Priority organic pollutants in the urban water cycle (Toulouse, France)

Caroline Sablayrolles, Audrey Breton, Claire Vialle, Christian Vignoles, Mireille Vignoles-Montrejaud

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ABSTRACT

Application of the European Water Framework Directive requires Member States to have better understanding of the quality of surface waters in order to improve knowledge of priority pollutants. Xenobiotics in urban receiving waters are an emerging concern. This study proposes a screening campaign of nine molecular species of xenobiotics in a separated sewer system. Five sites were investigated over one year in Toulouse (France) using quantitative monitoring. For each sample, polycyclic aromatic hydrocarbons, polychlorinated biphenyls, nonylphenols, diethelhexylphthalate, linear alkylbenzene sulphonates, methyl *tert*-butylether, total hydrocarbons, estradiol and ethinylestradiol were analysed. Ground, rain and roof collected water concentrations are similar to treated wastewater levels. Run-off water was the most polluted of the five types investigated, discharged into the aquatic environment. The wastewater treatment plant reduced xenobiotic concentrations by 66% before discharge into the environment. Regarding environmental quality standards, observed concentrations in waters were in compliance with standards. The results show that xenobiotic concentrations are variable over time and space in all urban water compartments.

Key words | quantification, pollution, screening, stormwater, wastewater, xenobiotics

C. Sablayrolles (corresponding author)
M. Montréjaud-Vignoles
Université de Toulouse,
INP-ENSIACET,
LCA (Laboratoire de Chimie Agro-industrielle),
F-31030 Toulouse, France
and
INRA, UMR 1010 CAI,
F-31030 Toulouse, France
E-mail: *Caroline.Sablayrolles@ensiacet.fr*

A. Breton
C. Vialle
CATAR-CRITT Agroressources – CRT n°96/7,
LCA (Laboratoire de Chimie Agro-Industrielle),
UMR 1010 INRA/INPT, ENSIACET,
4 allée Emile Monso,
BP 44 362, 31030 Toulouse cedex 4, France

C. Vignoles
Veolia Eau, Direction Technique,
1, rue Giovanni Battista Pirelli,
94410 Saint Maurice, France

INTRODUCTION

The European Water Framework Directive (EC 2000) and its affiliated directives, whose aim is better ecological and environmental quality, requires Member States to improve their understanding of priority pollutants' behaviour in urban areas. A list of 41 priority substances was defined, including polycyclic aromatic hydrocarbons (PAHs), polychlorinated biphenyls (PCBs), nonylphenols (NPEOs), Diethylhexylphthalate (DEHP), linear alkylbenzene sulphonates (LAS), hydrocarbons (TH), hormones (estradiol (E2) and ethinylestradiol (EE2)). Environmental quality standards (EQS) have been set up in order to ensure chemical quality of surface waters.

Xenobiotics in the environment originate from anthropogenic activities, both domestic and industrial. They are transferred to the different compartments of the environment, atmosphere, soil, and surface waters at certain points or through various inputs.

The main sources of PAHs originate from pyrolysis of organic matter under high temperature (Moilleron *et al.* 2001). PCBs have been used extensively in many industrial applications, including in fire-resistant transformers and insulating condensors (Waid 1996). Due to inconvenient storages, industrial incidents or handling oversights, PCBs have contaminated the environment. Actually, urban surfaces can receive deposits of PAHs and PCBs from different sources such as car traffic, industries, waste incinerators, and domestic heating via both atmospheric transport and local activity (Cailleaud *et al.* 2007).

Methyl *tert*-butylether (MTBE) is a volatile organic compound produced from natural gas. It is commonly selected by petroleum refiners and distributors for the oxygenation of fuel to reduce carbon monoxide emissions. It is introduced to the environment by leaking petroleum storage tanks, urban runoff, and motorized watercraft (Achten *et al.* 2001).

doi: 10.2166/wst.2011.580

LAS are the most important synthetic anionic surface active agents widely used as the principal constituents of commercial detergents, institutional cleaning and other industrial purposes. LAS are significant environmental pollutants, as their bio-degradation involves the consumption of bio-available oxygen resulting in an increase in chemical oxygen demand. LAS are not only toxic, but also contribute to the permeation of other pollutants into aquatic animals (Sanderson *et al.* 2006).

DEHP is the main plasticizer used to impart flexibility to plastics, e.g., polyvinylchloride which is often used for coatings on roofing. Phthalates can also be used in paints and sealants (Gasperi *et al.* 2008). Nonylphenols are used in the production of ethoxylates and as additives in polymer processing. NPEOs are used as additives in lubricants, fuel and car care products such as washing and degreasing agents, polish and wax. Vehicles are believed to be important sources of phthalates and NPEOs in urban stormwater (Peters *et al.* 2008). Other human activities in urban areas include diffuse sources such as shoe and textile wear, toys, paper and packaging, strollers and bicycles which may lead to emissions of phthalates and NPEOs.

Monitoring of priority substances is needed because data concerning concentrations found in urban receiving waters is scarce and knowledge of the quality of the receiving aquatic systems is important (Table 1). The case of Toulouse in France is particularly interesting since the town has a separated sewer system where organic

Table 1 | Reported concentrations of organic pollutants in waters

				Concentrations				
Xenobiotics	**Water type**	***n***	**Origin**	**Min.**	**Max.**	**Mean**	**Median**	**References**
PolyChlorinated biphenyls (µg L^{-1})								
PCBs (Σ12)	Raw wastewater	–	France	0.380	1.300	0.650	–	(Chevreuil *et al.* 1990)
	Treated wastewater	–		0.150	0.390	0.280	–	
PCBs (Σ7)	Raw wastewater	20	Greece	0.470	1.800	1.000	1.000	(Katsoyiannis & Samara 2004)
	Treated wastewater	20		0.130	0.390	0.250	0.250	
PCBs (Σ7)	Raw wastewater	5	France	0.020	0.036	0.029	0.031	(Blanchard *et al.* 2001)
PCBs (Σ85)	Rainwater	9	USA	$2 \cdot 10^{-2}$	0.189	–	–	(Offenberg & Baker 1997)
PCBs (Σ65)	Rainwater	5	USA	$8.5 \cdot 10^{-3}$	0.020	–	–	(Poster & Baker 1996)
PCBs (Σ7)	Ground water	49	Sweden	–	–	0.850	–	(Bremle *et al.* 1997)
PCBs (Σ2)	Roof collected water	30	Poland	0.020	2.680	0.427	–	(Tsakovski *et al.* 2009)
PCBs (Σ12)	Run-off water	89	Switzerland	$0.11 \cdot 10^{-3}$	0.403	–	–	(Rossi *et al.* 2004)
Polycyclic aromatic hydrocarbons (µg L^{-1})								
PAHs (Σ16)	Rainwater	10	Spain	–	–	0.103	–	(Olivella *et al.* 2006)
PAHs (–)	Run-off water	35	France	0.011	0.474	0.096	0.074	(Legret & Pagotto 1999)
PAHs (Σ14)	Run-off water	33	France	–	–	0.149	0.063	(Moteley-Massei *et al.* 2006)
PAHs (–)	Ground water	4	Norway	90,000	300,000	170,000	–	(Saether *et al.* 1997)
PAHs (Σ6)	Roof collected water	30	Poland	7.10^{-3}	0.875	0.200	–	(Tsakovski *et al.* 2009)
PAHs (Σ16)	Raw wastewater	4	France	1.277	3.240	1.998	1.737	(Blanchard *et al.* 2001)
PAHs (Σ16)	Raw wastewater (rainy weather)	10	France	0.03	0.34	–	0.11	(Gasperi *et al.* 2008)

(*continued*)

Table 1 | continued

Xenobiotics	Water type	*n*	Origin	Concentrations Min.	Max.	Mean	Median	References
	Raw wastewater (dry weather)	13		0.07	3.07	–	0.67	
PAHs (Σ16)	Raw wastewater	–	Finland	<0.05	3.4	–	–	(Marttinen *et al.* 2003)
	Treated wastewater	–		<0.05	0.12	–	–	
PAHs (Σ21)	Raw wastewater	10	Canada	–	–	1.55	–	(Pham & Proulx 1997)
	Treated wastewater	6		–	–	0.42	–	
PAHs (Σ15)	Ground water	1	Germany	–	–	$9.4 \cdot 10^{-3}$	–	(Popp *et al.* 2001)
	Rainwater	1		–	–	0.07	–	
PAHs (Σ14)	Rainwater	28	Macedonia	0.143	1.397	0.575	–	(Manoli *et al.* 2000)
PAHs (Σ12)	Rainwater	38	Hungary	0.156	1.993	0.571	–	(Kiss *et al.* 2001)
PAHs (Σ15)	Rainwater	6	France	0.031	0.105	0.060	0.061	(Bourdat-Deschamps *et al.* 2007)
Diethylhexylphthalate (μg L^{-1})								
DEHP	Ground water	17	China	0.570	1.1	–	–	(Zhang *et al.* 2009)
DEHP	Raw wastewater	–	Denmark	53.23	84.10	71.89	–	(Roslev *et al.* 2007)
	Treated wastewater	–		2.08	9.93	4.95	–	
DEHP	Raw wastewater	7	France	9	44	22.46	–	(Dargnat *et al.* 2009)
	Treated wastewater			3.4	7.5	5.02	–	
DEHP	Raw wastewater (rainy weather)	10	France	16	57	–	27	(Gasperi *et al.* 2008)
	Raw wastewater (dry weather)	13		5	188	–	22	
DEHP	Rainwater	6	France	–	–	0.42	–	(Teil *et al.* 2006)
DEHP	Rainwater	50	Netherlands	–	30.9	–	–	(Peters *et al.* 2008)
Nonylphenols ethoxylates (μg L^{-1})								
NP	Ground water	8	Denmark	–	4.2	0.6	–	(Juhler & Felding 2003)
NP	Raw wastewater	7	Switzerland	0.07	1.24	–	0.47	(Jonkers *et al.* 2009)
	Treated wastewater	14		0.003	0.28	–	0.12	
NP	Raw wastewater	3	Greece	0.05	0.46	–	–	(Gatidou *et al.* 2007)
NP_1EO				0.75	2.63	–	–	
NP_2EO				0.68	0.68	–	–	
NP	Roof collected water	2	Germany	0.078	0.123	–	–	(Fries & Püttmann 2004)
	Rainwater	6		0.03	0.950			
NP	Rainwater	17	Netherlands	–	0.26	0.04	–	(Peters *et al.* 2008)
NPEO		47		–	0.92	0.09	–	
Total hydrocarbons (mg L^{-1})								
TH	Run-off water	56	France	0.1	4.9	2.3	–	(Daligault *et al.* 1999)
TH	Run-off water	44	France	0.14	4.2	1.2	0.86	(Legret & Pagotto 1999)
TH	Run-off water	–	Europe	0.04	25.9	1.9	–	(Barraud *et al.* 2006)

(*continued*)

Table 1 | continued

Xenobiotics	Water type	*n*	Origin	Concentrations				References
				Min.	Max.	Mean	Median	
TH	Roof collected water	7	France	0.037	0.823	0.108	–	(Grommaire-Mertz *et al.* 1999)
TH	Groundwater	3	Norway	67	110	93	–	(Saether *et al.* 1997)
Linear alkylbenzene sulfonates (μg L^{-1})								
LAS (Σ C_{10}–C_{13})	Raw wastewater	24	–	3,400	10,700	6,329	5,850	(Crescenzi *et al.* 1996)
	Treated wastewater	24		21	290	68	56	
LAS (Σ C_{10}–C_{13})	Groundwater	5	Thailand	<1.6	7.5	–	–	(Kruawal *et al.* 2005)
LAS (Σ C_{10}–C_{13})	River water downstream a WWTP	8	UK	5	416	147	106	(Fox *et al.* 2000)
LAS (Σ C_{10}–C_{13})	Raw wastewater	16	Spain	104	1,920	837	–	(Gonzalez *et al.* 2004)
	Treated wastewater	16		11	595	90	–	
LAS (Σ C_{10}–C_{14})	Raw wastewater	3	USA	2,749	3,955	3,257	3,067	(Sanderson *et al.* 2006)
	Treated wastewater	3		1.331	2.910	2.061	1.943	
MTBE (μg L^{-1})								
MTBE	Rainwater	35	Germany	<0.010	0.085	0.032	0.024	(Achten *et al.* 2001)
	Run-off water	12		0.030	1.174	0.204	0.114	
	Raw wastewater	15		–	–	0.384	0.299	
	Treated wastewater	15		–	–	0.265	0.078	
MTBE	Ground water	66	Japan	0.003	5.9	0.35	–	(Tanabe *et al.* 2005)
	Raw wastewater	24		0.003	0.025	–	–	
	Treated wastewater	24		0.003	0.015	–	–	
MTBE	Ground water	1	Denmark	–	–	1.4	–	(Juhler & Felding 2003)
MTBE	Raw wastewater	–	Germany	–	0.18	–	–	(Rosell *et al.* 2006)
	Treated wastewater	–		–	0.17	–	–	
	Raw wastewater	–	Austria	–	121	–	–	
	Treated wastewater	–		–	5.6	–	–	
	Raw wastewater	–	Belgium	–	0.11	–	–	
	Treated wastewater	–		–	0.08	–	–	
Estradiol and ethynilestradiol (ng L^{-1})								
E2	Raw wastewater	6	Germany	–	–	15	–	(Ternes *et al.* 1999)
E2	Treated wastewater	16		–	–	1	–	
EE2	Treated wastewater	16		–	–	6	–	
E2	Raw wastewater	6	France	11.1	17.4	–	–	(Cargouët *et al.* 2004)
EE2	Raw wastewater	6		4.9	7.1	–	–	
E2	Treated wastewater	6		4.5	8.6	–	–	
EE2	Treated wastewater	6		2.7	4.5	–	–	
E2	Treated wastewater	6	Netherlands	<0.6	12	–	–	(Belfroid *et al.* 1999)
EE2	Treated wastewater	6		<0.2	7.5	–	–	

compounds in the wastewater system cannot mix with the stormwater. Thus, the aim of this screening campaign is (1) to investigate the removal of xenobiotics in the wastewater treatment plant, (2) to characterise the composition of different types of stormwaters, in order to establish the level of pollution in the Toulouse (France) urban catchment area.

MATERIALS AND METHODS

Sampling sites

Five sites were investigated in Toulouse in order to evaluate xenobiotics contamination. Figure 1 shows the locations of the sampling sites.

A main outlet fed from an urbanised catchment area of 439 hectares (impermeable coefficient: 0.7), was selected in order to evaluate run-off water quality. The address of the site was 'allée du Niger 31000 Toulouse, France' and GPS coordinates were (43.60; 1.43).

Groundwater was collected in the ground under an urban road. The address of the site was 'chemin de Ramelet-Moundi 31300 Toulouse France' and GPS coordinates were (43.58; 1.38).

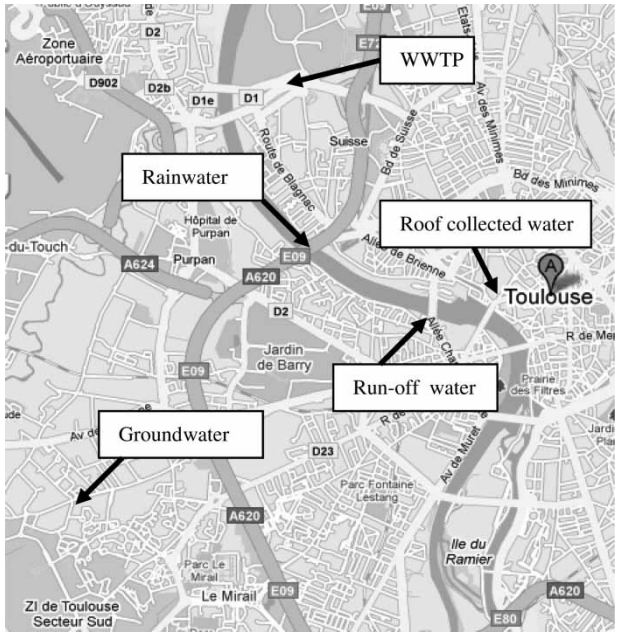

Figure 1 | Location of sampling sites.

Rainwater was collected in a zone free from any overhanging interference. The address of the site was 'rue Marcou Debax 31200 Toulouse France' and GPS coordinates were (43.61; 1.41).

Roof collected water was taken from buildings in the town centre ('34 rue Pargaminière 31000 Toulouse, France' (43.60; 1.44)). The cover of the roof consists of tile. This site was chosen because it is representative of a roof in a strongly urbanized zone.

The Toulouse wastewater treatment plant (WWTP) was also investigated. The town is equipped with a separated sewer system. Thus, wastewater and stormwater cannot mix together. The WWTP treats about 125,000 $m^3\ d^{-1}$ of wastewater and discharges its effluent into the River Garonne. It is composed of a pre-treatment grid, sand trap and degreaser plus three treatment units: G1 (400,000 EH), G2 (150,000 EH), G3 (250,000 EH), followed by a nitrification unit G4 (800,000 EH) which treats all water from G1, G2 and G3, before discharging it into the River Garonne. In this study, wastewater entering unit G1 (biological treatment using activated sludge) and treated wastewaters (after unit G4) were investigated. The address of the site was 'chemin de Ginestous 31200 Toulouse France' and GPS coordinates were (43.64; 1.41).

Sampling methods

Samples were collected from December 2006 to November 2009. Sampling dates and rain intensity is presented in Table 2.

For run-off water, an automatic sampler (ISCO 3700, Neotek) was used to sample ten events over 24 h; samples were collected between December 2006 and 2007.

For groundwater, samples were taken in dry weather in order to limit road scrubbing and were made in a sealed manhole chamber. Five samples were collected between November 2008 and 2009.

For rainwater, basins in high density polyethylene (l × w × h: 475 × 325 × 75 mm) were distributed on the ground in order to cover a large area. To be able to collect enough water for analyses, 40 basins were arranged on the ground which, with 3 mm of rain, represents taking a volume of 18 L of water. Collected waters were poured into a bin and homogenized in order to get a representative

Table 2 | Sampling dates and precipitation (in mm of rain)

	Number of samplings	Spring	Summer	Autumn	Winter
Raw wastewater	8	28/03/08 (3 mm)	20/06/08 (0 mm)	29/10/08 (0 mm)	21/01/09 (3 mm)
		20/03/09 (0 mm)	11/09/08 (4 mm)	25/11/08 (5 mm)	18/02/09 (0 mm)
Treated wastewater	8	28/03/08 (3 mm)	20/06/08 (0 mm)	29/10/08 (0 mm)	21/01/09 (3 mm)
		20/03/09 (0 mm)	11/09/08 (4 mm)	25/11/08 (5 mm)	18/02/09 (0 mm)
Rainwater	4	09/05/09 (5 mm)	20/09/09 (12 mm)	05/11/08 (9 mm)	23/01/09 (4 mm)
Roof collected water	4	9/04/09 (5 mm)	8/10/09 (12 mm)	24/11/08 (7 mm)	03/11/09 (7 mm)
Ground water	4	25/05/09 (7 mm)	02/07/09 (6 mm)	01/10/09 (5 mm)	16/02/09 (4 mm)
Run-off water	10	04/05/07 (0 mm)	12/07/07 (1 mm)	11/10/07 (12 mm)	02/02/07 (0 mm)
		07/02/07 (2 mm)	19/09/07 (2 mm)	23/10/07 (0 mm)	07/02/07 (2 mm)
				03/12/07 (3 mm)	26/02/07 (6 mm)

sample. Five samples were collected between November 2008 and 2009.

For roof collected water, samples were taken from the gutter down pipe. Each time, around 15 L of water was collected and then homogenized in order to obtain a representative sample. Five samples were collected between November 2008 and 2009.

For wastewater and treated wastewater, two automatic samplers (ASP 2000, Endress+Hauser) were used to sample four dry events and four rainy events over 24 h. Sampling was carried out between March 2008 and 2009.

Amber glass bottles of 1 L were filled with samples and stored at $-25\,^{\circ}C$ prior to analysis.

Analysis

The 16 priority polycyclic aromatic hydrocarbons (PAHs) of the Environmental Protection Agency were monitored. Analytical development was presented in Foan *et al.* (2010). PAHs were analysed using liquid-liquid extraction and a high performance liquid chromatograph and a fluorescence detector (Dionex, France); limit of quantification (LOQ) for individual PAHs was 0.01 µg L^{-1}.

Seven polyChlorinated biphenyls (PCBs) congeners (from three to seven chlorines), IUPAC numbers 28, 52, 101, 118, 138, 153, 180, were monitored. PCBs extraction was carried out using liquid-liquid extraction. The analysis was performed by gas chromatography coupled with mass spectrometry with a quadrupole type analyzer. Limit of quantification for individual PCBs was 0.05 µg L^{-1}.

MTBE was analysed using gas chromatography-mass spectrometry after head-space extraction with a limit of quantification of 1 µg/L.

Total hydrocorbons (TH) were analysed using liquid-liquid extraction with oil ether and a gas chromatograph equipped with a flame ionization detector. Limit of quantification was 0.10 mg L^{-1}.

LAS studied were the sum of C_{10}-LAS to C_{13}-LAS. After a solid phase extraction, chromatographic analysis was preformed on a high performance liquid chromatography and ultraviolet diode array (Dionex, France) at 224 nm. Limit of quantification for the sum of C10–C13 was 0.01 µg L^{-1}. The detailed protocol can be found in Breton *et al.* (2010).

DEHP was analysed using liquid-liquid extraction followed by a gas chromatography-mass spectrometry detector with a quadruple type analyzer (Thermo, France). Limit of quantification was 0.5 µg L^{-1}. The detailed protocol was published in Sablayrolles *et al.* (2005).

NP1EO were analysed using a gas chromatography-mass spectrometry detector (Thermo, France). Limit of quantification was 0.5 µg L^{-1}.

E2 and EE2 were analysed using solid phase extraction and liquid chromatography coupled to a tandem mass spectrometry detector. Limit of quantification for the two hormones was 5 ng L^{-1}.

Analytical protocol of the nine molecular species of xenobiotics investigated is presented in Table 3.

Table 3 | Analytical methods for xenobiotics

Xenobiotics	Standard	Extraction	Analysis	Column	Gradient	Quantification	LOQ
PAHs (16 individuals)	NF EN ISO 17993	Liquid – Liquid with *n*-hexane Lichrosolv (VWR, France)	HPLC – FLD (Dionex RF2000, France)	LC-PAH Supelcosil column (Supelco, France)	Flow rate = 1.5 mL min^{-1} Water/ acetonitrile elution gradient	Internal standards : anthracene d10, benzo*(a)*pyrene d12	0.01 µg L^{-1}
PCBs (7 individuals)	NF EN ISO 6468	Liquid – Liquid with *n*-hexane Suprasolv (VWR, France)	GC-MS (Thermo Trace 2000, France) Splitless injection (250 °C)	RTX-5MS column (Restek, France)	Flow rate = 1.2 mL min^{-1} Temperature program: 60 °C (2 min) to 230 °C (at 16 °C min^{-1}) to 282 °C (at 5 °C min^{-1}) − 1 min	SIM mode Internal standard : Tetrachlorometaxylene	0.05 µg L^{-1}
LAS (sum of C10-C13)	–	RP18 SPE – methanol elution + SAX SPE – hydrochloric acid/methanol (20/80; v/v) elution	HPLC – UV at 224 nm (Dionex, France)	Lichrospher 100 RP-18 column (VWR Merck, France)	Flow rate = 1.5 mL min^{-1} Water/ acetonitrile/ ammonium acetate elution gradient	Internal standard : C_8−LAS	0.01 µg L^{-1}.
DEHP	NF EN ISO 10301-3	Liquid – Liquid with *n*-hexane Suprasolv (VWR, France)	GC – MS (Thermo Trace 2000, France) Splitless mode (280 °C)	RTX-5MS column (Restek, France)	Flow rate = 1.2 mL min^{-1} Temperature program: 50 °C (1 min) to 310 °C (at 20 °C/min) 6 min	SIM mode internal standard : DEHP-d4	0.5 µg L^{-1}
NP1EO	–	RP18 SPE – methanol elution	GC – MS (Thermo Trace 2000, France) Splitless mode (250 °C)	RTX-5MS column (Restek, France)	Flow rate = 1.2 mL min^{-1} Temperature program: 50 °C (1 min) to 320 °C (at 20 °C/min) 5 min	SIM mode internal standard : 4-ter octylphenol	0.5 µg L^{-1}
MTBE	NF EN ISO 10301	Head-space	GC – MS (Thermo Trace 2000, France)	DB-VRX column (Agilent, France)	Flow rate = 1.2mL min^{-1} Temperature program: 35 °C (13 min) to 185 °C (at 13 °C/min) − 13 min to 255 °C (at 15 °C/ min) 10 min	Full SCAN mode Internal standard: MTBE-d_3	1.0 µg L^{-1}
TH	NF EN ISO 9377-2	Liquid-Liquid with oil ether (VWR, France)	GC – FID (Dani, France)			External calibration: C10–C40 solution	0.1 mg L^{-1}
E2/EE2	–	LiChrolut RP-18 cartridges SPE with methanol	LC – MS – MS (APPI 2000, Applied)	LiChrospher 100-RP18 column (VWR, France)	Flow rate = 1.5 mL min^{-1} Water/acetonitrile elution gradient	SIM mode	5 ng L^{-1}

Multivariate data analysis

The multivariate data analysis simulation was performed using the commercial software XL stat. The objectives of principal component analysis (PCA) are to find and interpret hidden complex and casually determined relationships between datasets. The key idea is to study the data structure in a reduced dimension while retaining the maximum amount of variability present in the data. A matrix of pairwise correlations among compound concentrations is decomposed into eigenvectors, which, are sorted in descending order of their corresponding eigenvalues. In this work, the variables were standardized in order to ensure that they have equal weights in the analysis (mean is equal to zero and the standard deviation is equal to the unit). Then, the calculation of the covariance matrix by identifying the eigenvalues and their corresponding eigenvectors was carried out.

RESULTS

Minimum, maximum, mean, median and standard deviation (SD) values of xenobiotic concentrations were calculated from the samples for each parameter (Table 4).

TH, MTBE and PAHs levels were quite low: compounds were either not quantified or only for one sampling site. All NP1EO samples were under the limit of quantification. PAH and TH values higher than those found in this study (0.011 to 0.474 µg L^{-1} and 0.14 to 4.2 mg L^{-1}) have already been reported for run-off water in France (Legret & Pagotto 1999). Observed values for MTBE were close to reported values (0.03 to 1.2 µg L^{-1}) for run-off water in Germany (Achten *et al.* 2001). PCB levels were close to those reported for river water (0.02 to 0.99 µg L^{-1}; Rossi *et al.* 2004) and for run-off water (0.0001 to 0.403 µg L^{-1}; Chevreuil *et al.* 1990). LAS levels were higher than literature values for estuary water (25.1 to 64.4 µg L^{-1}; Lara-Martin *et al.* 2006).

Concerning ground, rain and roof collected water samples, PCBs and MTBE were under the limit of quantification. Observed values for PAHs and TH in ground water samples were low compared with reported values for ground water in Norway (PAHs: 90 to 300 µg L^{-1}; TH:67 to 110 mg L^{-1}; Saether *et al.* 1997). A ground water study in Thailand reported values between <1.6 to 7.5 µg L^{-1} for the sum of LAS (Kruawal *et al.* 2005), and these values were higher than those observed in this study. Observed values for TH in roof collected water were lower than literature values for France (0.03 to 0.82 mg L^{-1}; Grommaire-Mertz *et al.* 1999). Mean concentrations of DEHP in rainwater samples were close to the mean value found for French rainwater (0.42 µg L^{-1}; Teil *et al.* 2006). Estradiol and ethinylestradiol were not detected in any samples.

Concerning the wastewater treatment plant, sampling was performed during raining and dry days. It was observed that the difference between rainy and dry events was not significant. This demonstrates the effectiveness of the separated sewer system. MTBE was not quantified for all samples. PCB levels in wastewater were higher than literature values for French wastewater (0.02 to 0.036 µg L^{-1}; Blanchard *et al.* 2001). Observed values for PAHs in wastewater were lower than values found in French wastewater (1.28 to 3.24 µg L^{-1}; Blanchard *et al.* 2001). A Spanish study reported LAS and NP1EO mean concentrations for wastewater (LAS: 837 µg L^{-1}; NP1EO: 18 µg L^{-1}) and treated wastewater (LAS: 590 µg L^{-1}; NP1EO: 4.4 µg L^{-1}) higher than those observed here (Gonzalez *et al.* 2004). Observed concentrations in DEHP for the two water samples were lower than mean values found in French wastewater (22.5 µg L^{-1}) and treated wastewater (5.0 µg L^{-1}) (Dargnat *et al.* 2009). Observed values for E2 and EE2 in wastewater were higher than values reported by a study in France (E2: 11.1 to 17.4 ng L^{-1}; EE2: 4.9 to 7.1 ng L^{-1}; Cargouët *et al.* 2004). In treated wastewater, levels of PCBs and of the two hormones were under the limit of quantification.

It is interesting to note that a large amount of data were lower than the limit of quantification while analytical methods performance were consistent with xenobiotics levels observed in waters.

DISCUSSION

Comparison of the different types of water studied

Run-off, rain, ground and roof collected water and treated wastewater levels of xenobiotics were compared. Only the parameters detected in the majority of samples are represented in Figure 2.

Table 4 | Statistical data for xenobiotic levels in run-off, groundwater, rainwater, roof collected waters, raw wastewaters and treated wastewaters

	Units	n	Min.	Max.	Mean	Median	SD
Run-off water							
Σ PAHs (16)	µg/L	10	<LOQ	0.067	<LOQ	<LOQ	–
Σ PCBs (7)	µg/L	10	0.06	0.51	0.28	0.30	0.18
Σ LAS (4)	µg/L	10	43	590	252	87	246
MTBE	µg/L	10	<LOQ	1.9	<LOQ	<LOQ	0.6
DEHP	µg/L	10	1.3	17	11	13	5
NP1EO	µg/L	10	<LOQ	<LOQ	<LOQ	<LOQ	–
TH	mg/L	10	<LOQ	1.5	0.2	0.0	0.5
Ground water							
Σ PAHs (16)	µg/L	4	<LOQ	0.035	0.012	<LOQ	0.020
Σ PCBs (7)	µg/L	4	<LOQ	<LOQ	<LOQ	<LOQ	–
Σ LAS (4)	µg/L	4	0.01	0.03	0.02	0.01	0.01
MTBE	µg/L	4	<LOQ	<LOQ	<LOQ	<LOQ	–
DEHP	µg/L	4	<LOQ	<LOQ	<LOQ	<LOQ	–
NP1EO	µg/L	4	<LOQ	<LOQ	<LOQ	<LOQ	–
TH	mg/L	4	<LOQ	0.23	0.14	0.14	0.13
E2	µg/L	4	<LOQ	<LOQ	<LOQ	<LOQ	–
EE2	µg/L	4	<LOQ	<LOQ	<LOQ	<LOQ	–
Rainwater							
Σ PAHs (16)	µg/L	4	<LOQ	<LOQ	<LOQ	<LOQ	–
Σ PCBs (7)	µg/L	4	<LOQ	<LOQ	<LOQ	<LOQ	–
Σ LAS (4)	µg/L	4	0.03	0.21	0.09	0.06	0.08
MTBE	µg/L	4	<LOQ	<LOQ	<LOQ	<LOQ	–
DEHP	µg/L	4	<LOQ	1.0	0.5	0.5	0.5
NP1EO	µg/L	4	<LOQ	<LOQ	<LOQ	<LOQ	–
TH	mg/L	4	<LOQ	4.0	1.1	0.2	1.9
E2	µg/L	4	<LOQ	<LOQ	<LOQ	<LOQ	–
EE2	µg/L	4	<LOQ	<LOQ	<LOQ	<LOQ	–
Roof collected water							
Σ PAHs (16)	µg/L	4	<LOQ	0.10	0.03	0.01	0.05
Σ PCBs (7)	µg/L	4	<LOQ	<LOQ	<LOQ	<LOQ	–
Σ LAS (4)	µg/L	4	0.02	0.09	0.04	0.03	0.03
MTBE	µg/L	4	<LOQ	<LOQ	<LOQ	<LOQ	–
DEHP	µg/L	4	<LOQ	1.10	0.28	<LOQ	0.55
NP1EO	µg/L	4	<LOQ	<LOQ	<LOQ	<LOQ	–
TH	mg/L	4	<LOQ	0.11	<LOQ	<LOQ	–
E2	µg/L	4	<LOQ	<LOQ	<LOQ	<LOQ	–
EE2	µg/L	4	<LOQ	<LOQ	<LOQ	<LOQ	–

(*continued*)

Table 4 | continued

	Units	n	Min.	Max.	Mean	Median	SD
Raw wastewater							
Σ PAHs (16)	µg/L	8	<LOQ	0.169	0.061	0.043	0.064
Σ PCBs (7)	µg/L	8	<LOQ	0.30	0.06	0.05	0.11
Σ LAS (4)	µg/L	8	2.7	6.8	3.8	3.4	1.4
MTBE	µg/L	8	<LOQ	<LOQ	<LOQ	<LOQ	–
DEHP	µg/L	8	<LOQ	11.0	7.9	9.5	4.1
NP1EO	µg/L	8	2.8	34.0	11.1	8.5	9.9
TH	mg/L	8	<LOQ	0.57	0.14	0.1	0.20
E2	µg/L	8	<LOQ	0.45	0.03	0.04	0.02
EE2	µg/L	8	<LOQ	0.011	<LOQ	<LOQ	–
Treated wastewater							
Σ PAHs (16)	µg/L	8	<LOQ	0.035	0.012	<LOQ	0.016
Σ PCBs (7)	µg/L	8	<LOQ	<LOQ	<LOQ	<LOQ	–
Σ LAS (4)	µg/L	8	0.08	0.14	0.11	0.11	0.02
MTBE	µg/L	8	<LOQ	<LOQ	<LOQ	<LOQ	–
DEHP	µg/L	8	<LOQ	1.5	<LOQ	<LOQ	0.5
NP1EO	µg/L	8	<LOQ	0.3	<LOQ	<LOQ	0.1
TH	mg/L	8	<LOQ	0.13	<LOQ	<LOQ	–
E2	µg/L	8	<LOQ	<LOQ	<LOQ	<LOQ	–
EE2	µg/L	8	<LOQ	<LOQ	<LOQ	<LOQ	–

As can be seen in Figure 2, quality of treated wastewater was equivalent to quality of roof-collected, rain and ground water for PAHs, DEHP, LAS and TH. Roof-collected water has a high concentration in PAHs compared to other waters, and one sample, taken after a long period of dry weather, was responsible for this. The roof studied must accumulate pollutants in dry weather. Run-off waters were the most polluted of the five waters investigated. The level of LAS in run-off water can be explained by wastewater discharged from carwashes into the stormwater network. Treated wastewater was less polluted than run-off water for these parameters.

Wastewater treatment plant (WWTP) – correlation study

For the WWTP, the results show no significant differences between sampling during dry or rainy events. All samples can be considered as representative WWTP sampling. Minimum, maximum, mean, median and standard deviation (SD) values were calculated from the eight samples for each parameter for the wastewater and treated wastewater (Table 5). Values less than the quantification limit were taken as LOQ and LOQ/2 for statistical calculations. Then, the removal percentage for each parameter was also calculated (Equation (1)).

The removal percentage (%) calculation (with $Ce_i =$ wastewater concentration at the date i and $Cs_i =$ treated wastewater concentration at the date i) is:

$$\text{Removal percentage} = \frac{\sum_{i=1}^{n}[((Ce_i - Cs_i)/Ce_i) \times 100]}{n} \quad (1)$$

The WWTP removal percentage was equal or greater than 85% for each parameter except for PAHs. Moreover, it is clear that the influence of LOQ assumption for statistical calculation was not very important. The treatment was efficient for removal of xenobiotics from water before discharge into the River Garonne.

In order to compare the quality of water samples over a year, PCA was carried out. It was performed on the nine

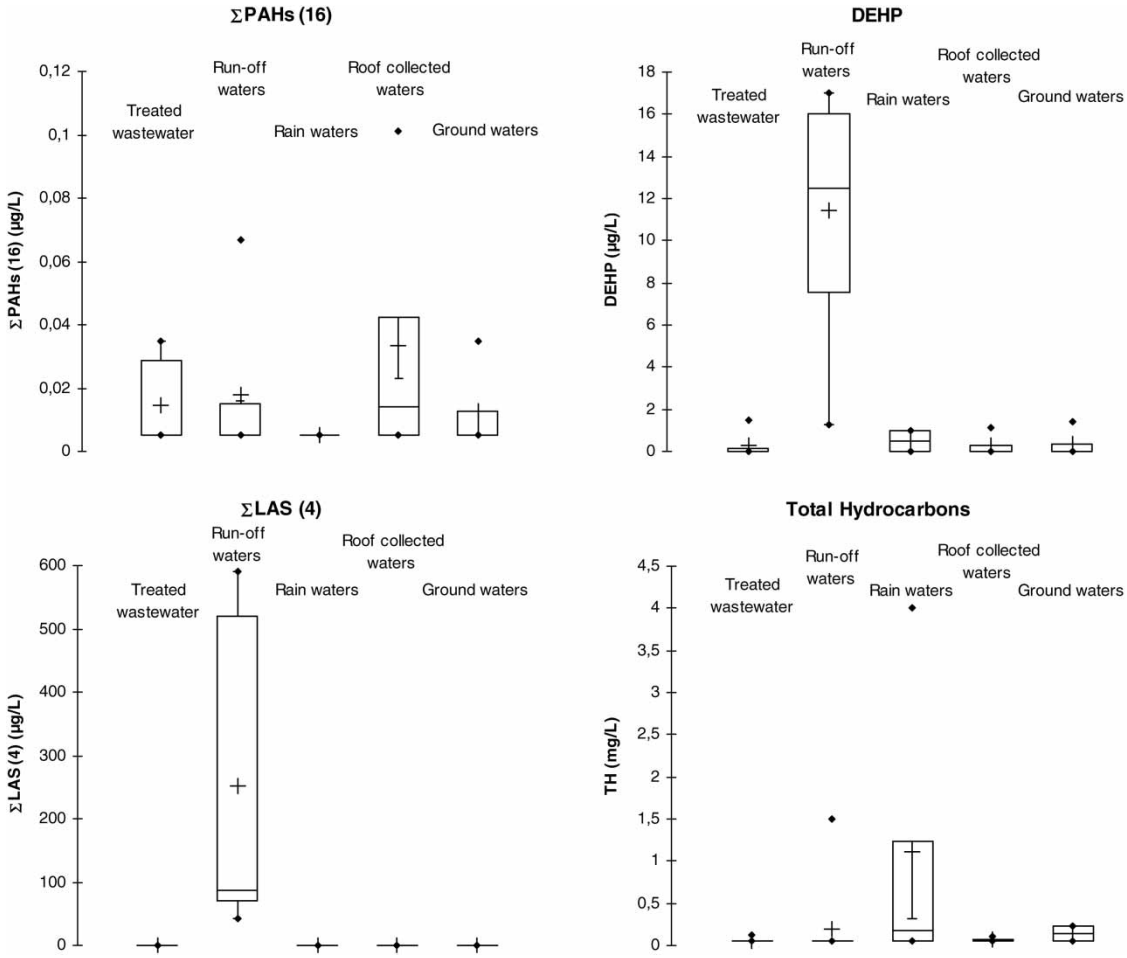

Figure 2 | Box plots of PAHs, DEHP, LAS and TH concentrations by sampling site, noting the minimum and maximum values, the median (—) and the mean (+).

Table 5 | Removal percentage of xenobiotic between wastewaters and treated wastewater

	Units	n	Removal percentage (with ' < LOQ' ' = LOQ')	Removal percentage (with ' < LOQ' ' = LOQ/2')
Σ PAHs (16)	%	8	64	66
Σ PCBs (7)	%	8	90	86
Σ LAS (4)	%	8	97	97
MTBE	%	8	–	–
DEHP	%	8	93	96
NP1EO	%	8	98	98
TH	%	8	85	92
E2	%	8	90	95
EE2	%	8	86	93

species of xenobiotics which were the 'variables' and for each sampling date, the 'individuals'. PCA identified three factors (F1, variance explained = 53.84%, F2 variance explained = 20.09%, F3 variance explained = 11.98%) that explained 85.92% of the variance of the original data set. PCA reveals that the quality of treated wastewater was the same for all the samplings while water entering the WWTP was of variable quality (Figure 3). No influence of LOQ values were identified with the PCA analysis indicating that no bias, linked to most of the results below the LOQ, was introduced in our conclusions. Water discharged by the WWTP into the River Garonne was of the same quality, in terms of xenobiotics, over the whole year.

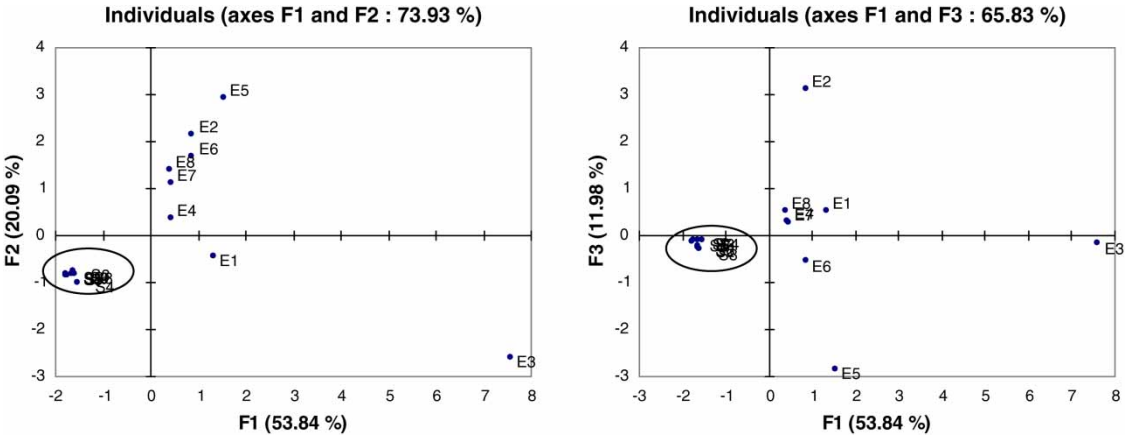

Figure 3 | Graphical representation of 'individuals'. E_{1-8} = wastewater samples; S_{1-8} = treated wastewater samples. 'Individuals' for treated wastewaters are circled.

Another PCA was carried out in order to find relationships between xenobiotics and global parameters of water pollution. Samples were measured for turbidity, chemical oxygen demand (COD) and suspended solid (SS). A data matrix, with columns representing the different samplings (observations) and rows corresponding to the measured parameters (variables), was constructed. A total of 16 complete observations were selected for analysis. The PCA showed that of the 9 components, the first component (F1) accounted for about 61.96% of the total variance, the second component (F2) accounted for about 15.83% of the total variance and the third component (F3) accounted for about 10.05% of the total variance of the dataset. The loadings for the three first components and square cosines are presented in Figure 4.

A variable is increasingly well represented by a component as the corresponding value of the square cosine approaches the unit. Almost all variables are well represented by the first three components, F1, F2 or F3, that collectively explain 87.84% of the total variance of the dataset. The variables that primarily contributed to the first eigenvector were principally turbidity, COD, SS, LAS, DEHP and NP1EO. F1 axis corresponded to the organic pollution load. A correlation between LAS, DEHP, SS, turbidity and COD was observed with $R^2 > 0.80$. It is interesting to note that the organic pollution (PAHs, TH, DEHP, LAS, NP1EO) was linked to suspended solid. Moreover, it is important to note that DEHP, LAS, NP1EO and E2 were negatively correlated ($R^2 = -0.80$) with NO_3^-. This can be seen in Figure 4 because they are symmetrically opposed regarding the center of the circle. This observation was consistent with the way analyses were performed. Indeed, nitrate analysis was performed on filtrate water. The second and third eigenvectors did not relate well to the other parameters such as PCBs and EE2.

Concentrations and EQS

The application of the European Water Framework Directive 2000/60/EC (EC 2000) aims to achieve surface waters with a 'good status', both ecologically and chemically. It defines priority substances considered as dangerous and defines EQS for these substances in order to preserve water resources. DEHP, nonylphenols and eight PAHs are considered as priority pollutants. Table 6 shows EQS values, mean concentrations and occurrence of these priority pollutants for the different types of waters studied, and discharged into the River Garonne.

Only two of the waters tested have a priority pollutant level higher than the EQS level. For run-off water, the DEHP value exceeds the 1.3 µg L^{-1} EQS level. Half of the samples could be quantified and observed levels are above the EQS. For roof collected water, mean concentrations of Benzo(g,h,i)perylene and Indeno(1,2,3-cd)pyrene exceeded the EQS values. These parameters were quantified on only one sample; other values are lower than LOQ. However the LOQ (0.01 µg L^{-1}) is greater than the EQS, therefore no clear conclusion can be drawn for an undetected compound as to conformity with EQS. For other parameters LOQ values are below the EQS, and observed values were

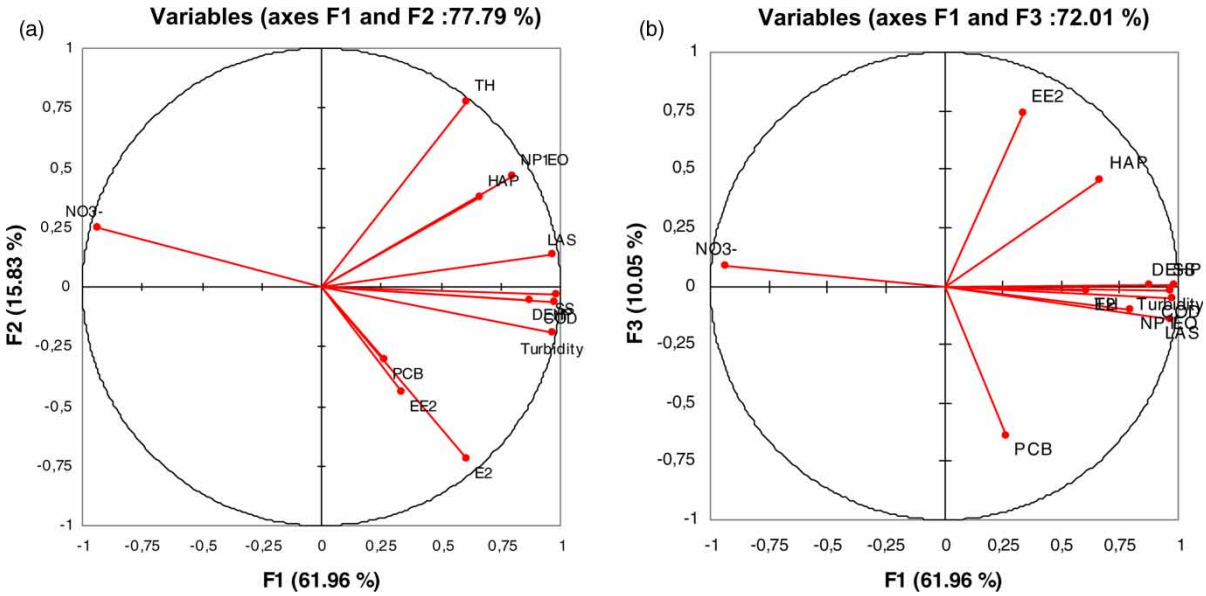

Figure 4 | The square cosines for all variables in (a) components F1 and F2 and (b) components F1 and F3.

Table 6 | Mean levels and occurrence (Oc.) of priority substances in run-off, ground, rain and roof collected waters and treated wastewaters and EQS

Compounds	units	EQS	Run-off water		Ground water		Rain water		Roof collected water		Treated wastewater	
			Mean	Oc.(%)	Mean	Oc.(%)	Mean	Oc.(%)	Mean	Oc.(%)	Mean	Oc.(%)
PAHs	–											
Anthracene	μg L^{-1}	0.1	<LOQ	0	<LOQ	0	<LOQ	0	<LOQ	0	<LOQ	0
Fluoranthene	μg L^{-1}	0.1	<LOQ	0	<LOQ	0	<LOQ	0	0.008	50	<LOQ	0
Naphthalene	μg L^{-1}	2.4	<LOQ	0	<LOQ	0	<LOQ	0	<LOQ	0	<LOQ	0
Benzo(a)pyrene	μg L^{-1}	0.05	<LOQ	0	<LOQ	0	<LOQ	0	<LOQ	0	<LOQ	0
Benzo(b)fluoranthene	μg L^{-1}	$\Sigma = 0.03$	<LOQ	0	<LOQ	0	<LOQ	0	0.012	25	<LOQ	0
Benzo(k)fluoranthene				0		0		0		25		0
Benzo(g,h,i)perylene	μg L^{-1}	$\Sigma = 0.002$	<LOQ	0	<LOQ	0	<LOQ	0	0.013	0	<LOQ	0
Indeno(1,2,3-cd)pyrene				0		0		0		25		0
DEHP	μg L^{-1}	1.3	11	50	0.35	25	0.49	50	0.28	25	<LOQ	25
NP1EO	μg L^{-1}	0.3	<LOQ	0	<LOQ	0	<LOQ	25	<LOQ	0	<LOQ	12.5

under the EQS. French legislation (Decree April 20th, 2005) gives the EQS for the sum of PCBs (0.001 μg L^{-1}) and TH (10 mg L^{-1}; Decree February 2nd, 1998). Levels observed for PCBs in run-off water are higher than the EQS. Other waters have concentrations in PCBs under the EQS. TH concentrations are lower than the EQS for all water samples.

Overall, the four types of water studied, and which are discharged into the environment, conformed to environmental standards.

CONCLUSION

This study aims to evaluate the level of pollution in different types of waters in a city equipped with a separated sewer system. Nine molecular species of xenobiotics were investigated: PAHs, PCBs, LAS, DEHP, MTBE, NP1EO, TH, estradiol and ethinylestradiol. Six types of waters were sampled: run-off water, rainwater, roof collected water, groundwater, wastewater and treated wastewater.

Xenobiotic concentrations observed for run-off, rain, roof collected and groundwaters were comparable with concentrations for these types of waters found in the literature. For the WWTP, the treatment efficiency was greater than 66% for all xenobiotics studied. PCA was performed on WWTP sampling results and revealed that treated wastewater samples maintained the same quality throughout the year. A comparison between treated wastewater, roof collected, rain, run-off and groundwaters shows that treated wastewater is of equivalent quality to other waters studied but less polluted than run-off water. Concentrations of xenobiotics were compared to Environmental Quality Standards for target compounds. Waters discharged into the environment were in conformity with the EQS. Urban water compartments were characterized by highly heterogeneous xenobiotic concentrations over time and space.

ACKNOWLEDGEMENTS

This work was supported by Veolia Water Technical Direction (Toulouse, France) with grant no. 20040101. We would like to thank Bernard Sentenac for his technical support.

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