

Supplementary Materials

1. Analytical Methods

1.1. PCBs

A sample of 100 mL of each waste water was filtered through 0,6 mm glass fibre filters to remove the fine particles and extracted three times using the liquid-liquid extraction method with 200 mL of dichloromethane/ hexane under ultrasonic conditions for 1 h (1:1, v/v). In total, the extracted volume was 180 ml of dichloromethane/hexane (1:1, v/v), the extracts were concentrated to 1 ml and were subjected to solvent exchange against hexane by a rotary evaporator. Concentrated extracts were sequentially submitted to multilayer silica gel, basic alumina and florisil chromatography columns for additional cleaning. This multilayer silica gel column was loaded from top to bottom with 4 g of anhydrous sodium sulfate, 2 g of activated silica, 8 g of acid silica (30% w/w), 1 g of activated silica, 4 g of basic silica (1.2% w/w), and 1 g of activated silica. These columns were preserved using dichloromethane/hexane (1:1, v/v) prior to loading the extracts. Les échantillons ont été élués à une vitesse de 1 ml/min sous vide. Ensuite, l'effluent a été collecté et évaporé à sec à l'aide d'un évaporateur rotatif. Final residue was dissolved in 1.0 mL of n-hexane containing 100 ng/L Isodrine (I.S) and then 2 µl of the reconstituted solution were injected onto the GC/MS.

1.2. PAHs

The Solid Phase Extraction (SPE) cartridges has been cleaned with 10 mL of deionized water and 5 mL of methanol. Subsequently, one hundred mL of wastewater sample aliquots have been stacked into the cartridges and went through a stream of about 5 mL/min. The cartridges were then washed with 5 mL deionized water preceding elution and dried at a low pressure for 14 minutes to eliminate any excess water. In the end, the cartridges were eluted using 4 mL of dichloromethane at a flow rate of 1 mL/min. The combined extracts were dried by evaporation using gentle nitrogen vapor. Results were passed to a 2 mL amber bottle.

1.3. Heavy Metals

Samples of wastewater (500 mL volume) were taken from various locations in polyethylene bottles pre-cleaned with de-ionized water, rinsed with the sample and immediately transported to the laboratory. Then put on the hot plate evaporate to almost dryness, making sure that the samples do not boil. Cool the beaker and add an additional 5 mL of acid; then cover it with glasses and put it back on the hot plate. Raise the temperature until a slight re-

flux occurs. Keep heating, adding additional acid if necessary, until the end of digestion; indicated by a slight coloured residue. Add 1 to 2 mL of nitric acid and heat the beaker slightly to dissolve the residue. Clean the walls of the beaker and the watch glass with distilled water and filter the sample from the blue band (Whatman 42). For the determination of metals, the volume was adjusted to 25 mL with de-ionized water. Heavy metal concentrations were measured by inductively coupled plasma optical emission spectrometry (ICP-OES).

Afterwards, 20 mL of this solution were placed in the sample tubes of the ICP-OES, the spectroscopic measurement was carried out under optimal instrumental parameters, using the standard addition method for the determination.

1.4. GC/MS working conditions

Gas chromatograph (Agilent 6890 series II) was used to analyze PAHs and PCBs. Temperature program: 1,000°C (10 min), 100-1,600°C (250°C/min), 160-2,700°C (50°C/min), 2,700°C isotherm (27 min). Injected volume: 1 µL/ splitless. Carrier gas: Helium (99.999 %), (8 psi). Column: BPX-5, 30 cm x 0.25 mm i.d. x 0.25 µm film thickness. Auxiliary (transfer line): 280°C. Detector: mass selective quadrupole – detector, Agilent 5973 N (MSD). Tuning masses: 69 / 219 / 502 m/z. Electron Impact Ionization, Ionization Energy: 70 eV. Calibration substance: Perflourotributylamine (PFTBA). Acquisition mode: Selective Ion Monitoring (SIM) – mode. Data analysis: HP MSD productivity Chemstation software. Mass was scanned at a range of 50 to 500 am at 0.5 s scan rate in total ion chromatogram (TIC) mode to identify the compounds in the standard mixture. For retention time designation purposes, mass spectrum for each analyte was compared with that published on data bases and also compared to the NIST mass spectral reference library for more confirmation. In sample analysis, SIM-mode was applied, where two ions were monitored for each analyte at its retention time range. The ratio between the ions abundances was used for identification purposes, while one of them was used for the quantitative analysis.

2. Status of Micropollutant Distribution in the Wastewater Treatment Plant

Table S1. The Status of Micropollutant Distribution in the Wastewater Treatment Plant

Micropollutants		N°1	N°2	N°3	N°4
		Sample ^a	Sample ^b	Sample ^c	Sample ^d
PAHs	Acenaphthene	+	+	+	+
	Acenaphthylene	+	+	+	+
	Anthracene	+	+	+	+
	Benzo (a) anthracene	+	+	+	+

	Benzo (a) pyrene	+	+	+	+
	Benzo (b) Fluoranthene	+	+	+	+
	Benzo (g,h,i) pyrene	+	+	+	+
	Benzo (k) Fluoranthene	+	+	+	+
	Chrysene	-	-	-	-
	Dibenzo (a,h) Anthracene	-	-	-	-
	Fluoranthene	+	+	+	+
	Fluorene	+	+	+	+
	Indeno (1,2,3,cd) Pyrene	+	+	+	+
	Naphthalene	+	+	+	+
	Phenanthrene	+	+	+	+
	Pyrene	+	+	+	+
	PCBs	PCB-28	-	-	-
PCB-52		-	-	-	-
PCB-77		+	+	+	+
PCB-81		+	+	+	+
PCB-101		-	-	-	-
PCB-105		+	+	+	+
PCB-114		+	+	+	+
PCB-118		+	+	+	+
PCB-123		-	-	-	-
PCB-126		+	+	+	+
PCB-138		-	-	-	-
PCB-153		-	-	-	-
PCB-156		+	+	+	+
PCB-157		-	-	-	-
PCB-167		+	+	+	+
PCB-169	+	+	+	+	
PCB-180	-	-	-	-	
PCB-189	+	+	+	+	
HMs	Cu	+	+	+	+
	Zn	+	+	+	+
	Fe	+	+	+	+
	Mn	+	+	+	+
	Cd	+	+	+	+
	Pb	+	+	+	+
	As	-	-	-	-
	Ni	+	+	+	+
	Ba	+	+	+	+
	Cr	-	-	-	-
Co	-	-	-	-	
Hg	+	+	+	+	

^a Raw wastewater.

^b Effluent at the end of pretreatment.

^c Effluent at the end of secondary treatment.

^d Effluent at the end of tertiary treatment.

+ Existent / - Inexistent.

3. Table Detection Limits

Table S2. Limit of Detection and Low Limit of Quantitation in (µg/L) for 46 Micropollutants Studied

Micropollutants	Limit of Detection (µg/L)	Lower Limit of Quantitation (µg/L)
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PAHs	Acenaphthene	0.002	0.007
	Acenaphthylene	0.001	0.005
	Anthracene	0.002	0.009
	Benzo (a) anthracene	0.001	0.003
	Benzo (a) pyrene	0.001	0.003
	Benzo (b) fluoranthene	0.001	0.003
	Benzo (g,h,i) pyrene	0.002	0.008
	Benzo (k) fluoranthene	0.003	0.009
	Chrysene	0.001	0.004
	Dibenzo (a,h) anthracene	0.002	0.007
	Fluoranthene	0.001	0.005
	Fluorene	0.008	0.025
	Indeno (1,2,3,cd) pyrene	0.002	0.006
	Naphthalene	0.003	0.008
	Phenanthrene	0.003	0.008
Pyrene	0.002	0.007	
PCBs	PCB-28	0.0009	0.0030
	PCB-52	0.0007	0.0020
	PCB-77	0.0008	0.0025
	PCB-81	0.0007	0.0025
	PCB-101	0.0008	0.0025
	PCB-105	0.0009	0.0030
	PCB-114	0.0008	0.0025
	PCB-118	0.0007	0.0025
	PCB-123	0.0015	0.0040
	PCB-126	0.0010	0.0035
	PCB-138	0.0015	0.0040
	PCB-153	0.0020	0.0035
	PCB-156	0.0010	0.0040
	PCB-157	0.0015	0.0035
	PCB-167	0.0025	0.0080
PCB-169	0.0015	0.0050	
PCB-180	0.0025	0.0065	
PCB-189	0.0010	0.0035	
HMs	Cu	0.0010	0.0050
	Zn	0.0020	0.0060
	Fe	0.0060	0.0200
	Mn	0.0001	0.0003
	Cd	0.0002	0.0009
	Pb	0.0020	0.0060
	As	0.0010	0.0040
	Ni	0.0002	0.0007
	Ba	0.0020	0.0060
	Cr	0.0005	0.0010
	Co	0.0025	0.0040
Hg	0.0001	0.0010	

4. Evolution of Flow of Wastewater during Sampling Campaigns

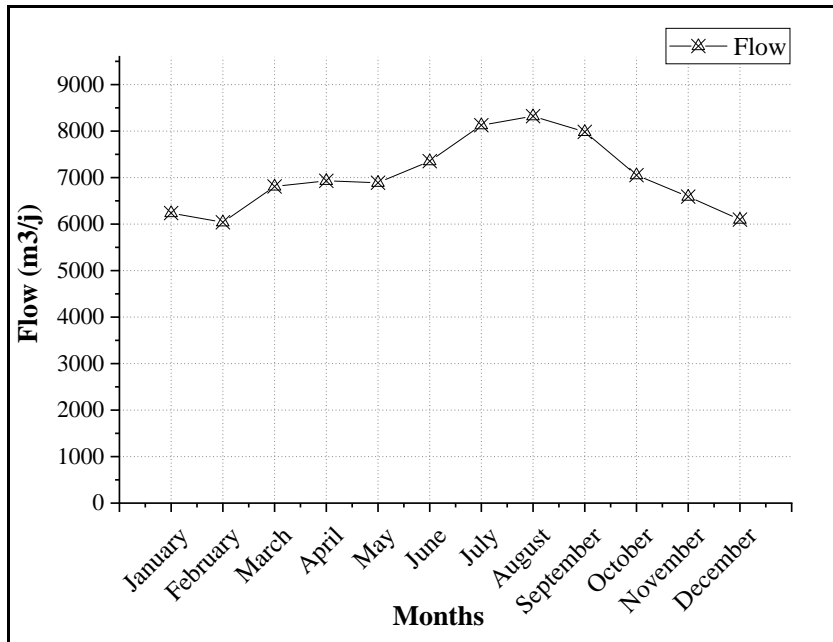


Fig. S1. Flow of wastewater during sampling campaigns.

5. Conventional Parameters of the Inlet and Outlet Wastewater (Monthly Mean Value)

The parameters monitored during this study are: total suspended solids (TSS), biologic oxygen demand (BOD₅), and chemical oxygen demand (COD) were analyzed every five-days for a year. Analyses were performed in the laboratory located on site according to international standard methods.

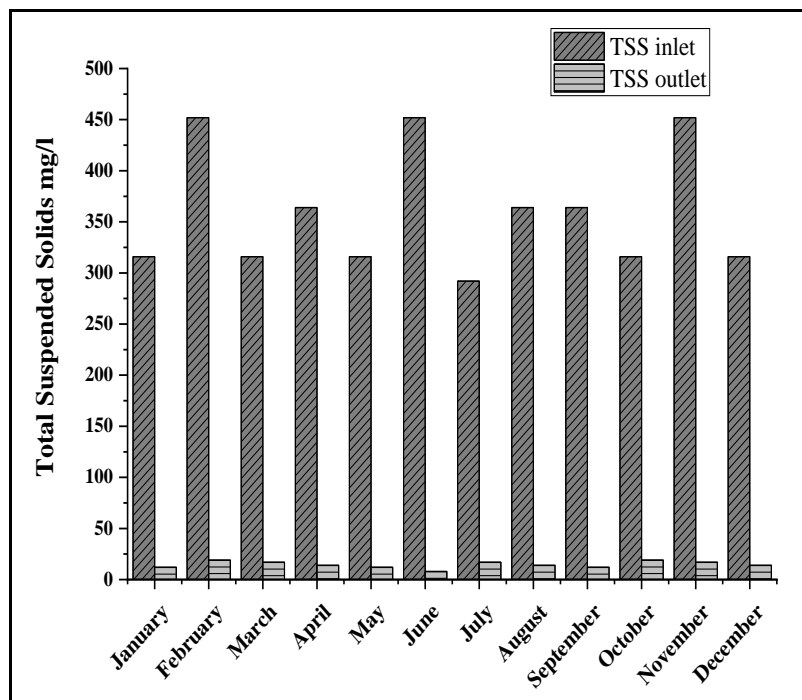


Fig. S2. Variation in TSS values between inlet and outlet.

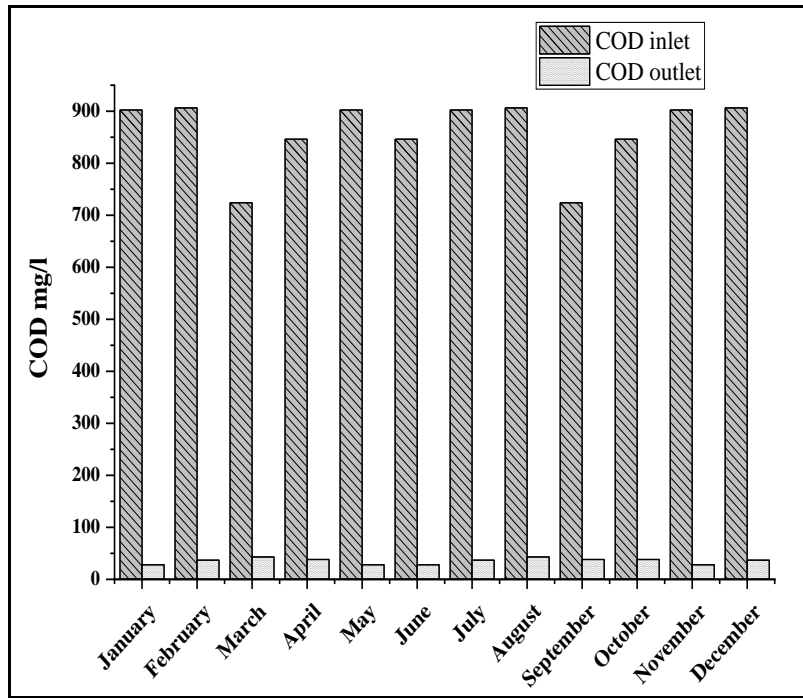


Fig. S3. Variation in COD values between inlet and outlet.

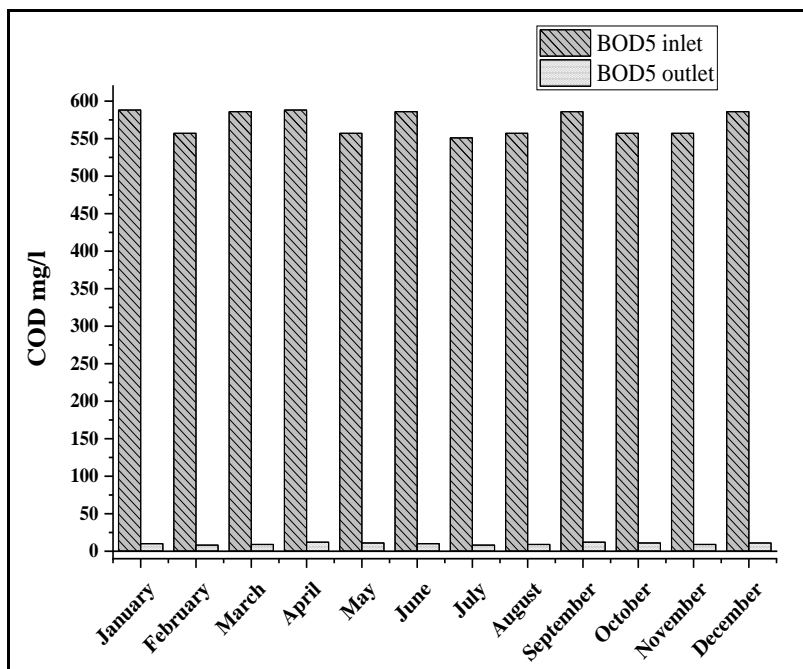


Fig. S4. Variation in BOD5 values between inlet and outlet.

Table S3. Linear Regression Structures Showing the Outlet Micropollutant Concentrations in Relation to the Macropollution Measured at the Inlet and Outlet of the WWTP

	Constant	TSS in	TSS out	COD in	COD out	TN in	TN out	TP in	TP out	BOD in	BOD out	r
Fe out	147.0336	13.2093	-193.3294	-0.0091	0.1700	0.1839	2.4678	-2.1439	1.7831	-0.0364	0.0470	0,832
Zn out	41.6780	-23.9305	-172.7978	-0.0002	0.1018	-0.1646	0,9285	1.5856	-0.3546	0.0666	-1.0733	0,589
Cu out	-79.5563	6.4874	-156.2270	-0.0266	0.1727	0.2268	1.5934	5.4971	3.0720	0.1381	-0.1206	0,691
Mn out	67.1772	-32.1102	163.3413	0.0215	0.1231	-0.1689	-0.2100	-3.5100	-1.5360	0.0098	0.1987	0,642
Ba out	57.0511	36.9297	548.4428	0.0039	-0.4002	-0.0074	0.1472	1.1167	-1.1519	-0.0451	0.9703	0,728
Pb out	-10.5564	-9.4411	-130.1518	-0.0017	-0.0714	0.0220	-0.1286	2.5765	-0.0704	0.0169	-0.5399	0,521
Ni out	-29.3927	-9.5579	-18.9956	0.0005	0.0349	0.0770	1.2639	-0.7812	1.0442	0.0419	0.0019	0,765
Cd out	-4.3745	1.4941	32.4380	0.0012	0.0283	-0.0036	0.2190	0.0960	-0.0632	0.0011	0.0606	0,822
Hg out	1.6109	0.9604	41.7266	0.0012	-0.0051	-0.0057	-0.1777	0.0186	-0.0912	-0.0039	0.0715	0,491
Naphthalene out	0.15670	0.00262	-0.41888	0.00002	-0.00001	-0.00027	-0.00312	-0.00309	-0.00023	-0.00011	-0.00002	0,662
Pyrene out	0.04551	0.02384	-0.22749	-0.00003	-0.00026	-0.00009	0.00232	0.00762	0.00338	-0.00008	-0.00033	0,762
Anthracene out	-0.01575	-0.00671	0.22310	-0.00006	-0.00007	-0.00001	0.00220	0.00362	-0.00055	0.00004	-0.00024	0,823
Fluorene out	-0.04155	-0.00303	-0.08063	-0.00002	0.00011	0.00018	0.00168	0.00315	0.00002	0.00004	-0.00035	0,842
Benzo (g,h,i) Pyrene out	-0.01811	0.00434	0.24473	0.00001	0.00020	-0.00012	-0.00180	0.00370	-0.00242	0.00001	0.00056	0,779
Benzo (a) Pyrene out	-0.03416	0.00459	-0.15750	-0.00002	0.00003	0.00007	0.00209	0.00289	0.00003	-0.00008	-0.00089	0,926
Indeno (1,2,3,cd) Pyrene out	-0.02071	-0.00290	-0.37267	-0.00002	-0.00017	0.00021	0.00218	0.00046	0.00461	0.00005	-0.00016	0,681

Table S4. Calculated Micropollutant Concentrations at the WWTP Outlet. Calculated Concentrations were Obtained by Eq. (3) and Table S3

	Fe cal	Zn cal	Cu cal	Mn cal	Ba cal	Pb cal	Ni cal	Cd cal	Hg cal	Naphthalene cal	Pyrene cal	Anthracene cal	Fluorene cal	Benzo (g,h,i) Pyrene cal	Benzo (a) Pyrene cal	Indeno (1,2,3,cd) Pyrene cal
Concentrations in µg/l	143.982	62.944	73.061	33.751	31.897	9.034	2.012	1.193	0.296	0.03197	0.04714	0.04300	0.01701	0.02216	0.04588	0.03203
	147.014	64.044	74.950	32.200	34.082	7.971	2.989	1.404	0.202	0.03424	0.04753	0.04397	0.01384	0.02641	0.04118	0.03266
	141.856	65.556	77.490	33.015	34.185	9.277	3.099	1.451	0.373	0.03492	0.04247	0.04500	0.01204	0.02250	0.04062	0.03210
	141.046	67.142	70.842	36.636	36.261	9.910	3.967	1.215	0.208	0.03602	0.04487	0.04099	0.01098	0.02086	0.04109	0.03197
	146.988	60.963	71.040	31.835	39.932	7.022	3.008	1.496	0.497	0.03616	0.04101	0.03998	0.01289	0.02093	0.04079	0.03377
	143.903	66.701	74.330	36.664	30.452	7.186	4.067	1.067	0.181	0.03084	0.04193	0.04201	0.01509	0.02301	0.04024	0.03581
	146.091	61.282	78.687	32.265	35.519	7.822	4.936	1.430	0.317	0.03616	0.04797	0.04298	0.01189	0.01989	0.04082	0.03576
	144.899	62.690	71.342	33.614	37.431	9.193	4.069	1.166	0.281	0.03799	0.04700	0.04200	0.01200	0.02200	0.04199	0.03300
	143.000	64.002	71.997	31.010	39.004	8.998	1.999	1.100	0.200	0.03782	0.04807	0.04201	0.01211	0.02315	0.04113	0.03324
	142.105	65.323	73.641	33.449	31.594	10.797	2.926	1.035	0.419	0.03799	0.04702	0.04200	0.01200	0.02202	0.04198	0.03300
	147.002	66.006	72.992	35.030	32.012	7.995	3.998	1.600	0.200	0.03781	0.04812	0.04201	0.01211	0.02321	0.04108	0.03325
	143.110	66.340	73.622	35.525	34.626	6.786	2.923	1.336	0.220	0.03799	0.04807	0.04201	0.01211	0.02315	0.04113	0.03324