Micropollutants reduction strategy at the scale of an urban area: comparison between effluents from stormwater overflows and from wastewater treatment plant

Stratégie de réduction des micropolluants à l'échelle d'une agglomération : comparaison entre les effluents d'exutoires pluviaux et d'une station d'épuration

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RÉSUMÉ

La gestion et la réduction des micropolluants ne peuvent être réalisées que dans le cadre d'une réflexion globale et par une stratégie intégrée. Dans ce contexte, Bordeaux Métropole, le LyRE-Suez et le laboratoire EPOC de l'Université de Bordeaux ont mis en œuvre à l'échelle de la métropole le "projet micropolluants" pour une période de 6 ans. Ce projet porte sur la question de la pollution de l'eau depuis la source de pollution jusqu'au milieu récepteur. L'objectif de cette communication est de mettre en évidence les contributions relatives des eaux usées, transitant par une station de traitement des eaux usées, et des eaux pluviales, issues de 3 exutoires, aux flux annuels de micropolluants reçus par une rivière périurbaine du territoire bordelais. Parmi les 162 substances recherchées 60 ont été retrouvées au moins 1 fois en sortie de station d'épuration et dans les exutoires pluviaux, 12 substances ont été retrouvées spécifiquement en sortie de station d'épuration, et 34 substances ont été retrouvées spécifiquement à la sortie exutoires des pluviaux. 56 substances n'ont pas jamais été retrouvées. Les résultats obtenus sont une première étape dans la connaissance des sources de micropolluants. Il s'agit d'un enjeu majeur dans l'objectif de maîtriser et réduire les flux de micropolluants à l'échelle d'un bassin versant.

ABSTRACT

The management and reduction of micropollutants can only be achieved within a framework of a global reflection and through an integrated strategy. In this context, Bordeaux Metropolis, LyRE-Suez and EPOC laboratory of Bordeaux University have implemented the "micropollutant project" for a period of 6 years at the scale of the metropolis. This project addresses the issue of water pollution as a whole, from the sources of pollution to the receiving environment. The aim of this publication is to compare the annual inputs of micropollutants from wastewater, passing through a wastewater treatment plant (85 000 population equivalent), and from rainwater, coming from 3 stormwater overflows, to a suburban river in the metropolis of Bordeaux. Among 162 substances looked for, 60 were found at least one time in wastewater treatment plant effluents and in stormwater overflows, 12 substances were only found in the outputs of wastewater treatment plant and 34 substances were only found in stormwater overflows. 56 substances were never found. The results obtained are a first step to understand the sources of micropollutants. This concern is of major importance in the objective to control and reduce micropollutant flows at the scale of a watershed.

KEYWORDS

Micropollutants, multi-sources, wastewater treatment plant, stormwater overflows, suburban river

1 INTRODUCTION

The management and the reduction of micropollutants can only be achieved within a framework of a global reflection and through an integrated strategy. The sources of micropollutants are multiple: rainwater runoff, agricultural runoff, wastewater from hospital or industrial activities, domestic wastewater etc. In this context, Bordeaux Metropolis, LyRE-Suez and EPOC laboratory of Bordeaux University have implemented the "micropollutant project" for a period of 6 years at the scale of the metropolis. The "micropollutant project of Bordeaux Metropolis" is an overall process addressing the issue of water pollution by micropollutants as a whole. Its aim is to characterize the fate of micropollutants, from their emission sources, such as the stormwater system for example, to their diffusion in the environment, in order to provide efficient actions allowing a flow reduction

From 2013 to 2015 the consortium was focused on the characterization and the quantification of micropollutants in the wastewater system of Bordeaux metropolis. The obtained results are a first step to understand the sources of micropollutants. This concern is of major importance in the objective to control and reduce the micropollutant flows at the scale of a watershed. The final objective is to identify and to understand the origins of emissions in order to propose appropriate actions of reduction. The second step, not presented here, will be the implementation of these actions of reduction such as new treatments (e.g. treatment of rainwater) or actions at the sources (e.g. change of behaviour change of practices).

The aim of this publication is to compare for a catchment area, the quantity of micropollutants which pass through stormwater overflows (SOs) and through a wastewater treatment plant (WWTP), 85000 population equivalent. More especially, the comparison is based on the annual outputs of micropollutants from 3 stormwater overflows and from one WWTP in a suburban river of the metropolis of Bordeaux.

2 MATERIALS AND METHODS

The samples have been collected over a three-year period (2013-2015). All water samples were 24 h composite samples (except stormwater samples which were collected during rain time). Only the rains which happened after five days of dry time and greater than 6 mm were selected. Three different processes were applied to analyse organic compounds: (1) liquid chromatography tandem mass spectrometry after a solid phase extraction for polar ones; (2) gas chromatography tandem mass spectrometry after a solid phase micro extraction for less polar; and (3) gas chromatography using an electron capture detector for non-polar ones. To insure the quality of the results, natural mineral water samples spiked with a known quantity of micropollutants, laboratory blank samples, analytical blanks and internal standards were used. These protocols enable us to reach quantification limits below the ng.L^{-1}. We considered a total of 162 organic substances. The number of substances by family are shown in Table 1.

Table 1 Overview of chemical detection results

	Number of substances looked for	Number of substances found			Number of substances not found
		only in WWTP	only in SO	In WWTP and SO	
Pharmaceuticals	43	11	7	19	6
Pesticides	62	0	23	16	23
OCP	14	1	2	0	11
PAH	11	0	3	6	2
VOC	8	0	1	2	5
PCB	8	1	0	5	2
Alkylphenols	7	0	0	7	0
PBDE	4	1	0	0	3
BTEX	4	0	0	4	0
Phthalates	1	0	0	1	0
TOTAL	**162**	**14**	**36**	**60**	**52**

OCP: Organochlorine pesticides, PAH: Polycyclic Aromatic Hydrocarbons, PBDE: PolyBrominated DiphenylEthers, PCB: PolyChloroBiphenyls, VOC: Volatile Organic Compounds.

Based on these analysis, the annual flow of micropollutants which pass through SOs has been estimated. Then, it has been compared with the annual flow from the WWTP output.

3 CASE STUDY

The study site is the catchment of the “jalle of Blanquefort” (Figure 1), a medium-size tributary of the left bank of the Garonne. This suburban river drains a catchment area of 347 km² area extending from the north west of Bordeaux with a total length of 176 km including its tributaries.

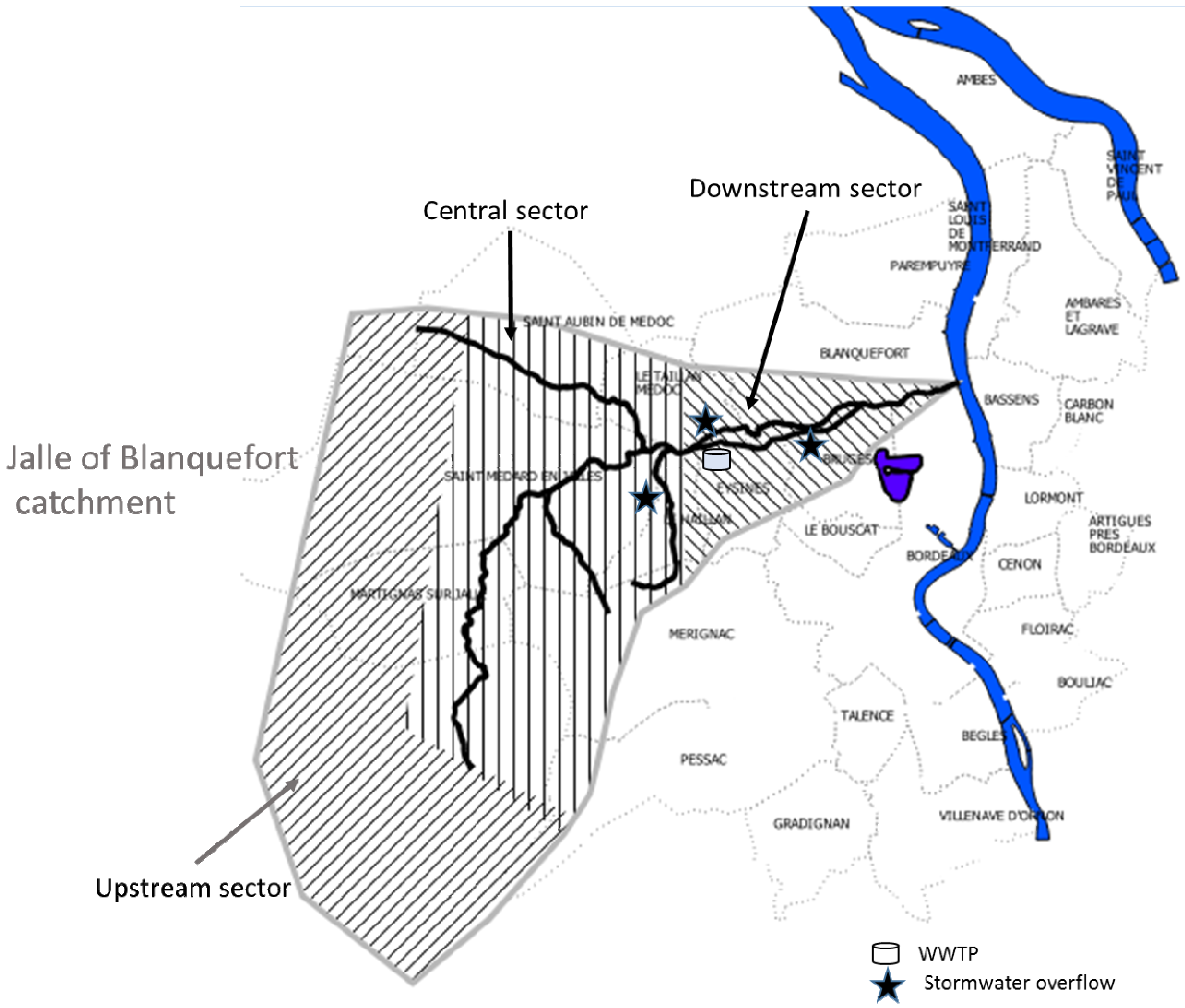

Figure 1 Major sectors on the jalle of Blanquefort catchment.

It crosses three major sectors:

- An upstream sector, a mainly forested area dominated by pine plantations. The upstream boundary of this watershed is occupied by corn fields but it remains difficult to assess due to a dense network of ditches often connected to neighboring watersheds.
- A central sector corresponding to a newly urbanized area.
- A downstream sector corresponding to the alluvial plain of the Garonne, bordered by hills. The land is dominated by the market gardening activity and grazed grasslands.

The studied micropollutants inputs into this rivers are:

- the three biggest SOs
- the outputs of a medium WWTP (sanitary sewage network of 85 000 population equivalent and an average discharge of 11 000 m^3/d) equipped with a biological secondary treatment.

4 RESULTS

Among the 162 substances looked for, 60 were found at least once time in the WWTP effluents and in stormwater overflows, 12 substances were found only in the outputs of wastewater treatment plant and 34 substances were found only in the SOs. 56 substances were neither found in the effluents of wastewater treatment plant nor in stormwater overflows (Table 1).

4.1 Stormwater overflows

The next table shows the minimum, maximum and average concentration of each measured substances in each overflow's outputs. The average annual quantity flowing through the three stormwater overflows has been estimated using the annual volume discharged by each SO.

Table 2. Minimum, maximum, average concentrations (n=3) and annual average dissolved flows found on stormwater overflow for each detected substances.

Substances	Families	Stormwater Overflow N°1				Stormwater Overflow N°2				Stormwater Overflow N°3				WWTP			
		min (ng/l)	max (ng/l)	mean (ng/l)	Average annual flows (mg/year)	min (ng/l)	max (ng/l)	mean (ng/l)	Average annual flows (mg/year)	min (ng/l)	max (ng/l)	mean (ng/l)	Average annual flows (mg/year)	min (ng/l)	max (ng/l)	mean (ng/l)	Average annual flows (mg/year)
Nonylphenols	AKP	102.6	961.4	367.0	67928.5	40.3	865.3	316.6	64593.2	89.2	489.0	210.4	114216.2	62.0	152.4	95.5	1127.8
NP1EC	AKP	48.3	97.0	68.6	14448.6	16.6	61.6	40.1	11830.8	62.9	208.3	122.7	85956.9	305.0	358.1	324.7	3889.2
NP1OE	AKP	16.7	227.1	103.0	21696.7	27.5	52.5	35.1	7779.3	8.5	76.6	55.4	32010.2	59.1	87.2	74.3	892.0
NP2OE	AKP	27.9	47.6	40.9	6772.6	11.4	33.4	22.0	5022.1	17.0	43.8	30.8	18608.6	14.6	39.8	24.2	293.4
Octylphenols	AKP	5.7	117.1	40.7	7031.7	<LoQ	8.6	5.4	803.4	<LoQ	18.1	9.8	3019.2	63.1	76.8	70.0	841.2
OP1OE	AKP	<LoQ	75.6	25.2	6706.9	<LoQ	7.0	3.1	703.1	<LoQ	18.4	7.7	6235.9	83.8	150.2	127.2	1521.6
OP2OE	AKP	5.4	9.6	7.4	1517.7	<LoQ	4.4	1.1	248.7	<LoQ	15.0	5.0	4442.4	125.7	374.7	263.5	3158.5
Benzene	BTEX	<LoQ	47.6	15.0	2211.6	<LoQ	<LoQ	<LoQ	<LoQ	<LoQ	71.0	20.1	10177.9	10.2	13.4	11.4	136.8
Ethylbenzene	BTEX	<LoQ	218.2	81.1	24300.6	5.7	524.6	142.4	63066.8	18.0	492.6	171.3	170934.6	28.1	64.1	50.2	600.5
Toluene	BTEX	171.9	770.9	407.2	82817.9	37.5	535.8	241.1	77605.3	<LoQ	1508.7	524.0	376446.8	77.3	205.2	121.1	1466.5
Xylenes	BTEX	<LoQ	426.4	249.2	61698.1	30.7	715.5	233.1	93133.2	58.9	755.6	399.6	320496.2	39.2	389.8	170.0	1968.7
Tetrachloroethylene	VOC	<LoQ	26.3	8.2	1706.9	<LoQ	14.7	5.6	1590.8	3.8	83.7	48.4	35053.8	3.2	3.7	3.5	42.5
Trichloroethylene	VOC	<LoQ	136.5	36.5	7182.2	<LoQ	<LoQ	<LoQ	<LoQ	42.7	225.8	119.4	54838.9	<LoQ	<LoQ	<LoQ	<LoQ
Trichloromethane	VOC	<LoQ	94.7	60.8	9784.2	<LoQ	233.0	82.2	5408.9	<LoQ	307.5	76.9	44113.7	110.4	141.6	125.3	1505.3
Anthracene	PAH	0.6	2.0	1.4	278.5	<LoQ	1.2	0.4	120.6	<LoQ	1.7	1.1	626.3	<LoQ	0.4	0.1	1.3
Benzo[a]anthracene	PAH	<LoQ	0.8	0.3	83.5	<LoQ	<LoQ	<LoQ	<LoQ	<LoQ	0.8	0.3	108.7	<LoQ	<LoQ	<LoQ	<LoQ
Benzo[b+j+k]fluoranthene	PAH	<LoQ	3.0	1.0	226.8	<LoQ	0.7	0.2	40.7	<LoQ	2.0	0.5	280.2	<LoQ	<LoQ	<LoQ	<LoQ
Benzo[g,h,i]perylene	PAH	<LoQ	0.5	0.1	23.5	<LoQ	<LoQ	<LoQ	<LoQ	<LoQ	0.6	0.1	79.8	<LoQ	<LoQ	<LoQ	<LoQ
Chrysene + Triphenylene	PAH	0.7	2.9	1.6	352.6	0.4	1.3	0.8	204.6	0.4	2.1	1.1	668.8	<LoQ	0.6	0.2	2.5
Fluoranthene	PAH	3.1	11.9	7.2	1541.6	1.9	5.4	3.4	876.3	2.2	7.9	5.4	3553.3	1.0	1.0	1.0	12.2
Naphtalene	PAH	8.7	14.0	11.3	1811.6	<LoQ	6.7	2.8	378.6	3.2	26.8	12.9	9696.2	<LoQ	22.0	9.7	112.5
Phenanthrene	PAH	8.5	22.7	14.4	2950.1	3.8	13.4	7.7	1551.0	4.0	17.0	9.5	6994.7	3.6	4.4	3.9	47.1
Pyrene	PAH	4.9	11.4	8.5	1643.3	2.0	7.3	4.5	1025.1	5.1	10.8	8.0	4007.1	4.0	5.3	4.8	58.0
Abacavir	Pharmaceuticals	<LoQ	<LoQ	<LoQ	<LoQ	<LoQ	<LoQ	<LoQ	<LoQ	<LoQ	<LoQ	<LoQ	<LoQ	8.6	22.3	17.6	210.1
Acebutolol	Pharmaceuticals	<LoQ	213.8	67.2	13073.7	<LoQ	234.3	89.6	20486.4	<LoQ	<LoQ	<LoQ	<LoQ	309.6	484.7	411.3	4932.5
4 Chlorobenzoic acid	Pharmaceuticals	<LoQ	167.5	63.2	16912.4	<LoQ	33.8	16.6	5740.7	13.8	88.4	51.1	30166.2	NC	NC	NC	NC
Clofibric acid	Pharmaceuticals	<LoQ	5.3	1.3	472.1	<LoQ	<LoQ	<LoQ	<LoQ	<LoQ	<LoQ	<LoQ	<LoQ	<LoQ	<LoQ	<LoQ	<LoQ
Fenofibric acid	Pharmaceuticals	<LoQ	225.7	100.7	25768.4	5.7	51.3	28.0	5919.3	<LoQ	10.0	3.8	1436.6	606.4	2261.4	1653.4	19730.1
Salycilic acid	Pharmaceuticals	110.6	11925.0	3381.3	608133.2	<LoQ	129.0	79.2	12192.0	41.1	523.8	187.9	39911.5	<LoQ	<LoQ	<LoQ	<LoQ
Atenolol	Pharmaceuticals	<LoQ	8.6	2.9	799.0	<LoQ	19.7	4.9	1112.6	<LoQ	<LoQ	<LoQ	<LoQ	664.4	909.7	794.1	9501.0
Atorvastatine	Pharmaceuticals	<LoQ	71.4	23.8	NC	<LoQ	<LoQ	<LoQ	<LoQ	<LoQ	<LoQ	<LoQ	<LoQ	<LoQ	<LoQ	<LoQ	<LoQ
Bezafibrate	Pharmaceuticals	<LoQ	<LoQ	<LoQ	<LoQ	<LoQ	12.8	3.2	723.2	<LoQ	9.1	2.3	1298.4	120.7	269.9	200.7	2388.7
Bisoprolol	Pharmaceuticals	<LoQ	639.2	169.8	32837.3	<LoQ	28.5	10.6	2572.6	<LoQ	<LoQ	<LoQ	<LoQ	177.9	205.5	189.9	2275.7
Caffeine	Pharmaceuticals	383.2	19690.0	5341.5	989568.2	175.8	1832.9	729.5	141445.4	360.9	1395.2	868.4	364234.8	71.2	176.6	108.0	1309.1
Carbamazepine	Pharmaceuticals	<LoQ	35.0	9.6	1784.6	<LoQ	8.9	2.2	501.9	<LoQ	<LoQ	<LoQ	<LoQ	762.7	933.2	843.6	10134.1
Cetirizine	Pharmaceuticals	<LoQ	3.8	1.0	340.2	<LoQ	11.6	4.0	900.5	<LoQ	<LoQ	<LoQ	<LoQ	513.0	596.1	548.2	6568.3
Clopidogrel	Pharmaceuticals	<LoQ	<LoQ	<LoQ	<LoQ	<LoQ	<LoQ	<LoQ	<LoQ	<LoQ	<LoQ	<LoQ	<LoQ	12.2	14.7	13.4	160.9
Diclofenac	Pharmaceuticals	<LoQ	6761.5	1737.6	328126.0	24.1	278.4	147.9	48813.1	21.7	268.3	139.0	100479.8	748.5	959.9	847.1	10178.1
Disopyramide	Pharmaceuticals	<LoQ	33.0	9.4	1933.2	<LoQ	7.2	1.8	408.1	<LoQ	<LoQ	<LoQ	<LoQ	248.3	354.0	286.8	3453.9
Fluoxetine	Pharmaceuticals	<LoQ	<LoQ	<LoQ	<LoQ	<LoQ	<LoQ	<LoQ	<LoQ	<LoQ	<LoQ	<LoQ	<LoQ	8.5	10.5	9.4	113.2
Gabapentine	Pharmaceuticals	<LoQ	<LoQ	<LoQ	<LoQ	<LoQ	<LoQ	<LoQ	<LoQ	<LoQ	<LoQ	<LoQ	<LoQ	7903.9	9602.3	8686.6	104029.6
Gemfibrozil	Pharmaceuticals	<LoQ	<LoQ	<LoQ	<LoQ	<LoQ	<LoQ	<LoQ	<LoQ	<LoQ	6.1	1.5	871.3	38.7	63.4	52.4	625.5
Hydroxy ibuprofene	Pharmaceuticals	<LoQ	2058.8	616.0	201474.3	107.9	332.4	246.3	48412.8	<LoQ	195.5	133.3	106350.5	1031.1	1933.9	1596.5	19071.7
Ibuprofene	Pharmaceuticals	<LoQ	74170.7	24778.1	6904283.0	38.0	130.8	91.6	16405.3	<LoQ	46.0	27.0	23643.6	<LoQ	<LoQ	<LoQ	<LoQ
Ketoprofene	Pharmaceuticals	<LoQ	123.9	80.7	10492.6	<LoQ	22.7	14.2	4888.0	12.6	36.4	25.7	18842.9	128.0	436.6	329.1	3925.2
Lamivudine	Pharmaceuticals	<LoQ	<LoQ	<LoQ	<LoQ	<LoQ	<LoQ	<LoQ	<LoQ	<LoQ	<LoQ	<LoQ	<LoQ	32.0	58.8	46.5	554.5
Losartan	Pharmaceuticals	<LoQ	<LoQ	<LoQ	<LoQ	<LoQ	<LoQ	<LoQ	<LoQ	<LoQ	<LoQ	<LoQ	<LoQ	147.5	176.2	159.6	1921.6
Meprobamate	Pharmaceuticals	<LoQ	<LoQ	<LoQ	<LoQ	<LoQ	103.8	25.9	12115.1	<LoQ	7.8	3.7	2580.1	<LoQ	<LoQ	<LoQ	<LoQ
Metoprolol	Pharmaceuticals	<LoQ	<LoQ	<LoQ	<LoQ	<LoQ	5.9	1.5	333.5	<LoQ	<LoQ	<LoQ	<LoQ	114.4	141.1	126.3	1511.5
Naproxene	Pharmaceuticals	<LoQ	<LoQ	<LoQ	<LoQ	<LoQ	93.6	39.5	13689.8	<LoQ	49.1	12.3	<LoQ	243.0	477.5	383.3	4574.5
Nevirapine	Pharmaceuticals	<LoQ	<LoQ	<LoQ	<LoQ	<LoQ	<LoQ	<LoQ	<LoQ	<LoQ	<LoQ	<LoQ	<LoQ	24.1	31.8	29.0	347.8
Nordazepam	Pharmaceuticals	<LoQ	<LoQ	<LoQ	<LoQ	<LoQ	<LoQ	<LoQ	<LoQ	<LoQ	<LoQ	<LoQ	<LoQ	18.7	22.5	20.3	244.0
Oxazepam	Pharmaceuticals	<LoQ	657.3	191.3	39791.8	<LoQ	20.3	11.4	3117.1	<LoQ	7.6	1.9	1093.8	1137.5	1307.8	1205.4	14444.5
Paracetamol	Pharmaceuticals	137.7	21694.2	6299.9	1226592.3	130.5	9041.6	2570.5	545738.3	137.2	727.8	392.7	189252.7	<LoQ	<LoQ	<LoQ	<LoQ
Pravastatine	Pharmaceuticals	<LoQ	<LoQ	<LoQ	<LoQ	<LoQ	<LoQ	<LoQ	<LoQ	<LoQ	<LoQ	<LoQ	<LoQ	76.5	88.5	81.3	977.4
Primidone	Pharmaceuticals	<LoQ	<LoQ	<LoQ	<LoQ	<LoQ	<LoQ	<LoQ	<LoQ	<LoQ	<LoQ	<LoQ	<LoQ	122.9	188.6	154.1	1852.0
Propranolol	Pharmaceuticals	<LoQ	105.3	28.1	9662.4	<LoQ	10.9	4.7	1550.2	<LoQ	<LoQ	<LoQ	<LoQ	625.8	709.2	662.7	7962.4
Ritonavir	Pharmaceuticals	<LoQ	<LoQ	<LoQ	<LoQ	<LoQ	<LoQ	<LoQ	<LoQ	<LoQ	<LoQ	<LoQ	<LoQ	47.2	59.9	54.7	655.4
Sotalol	Pharmaceuticals	<LoQ	416.7	207.4	55628.7	<LoQ	36.9	13.2	3355.7	<LoQ	14.2	3.6	2043.7	2450.7	2758.1	2630.9	31581.6
Theophylline	Pharmaceuticals	115.2	6647.5	3075.6	785988.0	218.2	662.5	364.6	84847.4	105.6	206.8	139.0	92593.9	203.8	358.8	264.0	3184.4
2,4'_DDD (+CB 154)	OCP	<LoQ	<LoQ	<LoQ	<LoQ	<LoQ	<LoQ	<LoQ	<LoQ	<LoQ	<LoQ	<LoQ	<LoQ	<LoQ	0.5	0.2	2.0
Dieldrine	OCP	<LoQ	<LoQ	<LoQ	<LoQ	0.5	0.6	0.6	135.6	<LoQ	0.6	0.3	<LoQ	<LoQ	<LoQ	<LoQ	<LoQ
Lindane	OCP	<LoQ	31.2	9.0	2995.4	<LoQ	<LoQ	<LoQ	<LoQ	<LoQ	<LoQ	<LoQ	<LoQ	<LoQ	<LoQ	<LoQ	<LoQ
BDE 100	PBDE	<LoQ	<LoQ	<LoQ	<LoQ	<LoQ	<LoQ	<LoQ	<LoQ	<LoQ	<LoQ	<LoQ	<LoQ	<LoQ	0.0	0.0	0.0
PCB 101	PCB	<LoQ	0.3	0.1	27.0	<LoQ	1.1	0.4	100.3	<LoQ	0.4	0.1	108.0	0.7	0.8	0.7	8.6
PCB 118	PCB	<LoQ	1.2	0.4	92.9	<LoQ	1.3	0.4	105.7	<LoQ	0.3	0.1	82.9	0.8	1.0	0.9	10.8
PCB 138	PCB	<LoQ	1.1	0.3	70.5	<LoQ	<LoQ	<LoQ	<LoQ	<LoQ	<LoQ	<LoQ	<LoQ	0.5	0.5	0.5	6.2
PCB 153	PCB	<LoQ	0.2	0.1	18.7	<LoQ	<LoQ	<LoQ	<LoQ	<LoQ	<LoQ	<LoQ	<LoQ	0.4	0.4	0.4	5.0
PCB 50	PCB	<LoQ	<LoQ	<LoQ	<LoQ	<LoQ	<LoQ	<LoQ	<LoQ	<LoQ	<LoQ	<LoQ	<LoQ	0.6	0.7	0.6	7.2
PCB 52	PCB	<LoQ	<LoQ	<LoQ	<LoQ	<LoQ	1.2	0.3	70.2	<LoQ	<LoQ	<LoQ	<LoQ	0.7	0.8	0.8	9.3
1_(3,4_dichlorodiphenyl)	Pesticides	<LoQ	22.9	5.7	1061.5	<LoQ	<LoQ	<LoQ	<LoQ	<LoQ	<LoQ	<LoQ	<LoQ	NC	NC	NC	NC
AMPA	Pesticides	1610.6	8768.7	4250.1	962848.7	124.1	2295.6	877.4	156004.6	278.7	1694.8	1065.9	645640.5	1226.5	1443.9	1335.8	16010.0
Atrazine	Pesticides	<LoQ	<LoQ	<LoQ	<LoQ	<LoQ	4.9	2.7	692.7	<LoQ	1.2	0.3	178.2	<LoQ	<LoQ	<LoQ	<LoQ
Atrazine 2 hydroxy	Pesticides	<LoQ	29.2	7.3	<LoQ	1.5	17.6	10.7	2704.6	1.2	32.4	20.5	13314.6	3.0	3.6	3.2	38.3
Atrazine deisopropyl (DIA)	Pesticides	<LoQ	24.9	6.2	2212.7	<LoQ	5.2	2.3	768.8	<LoQ	<LoQ	<LoQ	<LoQ	<LoQ	<LoQ	<LoQ	<LoQ

NC: Not calculable, LoQ: Limits of Quantification

The following of table is on the next page

Substances	Families	Stormwater Overflow N°1				Stormwater Overflow N°2				Stormwater Overflow N°3				WWTP			
		min (ng/l)	max (ng/l)	mean (ng/l)	Average annual flows (mg/year)	min (ng/l)	max (ng/l)	mean (ng/l)	Average annual flows (mg/year)	min (ng/l)	max (ng/l)	mean (ng/l)	Average annual flows (mg/year)	min (ng/l)	max (ng/l)	mean (ng/l)	Average annual flows (mg/year)
Atrazine desethyl (DEA)	Pesticides	<LoQ	<LoQ	<LoQ	<LoQ	<LoQ	9.20	6.02	1473.54	<LoQ	<LoQ	<LoQ	<LoQ	<LoQ	<LoQ	<LoQ	<LoQ
Azoxystrobine	Pesticides	<LoQ	22.89	8.43	2030.89	<LoQ	<LoQ	<LoQ	<LoQ	<LoQ	4.58	1.65	1499.89	<LoQ	<LoQ	<LoQ	<LoQ
Bifenthrine	Pesticides	<LoQ	1.35	0.34	119.37	<LoQ	<LoQ	<LoQ	<LoQ	<LoQ	<LoQ	<LoQ	<LoQ	<LoQ	<LoQ	<LoQ	<LoQ
Carbendazime	Pesticides	<LoQ	153.22	49.56	9707.32	<LoQ	11.45	3.76	646.04	24.09	126.56	61.39	45986.23	28.70	30.30	29.50	354.34
Chlorfenvinphos	Pesticides	<LoQ	5.16	1.29	457.85	<LoQ	<LoQ	<LoQ	<LoQ	<LoQ	<LoQ	<LoQ	<LoQ	<LoQ	<LoQ	<LoQ	<LoQ
DCPMU	Pesticides	<LoQ	82.30	26.51	8403.58	2.80	18.62	11.36	3061.61	7.75	102.53	39.67	34416.81	7.40	19.80	14.07	168.78
Diazinon	Pesticides	<LoQ	5.20	1.30	241.51	<LoQ	<LoQ	<LoQ	<LoQ	<LoQ	<LoQ	<LoQ	<LoQ	5.60	8.70	6.77	81.65
Difenoconazole A B	Pesticides	<LoQ	4.46	1.11	395.35	<LoQ	<LoQ	<LoQ	<LoQ	<LoQ	<LoQ	<LoQ	<LoQ	<LoQ	<LoQ	<LoQ	<LoQ
Diflufenican	Pesticides	6.30	29.40	17.03	4037.31	<LoQ	10.53	3.84	1017.66	3.00	4.12	3.51	2003.36	<LoQ	<LoQ	<LoQ	<LoQ
Diuron	Pesticides	18.40	179.31	78.97	17762.02	15.70	375.13	162.04	35262.11	53.80	354.53	142.85	122267.75	135.40	300.90	241.43	2886.11
DMSA	Pesticides	<LoQ	17.13	6.30	1683.93	<LoQ	1.40	0.64	144.99	<LoQ	3.42	1.88	1456.17	8.40	12.00	10.23	122.86
DMST	Pesticides	<LoQ	8.76	4.08	1123.09	<LoQ	<LoQ	<LoQ	<LoQ	<LoQ	<LoQ	<LoQ	<LoQ	4.50	5.40	4.90	58.88
Epoxiconazole	Pesticides	<LoQ	1.50	0.38	NC	<LoQ	<LoQ	<LoQ	<LoQ	<LoQ	1.90	0.48	<LoQ	<LoQ	<LoQ	<LoQ	<LoQ
Fipronil	Pesticides	<LoQ	5.90	1.48	274.03	<LoQ	<LoQ	<LoQ	<LoQ	<LoQ	1.00	0.25	143.44	39.20	42.10	40.60	488.14
Fipronil desulfinyl	Pesticides	<LoQ	1.40	0.35	65.02	<LoQ	<LoQ	<LoQ	<LoQ	<LoQ	<LoQ	<LoQ	<LoQ	0.60	1.00	0.80	9.67
Fipronil sulfide	Pesticides	<LoQ	<LoQ	<LoQ	<LoQ	<LoQ	<LoQ	<LoQ	<LoQ	<LoQ	0.64	0.24	190.13	1.60	2.10	1.83	22.03
Fipronil sulfone	Pesticides	<LoQ	2.40	0.60	111.47	<LoQ	<LoQ	<LoQ	<LoQ	<LoQ	<LoQ	<LoQ	<LoQ	4.00	5.00	4.33	52.15
Flazasulfuron	Pesticides	<LoQ	<LoQ	<LoQ	<LoQ	<LoQ	4.64	1.78	681.74	<LoQ	56.35	19.84	14902.25	<LoQ	<LoQ	<LoQ	<LoQ
Flutriafol	Pesticides	<LoQ	<LoQ	<LoQ	<LoQ	<LoQ	37.54	9.39	2118.33	<LoQ	<LoQ	<LoQ	<LoQ	<LoQ	<LoQ	<LoQ	<LoQ
Glyphosate	Pesticides	790.43	72824.07	27792.84	6950791.65	88.49	518.52	296.99	67406.99	580.68	6588.28	2624.63	2135619.90	250.70	384.30	322.60	3853.52
Hexazinone	Pesticides	<LoQ	<LoQ	<LoQ	<LoQ	<LoQ	1.26	0.61	214.27	<LoQ	<LoQ	<LoQ	<LoQ	<LoQ	<LoQ	<LoQ	<LoQ
Hydroxy-simazine	Pesticides	<LoQ	4.60	1.15	<LoQ	<LoQ	<LoQ	<LoQ	<LoQ	<LoQ	7.30	4.24	2461.42	<LoQ	<LoQ	<LoQ	<LoQ
Imidaclopride	Pesticides	<LoQ	6.50	1.63	<LoQ	<LoQ	4.10	1.03	231.35	<LoQ	6.70	2.50	473.36	135.70	152.10	142.93	1717.40
Lambda-cyhalothrine	Pesticides	<LoQ	2.36	0.79	209.28	<LoQ	<LoQ	<LoQ	<LoQ	<LoQ	<LoQ	<LoQ	<LoQ	<LoQ	<LoQ	<LoQ	<LoQ
Metolachlore	Pesticides	<LoQ	41.40	14.25	995.49	<LoQ	2.00	0.50	<LoQ	<LoQ	44.70	12.30	1069.98	<LoQ	2.50	0.83	10.32
Permethrine	Pesticides	<LoQ	8.25	2.06	383.20	<LoQ	<LoQ	<LoQ	<LoQ	<LoQ	<LoQ	<LoQ	<LoQ	NC	NC	NC	NC
Propiconazole	Pesticides	10.84	18.29	14.56	2629.08	4.70	258.96	131.83	29773.55	29.55	81.03	55.29	32474.09	NC	NC	NC	NC
Simazine	Pesticides	<LoQ	16.81	4.20	1490.99	<LoQ	3.60	2.21	522.13	<LoQ	10.92	2.73	1566.00	<LoQ	<LoQ	<LoQ	<LoQ
Spiroxamine	Pesticides	<LoQ	31.70	8.70	2812.58	<LoQ	<LoQ	<LoQ	<LoQ	<LoQ	1.60	0.75	409.22	<LoQ	<LoQ	<LoQ	<LoQ
Terbuthylazine	Pesticides	<LoQ	3.50	1.42	193.09	<LoQ	<LoQ	<LoQ	<LoQ	<LoQ	8.90	2.67	532.42	<LoQ	<LoQ	<LoQ	<LoQ
Terbuthylazine desethyl	Pesticides	<LoQ	11.20	2.80	<LoQ	<LoQ	3.18	1.52	535.03	<LoQ	9.00	4.31	2444.04	<LoQ	<LoQ	<LoQ	<LoQ
Terbutryne	Pesticides	1.01	4.80	3.01	690.95	3.60	20.89	9.70	3174.12	5.71	44.20	15.88	3642.02	56.00	65.40	60.30	724.50
Tetraconazole	Pesticides	<LoQ	4.71	1.18	418.07	<LoQ	<LoQ	<LoQ	<LoQ	<LoQ	2.50	0.62	738.99	<LoQ	<LoQ	<LoQ	<LoQ
Trifloxystrobine	Pesticides	<LoQ	3.23	1.08	286.83	<LoQ	<LoQ	<LoQ	<LoQ	<LoQ	1.45	0.36	429.04	<LoQ	<LoQ	<LoQ	<LoQ
DEHP	Phthalates	15.10	74.09	35.15	5523.81	11.09	53.16	34.29	6382.28	15.53	42.30	31.96	15544.34	46.44	103.27	76.27	915.78

4.2 Comparison with outputs by wastewater treatment plant

The relative contribution of WWTP and SO to the annual flow of micropollutants in the Jalle catchment is shown in Figure 2.

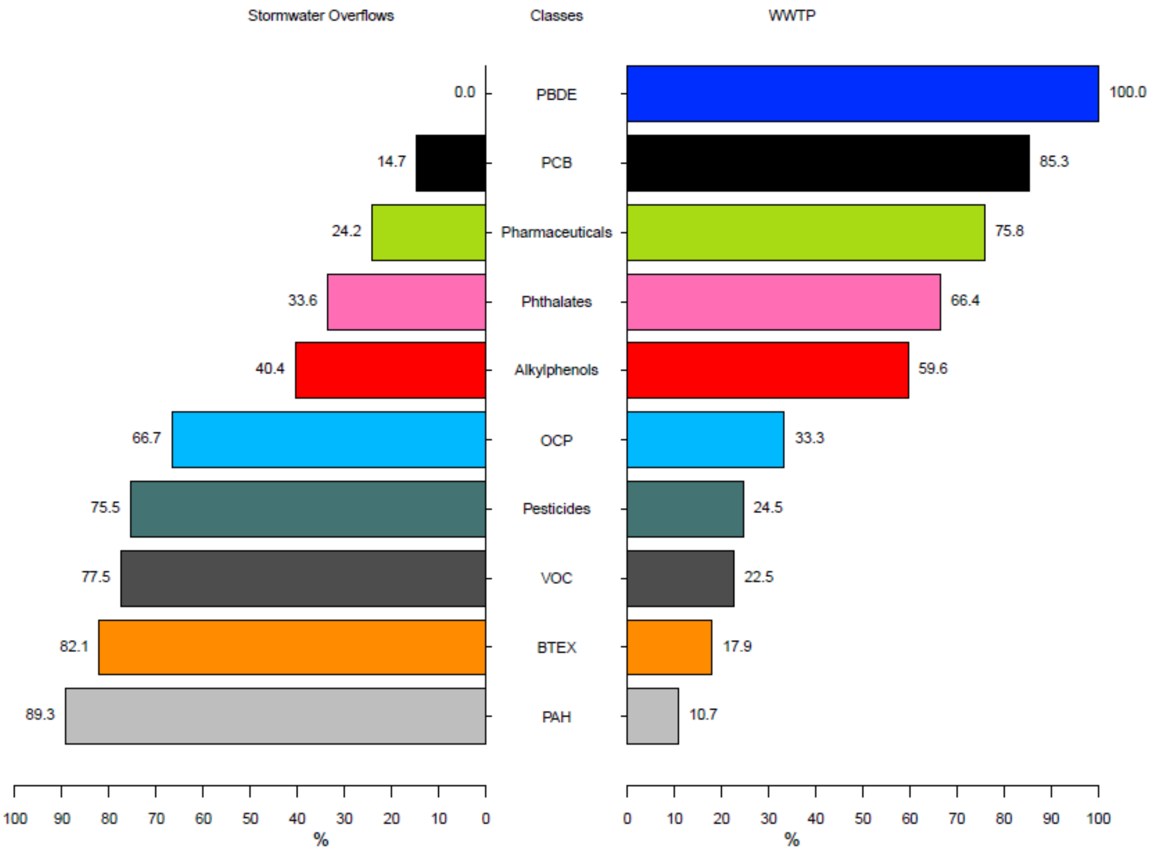

Figure 2 Comparison of the relative dissolved flows of micropollutants families from stormwater overflows and from the outputs of wastewater treatment plant.

These results allow to identify the main vectors of pollution for each family of substances. The contribution of each vector is mainly consistent with what it can be expected for most of the substances among each family. However, some of them exhibit a more complex pattern. The next figure shows the case of pharmaceuticals:

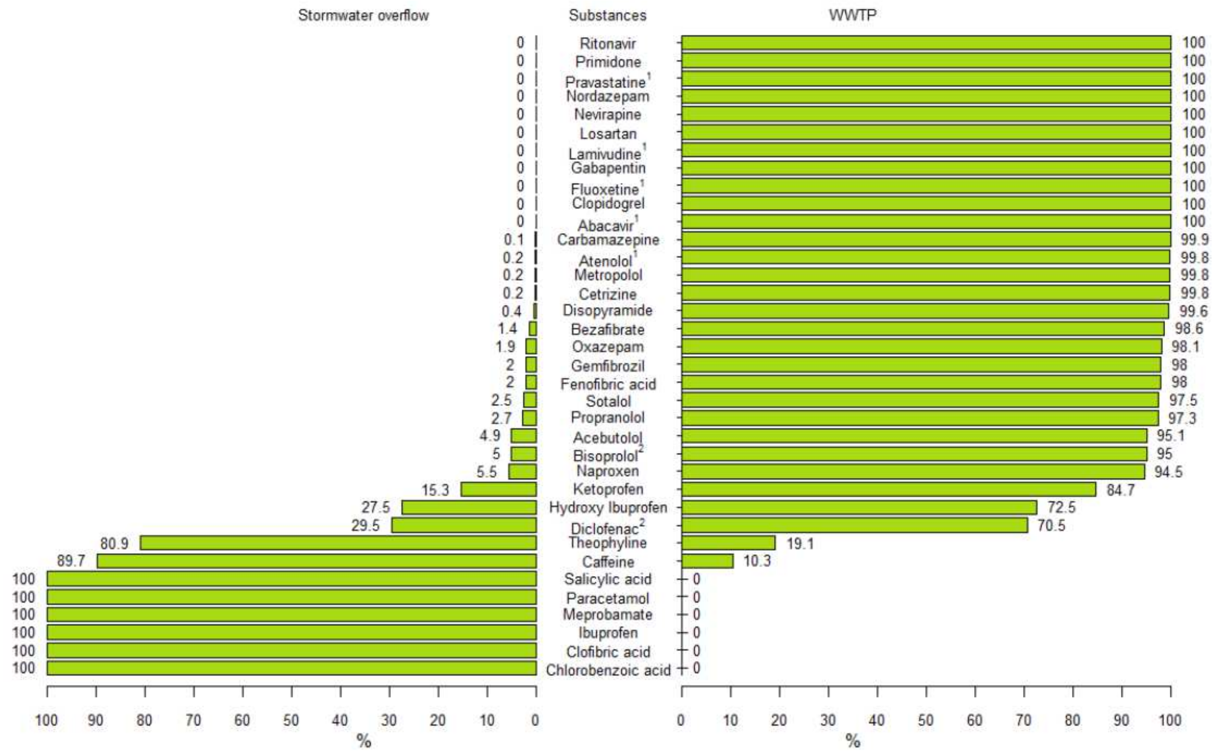

Figure 3. Contribution of the dissolved flow of pharmaceuticals chemicals transported by the outputs of the WTTP or SOs into the river "jalle of Blanquefort".

Figure 3 shows the relative part of each pharmaceuticals transported by the outputs of the WTTP or SOs. This graph shows contrasted pattern of emission for the pharmaceuticals:

- Some of them were exclusively emitted by SOs (*e.g.*, paracetamol, ibuprofen, clofibric acid).
- Some others come only from the WWTP (*e.g.*, ritonavir, primidone, nordazepam).
- From some other chemicals the interpretation remains unclear. In some cases, the main vector seems to be the WWTP, but the measure is slightly higher than the quantification limit (concentrations in this output do not exceed 2 times the quantification limit for SOs). Consequently, a decrease of the quantification limits could change the distribution (*e.g.*: the antidepressant fluoxetine). These substance are labelled "[1]" in the graph. In other cases, the high variability of the results among the samples do not allow a robust interpretation (*e.g.* diclofenac appears mainly in samples from the WWTP, but some values measured in the SO samples were much higher than in the WWTP outputs). Chemicals showing these limits of interpretation are labelled "[2]" in the graph.

Overall, 28 of the 36 measured pharmaceuticals pass through the wastewater treatment plant. These pharmaceuticals are emitted by the inhabitants and are transferred by the wastewater networks to the WWTP. These results demonstrate a low removal rate of pharmaceuticals (mostly hydrophilic) by the studied WWTP equipped with biological secondary treatment. They are consistent with the literature, as many publications from the national project AMPERES (Martin *et al.*, 2009; Budzinski *et al.,* 2009) show that many pharmaceuticals are not stopped by the wastewater treatment plants. Therefore, the contribution of the WWTP treated effluent seems predominant in the contamination of the river by these kinds of chemicals (gabapentin for example).

Furthermore, 8 substances are mostly transported by the stormwater overflows: chlorobenzoic acid, clofibric acid, ibuprofen, meprobamate, paracetamol, salicylic acid, caffeine, and theophylline. All these substances have been found in the inputs of the wastewater treatment plant but are well degraded during the different treatments processes in wastewater treatment plants (Miège *et al.,* 2009). The presence of these chemicals in the stormwater was verified for most of the rain events and

SO studied. They are suspected to originate from bad wastewater connections but further studies have to be considered to validate or invalidate this hypothesis as a source of pharmaceuticals in stormwater overflow networks.

5 CONCLUSION

In this study, the relative contribution of the three most important stormwater overflows and of the WWTP to the annual quantity of micropollutants entering into the catchment area of the “jalle of Blanquefort” has been investigated. The results show different behaviour according to the family of substances. In addition, among a single family, the contribution of these sources are not similar for all the substances. For example most of the pharmaceuticals are emitted through the WWTP, but the present results show that 8 substances are mostly released by the stormwater overflows. They are suspected to be related to bad wastewater connections. Consequently, a measure of these substances in stormwater could be a good indicator of wastewater inputs in stormwater network. In addition, the knowledge of the average consumption of these pharmaceuticals by humans, of the degradation rate in the organism and the network could be used as an indicator of bad connexions on all stormwater overflows.

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