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Occurrence of eight household micropollutants in urban wastewater and their fate in a wastewater treatment plant. Statistical evaluation

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HIGHLIGHTS

- Presence of eight household micropollutants in two different urban catchments was assessed.
- Concentration levels of the target compounds in sewage influent, treated wastewater and sludge were compared.
- The efficiency of a conventional activated sludge process was assessed.
- Statistical analyses have related the micropollution and macropollution in the WWTP.

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ABSTRACT

The occurrence in urban wastewater of eight micropollutants (erythromycin, ibuprofen, 4-nonylphenol (4-NP), ofloxacin, sucralose, triclosan, perfluorooctanoic acid (PFOA) and perfluorooctane sulfonate (PFOS)) originating from household activities and their fate in a biological wastewater treatment plant (WWTP) were investigated. Their concentrations were assessed in the liquid and solid phases (sewage particulate matter and wasted activated sludge (WAS)) by liquid chromatography–tandem mass spectrometry.

The analysis of sewage from two different urban catchments connected to the WWTP showed a specific use of ofloxacin in the mixed catchment due to the presence of a hospital, and higher concentrations of sucralose in the residential area.

The WWTP process removed over 90% of ibuprofen and triclosan from wastewater, while only 25% of ofloxacin was eliminated. Erythromycin, sucralose and PFOA were not removed from wastewater, the influent and effluent concentrations remaining at about 0.7 μg/L, 3 μg/L and 10 ng/L respectively. The behavior of PFOS and 4-nonylphenol was singular, as concentrations were higher at the WWTP outlet than at its inlet. This was probably related to the degradation of some of their precursors (such as alkylphenol ethoxylates and polyfluorinated compounds resulting in 4-NP and PFOS, respectively) during biological treatment.

4-NP, ofloxacin, triclosan and perfluorinated compounds were found adsorbed on WAS (from 5 ng/kg for PFOA to 1.0 mg/kg for triclosan).

The statistical methods (principal component analysis and multiple linear regressions) were applied to examine relationships among the concentrations of micropollutants and macropollutants (COD, ammonium, turbidity) entering and leaving the WWTP. A strong relationship with ammonium indicated that some micropollutants enter wastewater via human urine. A statistical analysis of WWTP operation gave a model for estimating micropollutant output from the WWTP based on a measurement of macropollution parameters.

1. Introduction

In the last decades, the use of pharmaceuticals and various chemicals present in many products used in our everyday life has become a source of environmental pollution transported by urban wastewater. Even though removal mechanisms for conventional macropollution (organic

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matter, nitrogen and phosphorus) in wastewater treatment plants (WWTPs) are understood and effective, this is not the case for most micropollutants (Kümmerer, 2001; Radjenović et al., 2009; Suarez et al., 2010; Richardson and Ternes, 2011). The removal of compounds such as pharmaceuticals, personal care products or detergents is usually not checked by plant managers or authorities because few or no regulations exist concerning their release into water bodies. The scientific interest in the environmental impact of these molecules, their behavior in WWTPs, and their occurrence in water bodies first emerged some ten years ago as showed in the literature review by Pasquini et al. (2013). Many of them are thought to be a possible threat to environmental health and safety.

Our research focused on eight micropollutants originating from different activities of our everyday life: erythromycin and ofloxacin (antibiotics), ibuprofen (anti-inflammatory drug), triclosan (biocide), 4-nonylphenol (4-NP is a mixture of branched isomers resulting from detergent degradation), sucralose (sweetener), and two perfluoroalkyl acids (PFAAs) (Buck et al., 2011)—perfluorooctanoic acid (PFOA) and perfluorooctane sulfonate (PFOS). PFOA and PFOS are employed in industrial and domestic products as floor cleaning agents and paints, but also in the manufacture of emulsifying agents, non-adhesive surfacing and waterproofing agent for textiles, leather and food packaging (Prevedouros et al., 2006).

The target compounds were chosen according to their:

i) occurrence in domestic use,
ii) physico-chemical properties in order to observe their possible partitioning between water and sludge in the WWTP. Erythromycin, 4-NP, triclosan and PFAAs which are hydrophobic compounds, and ofloxacin, are known to adsorb on sludge during biological treatment (Lindström et al., 2002; Picó and Andreu, 2007; Ochoa-Herrera and Sierra-Alvarez, 2008; Soares et al., 2008; Lillenberg et al., 2009). Ibuprofen and sucralose are hydrophilic compounds that should mostly remain in the aqueous phase,
iii) social and scientific interest: the French General Directorate for Health initiated in 2009 national campaigns to assess the occurrence of pharmaceuticals and perfluorinated compounds in water intended for drinking water production (surface water and ground water).

Our study focused on quantifying the target compounds in wastewater (in both the liquid and solid phases) from two urban areas and in the WWTP receiving wastewater from different catchments. The objective was *i*) to assess the occurrence of micropollutants released in two different types of urban areas, *ii*) to evaluate the removal (biodegradation or adsorption on sludge) of these compounds from wastewater by biological treatment in an urban WWTP, and *iii*) to examine by statistical methods if there is any relationship between micropollution and macropollution entering and leaving the studied WWTP.

2. Materials and methods

2.1. Sampling sites

Wastewater samples from two urban catchments in the area of Nancy, in the North-East of France, were studied. The first catchment is residential, with about 2100 lodgings and a sanitary sewage network. The second one is a mixed catchment composed of a hospital (about 1200 hospital beds), houses and administrations and with a combined sewage network. In both catchments, sampling was performed directly in the sewer.

The studied WWTP has a capacity of 500,000 p.e. (population equivalent). It treats urban wastewater from 21 municipalities (400,000 p.e.) including the two previously described catchments, and industrial wastewater from a brewery (100,000 p.e.). Urban wastewater is subject to pretreatment (grit, sand and oil removal followed by primary settling), biological treatment (pre- and post-denitrification combined with Biolift® technology), final clarification and then tertiary treatment (phosphorus precipitation). The sludge wasted from the final clarifier and the primary sludge are combined to get digested and dried after thickening.

Industrial wastewater represents less than 10% of the WWTP's daily inlet flow. It is pretreated separately to reduce its load to the same level as the urban wastewater and joins urban flows in the same biological treatment.

Samples were taken at the inlet (urban wastewater before pretreatment) and outlet of the plant (treated wastewater) and in the recycle line from the final clarifier.

Table S1, in Supplementary material, summarizes the sampling locations studied and the matrices analyzed.

2.2. Sample collection

Several sampling campaigns were performed in winter and summer. The wastewater and treated water samples were collected in dry weather with an automatic sampler (ISCO 3700, Teledyne ISCO, USA) over 24 h (1 l per hour and per bottle, time proportionnal). The 24 samples were always grouped by two consecutive; thus 12 samples were analyzed to determine concentrations of the target compounds. The sludge samples were manually collected. Before applying extraction procedures (described in Section 2.5.), wastewater and sludge samples were stored in two different bottles: part in HDPE (high density polyethylene) bottles for perfluorinated compounds analysis and part in amber glass bottles for the other six compounds. It was previously checked that the studied molecules did not adsorb on glass bottles.

2.3. Analysis of conventional wastewater parameters

Several conventional wastewater pollution parameters were assessed. Soluble chemical oxygen demand (COD) was measured by spectro-photocolorimetry (US EPA, 1993) following filtration on 0.45 μm pore size and chemical oxidation by a sulfochromic mixture. Ammonium content was determined by the Hach Nessler Method 8038 and measured on a Hach DR/2400 spectrophotometer (Hach Co., Colorado, USA) (error $\pm$ 0.5 mg/L N-NH_4+). Turbidity was measured by spectrophotometry at 450 nm and expressed in terms of formazin units. pH and conductivity were measured on a MeterLab ION 450 ion analyzer with two probes (Radiometer Analytical SAS, France).

2.4. Isotopic tracing of water sources

The infiltration of rainwater or groundwater into sanitary sewers can modify sewage chemistry by simple dilution of wastewater components, by addition of supplementary pollutants, or by a change of the deuterium/hydrogen ratio analysis (Houhou et al., 2010). Therefore the infiltration of rainwater or groundwater was checked in all sampling campaigns by ensuring that they were performed at a constant D/H ratio (more information and example in Supplementary material, Fig. S1).

The hydrogen isotopic composition (D/H ratio) of water was measured with an Isoprime mass spectrometer coupled with an elemental analyzer using a chromium reducing reactor (Morrison et al., 2001). The results were reported in δ-notation (δD) which represents the permil deviation of the measured isotopic ratio (D/H_{sample}) relative to a reference material (D/H_{SMOW}). Standard materials were V-SMOW (Vienna Standard Mean Ocean Water).

$$\delta D = \left(\frac{D/H_{sample}}{D/H_{SMOW}} - 1\right) \times 1000. \quad (1)$$