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BPA and phthalate fate in a sewage network and an elementary river of France. Influence of hydroclimatic conditions

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HIGHLIGHTS

- BPA and phthalates were characterized simultaneously in a sewage network and a river.
- WWTP removal occurred for BPA by degradation and for phthalates by decantation.
- The impact of the WWTP discharge for both pollutants upon river quality was proven.
- Opposite variations of BPA and phthalates with the hydro-climatic cycle were shown.

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ABSTRACT

Our purpose was to characterize the fate of bisphenol A (BPA) and phthalate contamination simultaneously in a sewage network and a watercourse, in relation with hydrological and climatic conditions. An elementary catchment of the Seine basin, receiving effluents from a wastewater treatment plant (WWTP), was chosen because of its basic hydrological features. BPA and DEHP concentrations in the WWTP inputs were 4 and 33 μg L^{-1} whereas in the outputs, they were only 0.4 and 2 μg L^{-1}, respectively. Contaminant ratios in the suspended sediment phase of the WWTP inputs ranged from 0.5% to 88%, related to their molecular properties. BPA and phthalates were effectively removed in the WWTP (>90% for both compounds), by degradation and decantation. Upstream of the discharge, river concentrations ranged from 0.002 to 0.175 μg L^{-1} for BPA and from 0.16 to 0.90 μg L^{-1} for DEHP. Downstream from the WWTP outputs, concentrations ranged from 0.11 to 0.79 μg L^{-1} for BPA and from 0.31 μg L^{-1} to 1.7 μg L^{-1} for DEHP: the WWTP discharge led to contaminant increases of 3.8 and 2 times, respectively. Far downstream, concentrations were lower ranging from 0.11 to 0.19 μg L^{-1} for BPA and from 0.36 μg L^{-1} to 1.1 μg L^{-1} for DEHP. BPA and phthalates displayed opposite seasonal variations with a decrease for the first one and an increase for the second one during summer. BPA contamination in the Charmoise river derived mainly from the WWTP, while phthalate contamination was attributed to both WWTP discharges and diffuse sources such as atmospheric bulk deposition.

1. Introduction

Bisphenol A (BPA) and phthalates are semi-volatile organic compounds widely used in industrial production and found in daily use products. The global BPA production was 4 million tons in 2006 and increased up to 5 million tons in 2008 (Chemical Weekly, 2009). The worldwide production volume of phthalates in 2008 was close to that of BPA and the di-ethyl-hexyl phthalate (DEHP) represented nearly 50% of the total phthalate consumption in the annual world market (German Federal Environment Agency, 2011). The wide use of BPA and phthalates led to their omnipresence in the different environmental compartments.

These compounds were frequently detected in wastewater discharged from municipal and industrial settlements from different countries (Fürhacker et al., 2000; Lee et al., 2004; Suzuki et al., 2004; Höhne and Püttmann, 2008; Sánchez-Avila et al., 2009). Removal efficiency of BPA by wastewater treatment plants (WWTPs) was incomplete, ranging from 30% to 90%, according to the treatment processes in use (Jin et al., 2008; Sánchez-Avila et al., 2009; Jafari et al., 2009).

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Phthalate removal efficiency was higher, ranging from 68% to 95% (Dargnat et al., 2009; Sánchez-Avila et al., 2009; Clara et al., 2010).

Consequently, residual contaminants were carried by WWTP effluents discharging to rivers, involving a pollution rise downstream of the discharges. Although BPA was reported to be quickly biodegradable in river water, under 2 d (Staples et al., 1998; Klečka et al., 2001; Flint et al., 2012), that compound was often found in river water with a wide range of concentrations: from 0.5 to 16 ng L^{-1} in Germany (Kuch and Ballschmiter, 2001) and from 90 to 12 000 ng L^{-1} in the USA including a wide range of sites with contrasted hydrological and climatic conditions (Kolpin et al., 2002). Close to WWTP discharge, it reached up to 1927 ng L^{-1} in Germany (Quednow and Püttmann, 2008). Several studies performed in China, Japan and Korea reported the presence of BPA in most of sediments (Khim et al., 2001; Kitada et al., 2008; Lui et al., 2010).

Phthalates in river water displayed a wide range of concentrations related to their physico-chemical characteristics and uses. DEHP was generally the prevailing compound ranging from 0.05 to 4.96 μg L^{-1} (Peñalver et al., 2001; Peijenburg and Struijs, 2006; Dargnat et al., 2009). Phthalates were easily found in sediment, especially the high molecular weight compounds such as di-n-butyl phthalate (DnBP), di-iso-butyl phthalate (DiBP), butylbenzyl phthalate (BBP) and DEHP (Peijenburg and Struijs, 2006; Huang et al., 2008; Fatoki et al., 2010).

In 2000, DEHP was listed among the 33 hazardous substances of the Water European Framework Directive (DCE, 2000/60/CE). Furthermore, the European Directive of December 16, 2008 (2008/105/CE) recommended for this compound, Norms for Environmental Quality (NEQ) in surface water, as acceptable annual mean concentrations of 1.3 μg L^{-1} and in sediment as acceptable maximal level of 4720 μg kg^{-1} dry weight.

In Europe, predictive environmental concentrations (PEC) for DEHP were estimated in rivers, downstream from WWTP discharges, to 3.2 μg L^{-1} in surface waters and to 30 mg kg^{-1} dry weight in sediments. These values were obtained from the EUSES model, on the basis of the DEHP contribution as follows: 2.5% from production, 2.5% from industrial uses, 32% from final by-products and 63% from waste treatments (EUR 23384 EN/2, 2008).

Our view was to improve knowledge about BPA and phthalate transfer mechanisms in relation with hydrological and seasonal conditions, at the scale of an elementary basin, equipped with a separate sewer network flowing to a WWTP. The Charmoise river (Ile-de-France) was selected because of its small surface basin (10.5 km^2) and its basic hydrography. The basin was equipped with a single sewage system which facilitated the investigation of WWTP impact upon river water quality.

In the present study, we considered BPA and phthalates in both dissolved and suspended sediment phases of wastewater and river water. First, we characterized their fates throughout the WWTP. Removal efficiencies of BPA and phthalates were determined, following seasonal variations. Then, the occurrence and the distribution of BPA and phthalates in the river water under contrasted hydrological conditions were investigated and the impact of WWTP discharge upon river water quality was considered. Last we focused on solid phase (suspended sediment and sediment) which integrated the contamination.

2. Materials and methods

2.1. Description of the study area

The study was conducted in a rural area around Fontenay-les-Briis (Essonne – France). The Charmoise river is an elementary tributary (Strahler stream order: 1) of the Orge river watershed, an affluent of the Seine river. The Charmoise river flow is usually low throughout the year although with unsteady variations, from 5 to 200 L s^{-1}. That small basin (surface: 10.5 km^2) is equipped with a separated sanitary sewer system, allowing to take into account the outputs of the WWTP of Fontenay-les-Briis that treats wastewaters of domestic (60%) and hospital (40%) origins (Fig. 1).

The WWTP working with a combined tank (decantation and activated sludge) treated 157 000 m^3 of wastewater by biological process and produced about 32 t $year^{-1}$ of dry sludge. The treatment capacity corresponded to 5000 inhabitant equivalents, while a population representing about 1715 inhabitant equivalents was connected, which indicates that the system was largely oversized. Wastewater fluxes entering the WWTP ranged from 270 to 532 m^3 d^{-1} in the 2010–2011 period and the transit time inside was about 17 h. The annual mean decrease between inputs and outputs for biological oxygen demand (BOD5), chemical oxygen demand (COD) and suspended matter were of 98%, 91% and 95.2%, respectively, during the study period, highlighting the efficiency of the Fontenay-les-Briis WWTP.

Water samples of WWTP inputs and outputs and of surface water, at three sites along the Charmoise river: upstream (50 m), downstream (15 m) and far downstream (1 km) from the WWTP discharge point were collected with a stainless steel bottle (Fig. 1). In view of investigating temporal variations of BPA and phthalate concentrations, 12 sampling campaigns, during different seasons, were carried out in the WWTP of Fontenay-les-Briis and in the Charmoise river, from February 2010 to February 2011. Contaminant distributions in dissolved and suspended sediment (S-Sed) phases were considered for all types of samples.

Also river sediment samples of about 200 g were taken with a sediment grab at the 3 sites along the river and stored in glass flasks.

2.2. Chemicals and reagents

Solvents for cleaning and extraction purposes were supplied by Merck-Chimie (Fontenay-sous-Bois, France). Superclean LC-Florisil (6 mL/1 g) cartridges for solid–liquid extraction (SPE) clean-up, were obtained from Sigma–Aldrich (Saint-Quentin Fallavier, France). Mobile phase for GC/MS, helium and nitrogen (99.999%), were purchased from Air–Liquide (Paris, France). Mobile phase for LC/MS/MS was prepared at the laboratory with methanol (liquid chromatography quality solvent – Merck) and ultrapure water from a Milli-Q system.

A standard solution of 6 phthalates in isooctane (dimethyl phthalate – DMP, diethyl phthalate – DEP, DnBP, BBP, DEHP, di-n-octyl phthalate – DnOP), was purchased from Supelco (*via* Sigma–Aldrich). DiBP and di-iso-decyl phthalate (DiDP) were added to the standard mixture of 6 phthalates at a final concentration of 8 μg mL^{-1} in isooctane, and di-iso-nonyl phthalate (DiNP) at a final concentration of 4 μg mL^{-1} in isooctane. Di-pentyl phthalate – DPP (Supelco) was used as internal standard (IS) and benzyl benzoate (Supelco) as surrogate standard (SrS).

BPA (98% purity assay) was obtained from Sigma–Aldrich and a solution of 2 μg mL^{-1} was prepared in methanol. BPA D_{16} from Supelco was used as IS for BPA quantification.

The internal standards were added to the different types of samples prior to extraction.

2.3. Sample treatment and extraction

3.5 L of water samples, except for wastewater entering the WWTP (250 mL), were filtered through glass fiber filters Whatman GF/F (Ø: 90 mm, porosity: 0.7 μm) to separate the dissolved and the S-Sed phases. In that concern, a wide range of filter pore size