Investigating sources of a wide range of organic micropollutants in urban wastewater

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Abstract. Urban wastewaters are often identified as major contamination vectors towards surface waters. The aim of this study was to investigate the presence of a wide range of pollutants (pesticides, biocides, pharmaceuticals, cosmetics, flame retardants, alkylphenols, phthalates …) in the sewage network of Bordeaux city in parallel to what was found in the rivers where the treated effluents are discharged. The study focused on various types of activities (industrial, domestic, hospital, …) in order to precise the main sources of compounds entering the WWTP. Waters from rainwater outlets were also studied. The results of this large-scale study showed the widespread contamination and allowed to establish presence of compounds in relation to main sources. Total concentrations in wastewaters ranged from 50 to 2000 µg.L-1. Contaminants were also quantified in rainwater at lower concentrations (2 – 160 µg.L-1) but with a higher variability. Compounds found at highest concentrations were often related to domestic origin. Finally, the cross-interpretation of all the results allows to provide a large picture of urban wastewater contamination that could help for a better understanding of pollutant dynamics and to identify source and transfer pathways in order to adapt correct management measures to make cities and territories more sustainable and safer.

Keywords: wastewater, rainwater outlets, sources, organic micropollutants, emerging contaminants

1. Introduction

The contamination of surface waters by chemicals such as pesticides, pharmaceuticals, perfluorinated alkylated substances (PFAS) or personal care products is now widely recognized (Loos *et al*., 2009). This became a major issue of public health concern, as this presence may be harmful to the freshwater resource (Malaj *et al*., 2014; Vörösmarty *et al*., 2010). Wastewater treatment plant (WWTP) effluents have been identified as important vectors of contamination. Indeed, WWTP are the receptacle of anthropic contamination, and as they were not designed to remove organic pollutants, some compounds are poorly degraded. 90 European WWTP effluents were analyzed and the results showed the presence of 125 substances over 156 polar organic chemical contaminants targeted (Loos *et al*., 2013). In this study, the presence of artificial sweeteners, pharmaceuticals and some pesticides was particularly showed. However, improving the WWTP technologies may not entirely reduce the micropollutant concern, and it is necessary to add source control measures (Neale *et al*., 2017). Indeed, the contamination is coming from the upstream of WWTP. For example, high levels of PFAS were observed in WWTP located in specific industrial areas (Xiao *et al*., 2012) and the hospital and domestic contribution to the pharmaceutical WWTP contamination was studied (Heberer and Feldmann, 2005; Quoc Tuc *et al*., 2017). These studies however considered separately different classes of contaminants and different types of wastewaters. Moreover, urban discharges such as separate or combined sewer overflows may also impact receiving waters (Barbosa *et al*., 2012). Pollutants such as polycyclic polycyclic aromatic hydrocarbons (PAH), alkylphenols or pesticides were indeed quantified in urban stormwaters (Gasperi *et al*., 2014).

The aim of this study was to investigate the presence of a wide range of pollutants (pesticides, biocides, pharmaceuticals, cosmetics, flame retardants, alkylphenols, phthalates …) in a small Garonne river tributary (near Bordeaux, south-west or France), the Jalle of Blanquefort, where treated effluents are discharged. In parallel, different type of effluents (industrial, domestic and hospital) of the sewage network of Bordeaux city and waters from rainwater outlets were studied.

2. Material and methods

2.1. Sampling

Time proportional 24 h composite water samples were collected at 4 points of a small Garonne river tributary (near Bordeaux, south-west or France, Figure 1), the Jalle of Blanquefort, between July 2013 and August 2015 (6 campaigns). This river is characterized by a low flow (≈ 3 $m^3.s^{-1}$) and is located in an urbanized area. It receives urban effluents such as wastewater treatment plants effluents and stormwater discharges. Flow proportional 24 h composite water samples from influent and effluent of a WWTP, discharging into the Jalle of Blanquefort were collected between July 2014 and November 2016 (6 campaigns were performed). The upstream of the sewage network of Bordeaux was also studied, with the collection of flow proportional 24 h composite effluent samples from industrial (2 campaigns performed at 15 sites in 2013-2015), hospital (2 campaigns performed for 9 effluents of the Bordeaux hospital in 2014-2015) and domestic areas (2 campaigns performed for 8 effluents in 2015). In parallel, flow proportional 24 h composite effluent samples were collected in separated sewer overflows (5 campaigns performed for 10 rainfall outlets, 2013-2015).

Upon arrival to the laboratory, surface water samples were filtered through glass fiber filter (pore size 0.7 µm, Whatman) and stored at -20°C in glass or Nalgene® bottles until analysis.

2.2. Extraction and analysis

A wide range of pollutants such as pesticides, biocides, pharmaceuticals, cosmetics, flame retardants, alkylphénols or phthalates was studied. Several extraction and analysis methods based on solid phase extraction (SPE), solid phase micro extraction (SPME), stir-bar sorptive extraction (SBSE) and liquid or gas chromatography coupled with mass spectrometry (LC/GC-MS) were implemented. All of them were sensitive in order to reach trace levels (0.1 – 100 $ng.L^{-1}$).

2.3. Control and quality insurance

Special attention was paid to quality insurance. All experiments were performed in dedicated room with dedicated materiel according to the level of contamination. For each experiment, spiked samples and blanks were performed in order to evaluate the trueness and the reproducibility of the method.

3. Results

2.1. Contamination of the Jalle of Blanquefort River

Total concentration in natural samples ranged from 2 to 6 µg/L (Figure 2). Pharmaceuticals and pesticides were the groups found at highest concentrations, with an increase in the downstream of the WWTP effluent. Indeed, despite the good removal for a large proportion of the contamination some molecules were still present in WWTP effluents. For example, the pharmaceuticals fenofibric acid (active form of fenofibrate, for cholesterol treatment), gabapentin (treatment for epilepsy and neuropathic pain), hydroxyl-ibuprofen (metabolite of ibuprofen, an analgesic), sotalol (cardiac arrhythmias treatment) and the metabolite of the glyphosate (herbicide), AMPA, were among the compounds found at highest concentration in the WWTP effluent (1-10 µg/L). These molecules were also along the most quantified in the river, in the downstream of the WWTP (0.2-1 µg/L). Other molecules were present at high concentrations in the river. For example, the DEHP (bis(2-ethylhexyl) phthalate) reached a concentration of 1 µg/L in the WWTP downstream (it is quantified at 1.8 µg/L in the WWTP effluent). 1-Nonyl-4-phenol (alkylphenol), toluene, vinyl chloride and tetrachloroethylene (volatile organic compounds) were also widely quantified in the upstream of the river, suggesting an earliest source. Moreover, some molecules were present at lowest concentrations but nevertheless of concern. For example the insecticide fipronil (used for urban applications such as flea treatments for pets or termite control) is quantified at concentrations comprised between 0.9 and 3.8 ng/L, which is higher than its predicted no effect concentration (0.77 ng/L, (AGRITOX, 2016)) particularly in the WWTP

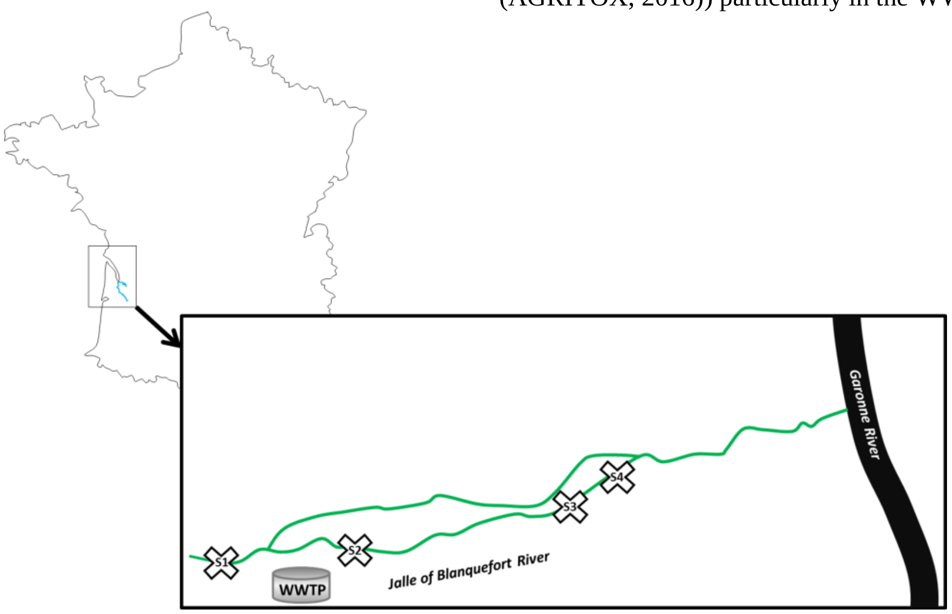

Figure 1. Location of sampling sites on the Jalle of Blanquefort River

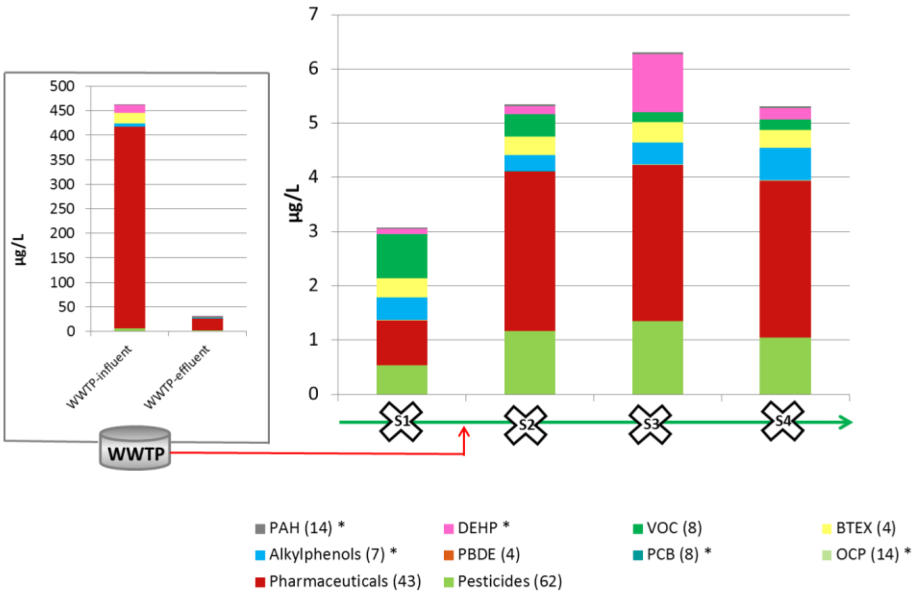

Figure 2. Total concentrations (µg/L) of organic compounds along the Jalle of Blanquefort River and in WWTP influent and effluent

downstream. Indeed, fipronil was quantified at 40 ng/L in the effluent.

Then, the Jalle of Blanquefort river was characterized by the presence of a wide range of molecules, and the impact of the WWTP effluent discharge on concentrations was showed. There is a need to investigate the upstream of the sewage network in order to identify the major sources of micro pollutants.

2.2. Contamination of wastewater

Total concentrations in wastewater effluents were high, and comprised between 50 and 2 000 µg/L. Concentrations in domestic effluents were comprised between 400 and 1 300 ng/L. Pharmaceuticals were predominant and represented more than 72 % of total concentration (93 % on average). DEHP represented from 1 to 12 % of total concentration. New classes of molecules such as UV filters, parabens, perfluorinated alkylated substances (PFAS) or triclosan (biocide) were specifically targeted in domestic effluents. UV filters were found at highest concentrations (2-7 µg/L), followed by parabens (2-5 µg/L) and triclosan (0.1-0.3 µg/L). PFAS concentrations were however significantly lower, inferior to 25 ng/L. It would therefore be interesting to investigate if these molecules are removed by WWTP treatments and if they are present in the river.

Total concentrations in industrial effluents were comprised between 200 and 900 µg/L. Surprisingly, pharmaceuticals were predominant and represented more than 75 % of total contamination. Industrial molecules such as alkylphenols or volatile organic compounds (including BTEX) only represented up to 12 % and 5 % of total contamination. Concentrations were comprised between 1-50 µg/L and 1-16 µg/L, respectively. The global fingerprint was then not significantly different from domestic one. This illustrated that these industrial effluents were more characterized by human activities than industrial ones.

Total concentrations in hospital effluents were comprised between 100 and 2 000 µg/L. Concentrations were higher in S2, S6 and S9 which were the services with a lot of medical activities (in contrast with administrative activity). Pharmaceuticals were predominant and represented more than 91 % of total contamination.

For all types of wastewater, paracetamol (analgesic) was identified as the major molecule. Indeed, it is the most distributed drug in France and it is also widely prescribed at hospital. Salicylic acid (metabolite of aspirin, analgesic), theophylline and caffeine (tracers present in coffea and tea) were also widely quantified, in relation with their large consumption. Other molecules however discriminate the different types of wastewater. Gabapentin was highly quantified at hospital while it was less quantified in industrial effluents and only quantified in one domestic effluent. Indeed this pharmaceutical is only supplied under prescription so it is not widespread. On the contrary, fipronil was quantified in higher concentration in domestic effluents while it was poorly quantified in hospital effluents. Finally, toluene concentrations were higher in industrial effluents and in some hospital effluents.

2.2. Contamination of separated sewer overflows

Total concentrations in separated sewer overflows were variable and comprised between 5 and 75 µg/L. Pesticides, DEHP et pharmaceuticals were found at the highest concentrations. The latter is surprising as the rainfall outlets were separeted sewer overflows, so no wastewater should be in there. This may be to bad connections within the wastewater network. Glyphosate (pesiticide) and its metabolites were major molecules. The parmaceuticals paracetamol, acid salicylic and the markers caffeine and theophilline were quantified at high concentrations, wich

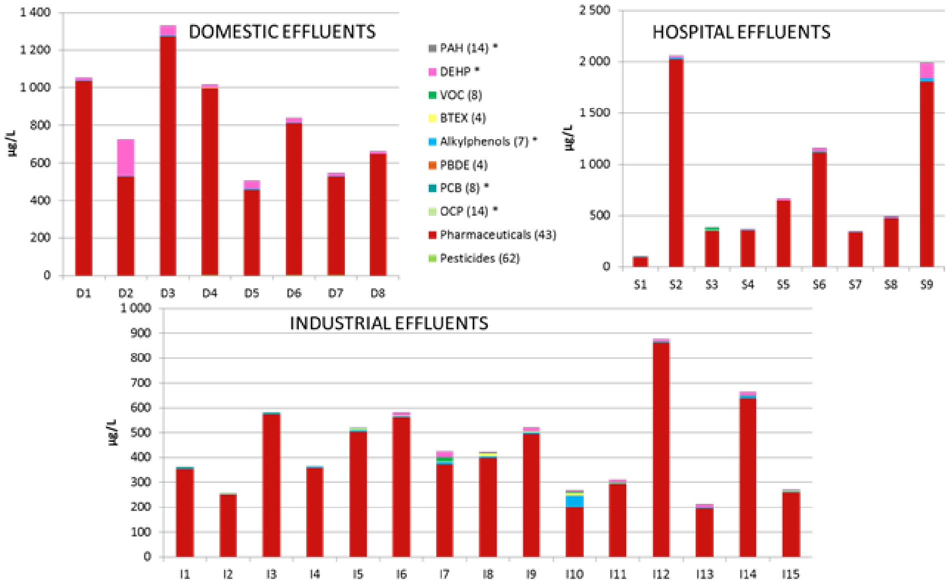

Figure 3. Total concentration (µg/L) of organic compounds in different type of wastewater (domestic, hospital and industrial effluents)

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Figure 4. Total concentration (µg/L) of organic compounds in separated sewer overflows

underlines the presence of non trated water. Nonyl-4-phenol (alkylphenol), and some volatile organic compounds were also widely quantified

4. Conclusion

In conclusion, the cross-interpretation of all the results allows providing a large picture of urban wastewater contamination. This will provide a better understanding of dynamics by identifying the main sources of each pollutant in order to add source control to make cities and territories more sustainable and safer.

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