, using a previously published method.[58] This technique involves a high-throughput sample introduction method reducing total analysis time to less than 15 s per sample. During operation, an infrared (IR) laser diode is focused on the back of the well, and the dried sample is then thermally desorbed, vaporizing itself into the gas phase. With a carrier gas, the uncharged analytes move along the transfer tube into the APCI area. The tube inserted into the well prevents sample losses. The analytes are ionized by the APCI when they reach its corona needle, just before being transferred into the MS inlet, where they are fragmented and quantified in positive mode. The LDTD (Laser set at 980 nm and 20 W, Laser power of 0.30 a.u., capillary temperature of 50ºC, carrier gas flow of 3.0 L min^{-1}, ion sweep gas at 0.3 a.u.) and MS/MS parameters were optimized previously[58]. Selected ions used for quantification are presented in **Table 2**. An exhaustive description of the analytical method (LDTD and MS/MS parameters) is presented in Table S2, S3 and S4.

Method Validation

Replicability values (before rejection of outliers) ranged from 3.8 % (ATZ) to 20.7 % (DCF). It was calculated with the experimental relative standard deviation (RSD) of a series of 5 measurements for each compound on the same sample of raw wastewater, and the acceptance threshold was fixed at 15% of RSD after the exclusion of outliers when meeting exclusion criteria. With six out of nine target compounds having values below the fixed threshold (<15%), results were deemed acceptable. Recovery values in the raw wastewater ranged from 81.9 to 114% except for SMX at 125%.

$$\%_{recovery} = \frac{C_{spiked} - C_{environmental}}{C_{expexted}} \times 100 \quad (2)$$

The spiking concentration of 200 µg L^{-1} corresponded to a value between LOQs and the initial experimental concentrations for all compounds. Replicability and recovery results are summarized in Table S5. The resulting LOD in the raw wastewater ranged from 0.4 (CBZ) to 10.0 µg L^{-1} (CAF) and the LOQ ranged from 1.3 (CBZ) to 33.3 µg L^{-1} (CAF); all values are summarized in Table S6. Both LOD and LOQ were calculated based on the signal-to-noise ratio.[80]

Rate constants and half-life calculation

The measured degradation of the nine target compounds in urban river water and wastewater was modelled using a pseudo-first order kinetics equation, where the time based pseudo-first-order constants (k) is reported in $days^{-1}$, as presented in Eq. (3):[81]

$$Ln\ \frac{C_0}{C_t} = kt \quad (3)$$

where t is the length of the degradation experiment in days, C_t is the residual concentration of target compound at time t and C_0 its initial concentration. Half-lifes $t_{1/2}$ were calculated using Eq. (4):

$$t_{1/2} = \frac{0.693}{k} \quad (4)$$

Previous authors[2, 6, 34, 36, 46, 49, 51, 55, 82] have successfully used the same model for those compounds in comparable environments. Concentrations considered to be part of the lag phase were not used for the calculation of the degradation constants.

Results and Discussion

Preliminary tests

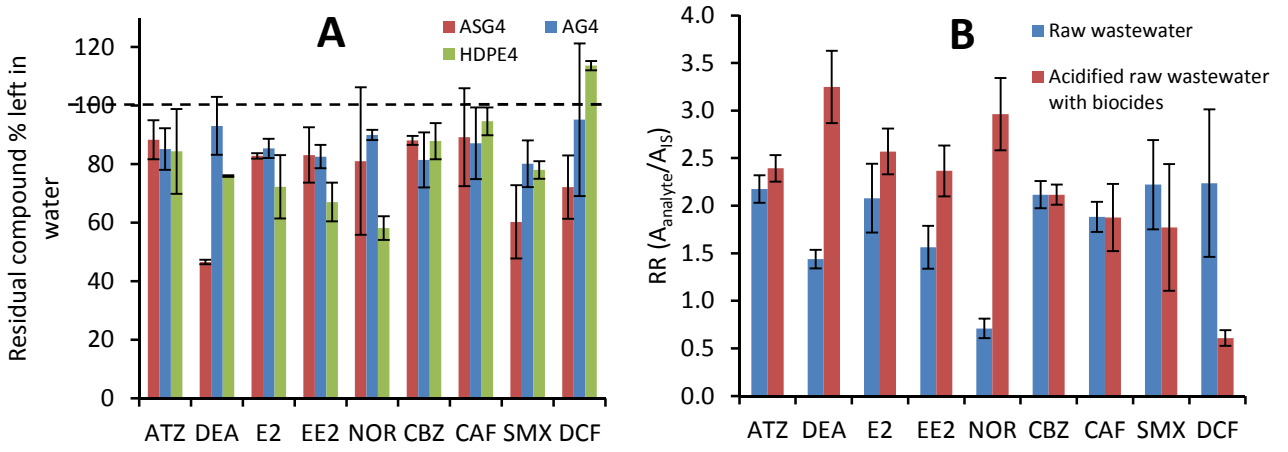


Figure 1. Method optimization figures. A. A comparison of compound losses due to sorption on internal bottle surfaces after 14 days of incubation at 4 °C for an initial concentration of ≈400 µg L^{-1} in distilled water where ASG = amber silanized glass bottle, AGB = amber glass bottle & HDPE = HDPE bottles B. Response ratio (Area $peak_{analyte}$/Area $peak_{internal\ std}$) of the 9 target compounds at 400 µg L^{-1} ± SD (n=5) in raw wastewater and in acidified (with formic acid) wastewater spiked with 150 µM of $CuSO_4$ and $AgNO_3$.

Compound sorption on the bottle surfaces

To optimize the experiments, we investigated which types of bottles sorbed the target analysts the least after 14 days of exposure, comparing amber glass bottles with and without salinization, as well as HDPE bottles.[83] Results of this comparison are presented in **Figure 1A** (a more exhaustive presentation of the results is presented in Figure S1). In general, there was no vial which consistently sorbed less than the others. We therefore chose the untreated amber glass, because of its capacity to block photo degradation, insignificant surface adsorption and no glass pre-treatment with silanizing agents is required. Hence, no correction was made for surface sorption artifacts.

Effects of biocides on the chemical analysis

The effect of the addition of copper sulfate and silver nitrate on the chemical analysis was measured by comparing the response ratio of the 9 target compounds in raw wastewater and in acidified raw wastewater with biocides (**Figure 1B**). Results showed that the biocides interfere with the chemical analysis of some compounds, increasing the signal of DEA, EE2, NOR, and decrease the signal strength of DCF. A calibration curve per condition was hence measured for each method before each quantification to ensure the integrity of the analysis. More details is available in the ESI (Figures S2-S3).

Laboratory bench-scale degradation experiments

Observed lag phases (Lp), pseudo first order disappearance rate constants (k) & half-lives ($t_{1/2}$) when observed in raw wastewater are presented in **Table 5** (the results in urban river water can be found in the ESI, Table S7). The residual compound percentage measured over time in urban river water and raw wastewater are presented in **Figures 2-3**. Reported degradation studies of the target compounds in comparable water systems are presented in **Table 1** and a more detailed overview can be found in the ESI (Table S8). Our measured results show that some compounds where persistent over the study period in all water samples, whereas other compounds readily degraded. Below we first present the appropriateness of using a first order model, followed by the results for the more persistent compounds, followed by the less persistent compounds.

First order kinetic validity

We calculated the degradation rate constants when significant degradation was observed. The 20 obtained rate constants from the linear regression analysis all followed the pseudo-first-order kinetic model, with 16 coefficients of determination (R^2) over 0.90 among which 14 were over 0.95. This was deemed satisfactory. The four lower R^2, between 0.85 and .90, are attributed to high analytical variability rather than non-compliance of the kinetic model.

Table 5 Lag phases (Lp), pseudo first order disappearance rate constants (k) & half-lives ($t_{1/2}$) ± standard deviation of duplicate incubations for the degradation experiments in raw wastewater. Refer to Table S7 in the ESI for an exhaustive presentation of the results.

Compound	Water type tested	Raw wastewater (PST outlet)								
	Characteristics of the incubation	4°C with biocides	4°C			21.5°C with biocides	21.5°C		
E2	Lp [days]		2 ≤ Lp < 8			2 ≤ Lp < 43	non significant		
	k [days^{-1}]	*b*	0.018	±	0.004	*d*	0.52	±	0.01
	$t_{1/2}$ [days]		40	±	9		1.30	±	0.03
EE2	Lp [days]						26 ≤ Lp < 66		
	k [days^{-1}]	*b*	*b*			*b*	0.036	±	0.003
	$t_{1/2}$ [days]						19	±	2
NOR	Lp [days]		8.5 ≤ Lp < 21.5				0 ≤ Lp < 8.5		
	k [days^{-1}]	*c*	0.022	±	0.002	*c*	0.11	±	0.00
	$t_{1/2}$ [days]		32	±	4		6	±	0
CAF	Lp [days]		0 ≤ Lp <8.5				0 ≤ Lp <8.5		
	k [days^{-1}]	*a*	0.011	±	0.003	*a*	0.037	±	0.004
	$t_{1/2}$ [days]		65	±	20		19	±	2
SMX	Lp [days]		21.5 ≤ Lp < 71				0 ≤ Lp < 8.5		
	k [days^{-1}]	*a*	0.0082	±	0.0008	*a*	0.035	±	0.003
	$t_{1/2}$ [days]		85	±	8		20	±	2

No significant disappearance observed after [a]130, [b]72 or [c]66 days (experiment length).

[d] data excluded due to poor reproductibility.

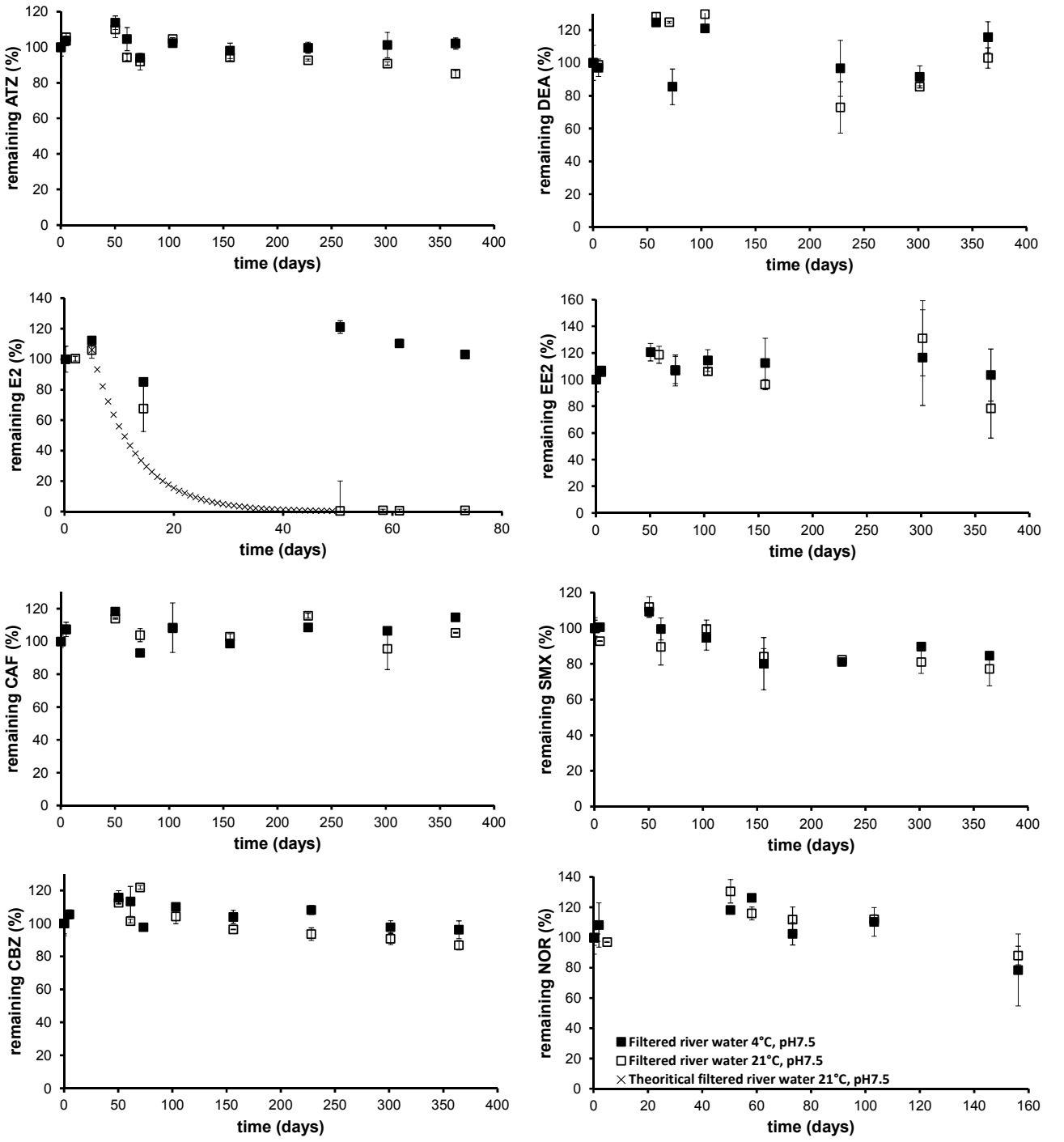


Figure 2. Residual ATZ, DEA, E2, EE2, NOR, CBZ, CAF and SMX (%) over time (days) in a 0.45 µm filtered urban river (surface water) measured over time at 4 °C (filled squares) and 21.5 °C (open squares), with an initial spiked concentration of 400 µg L^{-1}. Error bars represent relative standard deviation of duplicates measurements. Only degradation of E2 was considered significant, for which a theoretical pseudo first-order kinetic model is plotted (dashed line), using the calibrated constant presented in Table 5. Results of DCF are presented in the ESI to ease the graphical representation and due to poorer analytical precision (Figure S4).

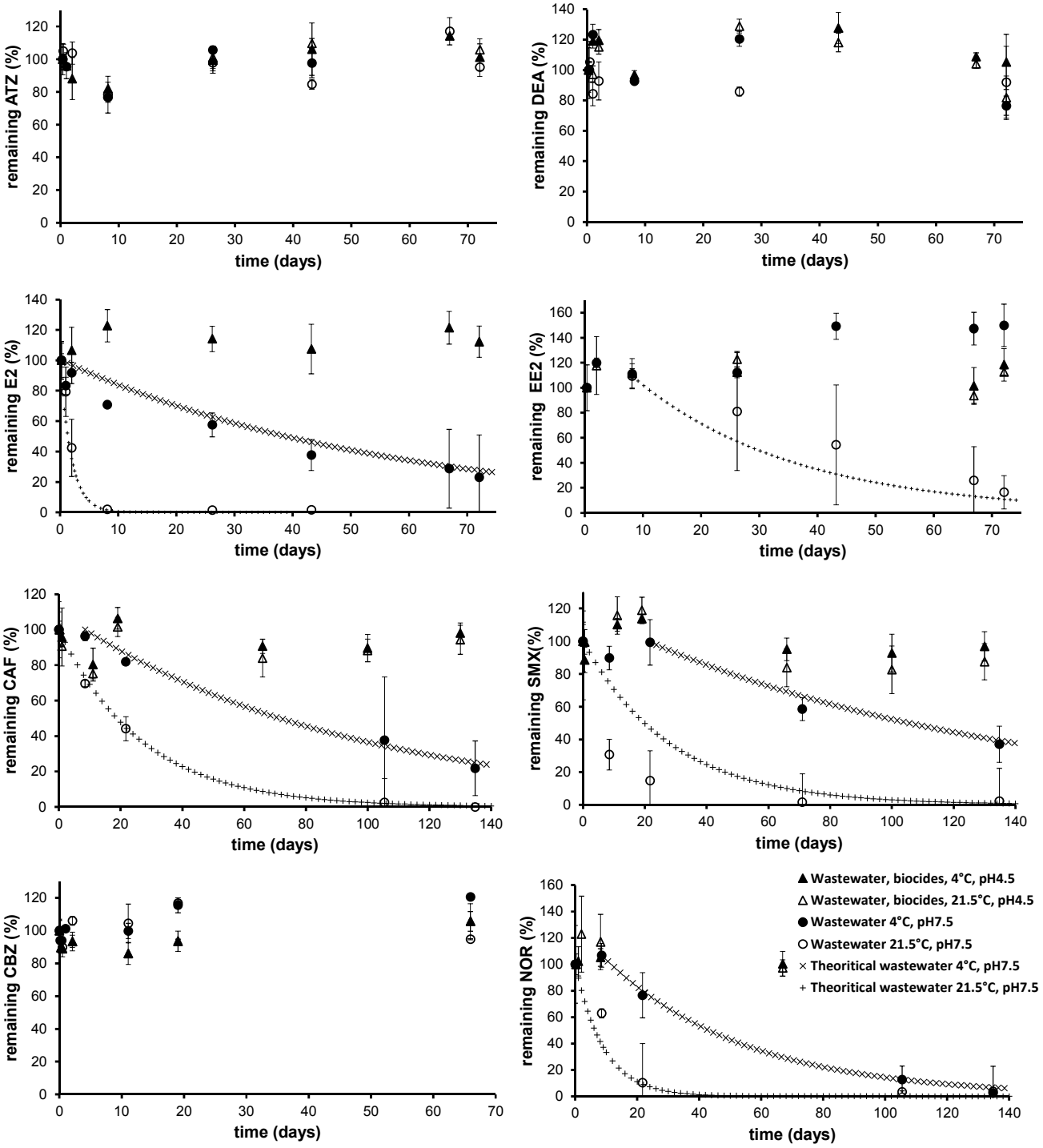


Figure 3. Residual ATZ, DEA, E2, EE2, NOR, CBZ, CAF and SMX (%) over time (days) in a raw wastewater (primary settling tank outlet) with an initial spiked concentration of 400 µg L^{-1} in the presence of biocides at pH 4.5 (triangles) and in raw wastewater at pH 7.5 (circles), measured over time at 4 °C (filled symbols) and 21.5 °C (open symbols). In cases where degradation was considered significant, a theoretical pseudo first-order kinetic model is plotted (dashed line), using the calibrated constant presented in Table 5. Error bars represent relative standard deviation of duplicates measurements. Results of DCF are presented in the ESI to ease the graphical representation and due to poorer analytical precision (Figure S4).

Persistent Compounds

Atrazine, desethylatrazine, carbamazepine and diclofenac were stable in all aqueous systems, with no significant decrease over 365 days (urban river waters) and 71 days (wastewaters) (**Table S7**, **Figures 2-3 and S7**). They are therefore considered persistent compounds.

Atrazine (ATZ) & desethylatrazine (DEA)

Our results suggest that the abiotic degradation of atrazine is either extremely slow or non-significant in natural aqueous

systems. These results correspond with reported literature where no loss of atrazine was measured in an autoclaved estuarine water after 128 days;[22] the same authors reported a hydrolysis half-life of 742 days in a water sample containing 5 mg L^{-1} of fulvic acid at pH=7. Hydrolysis of ATZ was also not considered significant in a sterile buffered water at pH=7 (**Table 1**).[32]

Results were similar for atrazine in the wastewaters with and without biocide (Table S7 and **Figure 3**) Its persistence in such dirty waters after 71 days leads us to conclude that typical microbial populations in PST outlet waters with an initial high number of bacteria (10^{10} L^{-1}) are not sufficient to induce disappearance at temperatures representing seasonal variations. With low aqueous photolysis values reported in natural conditions[22, 33] (Table S8) and physicochemical properties disfavouring sorption onto suspended particulates as can be seen in **Table 2,** we can fairly assume that atrazine will persist in similar aqueous systems. Among the compounds included in this study, atrazine is probably the most studied. However, only a few studies have reported degradation in aquatic environments, such as one study downstream from a sugar refinery (10 ppm sugar) that showed complete degrataion.[32] Short half-lives for ATZ have mainly been reported for sludge, sediments or soils (Table S8) which contain significantly higher local bacterial densities relative to the distribution observed in aqueous systems.[84] Extensive biodegradation studies have been done in pure bacterial cultures and bioreactors. Reported values vary largely, and range from partial to complete elimination in minutes, hours, days and weeks (Table S8).[85] Our results are comparable to a previous study[37] in aerobic synthetic river waters at pH=6.4 where biodegradation was not observed at an initial ATZ concentration of 500 µg L^{-1}. Nonetheless, the study[32] reporting a complete biodegradation of ATZ in an aerobic water located downstream from a sugar refinery (10 ppm sugar) suggests that biodegradation is highly dependent on the composition of the studied system (**Table 1**).

Desethylatrazine (DEA) is the main metabolite of ATZ from microbial degradation and is considered similarly toxic.[86] DEA behaved like its precursor ATZ in our studied system, in that it did not degrade (Table S7**, Figures 2-3**), which is comparable to previous studies that used different types of water and short test periods[38-40] (**Table 1**). The environmental fate of DEA in aqueous systems is poorly documented and sometimes contradictory. Some results have shown that it can sometimes be present in surface waters at concentrations above that of atrazine, as noted in the St-Lawrence River[19], which could mean that DEA is more persistent than ATZ in aqueous systems. This issue is under debate, as others suggested that ATZ is more persistent than DEA in environmental water samples.[87]

Carbamazepine (CBZ)

We observed little to no disappearance of CBZ in all water samples tested **(**Table S7**, Figures 2-3**), suggesting that both chemical and biological degradation are limited. CBZ's low capacity to degrade by photolysis[88] indicates that it can persist in surface waters of urban rivers and wastewater. Based on results of tests made to measure the capacity of the compound to biologically degrade in bioreactors and activated sludge processes, CBZ has been categorized as not readily biodegradable.[30] Since CBZ has a relatively low affinity for suspended particles (**Table 2**), its concentration in water could only be slightly decreased by sorption. Our results are consistent with previous studies, where neither hydrolysis nor biodegradation of CBZ was significant in an aquatic microcosm[45], in different types of wastewaters[47] and in oxic muddy waters (**Table 1**).[46] The hydrolysis half-life of CBZ was estimated to be more than a year in aqueous systems at 25ºC at pHs between 5 and 9.[48]

Diclofenac (DCF)

DCF did not show any signs of abiotic or biological degradation, neither in the controls nor in the studied water samples. This agrees with previous observations that DCF removal by biodegradation in a full-scale activated sludge plant is low[89] and that no degradation was observed in activated sludge over 28 days[2] as well as in sterile and raw liquid phases of wastewater sludge[52] (**Table 1**). Photo-degradation has been reported to be extremely effective on DCF with a reported disappearance to a concentration below 129 µg L^{-1} in pure water initially spiked at 1 mg L^{-1} after a few minutes of UV irradiation.[90] A 90% removal through natural irradiation was also observed in the surface water of a Swiss lake spiked at 100 ng L^{-1}.[54] The authors also reported that chemical and biological degradation should not be significant in such surface waters. . Thus, exposure to sunlight is likely the only way to assist the disappearance of DCF in surface waters or in any wastewater receiving natural or artificial UV light.

Our study highlights that ATZ, DEA, CBZ and DCF will persist as they transit through water systems that are isolated from sunlight.

Degradable compounds

Compound lag phases

The microbial adaptation period, i.e. the lag phase, corresponds to the time required for the bacteria to produce the specific degradation enzymes necessary for their growth and consumption of their surrounding medium. A lag phase is often observed in biodegradation experiments, because the aqueous systems tested needs to adapt to the disturbances caused by the addition of the tested chemicals. According to the OECD standardised method 309[57] used, a system is not considered viable in terms of active bacterium if the lag phase exceeds 60 days and no biodegradation is observed until 90 days, in which case the studied system has biologically depleted and a renewal is necessary to continue the studies.

16 out of the 18 observed degradation in raw wastewater were preceded by a lag phase (Table S7), varying from 0.5 to 71 days, showing that the studied raw wastewaters were biologically viable during all the duration of the biodegradation experiments. No lag phases exceeding 60 days were observed in the wastewater samples without biocide (confirming that the biocide was sufficient in inhibiting microbial activity, as expected[57]).

Not surprisingly, within the same systems for the degradable compounds, lag phases were shorter at higher temperatures. Bacterial growth is more efficient at 20°C than at 5°C.[91] It has been demonstrated that systems with lower nitrogen and phosphorus concentrations exhibit longer microbial adaptation to newly exposed chemicals,[92] which is an additional reason why lag times in the urban river samples may have been longer.

Waiting 48 hours after water collection to start the kinetic experiments may have also slowed bacterial growth, as the microorganisms would have been in an enzymatic sleeping mode, hence requiring more time to re-establish themselves.[91] Finally, spiking compounds at concentrations higher than environmentally pertinent concentrations could have also extended the adaptation period, as a larger portion of bacteria would need to be present to observably degrade the target compounds.[93]

Estradiol (E2), ethinylestradiol (EE2) and norethindrone (NOR)

The three tested hormones showed no significant disappearance in wastewater effluents treated with biocide (**Table 5, Figure 3**) at the temperatures tested for 72 days (E2 and EE2) and 66 days (NOR). No significant degradation in 0.45 µm filtered river surface waters was noted for E2 at 4°C for 72 days (Table S7**, Figure 2**) and NOR at both temperature tested for 156 days. These results tend to suggest that E2, EE2 and NOR are not readily amenable to abiotic degradation. However, significant degradation of E2 was noted in the same urban river water at ambient temperatures, contradicting our results of the control samples of wastewater effluents (with biocides) and previously reported values (**Table 1**).[34, 42, 44] This may be due to the reestablishment of bacteria in the surface water samples after 0.45 µm filtration. The results may hence be attributed to microbial degradation but should be interpreted carefully. In one previous study[43], a diminution of 38.9% of the initial E2 concentration (not given) in raw potable water was noted after 10 days, which suggests that E2 does not need a high number of microbial populations to be biodegraded (**Table 1**). Results in wastewaters were conclusive, with microorganisms being able to degrade these 3 compounds within less than two months (**Table 5, Figure 3**). The half-life of E2 averaged 40 days at 4°C and 1.2 days at 21.5°C, which was consistent with reported data[41] (**Table 1**). We observed that EE2 was more persistent under cold conditions since no degradation was noted at 4°C, while the half-lives of NOR averaged 20 days at 4°C and 7.2 days at ambient temperatures. Although no biodegradation data were previously reported in wastewater systems for EE2 (a synthetic hormone), it is known to be more persistent than E2 (a naturally-occurring hormone)[34] as observed here. No degradation data in aqueous systems was previously reported for NOR but its biodegradation was observed by Morissette in sludge of the same wastewater.[16]

Conclusions

In our experimental setup, the contaminants ATZ, DEA, CBZ & DCF were persistent. Hence, abiotic degradation is not expected to be significant for the losses observed for these compounds in typical surface river waters and in wastewater streams isolated from sunlight. The results also suggest that biodegradation was not significant for these 4 compounds in wastewaters. Unlike CBZ & DCF that have significant reported photolysis rates in aqueous systems,[2, 35, 56] the reported rates of photolysis of atrazine are extremely slow[32, 33] and it is most likely that only biologically rich aqueous systems could significantly degrade atrazine. No degradation was observed in control samples for EE2, NOR, CAF and SMX, suggesting that abiotic degradation (i.e. hydrolysis at the ambient pH and natural oxidation) is not significant. However, E2 showed important losses related to chemical processes in surface river water systems at 21ºC, contradicting previous studies. This may indicate that microbial contamination occurred throughout our time series, especially since it has been reported that biodegradation of E2 can occur in potable water, a system poor in bacterial population. Biological degradation occurred at different levels for E2, EE2, NOR, CAF and SMX in wastewaters with k ranging 0.0082-0.52 d^{-1} and half-lives of 1.3-85 days, E2 degrading the fastest at 21.5ºC and SMX the slowest under colder conditions (4ºC). The current results must still be interpreted carefully since half-lives and degradation rate constants are highly dependent on environmental conditions and because there are not enough reported degradation data of the studied compound in environmental aqueous systems. Further studies would be required to adequately characterize the degradation rates that could occur under field conditions for such compounds in real systems. Even if as many precautions as possible have been considered, bench-scale simulation tests never

Caffeine (CAF)

Caffeine was persistent in river waters after 365 days and in wastewater treated with biocide after 130 days (**Table 5** and **Figures 2-3**), suggesting that chemical processes are not expected to significantly contribute to the loss of CAF in environmental aqueous systems. These conclusions concur with a previous study that suggested that CAF can be used as an anthropogenic marker in surface waters because of its persistency in aqueous systems,[6] as that study measured no loss related to chemical processes in lake waters at 20°C. A previous study reported that typical concentrations of microorganisms in surface waters are not expected to be sufficient to induce rapid biodegradation (few hours or days) of caffeine, based on measurements in rivers up-stream and down-stream of 3 WWTPs at 23°C (**Table 1**).[50] However, significant losses were measured in the wastewater sample, with estimated biodegradation half-lives ranging from 12 days at 4°C to 7.9 days at 21.5°C. This suggests that microorganisms can degrade CAF when biological conditions are appropriate. A previous study that reported complete biodegradation values of CAF at 19 °C in 3 and 10 days in a WWTP's affluent and effluent respectively[49] support this observation (**Table 1**).

Sulfamethoxazole (SMX)

Results (**Table 5** and **Figures 2-3**) suggest that abiotic degradation does not contribute to the loss of SMX in aqueous systems, with no concentration decrease observed in urban river waters after 365 days and in wastewaters treated with biocides at 4°C and 21.5ºC after 130 days. These results match with previous studies where no hydrolysis was reported in typical aquatic microcosms[45], natural waters[36] and sediment slurries[36] (**Table 1**). Our results indicate that biodegradation contribution is important in wastewaters, with an average half-life of 85 days at 4ºC and 20 days at 21.5 °C (**Table 5, Figure 3**), which is consistent with the literature[36, 49, 51] (**Table 1**). It was elsewhere reported that >90% of SMX was degraded after ≈25 days in a WWTP equalization tank, which is a system richer in nutrients than our wastewater samples, while no degradation was noted in the WWTP effluent after 56 days, a system that is expected to be cleaner than our wastewaters.[49]

perfectly recreate environmental compartments because of the multitude of uncontrolled factors. Nonetheless, the data offer a general picture of the importance of degradation processes in urban and wastewater streams isolated from sunlight.

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† Electronic Supplementary Information (ESI) available: [The tables S1-S8 and figures S1-S4 mentioned above, as well as further explanations of the laboratory bench-scale experiments and the analytical method]. See DOI: 10.1039/b000000x/

‡ Room temperature for experiments in urban river waters

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