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Phthalate Fate in the Hydrographic Network of the River Seine Basin (France) Under Contrasted Hydrological Conditions

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Abstract Our main objective was to characterize phthalate transfer mechanisms in the river Seine basin (France) under contrasted hydrological conditions. Phthalates were present in rural as well as in urban areas, and di-(2-ethylhexyl) phthalate (DEHP) was always prevailing. Hotspots of DEHP water concentrations were identified along the river Seine at wastewater treatment plant (WWTP) and combined sewer overflow discharge locations. A spatial concentration increase was found (×2 for di-ethyl phthalate and di-*n*-butyl phthalate and ×3.5 for DEHP) from upstream to downstream of the urbanized areas. Comparing hydrological conditions in the river Seine, from low to high water, a six-time increase in concentrations was found downstream of the urbanized areas, while a dilution process occurred at the rural station due to slightly contaminated inputs. A strong enhancement of annual specific flux for DEHP was estimated from upstream (33 g km^{-2} $year^{-1}$) to downstream (114 g km^{-2} $year^{-1}$) of the urbanized areas, corresponding to annual inputs of 4.9 t. The monitoring of a combined sewer overflow discharge, following a strong storm event, showed a preferential distribution of compounds in the surface microlayer. DEHP enrichment ratios between subsurface and surface microlayer were for the dissolved and the particulate phases 2.7 and 15, respectively. Even at the very upstream part of a rural elementary basin, impact of runoff input prevailed against that from WWTP discharge. Moreover, in a suburban basin equipped with a separate sewer system, increase in phthalate concentrations under high flow conditions was strictly related to runoff processes. Comparison of inputs between separate (Orge) and combined (Seine) systems indicated a 9.7-times higher pollutant inputs as square kilometer of surface basin from the combined one.

Keywords Phthalate · River Seine · Combined sewer overflow · Runoff · Wastewater

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1 Introduction

Phthalic acid di-esters have been synthesized as plasticizers since the 1930s. Their worldwide production is growing from 1.8 million tons in 1975 to 4.3 million tons in 2006, the quarter of which is represented by the di-(2-ethylhexyl) phthalate (DEHP) (Peijnenburg and

Struijs 2006). That compound, mainly used as plasticizer of polyvinyl chloride (PVC), is manufactured up to 60,000 tons yearly in France and accounts for 10 % of the European production (INERIS 2005).

Phthalates are of particular concern as they are found in a wide range of products used in day-to-day life: indoor coverings, motor car components, clothing, cosmetics, medical disposals, and various household appliances. Contrary to other additives, they are not chemically bound to polymer matrix and, thus, might get easily dispersed to the close environment. Most plastic or polymeric materials containing DEHP are typically disposed of in landfills, where they are subjected to dynamic physicochemical and biological deterioration and degradation (Latorre et al. 2012). Moreover, a new phthalate source could be linked to PVC recycling activities, which represent a growth sector in Europe, from 14 255 tons treated in 2003 to 194 950 tons in 2008 (Sadat-Shojai and Bakhshandeh 2011).

Phthalates were involved in toxic processes, namely as endocrine disruptors in rodent (Harris et al. 1997) and in fish (Norrgren et al. 1999). In humans, the main concerns are fertility and postnatal development (Kavlock et al. 2002a, b, c, d). The new European Registration, Evaluation, Authorisation & Restriction of Chemicals (REACH) listed di-*n*-butyl phthalate (DNBP), benzylbutyl phthalate (BBP), and DEHP among hazardous substances of high concern for humans and environment. For drinking water, a maximal concentration value of 8 μg L^{-1} was recommended by the World Health Organization (WHO 1998) and of 6 μg L^{-1} by the US Environmental Protection Agency (EPA 2002).

In 2000, DEHP was listed among the 33 hazardous substances of the Water European Framework Directive (DCE 2000/60/CE). Furthermore, for DEHP, the European Directive of December 16, 2008 (2008/105/CE) recommended 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 levels of 4,720 μg kg^{-1} dry weight.

For that reason, phthalates were proposed in a list of selected storm water priority pollutants for evaluation of the chemical risks (Eriksson et al. 2007). Although significant improvements of wastewater treatment were performed, notably by the Syndicat Intercommunal d'Assainissement de l'Agglomération Parisienne in the Paris area, according to the European Directive on Urban Residual Waters, urban waste discharge under high rainfall pattern conditions, particularly in case of unitary sewers and storm overflows, might represent a major pollutant input source to surface water (Gasperi et al. 2012). Previous studies in the river Seine basin reported different processes occurring in river water, next to unitary overflow discharge, leading to strong hypoxia (Servais et al. 1999). Those questions are of major concern since the river Seine surface water constitutes a resource for drinking water production in the Ile-de-France area. Up to now, phthalate dynamics in surface and urban storm water were poorly documented and knowledge improvements about their distribution processes are needed. Moreover, the urban water system appeared to be an important sink for the nonpoint source of phthalates (Björklund et al. 2009).

In that context, our view was to improve knowledge of transfer mechanisms involved in phthalate distribution through the river Seine basin in the Ile-de-France district that displays particularly contrasted areas. The upstream parts of the small suburban basins are covered by intensive agriculture and receive atmospheric and runoff inputs, while downstream, they are densely populated (990 inhabitants/km^2 representing altogether 30 % of the national population) with a lot of industrial settlements and wastewater discharges. A combination of strong human pressures with limited dilution by the river Seine, due to its low flow rate, leads to heavy contamination downstream of the Paris conurbation (Gasperi et al. 2009).

Firstly, hotspots of phthalate concentrations along the river Seine were characterized and pilot stations were identified for investigating impacts of the densely urbanized Paris area upon the river contamination.

Secondly, the influence of hydrological conditions upon phthalate distribution in the river Seine was investigated over 2 years, upstream (one rural station) and downstream (two urban stations) of the Paris area. In addition, phthalate behaviour in a water body, discharged by a main urban combined sewer overflow in the river, during a strong rainy event, was monitored.

Thirdly, we attempted to specify the respective parts played upon phthalate transfers in rural and urban areas, by runoff and domestic wastewater through a separate or a combined sewer system, under dry and rainy weather conditions. Thus, we focused on phthalate distribution at the scale of one tributary basin, the river Orge (937 km^2) including the basin of its affluent, the Prédecelle (41 km^2).

2 Material and Methods

2.1 Sampling Schedule

The river Seine has a 777-km long course and runs through the Ile-de-France area, including Paris and its suburbs, which are densely industrialized and populated (11.5 million inhabitants) and last, flows into the channel. The river Seine and its tributaries are ruled by a pluvial-oceanic hydrologic regime, i.e., rainfall events are distributed throughout the year with a low flow period, from June to September and a high flow period, from December to April. Their hydrologic parameters, recorded for 35 years at gauging stations, are indicated in Table 1 and give information about the river system.

Three monitoring campaigns were carried out at different time scales in the river Seine:

1. In order to determine the hotspot locations and to precise the relative impacts of industrial and domestic discharges in the urbanized areas, water contamination was investigated during a high flow period in April 2008 at 17 stations from Marnay to Poses (Fig. 1a, Table 2). The river flow was 671 $m^3\ s^{-1}$ on the sampling day and the rainfall pattern including the previous days was 46.2 mm.
2. The spatial long term distribution of phthalate concentrations was investigated along the river Seine from 2009 to 2010, through complete hydrological cycles at three stations, one upstream (Marnay—station 1) and two downstream of highly urbanized areas (Bougival—station 8; Triel—station 12). Sampling locations are mentioned on Fig. 1a.
3. In addition, the monitoring of a water body from the combined sewer overflow of Clichy started on August/07/2008 (10 h, A.M.) and ended on August/08/2008 (3h 35, A.M.), during a strong storm event (rainfall, 19.2 mm) following a low flow period (17 days without raining) at the Clichy overflow discharge, downstream of the Paris area. The river flow increased from 150 to 356 $m^3\ s^{-1}$ in 1 h, and a water body of 577,000 m^3 poured into the river Seine with a 37 $m^3\ s^{-1}$ flow. The samples (A–D) were taken at successive times in order to study the becoming of the water body following the water flow. Two kinds of samples were collected, a surface micro-layer (SμLy, n=2) by means of a stainless steel sieve (0.5 m^2 surface; 100–150 μm pore diameter) and a subsurface (SbSu, n=4) by means

Table 1 Hydrological parameters of the river Seine and four tributaries (mean data over 35 years)

River		Unit	Prédecelle	Orge	Marne	Oise	Seine				
River length		km	19.1	50	525	341			777		
Basin surface		km^2	41	937	12,920	16,667	8,760	30,800	43,800	61,820	65,000
Gauge station			Outlet	Outlet	Outlet	Outlet	Marnay	Alfortville	Paris	Triel	Poses
River flow	High water	December–April	$m^3\ s^{-1}$	2	4.4–6.03	89.4–183	87.7–187	87–110	260–387	402–549	560–660	630–740
	Low water	June–September	$m^3\ s^{-1}$	0.33	2.29–2.83	56–79	47.4–76.3	45–64	102–107	140–191	253–322	340–460
	Average flow		$m^3\ s^{-1}$		3.9	110	110	76	214	310	483	538
	Specific flow		L $km^2\ s^{-1}$	8.1	4.2	8.5	6.6	8.7	6.9	7.1	7.8	8.3

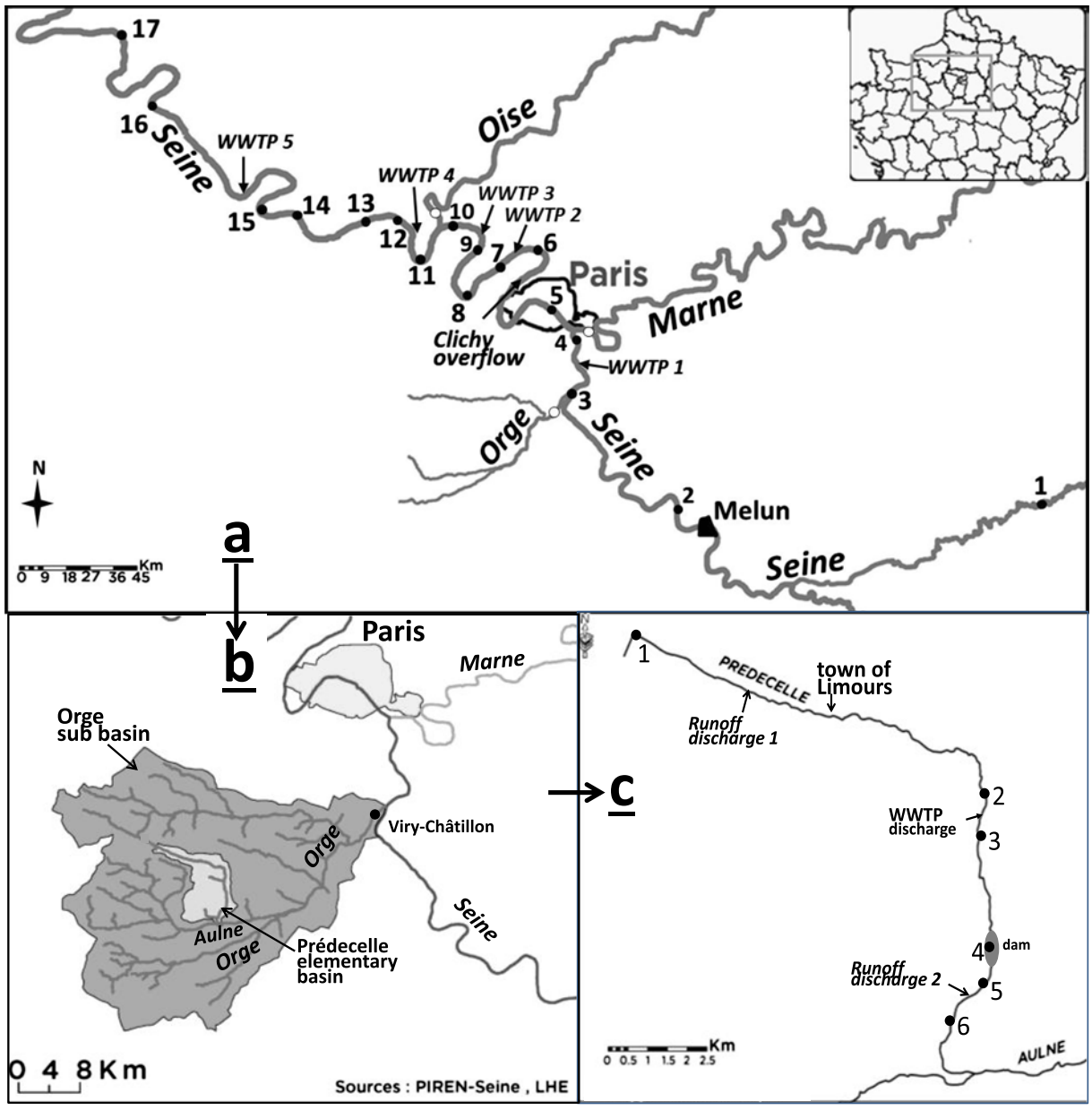

Fig. 1 Location of the 17 sampling stations (*filled circle*) and the tributary outlets (*empty circle*) along the river Seine from upstream to downstream of urbanized area (**a**). Locations of the sampling station of Viry-Châtillon at the outlet of the river Orge (**b**) and of the six sampling stations along the river Prédecelle (**c**)

of an amber glass bottle at 30 cm depth (Table 3). The occurrence of large amounts of organic matter in the discharge might involve the emergence of surface films that displays a high affinity for organic micro pollutants and alter the air/water interface of the river (Chi et al. 2003). Both types of samples from the water body, allowed investigating phthalate distribution between the dissolved and particulate phases and their fate in the single discharge plume.

Moreover, two sub-basins were investigated:

1. The river Orge tributary with a surface basin of 937 km^2, flows through uncultivated lands, such as woods and meadows in the upstream part (292 km^2, representing 31 % of total), then

Table 2 Sampling stations of the river Seine (light types), the tributaries (bold types), and the Clichy combined sewer overflow (italic) as reported on Fig. 1

Sample number	Sampling station	Site characteristics	Kilometric point from Paris (km)	DEHP concentration ng L^{-1}
1	River Seine (Marnay)	Reference site	−149	70
2	Seine (St Fargeau-Ponthierry)	Downstream city of Melun	−52	83
	River Orge (Viry-Châtillon)	**Outlet of river Orge**		**1,519**
3	Seine (Ablon)	Downstream river Orge confluence	−20	114
4	Seine (Port à l'Anglais)	Downstream WWP 1	−7	127
	River Marne (S^{t} Maurice)	**Outlet of river Marne**		**115**
5	Seine (Paris)	Downstream river Marne confluence	0	84
	Clichy combined sewer overflow	*Discharge*	*+24*	*1,741*
6	Seine (Epinay-sur-Seine)	Downstream Clichy overflow discharge	+32	266
7	Seine (pont de Bezons)	Downstream WWP 2	+39	321
8	Seine (écluse de Bougival)	Downstream tire industry	+49	297
9	Seine (Maisons-Laffitte)	Downstream WWP 3	+59	466
10	Seine (Conflans)		+70	225
	River Oise (Conflans)	**Outlet of river Oise**		**387**
11	Seine (Poissy)	Downstream motor car industry and river Oise confluence	+78	286
12	Seine (Triel)	Downstream motor car industry and WWP 4	+85	636
13	Seine (Les Mureaux)	Downstream aerospace industry	+93	588
14	Seine (Mantes-la-Jolie)		+109	285
15	Seine (barrage de Méricourt)		+121	168
16	Seine (Gaillon)	Downstream WWP 5	+164	190
17	Seine (Poses)	Upstream Poses dam	+202	180

Corresponding DEHP concentrations as ng L^{-1} during the campaign of April 2008, under high flow and rainy conditions

through intensive agriculture area in its middle course (425 km^2, 45 % of total), and last, through urban area downstream (220 km^2, 23 % of total) gathering most of the basin population (87,000 inhabitants). The impervious surfaces were estimated to 23 % of total. WWTP discharges are also present in the upstream rural part of the basin (Fig. 1b, Table 1). The downstream area is

Table 3 Sampling characteristics for monitoring of the combined sewer overflow of Clichy and suspended sediment concentration for the two types of samples collected, the surface microlayer (SμLy) and the subsurface (SbSu), at different sampling times following the river flow

	Combined sewer overflow of Clichy	Seine river					
		Upstream of the overflow	Downstream of the overflow				
Sample name	CSO	TA-SbSu	TB-SμLy	TB-SbSu	TC-SμLy	TC-SbSu	TD-SbSu
	Subsurface	Subsurface	Surface layer	Subsurface	Surface layer	Subsurface	Subsurface
Location	Km 0	Km −1	Km +14		Km +34.5		Km +52.5
Sampling time	t 0	t 0	t +4h40	t +4h40	t +11h30	t +11h30	t +17h30
Suspended sediment (mg L^{-1})	188	17.0	27.8	18.7	19.4	8.4	13.4

connected to a separate sewer system flowing to a WWTP that do not discharge in the river Orge. Inputs under rainy conditions occur in that area, mainly from urban runoff upon the impervious surfaces. At the outlet of the river Orge (Viry-Châtillon) in 2009–2010, 11 series were carried out under low flow (n=6, 2.29 to 2.83 m^3 s^{-1}) and high flow (n=5, 4.4 to 6.03 m^3 s^{-1}) conditions to precise the impact of hydrological conditions in a subbasin equipped with a separate system.

2. The river Prédecelle (elementary tributary of the river Orge) flowing mainly through rural areas (85 %) with 75 % intensive culture and 25 % of uncultivated lands was also considered. The impervious surfaces were estimated to 4 % of total. A WWTP (Briis-sous-Forges, 5,000 inhabitant equivalents, flow of 0.027 m^3 s^{-1}), discharges directly into the river (Fig. 1c, Table 1). The impact of discharges from the different sewer systems upon this small subbasin of 41 km^2 were studied in 2008 under low (n=2) and high (n=2) flow conditions. Surface waters, runoff discharges, domestic wastewaters, and WWTP discharges were carried out.

2.2 Sample Collection and Analyses

Use of plastic materials was prohibited throughout the procedures. All the solvents were of pico-grade quality for trace analysis and free from phthalates (Merck, Darmstadt, Germany). Samples were treated as described by Dargnat et al. (2009a). Water samples were collected with a stainless steel flask and stored in amber glass flasks with Teflon® stoppers. Aliquots of raw water were filtered through a glass fibre filter (Whatman GF/F), with pore diameter of 0.7 μm. After addition of the internal standard (IS), phthalates were extracted from 3.5 L of raw or filtered water with a solvent mixture (3 vol hexane–1 vol dichloromethane) and then, concentrated to 500 μL.

Freeze-dried filter samples were spiked with IS in a 40 mL centrifuge glass tube, extracted by ultrasonic treatment with 20 mL of hexane/acetone (80⊗20, v/v) then centrifuged (5 min, 970×g), and supernatants were collected. This procedure was performed twice and both extracts were combined and concentrated under nitrogen stream.

Prior to analysis, the extracts were purified with 1 g LC-Florisil cartridges (Supelco, from Sigma-Aldrich, Saint Quentin Fallavier, France), concentrated under a nitrogen stream to 250 μL and 100 ng of benzyl benzoate were added as syringe standard. Suspended matter (SM) contents were determined by gravimetry.

Sample analyses were performed by gas chromatography–mass spectrometry with a 7890 A gas chromatograph (Agilent Technologies, Massy, France) coupled to a 5975 A mass spectrometer (Teil et al. 2012). Analytical conditions were as follows: splitless at 290 °C, 1 μL injected, column ZB-7HG (30 m, 250 μm ID, 0.25 μm film thickness, Phenomenex, France), oven temperature of 50 °C for 1 min then 30 °C/min to 280 °C and 15 °C/min to 310 °C for 4 min, 1 mL min^{-1} helium, electronic impact detector, quadrupole at 150 °C, interface at 200 °C, source at 230 °C. Quantification and qualification ions were as follows: 163, 194 [di-methyl phthalate (DMP)]; 149, 177/105 [di-ethyl phthalate (DEP)]; 149, 223 (DnBP); 149, 104 (DPP); 149, 104/206 (BBP); 149, 279/293 (DEHP); and 149, 279 [di-n-octylphthalate (DnOP)].

Calibration was realized with a mixed solution of six phthalates in isooctane (DMP, DEP, DnBP, BBP, DEHP, and DnOP from Supelco, Sigma-Aldrich) and dipentyl phthalate (DPP) as internal standard. Reproducibility was checked by standard deviation (as %) considering 12 different calibration curves. Results were 28 for DEP, 31 for DnBP, and 21 for DEHP. Instrument detection limits (IDLs) were considered, for the standard solutions, as the concentration with a signal/noise ratio of 3 (peak to peak). Method detection limits (MDLs) corresponded to concentrations of signal/noise ratios of 9 (peak to peak). Analytical blanks were performed simultaneously for each series (about one blank for five or six samples). Sample measurements were corrected by the concomitant blanks and limits of quantification were corresponding to the average blank values. When blanks were below IDLs, MDLs were considered. IDLs, recovery rates and MDLs were 37.5 pg, 68.5 % and 29 ng L^{-1} for DEP; 3.6 pg, 91.5 % and 54 ng L^{-1} for DnBP; and 4.5 pg, 92.5 % and 50 ng L^{-1} for DEHP.

Samples were sorted according to low and high river flow conditions. Concentrations were expressed as nanograms per liter, and fluxes (kilograms per day) were estimated from river flows (cubic meter per second) provided by Eaufrance. River specific flows as liters per square kilometre per second were calculated as ratios between river flows as cubic meter per

second and basin surface as square kilometer. Specific catchment area emission factors (SCAEFs as grams per square kilometre per year) were calculated as ratios between river concentrations and specific flows. Statistical analyses were performed with XLSTAT 7.1 software (Addinsoft). Correlation significances were expressed by the Pearson *r* coefficient and corresponding p values were read in the table of Fisher and Yates. Comparisons of series were performed with the Student's *t* test or for particular data distribution, with the Kruskall–Wallis and the Mann–Whitney nonparametric tests.

3 Results

3.1 Urban and Industrial Hotspot Locations

The spatial monitoring at the scale of the river Seine basin showed that DEHP clearly prevailed at all sites. The part played by the main inputs under high flow condition (671 $m^3 s^{-1}$ at Paris) and rainy weather (rainfall 4.6 mm) was determined. From Marnay upstream to highly urbanized areas to Poses far downstream, successive rises of DEHP concentrations were observed next to lateral inputs from WWTP discharges or storm overflows and industrial activities (Table 2).

A succession of events such as tributary or WWTP and industrial (tire and motorcar factories) discharges led to the maximum DEHP concentration, up to 636 ng L^{-1} at Triel. A first impact was observed at the confluence of the river Orge tributary due to its highest DEHP concentration. As a matter of fact, the NEQ was exceeded for this tributary. The three tributaries showed contrasted impacts to the river Seine with dilution by the river Marne and enrichment by the river Orge and Oise (Table 2).

The highest DEHP increase (three times) was observed at the station 6, downstream of the combined sewer overflow discharge of Clichy.

WWTP 1 and WWTP 2 discharges were of negligible importance, while WWTP 3, which drains a large part of the wastewaters from the Paris conurbation, led to a 1.5 times increase at the station 9. A strong enhancement occurred at the station 12 related to the conjunction of river Oise, car industries, and WWTP 4 discharges. Thus, the combined sewer system of the Parisian area leads to important discharges by rainy weather.

Next, concentrations decreased and remained steady until Poses that might be linked to minor lateral inputs in that less industrialized and urbanized area. Moreover, sediment deposit and degradation processes might be involved (Table 2). Indeed, phthalates are partly associated to particulate matter and deposit mechanisms occurred in this section, not channelized of the river Seine (Gasperi et al. 2009). Last, biodegradation processes exist in river sediment under aerobic (Chang et al. 2004a) and anaerobic conditions (Chang et al. 2004b) as in river water (Hashizume et al. 2002).

Evidence was given for the prevailing influence of the urbanization, particularly at the outlet of the river Orge basin and at the combined sewer overflow discharge at Clichy, as compared to that of industrial settlements downstream of Paris.

3.2 Impact of Hydrological Conditions on Phthalate Distribution in the River Seine

The impact of low and high flow conditions was investigated at the rural station of Marnay upstream and at Bougival and Triel downstream of the Paris conurbation (Table 4). DEP, DnBP, and DEHP were detected in all samples. DEHP prevailed at concentrations from 22 to 261 ng L^{-1} at the rural station of Marnay and from 50 to 814 ng L^{-1} downstream of the Paris area, as reflect of the industrial production pattern. In that way, DEHP was the predominant compound in water and settleable particles of the river Seine in 2006–2007, at median concentrations of 1 μg L^{-1} and 5.1 μg g^{-1}, respectively (Gasperi et al. 2009). Moreover, our DEHP observations were consistent with the lowest phthalate concentrations reported in the literature for surface water from other countries worldwide, particularly in Canada (0.2–270 ng L^{-1}, Fromme et al. 2002), and in USA (10–700 ng L^{-1}, De Leon et al. 1986).

In Europe, a similar concentration (700 ng L^{-1}) was reported in the Ebro river (Spain) by Peñalver et al. (2000). Higher values than for river Seine were observed in other European countries like Germany (80–10,000 ng L^{-1}, Fromme et al. 2002), The Netherlands (50–4960 ng L^{-1}, Peijnenburg and Struijs 2006), and Italy (280–3,000 ng L^{-1}, Vitali et al. 1997). Concentrations of only 1,600 ng L^{-1} were reported in rivers from strongly contaminated sites in England

Table 4 River flow ($m^3\ s^{-1}$), suspended sediment (S-Sed, mg L^{-1}), dissolved organic carbon (DOC) and particulate organic carbon (POC, mg L^{-1})

Sampling location	Marnay			Bougival			Triel		
Sampling frequency	11	7	4	9	5	4	13	7	6
Mean±SD	Annual	Low water	High water	Annual	Low water	High water	Annual	Low water	High water
River flow ($m^3\ s^{-1}$)	36±16	26.3±8.9	53±7.5	173±73	121±25	238±55	311±110	228±60	408±64
S-Sed (mg L^{-1})	10.1±5.7	6.5±2.1	16.3±4.3	17.4±14.3	14.8±7.9	20.7±9.6	13.9±6.4	10.6±2.2	17.9±7.5
DOC (mg L^{-1})	2.1±0.22	2.1±0.25	2.1±0.21	2.9±0.41	2.6±0.22	3.1±0.4	3.5±0.24	3.3±0.17	3.6±0.23
POC (mg L^{-1})	0.68±0.28	0.52±0.23	0.91±0.19	1.8±1.37	1.8±0.86	1.8±1.9	1.2±0.6	1.0±0.34	1.5±0.8
DEP (ng L^{-1})		328±158	<LQ		480±231	<LQ		411±280	<LQ
DnBP (ng L^{-1})	60±42	47±49	78±36	101±83	70±57	124±99	121±119	102±131	140±121
DEHP (ng L^{-1})	120±74	128±82	107±75	484±251	459±299	515±214	465±270	380±286	636±151
DEP (kg day^{-1})		7.2±1.5			7.2±1.5			11.1±2.7	
DnBP (kg day^{-1})	0.19±0.06	0.36±0.02	1.51±0.52	1.5±0.52	0.7±0.13	2.6±0.47	3.2±1.1	2.8±0.63	3.6±0.73
DEHP (kg day^{-1})	0.37±0.10	0.29±0.06	0.49±0.05	7.2±1.6	4.8±0.66	10.6±1.0	12.5±2.6	7.5±1.5	22.4±0.84

DEP DnBP and DEHP concentrations (ng L^{-1}) and fluxes (kg day^{-1}) at the stations of Marnay, Bougival, Triel (2009–2010) as annual, low and high water means

receiving direct and indirect discharges from plastic factories (Fatoki and Vernon 1990) .

Last, river Seine varied little since 2004, where DEHP concentrations ranged from 323 to 779 ng L^{-1} (Dargnat et al. 2009b), while the trend was to replace the main phthalate compounds by esters of polylactic acid and starch based materials.

Considering the spatial distribution from Marnay upstream to Triel downstream of Paris, an important increase in water concentrations as annual means was noticed: 2 times for DnBP and 3.5 times for DEHP.

Distribution ratios between particulate and dissolved phases were 33.6 % for DEP, 48.3 % for DnBP, and 66.4 % for DEHP, and significant relationship was found between particulate organic carbon and DEHP contents of the particulate phase (Fig. 2). The increase of log octanol–water partitioning coefficient for phthalates with their molecular weight, leads to a predominant DEHP partitioning in the suspended sediment (S-Sed) and organic matter (Cousins and Mackay 2003). In addition, a significant correlation was observed between dissolved organic carbon and DEP concentrations of the dissolved phase (Fig. 2). More, S-Sed from the river Seine was mainly of organic nature with a high correlation between the particle levels and the particulate organic carbon contents ($p<0.001$, $r=0.934$, $n=18$). These results pointed out the WWTP discharge and the combined sewer overflow contributions to the river phthalate contamination.

At Marnay, DEP and DEHP concentrations were the lowest found under high flow conditions. A dilution process corresponding to little lateral inputs and the lack of runoff at this rural station occurred. On the contrary, we observed that DnBP and DEHP concentrations increased under high flow conditions in the urban areas of Bougival and Triel affected by significant contamination inputs (Table 4).

DEHP concentration discrepancies were found between low and high water conditions from Marnay to Poses, with three times higher values under low water and six times under high water conditions. More than 200 sewer overflows were identified in the Paris area, the main one being situated at Clichy, which were accountable of important discharges of the combined

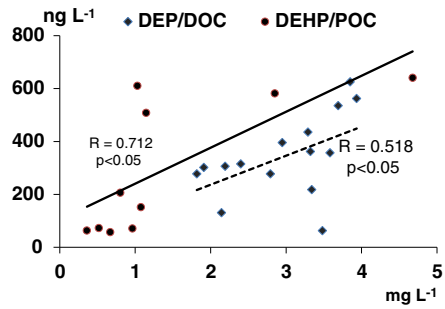

Fig. 2 Relationship between DEP concentration in dissolved phase and dissolved organic carbon and between DEHP concentrations in particulate phase and particulate organic carbon in the river Seine ($n=18$)

sewer system to the river during rainy periods. Furthermore, turbulent flow involving resuspension of contaminated sediment deposits in the different overflows as in the river might contribute to the failure of dilution effect in the river Seine during high flow periods. In addition, inputs might occur *via* rainwater. Indeed, DEHP concentrations of 423 ng L^{-1} were found in the rainwater of Paris area, corresponding to a flux of 274 μg m^{-2} $year^{-1}$ (Teil et al. 2006). The three phenomena might involve additional contributions to water concentrations during flood and rainy conditions and offset dilution due to water inputs under high flow period.

The annual specific flux of DEHP estimated to 33 g km^{-2} $year^{-1}$ at Marnay, upstream of the urbanized areas. A strong enhancement was observed at Bougival (108 g km^{-2} $year^{-1}$) and Triel (114 g km^{-2} $year^{-1}$). Björnklund et al. (2009) reported a considerable higher value of DEHP specific flux of 21×10^4 g km^{-2} $year^{-1}$ in a Swedish urban area with large impervious surfaces. Specific flow increased with the extent of impervious surfaces and allowed to estimate the pollutant exportation at basin scale and to assess the urbanization level. The mass balance estimation of phthalate loads to the river Seine indicated the part played by each type of input: WWTP discharge or sewer overflow whether separated or combined. Annual DEHP transportation calculated from the annual specific flux and the surface basin at the location supplied a value of 2039 kg at Paris and 7047 kg at Triel. The annual input of 5,008 kg might be attributed to the presence of many WWTP and combined sewer overflow discharges in that section of the river. An estimation of 13 t $year^{-1}$ for 100,000 km^2 for total emission of DEHP to surface water was reported by Cousins and Mackay (2003) on the basis of a predictive model developed from selected industrialized regions from USA and Europe. Moreover, the total amount of DEHP brought by atmospheric fallout to the river Seine basin, upstream from Paris, was previously estimated to 4.3 t $year^{-1}$ for a surface basin of 43,800 km^2 (Dargnat 2008) that might contribute significantly to river contamination via runoff processes.

3.3 Impact of a Main Storm Overflow Discharge upon the River Seine Contamination Downstream of Paris

In order to investigate the mechanisms involved in the fate of phthalates brought by a combined sewer overflow, during a brief and strong rainy event following a low flow period, a water body discharged to the river Seine at Clichy was studied. Although a significant progress was realized in term of performance in wastewater treatment plants, particularly in the Paris area, combined sewer overflows constituted a considerable source of pollutant inputs to the river. Gasperi et al. (2012) observed higher concentrations in a combined sewer overflow than in separated storm water and wastewater partly due to the erosion of the sewer deposit.

Indeed, investigations of trace metal and S-Sed levels in the same area of the river Seine by Estèbe et al. (1998) highlighted a strong impact of discharge under particulate phase to the water quality. Moreover, Zgheib et al. (2011) encountered at the outlet of storm sewers in the Paris area significant DEHP concentration of 22 μg L^{-1}. Norin and Strömvaix (2004) identified recycled asphalt and vehicle components as potential sources of phthalates to urban runoff. Moreover, DEHP occurred in highest amounts in the vicinity of traffic route, as compared to residential areas in Stockolm (Sweden) and at concentrations up to 5 μg L^{-1} (Björnklund et al. 2009).

The different water samples collected during the rainy event corresponded to a mixture of river water just upstream of the overflow discharge point and the water body discharging to the river.

The overflow presented higher S-Sed levels the surface microlayer (SμLμ) at TB located just downstream of the discharge (Fig. 3). At this location, mixing between river and overflow water was not yet achieved. Globally, we found that phthalates were preferentially distributed in dissolved phase of the overflow or of the river water, whatever the layer. However, differences were observed between DEP, a light compound like that was essentially in dissolved phase (99 %) and DEHP. The latter displayed higher ratios in particulate phase, particularly in the overflow (26 %) and the SμLμ (36 % at TB and 12 % at TC) than in the subsurface layer (SbSu) of river water: 3 % at TA, 6 % at TB, 6 % at TC, and 10 % at TD (Fig. 3). DEHP was the main compound in particulate phase, in accordance with its affinity for particles. On the other hand, the SμLμ showed an enrichment of DEHP in particulate phase, as compared to that of the overflow. Substances with low water solubility and high lipid/water partitioning such as phthalates display a strong interfacial affinity. In this way, Chi et al.

(2003) found that DEHP concentration in the SμLμ of a small eutrophic lake was higher than that of the corresponding subsurface water and that the temperature was an important factor controlling DEHP distribution between the two layers.

Concerning the dissolved phase, the SμLμ showed also a high DEP concentration close downstream of the overflow discharge (Fig. 3). DnBP, which has higher water solubility than DEHP, was predominant in the dissolved phase of the SμLμ at the two sites, TB and TC, downstream of the overflow. The SbSu showed higher phthalate concentrations downstream of the overflow discharge (up to 9 times), for the dissolved phase and 32 times for the particulate phase as compared to the river Seine upstream that location. The homogenization of the water column was not completely achieved at site TC, 11 h and 30 min after the beginning of the discharge.

Enrichment ratios were calculated between the SbSu and the SμLμ concentrations. For DEP, the enrichment ratio was only for the dissolved phase: 2.4. For DnBP and DEHP, they were 9.4 and 2.7 for the dissolved phase and 17.6 and 15 for the particulate phase. Indeed, the highest ratios were found for the high molecular weight compounds, especially for the particulate phase. Cincinelli et al. (2001) reported similar observations for a marine environment in the Tyrrhenian Sea. On the contrary, an enrichment factor for DEHP of 1.35 only, between the SbSu and the SμLμ, was reported by Chi et al. (2003) in a eutrophic lake.

3.4 Phthalate Transfers at the Scale of 2 Encased Subbasins Under Dry and Rainy Periods

3.4.1 Prédecelle Basin

At the small scale of the elementary river Prédecelle sub-basin, all sites, whatever the conditions, DEHP prevailed (Fig. 4). Under low water conditions, the

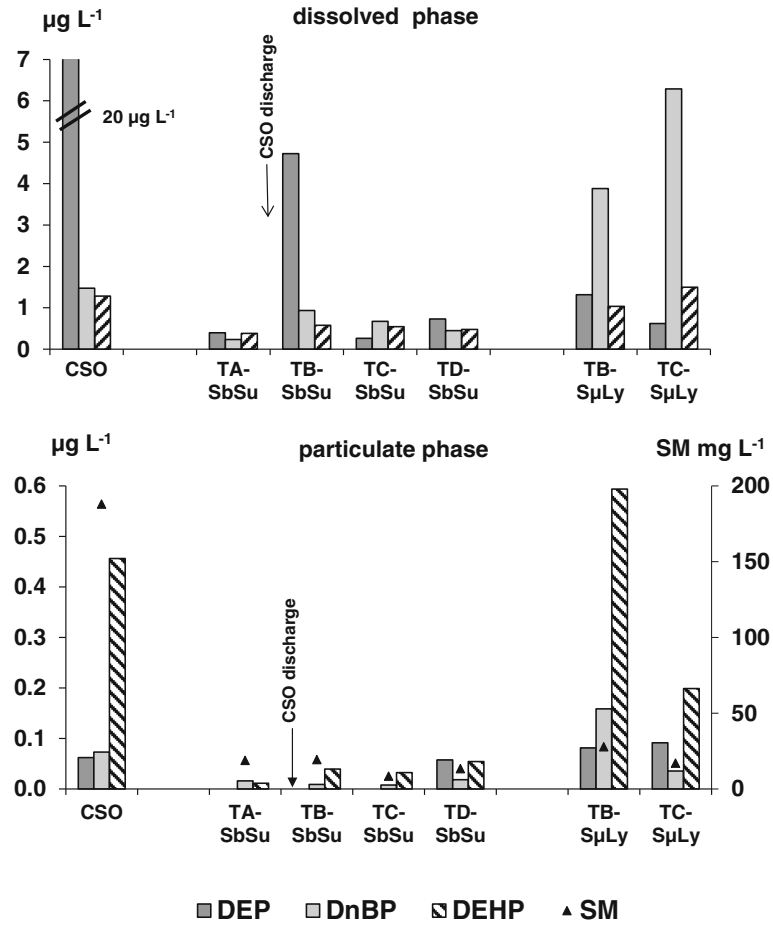

Fig. 3 Phthalate distributions (μg L^{-1}) in the dissolved and the particulate phases of the combined sewer overflow of Clichy (*CSO*), the subsurface samples (*SbSu*), and the surface microlayer (*SμLy*)

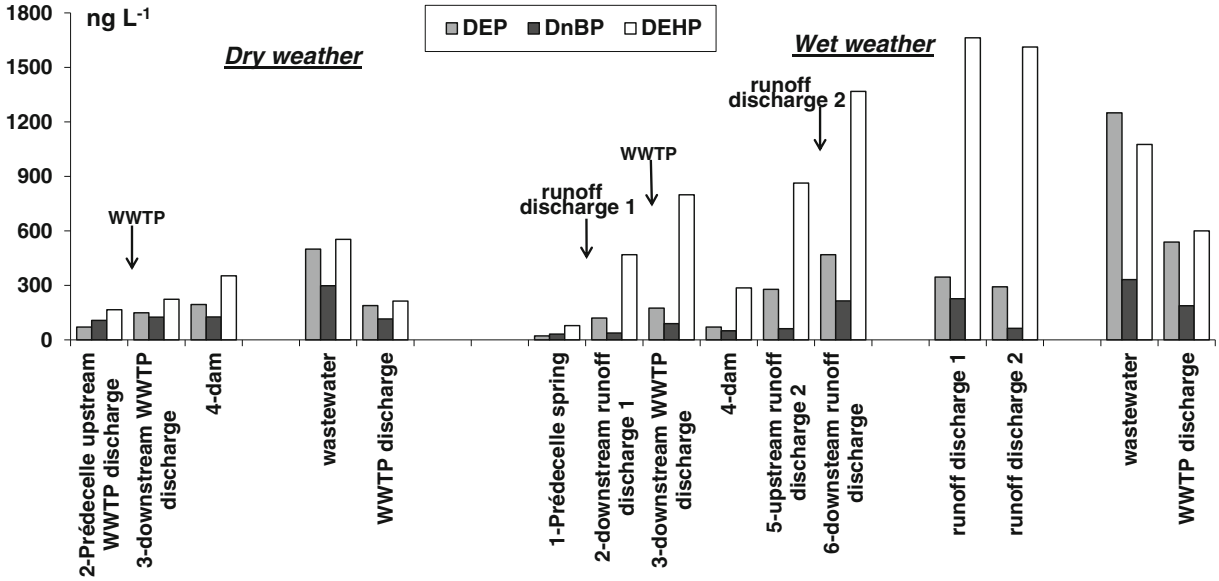

Fig. 4 Phthalate concentrations in the river Prédecelle, during dry weather–low flow period (sampling stations 2–4) and wet weather–high flow period (sampling stations 1–6) in the wastewater and the WWTP discharge and in the runoff from impervious areas (runoff discharges 1 and 2)

first pollutant rise (two times for all compounds) originated from the WWTP discharge. Under high water and rainy conditions, the river Prédecelle that flows through rural areas in its upper section, displayed initially high phthalate concentrations. Runoff from the impervious surface of an artisanal and commercial activity area (runoff discharge 1), involved pollution flushes to the river at station 2, with a six-time increase for DEHP, corresponding to a concentration even higher than those observed in the river Seine downstream of Paris (Fig. 4, Table 4). Far downstream (station 6), a second direct input to the river was identified, corresponding to a sewer receiving runoff from a peri-urban area that clearly impacted the water quality and involved maximum concentrations observed in the river Prédecelle (Fig. 4).

Indeed, the water brought by the runoff displayed a DEHP concentration of 1.6 μg L^{-1}, which was consistent with literature data from England: 0.75–1.25 μg L^{-1} (Rule et al. 2006). In addition, the WWTP of Briis-sous-Forges (5,000 inhabitant equivalents,) discharged into the river and constituted another source of inputs, whatever the conditions. DEHP was the main compound with a concentration of 600 ng L^{-1}. Vethaak et al. (2005) found in WWTP effluents of the Netherlands DEHP concentrations up to 2.4 μg L^{-1} only, followed by DEP up to 0.84 μg L^{-1}, without any differences between domestic and industrial wastewaters. Moreover, DEHP in new housing estate wastewater was five times higher than in the ancient ones (Rule et al. 2006).

An increase in phthalate concentrations of 54 ng L^{-1} for DEP, 19 ng L^{-1} for DnBP, and 60 ng L^{-1} for DEHP was found from upstream to downstream of the WWTP discharges. Under low water conditions, the effluent flow (0.027 m^3 s^{-1}) corresponded to 1/10 of the total river flow (0.33 m^3 s^{-1}), and estimations of the discharge impact upon river concentrations were 53 ng L^{-1} for DEP, 52 ng L^{-1} for DnBP, and 329 ng L^{-1} for DEHP. Differences observed between measured and estimated concentrations might be explained by unidentified runoff inputs. Indeed, a detection frequency of 100 % for DEHP both as particulate and dissolved phases in storm water from a small residential catchment in Paris and as total concentrations ranging from 15 to 61 μg L^{-1} that contributed to pollution during storm events was reported by Zgheib et al. (2011).

Our limited WWTP impact occurring under low river flow became of major importance during rainy periods, partly due to untreated by-pass wastewater discharged directly to the river. On the whole, a two-time concentration rise was observed in the Prédecelle for the three compounds which was previously noted

in a urban area about WWTP impact upon the Marne river (France) during same conditions (Dargnat et al. 2009b). In that way, we observed removal efficiency of 62 % for the three compounds in the WWTP, during the low flow period and of only 46 % for DEP and 43 % for DnBP and DEHP, during the high flow (Fig. 4).

Moreover, DEHP concentrations remained lower in the WWTP discharge (2.7 times) and in the domestic wastewater (1.5 times) than in the runoff discharges. In the same way, Clara et al. (2010) found DEHP concentrations in WWTP effluents up to 48 times lower than in runoff from a motorway and up to 17 times lower than in runoff from a suburban area. The results of the present study confirm the prevalence of runoff inputs against those of WWTP discharges upon surface water contamination even in the upstream part of the catchment basin.

3.4.2 Orge Basin

At the scale of the Orge subbasin, phthalate distribution in surface water and wastewater under low (2.29–2.83 $m^3\ s^{-1}$) and high (4.4–6.03 $m^3\ s^{-1}$) flow conditions are presented on Fig. 5 a and b. For all compounds, phthalate concentrations in river water increased clearly under high flow conditions, up to 2.8 times. Under low flow conditions, phthalate ratios between dissolved and particulate phases varied from 3.5 for DEP to 0.3 for DEHP, related to compound molecular weight. Under high water conditions, an important rise of phthalate concentrations in dissolved phase was observed: from 73 to 95 % for DEP, from 32 to 81 % for DnBP, and from 23 to 68 % for DEHP, which were typical of atmospheric washout origin (Fig. 5a). Indeed, phthalates occur mainly in the vapor phase of ambient air in Paris, from 93.8 % for DEP to 64.9 % for DEHP (Teil et al. 2006).

An increase up to 4.8 times for wastewater concentrations might partly be explained by resuspension of contaminated particles in the sewer network. For wastewater mainly collected by a separate system, also partition between the two phases depended on the molecular weight of the compounds and varied from 2.7 for DEP to 0.6 for DEHP but phthalate ratio between the two phases remained constant whatever the conditions.

Under high flow period, the rises of phthalate fluxes in river Orge were of 6.6 times for DEP (from 45 to 294 g day^{-1}), 5.2 times for DnBP (from 12 to 64 g day^{-1}), and 5.2 for DEHP (from 110 to 575 g day^{-1}) whereas for wastewater, they were only 3.6 times for DnBP (from 113 to 407 g day^{-1}) and 4.9 for DEHP (from 596 to 2,904 g day^{-1}).

On the whole, inputs during high flow conditions occurred mainly under dissolved phase to river water, which might indicate a main source by atmospheric washout. For other organic families, such as polycyclic aromatic hydrocarbons and polychlorobiphenyls, atmospheric inputs in similar area, accounted for 40 % and for 100 % of total levels, respectively (Bressy et al. 2012).

At the outlet of the river Orge, during low flow periods, the annual loads transferred were 13.3, 3.6, and 32.4 kg for DEP, DnBP, and DEHP, respectively, and during high flow periods, they increased up to 20.8, 4.5, and 40.3 kg, for DEP, DnBP, and DEHP,

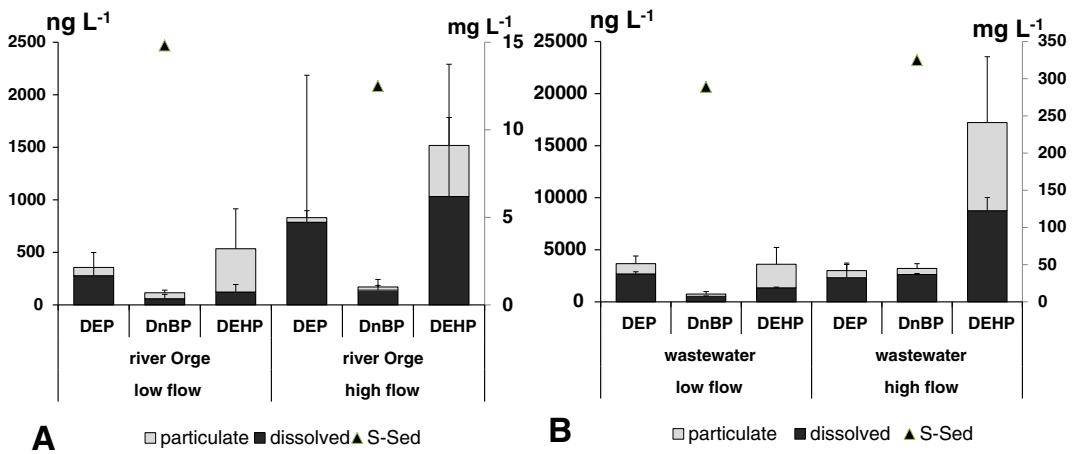

Fig. 5 Phthalate concentrations in particulate and dissolved phases and S-Sed in the river Orge at the station of Viry-Châtillon (**a**) and in domestic wastewater (**b**) during low (n=6) and high (n=5) water conditions

respectively. Considering that this area is equipped with separate system and that no WWTP discharges occur in a large portion downstream of the river, the differences observed yearly between the two hydrological periods might correspond to runoff inputs: 7.5 kg for DEP, 0.87 kg for DnBP, and 7.8 kg for DEHP. However, at the scale of the two basins, comparison of inputs as square kilometer of surface basin, between separate (Orge) and combined (Seine) systems indicated a 9.7 times higher pollutant inputs from the combined system.

4 Conclusion

Phthalates were present in rural as well as in urban areas of the river Seine basin, and DEHP was always prevailing. Globally, the river Seine contamination by phthalates, remains below the NEQ and lower than that of other European river courses, in spite of the high population density of the Parisi area.

Our results are original since they take into account the whole river Seine basin by means of scale transposition from elementary sub-basins and stretch over a couple of year including contrasted hydrological conditions. Particularly, the impact of a strong storm event upon phthalate contamination of a main overflow discharge could be proved. Phthalates are ubiquitous as well in rural as in urban areas of the river Seine basin.

WWTP discharges and storm overflow emissions constitute the main sources of phthalates to surface water. It appears that, during strong rain events, in densely urbanized areas, the combined sewer system exerts a considerable impact upon river water quality. The present findings highlight the influence of runoff inputs to surface water, even in the very upstream section of an elementary basin in rural environment of a subbasin of the river Seine. Consequently, the use of a mass balance index is a helpful tool for suited strategies for minimizing phthalate inputs to the river Seine. At present, these compounds are gradually substituted by phthalates of higher molecular weight or other chemicals. However, new potential sources of phthalates to the environment might arise from ancient polymer (e.g., PVC) recycling activities

Further studies are needed to investigate the long term impact of episodic runoff water inputs during rainy events. These findings might be useful for the development of predictive models for phthalate fate in storm drainage system and their subsequent impact upon surface water quality.

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