Phthalate and alkylphenol removal within wastewater treatment plants using physicochemical lamellar clarification and biofiltration

A. Bergé[1, 2], J. Gasperi[2], V. Rocher[3], A. Coursimault[1] &
R. Moilleron[2]
[1]Central Laboratory of Police Department, Paris, France
[2]LEESU, Paris-Est University, France
[3]SIAAP, Colombes, France

Abstract

Endocrine disrupting compounds (EDCs) have been found in surface waters worldwide. They are known for exerting adverse effects on animals of many species, including humans. EDCs comprise compounds of anthropogenic origin. They can enter waterways via either discharges from wastewater treatment plant (WWTPs), combined sewer overflows (CSO) or atmospheric deposition. In this work, the fate and removal of four phthalates and two alkylphenols: Diethyl phthalate (DEP), Di-n-Butyl phthalate (DnBP), Butyl Benzyl phthalate (BBP), Di-(2-ethylhexyl) phthalate (DEHP), nonylphenol (NP) and octylphenol (OP) were investigated within a wastewater treatment plant (WWTP) using lamellar clarification and biofiltration. This plant receives about 240,000 m^3 d^{-1} of wastewater. The whole treatment process comprises: screening, grit removal, primary sedimentation using coagulant and flocculant, followed by biofiltration units. Phthalates and alkylphenols were monitored at three locations, including raw sewage, before primary treatment, decanted effluents, before biological treatment, and final effluents, just before discharge to receiving waters. Nine campaigns were performed in 2011 during different seasons.

In raw wastewater, DEHP was the major compound (32.42 to 71.88, median 42.95 $\mu g.l^{-1}$), followed by DEP (7.00 to 36.03, median 21.00 $\mu g.l^{-1}$) and NP (4.08 to 10.63, median 5.95 $\mu g.l^{-1}$). Other compounds averaged few $\mu g.l^{-1}$. During the WWTP treatment, DEP becomes major contaminant (0.46 to 6.77, median

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2.95 $\mu g.l^{-1}$), followed by DEHP (0.95 to 6.43, median 2.30 $\mu g.l^{-1}$) and NP (0.31 to 1.36, median 0.63 $\mu g.l^{-1}$). Contaminant removal depends on the physicochemical characteristics of the compounds. For example, for lamellar clarification, removal efficiency was found to be strongly dependent to log Kow and, hence, to be highly correlated with their sorption coefficient (Kd). As a consequence, compounds with high log Kow (>3) were removed to a significant extent. DEHP was highly removed by lamellar clarification (68.8%), followed by BBP (61.5%) and NP (51.0%). Besides, DEP (log Kow < 3) was slightly removed (13.8%). During biofiltration, both hydrophilic and hydrophobic compounds were equally eliminated. Therefore, DEP (87.3%), OP (88.0%) and DEHP (81.9%) were mostly removed during biological treatment.

Keywords: phthalates, alkylphenols, endocrine disrupting compounds, lamellar clarification, biofiltration.

1 Introduction

The European Water Framework Directive (WFD) aimed to reach the good ecological and chemical status for the aquatic environment [1] by 2015. The assessment of chemical status of these water bodies was based on the monitoring of about forty priority substances for which environmental quality standards (EQS) have been established in 2008 [2]. Among these substances, phthalates and alkylphenols, especially di-(2-ethylhexyl) phthalate (DEHP) and nonylphenols (NP) were and still are of particular concern.

Phthalates are industrial chemicals that are widely used as additives to improve flexibility in polyvinyl chloride (PVC) [3]. In the world, Xie *et al.* [4] reported that approximately 6,000,000 tons per year are produced which has been at a constant level for 20 years. Phthalates are typically used in industrial and household products such as adhesives, plasticizers, building materials, home furnishing, food packaging and clothing and also in cosmetics, fragrances and personal care products [5, 6]. Alkylphenols are used as nonionic surfactants in a large range of domestic and industrial applications. Their predominant uses are in pulp and paper production, textile manufacturing and in the production of crop protection chemicals [7]. Besides, they have also applications in detergents, paints, herbicides, emulsifiers, wetting and dispersing agents [8–10]. Moreover, they are principally used to prepare nonylphenol ethoxylates (NPE). Despite their miscellaneous uses recent studies showed a stagnation in the American, Canadian and European productions of NPE, mainly owed to highly restrictive regulations [11, 12], while worldwide production increased from 300,000 in 1994 to 500,000 tons in 2002 [9, 13]. This was explained by the increase of emerging nation consumptions such as Brazil, Russia, India and China.

This work as a part of the third phase of the OPUR program focuses on the fate of phthalates and alkylphenols within the wastewater treatment plant (WWTP) of Seine Centre (Colombes, France). This study complete a previous work dealing with the removal of WFD priority substances [14, 15]. The main advantages of this WWTP compared to conventional activated sludge WWTP lies in their compactness and their high biomass content and its volumetric reaction rates [16, 17]. Therefore, biofilters became an alternative to activated sludge tanks and they perfectly suit the treatment plants that were built in large urbanized areas where the building pressure made available lands scarce [16]. The main objectives of this study were: (i) to achieve the quality of raw wastewater as regard phthalates and alkylphenols, (ii) to identify processes and routes of elimination in WWTP for these contaminants, with a focus on the physicochemical lamellar clarification and the biofiltration and (iii) to evaluate the WWTP efficiency by following the quality of discharges into receiving waters.

2 Materials and methods

2.1 Description of the sampling site

The wastewater treatment plant of Seine Centre (Colombes, France) is managed by the Interdepartmental Association for Sewage Disposal in the Paris Conurbation (SIAAP) and daily treats about 240,000 m^3 of urban wastewater of Paris and its suburbs. Treatment begins with a pretreatment step. Pretreatment step includes screening and cursory grit/oil removal. Primary treatment consists of a physicochemical lamellar clarification. Total Suspended solids (TSS) are eliminated by addition of ferric chloride (causing destabilization of colloid particles) and anionic polymers (promoting floc formation). This clarification also allows the elimination of phosphorous pollution. This physicochemical clarification is followed by biological filtration performed on three levels of biofilters. The first two stages are respectively aerated for the treatment of carbonated pollution and nitrification process (NH_4^+ to NO_3^-). The last biofilter is not aerated to allow denitrification of wastewater and requires the addition of an exogenous carbon source (methanol). In order to follow the efficiency of these two treatment processes (physicochemical lamellar clarification and biofiltration), automatic and refrigerated (4°C) samplers were used upstream and downstream of each processing units. Three sampling points were considered: raw wastewater (RW), settled wastewater (SW) and final effluents (FE). A total of nine sampling days were carried out in winter (n=3, from January 31 till February 3), spring (n=3, from 9 till 12 May) and autumn (n=3, from 21 till 24 November).

2.2 Analysis of wastewater quality parameters, phthalates and alkylphenols

2.2.1 Wastewater quality parameters analysis

For each sample, parameters commonly used to represent water quality, have been analyzed. These parameters include chemical and biological oxygen demands (COD and BOD_5), total suspended solids (TSS), ammonia nitrogen (NH_4^+), nitrates (NO_3^-), nitrites (NO_2^-) and orthophosphates (PO_4^{3-}). These analyzes were performed by the SIAAP accredited laboratory. In this study, we focused only towards organic contaminants and not to wastewater quality parameters. However, overall, these analyzes have shown the representativeness of our campaigns compared with SIAAP chronicles for 2011.

2.2.2 Phthalate and alkylphenol analysis

After sampling, samples were analyzed within 24 hours for the dissolved phase and after lyophylization (freeze drying) for the particulate phase in the Central Laboratory of the Police Department (LCPP) of Paris. The samples were homogenized and then filtrated at 0.7 µm to separate dissolved and particulate phases. Phthalates in the dissolved phase were analyzed according to NF EN ISO 18856 French standard (December, 2005). The alkylphenols in the dissolved phase and phthalates and alkylphenols in the particulate phase were analyzed according to an internal method developed in the LCPP. Thus, for the dissolved phase, a volume of 100 ml (RW and SW) to 250 ml (FE) of the sample was extracted by solid phase extraction (SPE). The extraction of phthalates and alkylphenols was performed on C18 cartridge (Supelclean). The cartridge was conditioned by ethyl acetate (6 ml) and methanol (2 x 6 ml). All chemicals and solvents used for extraction were pesticide residue grade. The sample was then loaded onto the cartridge. After rinsing and dying, the C18 cartridge was eluted with 2 ml of ethyl acetate containing two internal standards (DnBP D4 RING, deutered and 4-n-NP, linear nonylphenol). For the particulate phase, about 50 mg dry weight of TSS was extracted by sonication in 20 ml of ethyl acetate. This step was repeated a second time to ensure complete extraction of the compounds. The dissolved and particulate extracts were then purified on an alumina column (1 g), previously conditioned with 6 ml of ethyl acetate. During the extraction of the particulate phase, the extracts were concentrated under a stream of nitrogen to a final volume of 1 ml. the concentrate was taken up in 1 ml of ethyl acetate containing the internal standards.

A total of 4 phthalates (including DEP, DnBP, BBP and DEHP) and 2 alkylphenols (including NP and OP) were analyzed by gas chromatography coupled to a mass spectrometer (single quadruple, Agilent Technologies), equipped with a DB-5MS column (Agilent Technologies, 30 m). These molecules were ionized by electron impact. The analysis was performed by single ion monitoring (SIM) and the quantification was based on two or three specific masses depending on the molecule. Control solutions (low and mid-range points) were injected every ten samples and a drift of less than 20% of the target value validated results. Extraction blanks were also carried out, if measured concentrations in blanks were superior to quantification limits (0.20 $\mu g.l^{-1}$ for all compounds), those values were subtracted from the sample concentrations. Finally, analytical and extraction techniques have been validated by interlaboratory tests (AGLAE).

3 Results and discussion

3.1 Raw wastewaters quality

The total concentrations found for phthalates and alkylphenols in raw wastewaters (RW) are summarized in Table 1. Minimal, median and maximal concentrations are provided. In addition, the pollutant patterns are illustrated in Figure 1. As expected, DEHP had the highest median concentration with 42.95 µg.l^{-1}, followed by DEP (21.00 µg.l^{-1}), DnBP (3.81 µg.l^{-1}) and BBP (1.57 µg.l^{-1}). Concentrations measured in RW were of the same order of magnitude than those reported by different studies in WWTP influents: in Canada by Barnabé *et al.* [18] (41.00 to 70.00 µg.l^{-1} of DEHP), by Sanchez-Avila *et al.* [19] in Spain (50.70 ± 19.00 µg.l^{-1} for DEP and 47.90 ± 25.00 µg.l^{-1} for DEHP), in France by Dargnat *et al.* [20] on the Marne Aval WWTP influents (22.46 ± 13.22 µg.l^{-1} for DEHP, 7.71 ± 5.21 µg.l^{-1} for DEP and 1.12 ± 0.54 µg.l^{-1} for BBP) and by Choubert *et al.* [21] in 21 French WWTP (52,80 ± 54,90 µg.l^{-1} for DEHP), but were slightly higher than those reported by Clara *et al.* [22] in raw materials from Austria (1.20 to 2.70 µg.l^{-1} for DEP, 0.15 to 0.47 µg.l^{-1} for DnBP and 4.10 to 13.00 µg.l^{-1} for DEHP) and by Jackson and Sutton [6] in the United States (9.20 to 33.00 µg.l^{-1} for DEHP and up to 10.00 µg.l^{-1} for DEP).

Table 1: Concentrations of phthalates and alkylphenols in WWTP of Seine Centre (concentrations min - max and (median) in µg.l^{-1}).

	DEP	DnBP	BBP	DEHP	NP	OP
RW (n=9)	7.00 – 36.06 (21.00)	1.86 – 6.01 (3.81)	0.97 – 2.29 (1.57)	32.42 – 71.88 (42.95)	4.08 – 10.63 (5.95)	0.17 – 1.88 (1.08)
SW (n=9)	5.45 – 37.90 (21.20)	0.82 – 4.01 (1.35)	< loq – 0.93 (0.56)	5.85 – 22.16 (12.80)	2.39 – 4.53 (3.22)	< loq – 1.00 (0.50)
FE (n=9)	0.46 – 6.77 (2.95)	< loq – 0.93 (0.31)	< loq – 0.21 (0.10)	0.95 – 6.43 (2.30)	0.31 – 1.36 (0.63)	< loq – 0.33 (< loq)

< loq: inferior of the limit of quantification

The concentrations of alkylphenols in the influents of the wastewater treatment plant of Seine Centre highlight the preponderance of NP (5.95 µg.l^{-1}) against 1.08 µg.l^{-1} for OP. However, Gilbert *et al.* [23] found lower concentrations on the same site (0.81 µg.l^{-1} for NP and 0.25 µg.l^{-1} for OP). As suggested by Choubert *et al.* [21], this can reflect the high variability of wastewater quality entering the WWTP. Concentrations measured in RW are in the same order of magnitude than WWTP influents concentrations reported by Isobe and Takada [24] in Japanese influents (1.00 µg.l^{-1} for NP), by Jackson and Sutton [6] in American influents (up to 5.00 µg.l^{-1}) but are lower than those reported by Céspedes *et al.* [25] (5.59 to 17.5 µg.l^{-1} for NP and from 1.26 to 3.98 µg.l^{-1} for OP) and Vega-Morales *et al.* [26] (9.70 µg.l^{-1} for NP and 6.10 µg.l^{-1} for OP) in Spanish influents and by Martin-Ruel *et al.* [27] in France (15.7 µg.l^{-1} for NP and 5.60 µg.l^{-1} for OP).

For DEP, an important variability of concentrations in the influents of Seine Centre was observed. Indeed, a factor of 4 was observed for DEP in RW between the first (January/February) and the third (November) sampling campaigns but no explanation can be provided so far. As illustrated by Figure 1, whatever the sampling period (January/February, May and November), similar distribution can be observed in RW dominating by DEHP (64.2%) and DEP (28.5%). The DnBP and the BBP account for 2.5 and 2.2% of the remaining phthalates, respectively. As expected by uses of alkylphenols, NP represents more than 84% of the total alkylphenols.

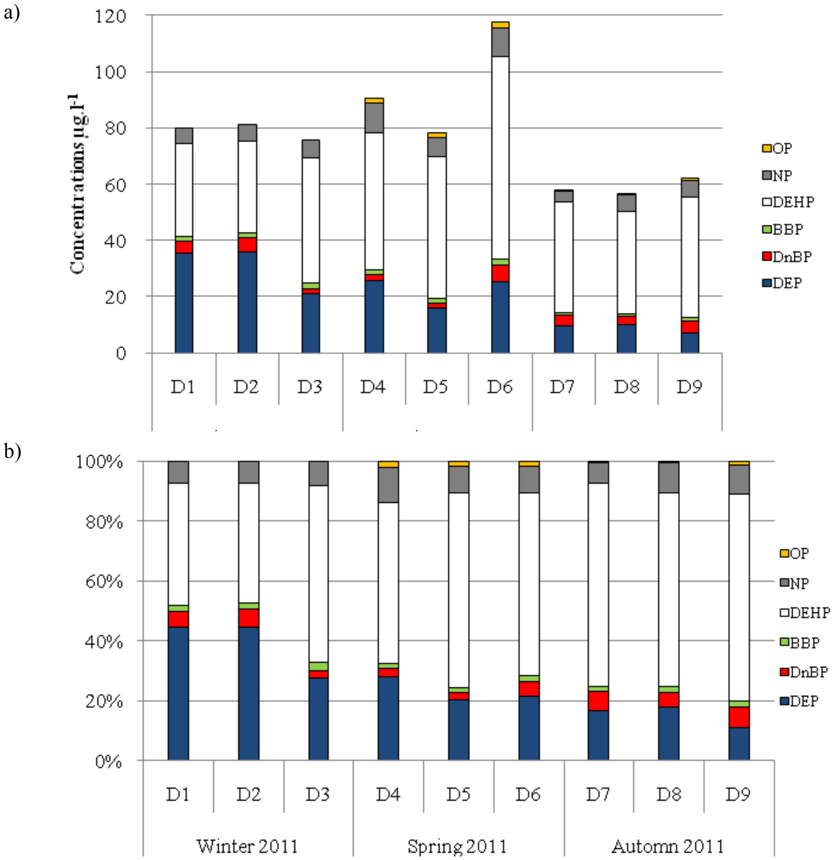

Figure 1: Total concentrations (a) and distributions (b) of phthalates and alkylphenols in RW.

The pollutant patterns are in good accordance with the extensive uses of DEHP and NP in domestic and industrial applications. In addition, restrictions on the uses of DnBP and BBP, contributed to the large spreading of DEP, DEHP in wastewater. Moreover, the scarce available data on production and consumption of these compounds worldwide also confirmed the trend observed in the influents of Seine Centre. Because of their physicochemical properties, three profiles were observed for the partition between the dissolved and particulate phases for phthalates and alkylphenols. Indeed, the lightest molecular weight compounds such as DEP (log Kow 2.42) were mainly present in the dissolved fraction (90.3%). DnBP (log Kow 4.57), NP (log Kow 4.48) and OP (log Kow 4.12) were equally distributed between both phases (DnBP: 47.2 and 52.8%; NP: 46.5 and 53.5% and OP: 49.7 and 50.3%, respectively). Finally, the heavier compounds, such as BBP and DEHP (log Kow respectively equal to 4.84 and 7.50), were preferentially associated with the particles (up to 70.0% for BBP and

93.0% for DEHP), as most of hydrophobic pollutants with log Kow > 5.00. Besides, no correlations were found between wastewater quality parameters and contaminants.

3.2 Efficiency of the physicochemical lamellar clarification and the biofiltration

Figure 2 illustrated the phthalate and alkylphenol removals in the different stages of treatment processes (physicochemical lamellar clarification, biofiltration and global removal). The removals were calculated for each stage, as the ratio of the difference between upstream and downstream concentrations of the unit processes to the upstream concentration.

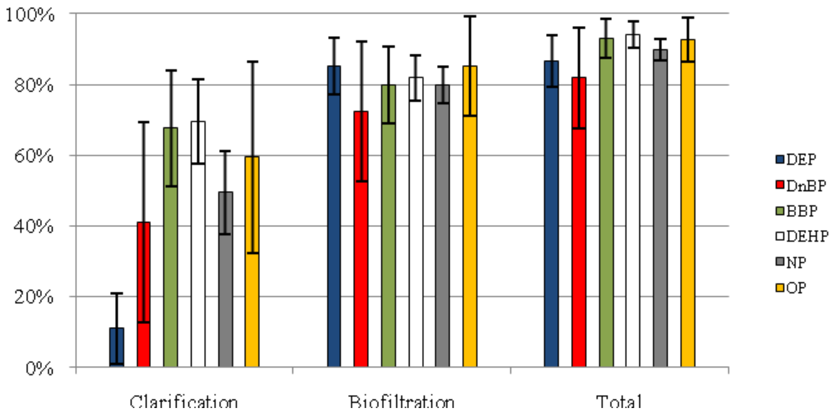

Figure 2: Mean (± standard deviation) removals (in %) of phthalates and alkylphenols in the WWTP of Seine Centre (n=9).

3.2.1 Efficiency of the physicochemical lamellar clarification

Thus, for the lamellar clarification, the removal is calculated by 100 x ([RW] - [SW]) / [RW]. In order to better understand the behavior of phthalates and alkylphenols at each stage, the discussion on the removal dealt with the total concentrations and the concentrations of both the dissolved and particulate phases. During the physicochemical lamellar clarification, based on the total concentrations, three behaviors were observed for median removal of the nine sampling days. DEP was poorly eliminated (about 13.8%), DnBP, NP and OP moderately (39.9%, 51.0% and 49.6%, respectively), while BBP and DEHP were more highly removed from 61.5 up to 68.8%, respectively. These eliminations were directly related to particulate bound compounds. Actually, TSS was well removed during clarification. Median removal was estimated at 87%. Interestingly, we noted an increase in the removal of DnBP between the first and the third campaign, which was correlated with the increase of its particulate fraction.

Moreover, the specific study of both the dissolved and particulate phases highlighted the minor elimination of dissolved compounds and the major elimination of particulate compounds. The removal of particulate DnBP, BBP and DEHP is above 61.7%, 77.8% and 70.9%, respectively, and accounted for 47.1% for the DEP. Additionally, NP and OP particulate removal accounted for 72.2% and 84.9%. Comparatively, the elimination of the dissolved fraction during the physicochemical lamellar clarification varies between 13.6 and 14.1% for DEP and DnBP, between 16.5% and 17.8% for BBP and DEHP and between 21.2% and 21.5% for OP and NP. Gilbert *et al.* [23] and Song *et al.* [28] reported the same observations associated to the removal of colloids for some alkylphenols and PBDE, respectively.

As a results of particle elimination, an increase in the dissolved fraction for DEHP, BBP, DnBP, NP and OP was observed between RW and SW (DEHP: 6.6 to 15.7%; BBP: 50.7 to 70.4%; DnBP: 33.5 to 50.4%; NP: 45.2 to 73.2% and OP: 51.7 to 63.6%) except for DEP (close to 90%). Additionally, the median total concentrations in SW (dissolved + particulate) were still above 20.00 $\mu g.l^{-1}$ for DEP and 10.00 $\mu g.l^{-1}$ for DEHP. Finally, the pollutants predominantly present in the particulate fraction (BBP, NP, OP and DEHP) are preferentially removed by the physicochemical lamellar clarification.

3.2.2 Efficiency of the biofiltration

As previously done for the physicochemical lamellar clarification, removals were calculated using the following equation: 100 x ([SW] - [FE]) / [SW]. Whatever the compound under consideration, removals by biofiltration are high, up to 67.6%: OP (88.0%) ≈ DEP (87.3%) > DEHP (81.9%) ≈ NP (81.5%) ≈ BBP (81.0%) > DnBP (67.6%). This elimination might be explained either by: (i) TSS retention in biofilters, (ii) a strong biodegradation of the compound, (iii) its volatilization, or (iv) its adsorption on the biofilters biomass. For the particulate fraction, the elimination was about 85%: DEP (92.5%) ≈ DEHP (92.2%) ≈ DnBP (91.3%) > NP (85.4%) ≈ OP (82.8%) ≈ BBP (81.0%) and could be certainly linked to high removals of TSS by biofiltration (87%). The removal of the dissolved fraction presented contrasting values, between 25.0% (BBP) and 86.9% (DEP), with intermediate values for DnBP (41.7%), NP (79.8%), OP (57.7%) and DEHP (48.6%).

In final effluents, when compared to SW, particulate fractions of DnBP, BBP and DEHP decreased significantly (DnBP: 29.6 to 6.5%; BBP: 49.6 to 34.0% and DEHP: 84.3 to 51.4%), while those for DEP and NP decreased moderately (DEP: 5.7 to 4.4% and NP: 26.8 to 19.0%). Interestingly, OP was not quantified in the particulate fraction of FE. Overall, the median total concentrations (dissolved + particulate) in FE were on the same order of magnitude than those observed in the final effluents of the Parisian Marne Aval WWTP [20]: 0.78 ± 0.22 $\mu g.l^{-1}$ for DEP and 5.02 ± 1.53 $\mu g.l^{-1}$ for DEHP. Moreover, median concentrations measured in FE were closed to those reported by Clara *et al.* [22] in effluents from Austria (DEP up to 1.10 $\mu g.l^{-1}$ and DEHP ranging from 0.08 to 6.60 $\mu g.l^{-1}$) and by Martin-Ruel *et al.* [27] for French effluents (4.20 $\mu g.l^{-1}$ for DEHP). However, median concentrations measured in our study were lower than those reported for Spanish effluents (9.43 µg.l^{-1} for DEHP and 49.80 µg.l^{-1} for DEP) by Sanchez-Avila *et al.* [19] and for Canadian effluents (54.00 µg.l^{-1} for DEHP) by Barnabé *et al.* [18]. In final effluents, NP and OP concentrations vary from 0.31 to 1.36 µg.l^{-1} for NP and do not exceed 0.33 µg.l^{-1} for OP (Table 1). These concentrations were similar than those reported by Martin-Ruel *et al.* [27] for French effluents (1.30 µg.l^{-1} for NP and 0.21 µg.l^{-1} for OP) and by Nakada *et al.* [29] for Japanese effluents (up 1.10 µg.l^{-1} for NP and up to 0.20 µg.l^{-1} for OP). However, median concentrations measured in FE were lower than those reported for Spanish effluents by Vega-Morales *et al.* [26] (18.70 µg.l^{-1} for NP and 9.30 µg.l^{-1} for OP) and by Sanchez-Avila *et al.* [19] (21.90 µg.l^{-1} for NP and 53.80 µg.l^{-1} for OP) and by Arditsoglou and Voutsa [30] for WWTP effluents from Greece (up to 37.90 µg.l^{-1} for NP).

4 Conclusions

This study was designated to provide information regarding phthalates and alkylphenols contamination levels in raw wastewaters, as well as to evaluate the removal performance of physicochemical lamellar clarification and biofiltration. Monitoring phthalates and alkylphenols in the WWTP of Seine Centre highlighted three different behaviors as regard their elimination. The first concerned the removal of heavy compounds such as BBP, NP, OP and DEHP during the physicochemical lamellar clarification. The second related to light compounds such as DEP, which underwent further degradation during biofiltration. The latest concerned the DnBP, which following its distribution between dissolved and particulate fractions in the raw materials, shifted from a significant removal of the dissolved phase to an important elimination of the particulate phase. This change in profile turned out to be in adequacy with the change in distribution observed for this compound at different sampling campaigns. Indeed, this peculiar phthalate primarily dominated in the dissolved phase, whereas in the last campaigns it appeared to be mainly bound to particles.

Although both processes removed a significant proportion of the total pollution (Figure 2), with median removal up to 83% for all compounds, concentrations in final effluents were 2.95 µg.l^{-1} for DEP, 2.30 µg.l^{-1} for DEHP and 0.63 µg.l^{-1} for NP. NP and DEHP concentrations even exceeded the current EQS (1.30 µg.l^{-1} for DEHP and 0.30 µg.l^{-1} for NP) [2]. Besides, the discharge of Seine Centre WWTP represents only a small part of the total flow of the Seine River (about 1%). Therefore, final effluents undergo a significant dilution effect when discharge in the receiving waters. Removal and concentrations for DEHP measured during those different campaigns were in adequacy with the values reported by Gasperi *et al.* [14] on the same WWTP (between 50 to 80% for the physicochemical lamellar clarification and between 20 and 50% for the biofiltration) and more generally by Martin-Ruel *et al.* [27] and Dargnat *et al.* [20] for several French WWTP (from 78.1% for DEHP to 93.4% for DEP). However, alkylphenol concentrations measured during our three campaigns were significantly higher than those reported by Gilbert *et al.* [23] on the same site (0.81 µg.l^{-1} for NP and 0.25 µg.l^{-1} for OP) whatever the season. This difference could be explained by the strong variability of concentrations existing in urban wastewaters. In addition, alkylphenol removal efficiencies reported by these authors were of the same order of magnitude that efficiencies reported in this study (83% for NP and 72% for OP). Finally, though the removal efficiencies of phthalates and alkylphenols in the water treatment units were important, further investigations concerning the transfer of these pollutants in sludge and others biosolids (TSS, cursory grit/oil removal,…) generated by waste treatment units are needed. The same remained true for the gaseous phase above treatment units, especially for DEP, the most volatile compound among the ones studied.

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