Alkylphenol ethoxylates and bisphenol A in surface water within a heavily urbanized area, such as Paris

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Abstract

This work focused on alkylphenol ethoxylates (APEOs) and bisphenol A (BPA) in surface water at the scale of the upper part of the Seine basin. Although this basin is vulnerable, since it undergoes a combination of strong human pressures (Paris conurbation) with very limited dilution via the Seine River, no comprehensive data was available for these compounds. In this context, the evolution of the pollutant concentrations and loads was assessed during two sampling campaigns (April and July 2009) along a 300 km-transect. Hence, 18 stations (10 sites on the Seine River, four tributaries and four wastewater treatment plants – WWTPs) were considered. Additional campaigns were also conducted over 2009 on four sites on the Seine River. The BPA concentrations range from 7.2 to 127 $ng.l^{-1}$ in surface water, while higher concentrations of APEOs (324 ± 153 $ng.l^{-1}$) were observed. Based on our first results, no spatial variability of concentrations between up- and downstream sites, or any seasonal variability, were highlighted. During the longitudinal campaigns, an increase of the pollutant loads between up- and downstream sites was clearly noticed. Contrary to BPA, for which a limited seasonal variation of loads was observed at the basin outlet (1,400 and 1,500 $g.d^{-1}$), the APEO loads significantly vary (10,000 and 5,500 $g.d^{-1}$). Mass balances between the inputs (tributaries + WWTPs) and the exported loads reveal that the BPA inputs are lower than the exported loads, suggesting that other inputs have to be considered along the transect studied. For APEOs, the inputs appear higher than the exported loads, underscoring the in-stream removal of APEOs. Globally, the results reveal that the removal of APEOs and the number of ethoxylate units are correlated – the longer the ethoxylate chain, the higher the removal.

Keywords: alkylphenol ethoxylates, bisphenol A, endocrine-disrupting compounds, mass load, nonylphenol, octylphenol, surface water.

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1 Introduction

Among the endocrine-disrupting compounds commonly pointed out in the literature, alkylphenol ethoxylates (APEOs) and bisphenol A (2,2-bis(4-hydroxyphenyl)propane, BPA) deserve special attention, not only because of their disrupting properties but also for their widespread distribution in the environment [1, 2].

APEOs, mainly composed of nonylphenol ethoxylates (NPEOs, 80%) and octylphenol ethoxylates (OPEOs, 20%), are widely used for industrial, domestic and commercial applications, such as lubricating, oil additives, detergents and antistatic agents. Similarly, BPA is mainly used as a monomer in the synthesis of epoxy resins and polycarbonate plastics [3, 4]. Due to these applications, the worldwide annual production is approximately 500,000 tons for APEOs (in 2002, according to Ying *et al.* [5]) and 450,000 tons for BPA (in 2007, according to Vandenberg *et al.* [4]).

The occurrence of APEOs and BPA in the environment is closely correlated with anthropogenic activities. Many studies suggested that these chemicals preferentially enter into environment through the effluents of wastewater treatment plants (WWTPs) [5, 6].

Contrary to BPA, for which the estrogenic activity was clearly observed [1, 2], APEOs are of concern because their degradation products are found to be more toxic than their precursors [7, 8]. Biotransformation pathways of alkylphenol ethoxylates are well documented [9, 10]. This biodegradation can occur through the oxidative hydrolytic (aerobic) or non-oxidative hydrolytic pathways. This last pathway leads to the reduction of the number of ethoxy units generating APEOs with shorter ethoxylate chains, such as alkylphenol diethoxylate (NP_2EO and OP_2EO) and alkylphenol monoethoxylate (NP_1EO and OP_1EO). Ultimately, the last products of biodegradation are 4-nonylphenol (NP) and 4-tert-octylphenol (OP), which are identified as endocrine-disrupting compounds [1, 11].

The Seine Basin, located in north-western France and responsible for draining approximately 32,000 km² from its headwaters to Paris, can be considered as representative of river basins exposed to the impacts of intense human activity (Meybeck *et al.* [12]). This basin accommodates a combination of strong human pressures with very limited dilution via the Seine River, due to its low flow rate. However, no comprehensive data on the occurrence of APEOs and BPA is presently available for the upper part of the Seine basin. As regards the environmental issue of these chemicals, an accurate knowledge at the scale of the Seine Basin, and more especially within the Paris Region, corresponding to the most heavily urbanised area (with a density of roughly 3,540 inhabitants.km^{-2}), has definitely proved necessary.

As a consequence, this study was launched to provide the first relevant information on the occurrence and significance of the concentrations of APEOs and BPA in surface water at the scale of the upper part of the Seine basin. In this paper, we particularly examine (i) the concentrations in surface water and

WWTP effluents, (ii) the spatio-temporal variability of loads and finally (iii) the environmental behaviour and fate of APEOs and BPA along the Seine River.

2 Materials and methods

2.1 Sampling sites

Two sampling campaigns, corresponding to the median-water period (14/04/09, median flow at 154 $m^3.s^{-1}$) and the low-water period (07/07/09, median flow at 83 $m^3.s^{-1}$), were carried out along a 300-km transect of the Seine River. For each campaign 14 sites, including 10 stations on the Seine River (S_{1-10}) and four main tributaries (T_{1-4}), were considered (Figure 1). In parallel, the effluents of the four major WWTPs along this section were investigated ($WWTP_{1-4}$). The main characteristics of these WWTPs (type of treatment, population equivalent, capacity, etc.) are reported in Figure 1. Two additional campaigns were also performed on 11/05/09 and 28/09/09 on four sites (S_1, S_3, S_5 and S_8 stations).

2.2 Analytical procedure

For each site, a 2L-sample was manually collected and stored in glass amber bottles until analysis. After filtration on glass fibre filters (GF/D 2.7 µm and GF/F 0.7 µm), dissolved and particulate phases were individually analyzed.

2.2.1 Dissolved phase

Each water sample was spiked with internal standards (BPA-d6; n-OP-d17 and NP_1EO-d2) for extraction follow-up and stored overnight at 4 °C to reach an equilibrium state. Volumes of 250 ml were extracted by solid phase extraction

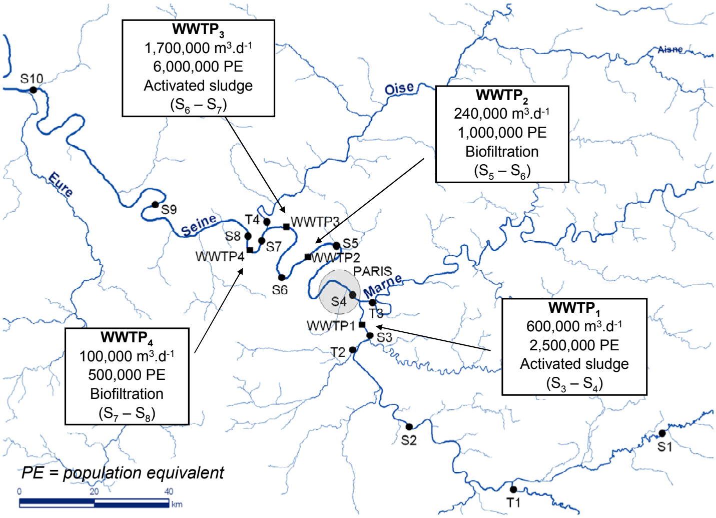

Figure 1: Sampling sites along the Seine River.

(Autotrace SPE Workstation, Caliper LifeScience) using Oasis HLB (200 mg, 6 ml) cartridges. After conditioning with 10 ml of methanol and 10 ml of ultrapure water, samples were extracted at neutral pH. After drying under vacuum, elutions were performed with 12 ml of a mixture methanol/dichloromethane/ethylacetate (40:40:20, v/v).

2.2.2 Particulate phase

After freeze-drying, the filters spiked with internal standards are extracted by microwave assisted extraction (MAE) with 20 ml of dichloromethane/methanol (90:10, v/v) (Multiwave 3000, Anton Paar) during a 30 min-cycle. Extracts are then filtered and evaporated until dryness under nitrogen for subsequent clean up using silica gel cartridges. These cartridges are conditioned with 5 ml of heptane before deposing the sample. Elution is done sequentially in three steps: 18 ml of heptane/dichloromethane (98:2, v/v), 10 ml of heptane/dichloromethane (80:20, v/v) and 10 ml of heptane/dichloromethane/ ethylacetate (10:30:60, v/v). Only the last fraction is kept for BPA and APEOs analysis.

2.3 LC-MS-MS conditions

Before analysis, both extracts are spiked with internal standard for quantification (BPA-d16, n-NP and n-NP$_1$EO). The analysis is performed by liquid chromatography coupled to a tandem mass spectrometry, LC-MS-MS (AQUITY UPLC / TQD, Waters). APEOs and BPA are separated on an AQUITY UPLC / BEH C$_{18}$ column, heated at 40 °C, with ultrapure water containing 4.5 mM NH$_4$OH (A) and methanol containing 4.5 mM NH$_4$OH (B) as mobile phase. Equilibration takes place with 50% B at 0.4 ml.min^{-1} and 10 µl are injected. The mass spectrometer is equipped with an electrospray interface used in positive ionization mode (ESI+) for NP$_{1-2}$EO and OP$_{1-2}$EO and negative ionization mode (ESI-) for all other analytes. The compounds were detected in multiple reactions monitoring mode (MRM) with two mass transitions for each analyte. Cone voltage and collision energy were optimized for all analytes (Table 1).

Table 1: Optimized parameters for LC-MS-MS analysis.

Compound	M (g.mol^{-1})	ESI Mode	Retention time (min)	Quantification		Qualification		Cone voltage (V)
				Transition (m/z)	Collision energy (eV)	Transition (m/z)	Collision energy (eV)	
BPA	228	ESI-	1.82	226.9 → 133.0	25	226.9 → 212.2	25	30
OP	206	ESI-	3.25	205.5 → 134.2	17	205.2 → 133.2	30	45
OP$_1$EO	250	ESI+	3.34	268.2 → 113.4	10	268.2 → 139.2	12	20
OP$_2$EO	294	ESI+	3.38	312.3 → 183.3	10	312.3 → 121.2	18	20
NP	220	ESI-	3.52	219.2 → 147.2	26	219.2 → 133.2	26	40
NP$_1$EO	264	ESI+	3.58	282.4 → 127.3	8	282.4 → 85.4	15	20
NP$_2$EO	308	ESI+	3.61	326.4 → 183.3	10	326.4 → 71.2	20	40

2.4 Quantification and quality control

The quantification was performed using internal calibration based on areas relative to the internal standards. Internal standard n-NP was used for the quantification of NP, OP and n-OP-d17. Similarly, BPA-d16 was used for BPA and BPA-d6 and n-NP$_1$EO for OP$_1$EO, OP$_2$EO, NP$_1$EO, NP$_2$EO and n-NP$_1$EO-d2. For each compound, calibration curves were drawn and satisfactory determination coefficients were obtained ($r^2 > 0.99$). Experimental blanks for SPE and MAE extractions, as well as mobile phase blanks were processed. No quantifiable contamination was observed. During a sequence, two calibration controls (lower and higher concentrations) were injected every 10 samples. A deviation between the control and the calibration curve lower than 20% validates the quantification.

3 Results and discussion

3.1 APEO and BPA in surface water and WWTP effluents

3.1.1 APEO and BPA concentrations

Total concentrations (median ± standard deviation, SD) measured for the Seine River, its tributaries and the WWTP effluents are shown in Figure 2.

As illustrated in Figure 2, BPA concentrations are quite similar in surface water (from 7.2 to 127 ng.l^{-1}, median concentration being 50 ng.l^{-1}) and in WWTP effluents (from 24 to 163 ng.l^{-1}, median concentration being 36 ng.l^{-1}). No significant difference was also observed between the Seine River and its tributaries. For APEOs, the distributions within surface water are featured by the predominance of NP, followed by NP$_2$EO and NP$_1$EO while OPEOs exhibit far lower concentrations (< 1 ng.l^{-1} for OP$_1$EO to 20 ng.l^{-1} for OP). The relative concentrations of NPEOs and OPEOs reflect their consumption pattern and are consistent with ratio reported in literature [6] but are slightly different from

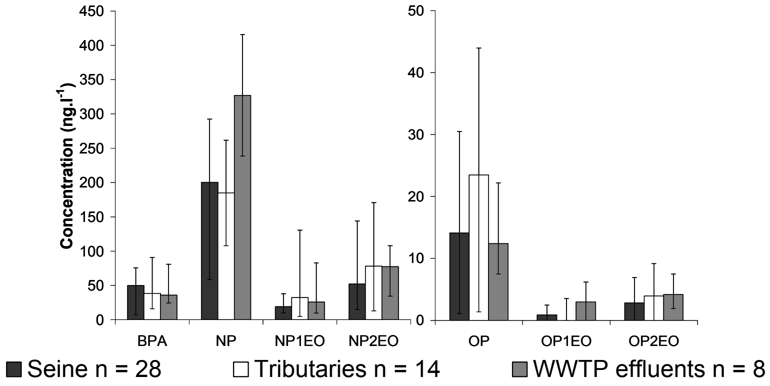

Figure 2: Total concentrations in surface water (Seine River and tributaries) and in WWTP effluents.

Table 2: Concentrations (ng.l^{-1}) in surface water, this study *vs*. literature.

Location	BPA	NP	NP_1EO	NP_2EO	OP	OP_1EO	OP_2EO	Reference
Glatt River	9.4	64	18	9.4	2.4	-	-	[15]
Masan Bay	-	18.9	24.2	115.4	-	-	-	[18]
Seine River downstream	-	168	82	59	-	-	-	[13]
Jamaica bay	-	201	157	320	3.3	26	4.9	[19]
Tiber River	80	240	360	270	-	-	-	[20]
Seine River upstream*	50 7-127	200 58-426	19 10-79	52 15-414	14 1-81	1 < 1-4	3 < 1-14	This study

* *Median, min – max values.*

values given by Ying *et al.* [5], i.e. 80% for NPEOs and 20% for OPEOs. As regard the Water Framework Directive, the total concentrations for NP (200 ± 92 ng.l^{-1}) and OP (14 ± 16 ng.l^{-1}) do not exceed the environmental quality standards (300 and 100 ng.l^{-1} for NP and OP, respectively). Concentrations found in this study on the upper part of the Seine basin are in good agreement with concentrations reported in the lower part by Cailleaud *et al.* [13]. Moreover, and in spite of the strong human pressures on the Seine basin, the BPA and APEO concentrations measured in the Seine River appear in the same order of magnitude than concentrations reported in literature (Table 2). Contrary to some studies emphasising higher levels of APEOs and BPA in WWTP effluents comparatively to surface water [14-16], comparable concentrations were found in WWTP effluents and in surface water, except for NP which is more concentrated in WWTP effluents. Comparatively to other studies, the WWTP effluent concentrations found in this study are similar to the results reported by Jonkers *et al.* [15] in Switzerland but far lower than those reported in China and Austria [16, 17]. The low concentrations in WWTP effluents probably reflect the decrease of APEO consumption for both industrial and domestic applications due to the European Directive 2003/53/CE.

In spite of their hydrophobicity (log K_{ow} ranging from 3.2 for BPA to 4.6 for NP, Ahel and Giger [21]), APEOs and BPA are weakly associated with suspended solids, except for OP. Indeed, particulate phase only represent 20% of total concentration of APEOs and 5% of BPA for each surface water and WWTP effluents. Similar distributions between dissolved and particulate phase were found in the downstream part of the Seine basin by Cailleaud *et al.* [13]. The higher particulate proportion of OP (between 40 and 50%) could probably be explained by the sorption of this compound on suspended solids. Indeed, Johnson *et al.* [22] demonstrated that up to 40% of OP can be sorbed onto suspended solids under low flow condition.

3.1.2 Evolution of the pollutant concentrations along the Seine River

The individual concentrations along the 300-km transect of the Seine River (S_{1-10}) are illustrated in Figure 3. For stations downstream of $WWTP_{1,\ 2,\ 4}$, no significant impact on the concentrations was noticed. This is mainly related to the low concentrations of WWTP effluents and low volumes discharged (1 - 4

$m^3.s^{-1}$) comparatively to the Seine River (about 150 $m^3.s^{-1}$). To the opposite, a significant increase of concentrations is observed at S_7 downstream of $WWTP_3$ (from 324 at S_6 to 751 $ng.l^{-1}$ at S_7 in April and from 304 to 526 $ng.l^{-1}$ in July). This impact is related to higher volume discharged (17 $m^3.s^{-1}$ against 150 $m^3.s^{-1}$ for the Seine River) and to a lesser extent to the higher concentrations measured in the effluents. Actually, the $WWTP_3$ is the biggest plant of the Parisian conurbation treating approximately 75% of the Parisian wastewater, i.e. 1.7 million m^3 (6.0 millions of population-equivalents). This impact is clearly visible at S_7 but becomes less perceptible at S_8 due to the Seine River dilution by the Oise tributary (T_4, Figure 1), accounting for 40% of total river flow.

3.2 Alkylphenol ethoxylate and bisphenol A mass loads

For both sampling campaigns, daily mass loads ($g.d^{-1}$) were calculated according to the total concentrations ($ng.l^{-1}$) and the river flows ($m^3.s^{-1}$). These values were obtained from different river monitoring stations.

3.2.1 Temporal variation of the pollutant loads

In order to assess the temporal variation of the pollutant loads, the loads ($g.d^{-1}$) at S_8 and S_{10} for all sampling campaigns available were examined (Figure 4). The distance between S_8 and S_{10} is about 150 km and the hydraulic time is evaluated between 3 and 5 days.

As underlined by Figure 4, a limited temporal variation is observed for BPA between median- and low-water periods. While the BPA loads in April (S_8 and S_{10}) or in May (S_8) ranged from 1,360 to 1,776 $g.d^{-1}$, those observed during low-water period are comprised between 611 and 1,370 $g.d^{-1}$. In contrast, the APEO loads significantly vary between spring and summer. While the APEO loads (sum of 6 congeners) in April reach 10,741 and 10,108 $g.d^{-1}$ at S_8 and S_{10}, far lower loads are indeed observed in July (3,822 and 3,931 $g.d^{-1}$, Figure 4). This temporal variability is mainly explained by the important decrease of Seine River

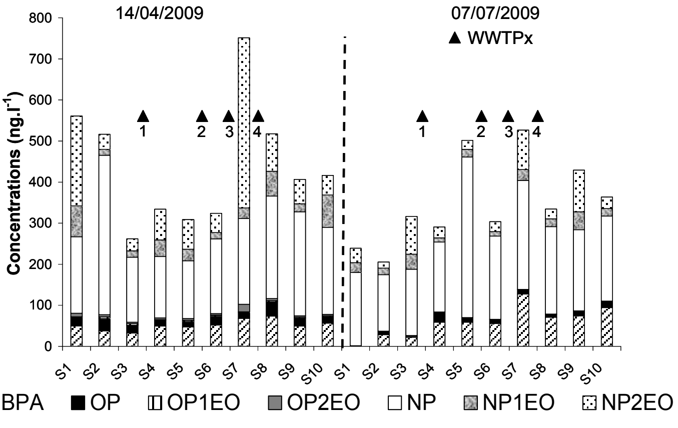

Figure 3: APEO and BPA concentrations in the Seine River.

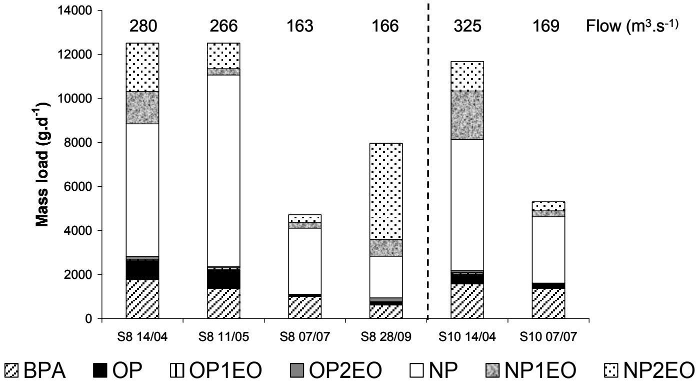

Figure 4: Temporal variation of the APEO and BPA loads.

flow between both dates (280 *vs*. 163 $m^3.s^{-1}$, i.e. 58%) and to a lesser extent by the difference of concentrations at S_8. Whether no clear seasonal variation of APEO concentrations was highlighted in our study, the lower concentration at S_8 was however noted in July (263 $ng.l^{-1}$) comparatively to April (444 $ng.l^{-1}$).

Figure 4 also underlines an evolution of the $NP_{1\text{-}2}EO$ and $OP_{1\text{-}2}EO$ distributions between S_8 and S_{10}. This change probably results from *in-situ* processes, more likely through biodegradation. It is actually known that the biodegradation leading to the formation of APEOs with shorter ethoxylate chain affect the distributions of the different congeners (John and White [9]). As attested by the change of $NP_{1\text{-}2}EO$ and $OP_{1\text{-}2}EO$ proportions between both stations, biodegradation seems to be more important in April than in July.

3.2.2 Evolution of pollutant loads along the Seine River

Figure 5 illustrates the evolution of the pollutant loads along the Seine River (from S_1 to S_{10}) for both sampling campaigns. Whatever the campaign considered, results show an increase of the pollutant loads from up- (S_1) to down-stream (S_{10}) stations. Typically, the BPA loads in April rise from 154 $g.d^{-1}$ at S_1 to 1,576 at S_{10} while the APEO loads increase from 1,580 to 10,108 $g.d^{-1}$ in the same time (Figure 5).

At the Seine basin outlet (S_{10}), the exported loads in April and July to the lower part of the Seine basin were respectively evaluated at 1,576 and 1,373 $g.d^{-1}$ for BPA and at 10,108 and 3,931 $g.d^{-1}$ for APEOs. The $WWTP_{1,2,4}$ seem to have a moderate impact on the pollutant loads conveyed by the Seine River. As previously mentioned, this can be mainly related to their low effluent discharges comparatively to the Seine River and their low concentrations.

To the opposite, the $WWTP_3$ has a significant impact on the Seine River pollutant loads. Due to the $WWTP_3$ discharge, the APEO and BPA loads between S_6 and S_7 increase from 5,173 to 11,681 $g.d^{-1}$ in April and from 2,576 to 5,240 $g.d^{-1}$ in July. As previously explained, this impact is related to the high flow of the $WWTP_3$ effluents (17 $m^3.s^{-1}$) representing up to 15% of Seine River flow (S_7). Contrary to the results found for concentrations, the $WWTP_3$ impact

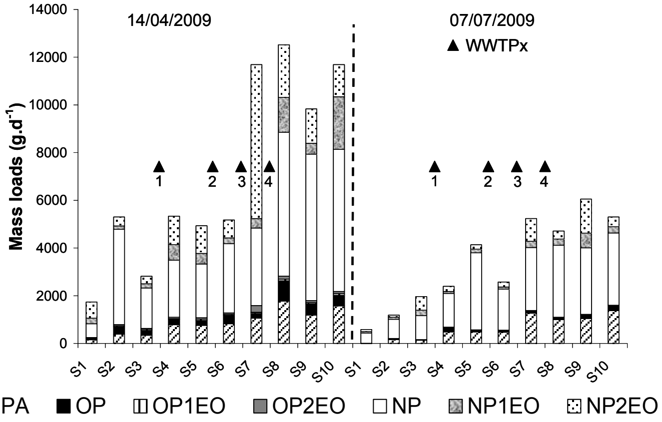

Figure 5: Evolution of pollutant loads along the Seine River.

on the pollutant loads is still visible on the downstream stations. A comparison between the WWTP loads (sum of 4 WWTPs) and the total inputs to the Seine River system (S_1, tributaries and WWTPs) attests to the higher contribution of the WWTPs in July comparatively to April. For instance, the contribution of WWTP effluents to total inputs rises from 13% to 36% for BPA and from 10% to 40% for APEOs. These results are mainly related to the decrease of tributaries and S_1 flows between spring and summer whereas the WWTP discharge flows are constant.

3.2.3 Inputs and exported pollutant loads at the scale of the Seine basin

To assess the dynamic of the pollutants within the Seine River, mass balances between the inputs (S_1, tributaries and WWTPs) and the pollutant loads measured at the basin outlet (S_{10}) were carried out. Thus, the ratio between the inputs and the exported loads were calculated for both campaigns (Table 3).

The comparison between the inputs and the exported loads highlights two different cases. For BPA, the inputs for both campaigns appear lower than the exported loads (ratio inputs *vs.* exported loads respectively equal to 0.7 and 0.5). Considering that a production of BPA cannot occur within the Seine River [4], these ratios indicate that not all sources were account for. To asses more accurate mass balances, the other WWTPs present in the Seine basin (about 250 plants with capacity below 2,000 population-equivalents) have to be considered along the Seine transect.

To the opposite, APEOs exhibit ratios above 1 suggesting that the inputs are higher than the exported loads (Table 3). These values point out the in-stream removal of APEOs along the Seine River, probably through *in-situ* processes such as adsorption on particles and sedimentation [22] and/or biodegradation [9, 10]. Out of these different processes, the biodegradation is likely the predominant one [5]. Results found in April and to a lesser extent in July reveal that the removal of APEOs and the number of ethoxylate units are correlated – the longer ethoxylate chain, the higher the removal (3.5 for NP_2EO > 1.7 for

Table 3: Inputs and exported loads (g.d^{-1}) in the Seine River.

compound	April		July		Inputs / exported	
	Inputs	exported	Inputs	exported	14/04/09	07/07/09
BPA	1,164	1,576	728	1,373	0.7	0.5
OP	544	447	135	235	1.2	0.6
OP$_1$EO	132	68	10	NC	2.0	-
OP$_2$EO	282	87	20	NC	3.2	-
NP	6,138	5,959	3,466	3,019	1.0	1.1
NP$_1$EO	3,282	2,205	467	268	1.7	1.7
NP$_2$EO	5,175	1,342	676	409	3.5	1.7

NC = not calculated since concentrations are below the detection limit.

NP$_1$EO > 1.0 for NP in April, Table 3). Considering the views of transformation reactions of nonylphenol ethoxylates provided by Giger *et al.* [23], results implied that the transformation of NP$_2$EO into NP$_1$EO or nonylphenolethoxyacetic acid (NP$_2$EC) is faster than its formation from NPnEO. Similarly, our results suggest that the transformation of NP$_1$EO into NP or nonylphenolacetic acid (NP$_1$EC) is faster than its formation from longer homolog.

4 Conclusion

This study provides first relevant information on the occurrence and fate of APEOs and BPA at the scale of the upper part of the Seine basin. BPA concentrations range from 7.2 to 127 ng.l^{-1} in surface water. For APEOs, higher concentrations for surface water (324 ± 153 ng.l^{-1}) were observed. Based on our first results, no spatial variability of concentrations between up- and downstream sites as well as any seasonal variability were highlighted. To the opposite, an increase of the pollutant loads between up- and down-stream sites was noticed. Contrary to the limited seasonal variation of BPA, the APEO loads significantly vary (10,108 and 3,931 g.d^{-1}). At present, this seasonal variation has to be better examined in relation to the hydrological dynamic conditions. Therefore, further investigations will be soon carried out.

The assessment of the pollutant mass balances between the inputs and the exported loads reveal that the BPA inputs are lower than the exported loads suggesting that not all sources were considered. For APEOs, the inputs appear higher than the exported loads, underscoring their in-stream removal during their transport within the Seine River. Results reveal that this removal and the number of ethoxylate units are correlated – the longer ethoxylate chain, the higher the removal. Whether our result do not allow the identification of the transformation reactions involved in the aquatic system, our sampling approach nevertheless enables a better understanding of the APEO behaviour. In the future, the analyses of NP$_{1\text{-}2}$EC intermediates will improve this understanding.

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