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Abstract

Assessing the fate of endocrine disrupting compounds (EDC) in the environment is currently a key issue for determining their impacts on aquatic ecosystems. The 4-nonylphenol (4-NP) is a well known EDC and results from the biodegradation of surfactant nonylphenol ethoxylates (NPnEO). Fate mechanisms of NPnEO are well documented but their rate constants have been mainly determined through laboratory experiments.

This study aims at evaluating the *in-situ* fate of 4-NP, nonylphenol monoethoxylate (NP_1EO) and nonylphenolic acetic acid (NP_1EC). Two sampling campaigns were carried out on the Seine River in July and September 2011, along a 28 km-transect downstream Paris City. The field measurements are used for the calibration of a sub-model of NPnEO fate, included into a hydro-ecological model of the Seine River (ProSe). The timing of the sampling is based on the Seine River velocity in order to follow a volume of water. Based on our results, *in-situ* attenuation rate constants of 4-NP, NP_1EO and NP_1EC for both campaigns are evaluated. These rate constants vary greatly. Although the attenuation rate constants in July are especially high (higher than 1 d^{-1}), those obtained in September are lower and consistent with the literature. This is probably due to the biogeochemical conditions in the Seine River. Indeed, the July sampling campaign took place at the end of an algal bloom leading to an unusual bacterial biomass while the September campaign was carried out during common biogeochemical status. Finally, the uncertainties on measurements and on the calibration parameters are estimated through a sensitivity analysis.

This study provides relevant information regarding the fate of biodegradable pollutants in an aquatic environment by coupling field measurements and a biogeochemical model. Such data may be very helpful in the future to better understand the fate of nonylphenolic compounds or any other pollutants at the basin scale.

Keywords:

Nonylphenol and nonylphenol ethoxylates, attenuation rate constant, endocrine disrupting compounds modelling, surface water

1. Introduction

Over the last 20 years, the scientific community paid a special attention to endocrine disrupting compounds (EDC) due to their toxicity on aquatic wildlife (Petrovic *et al.*, 2004). Among these compounds, the nonylphenol ethoxylates (NPnEO), and especially the 4-nonylphenol (4-NP), are of prime interest since concentrations of several hundred nanogrammes per liter were measured in all environmental and urban waters (Giger *et al.*, 1984; Ahel *et al.*, 1994). 4-NP is more estrogenic and more toxic than NPnEO (Soto *et al.*, 1991). Jugan *et al.* (2009) and Fenet *et al.* (2003) have reported the role played by the 4-NP in the estrogenic activity occurring in both surface water and sediment compartments. Due to its toxicity, the 4-NP have been included in the list of the 33 priority pollutants in the European water framework Directive 2000/60/EC (European Commission, 2000). More recently the European Directive 2008/105/EC established the environmental quality standard for 4-NP at 300 ng/L in surface water (European Commission, 2008). The 4-NP mainly originates from the biodegradation of NPnEO (readily biodegradable compounds) which are used as non-ionic surfactants in many industrial and domestic applications. The worldwide production of NPnEO reached 500,000 tons in 2000 and is decreasing because of regulations (Ying *et al.*, 2002). The biodegradation pathways of NPnEO are currently well known (John and White, 1998; Jonkers *et al.*, 2001; Giger *et al.*, 2009). Basically, the NPnEO can be biodegraded into 4-NP through an oxidative pathway leading to nonylphenolic acids (e.g. nonylphenol acetic acid: NP_1EC) as biodegradation intermediates, or through a non-oxydative pathway leading to short chain nonylphenol ethoxylates (e.g. nonylphenol mono ethoxylates: NP_1EO) as intermediates (Giger *et al.*, 2009). Finally, the 4-NP can be mineralized under well oxygenated conditions (Gabriel *et al.*, 2005). The biodegradation rate constants of NPnEO have been mostly determined through bioreactor laboratory experiments (Staples *et al.*, 2001; Jurado et al., 2009; Karahan *et al.*, 2010). However, such experiments fail to represent the complexity of freshwater ecosystems, including the spatial and temporal heterogeneity and the numerous biological, physical and chemical parameters which may interfere with the dynamics of the NPnEO degradation. Jurado *et al.*, (2009) used NPnEO mixture as the sole source of carbon for microorganisms and found biodegradation rate constants of NPnEO about 0.2 h^{-1}, while Staples *et al.*, (2001) used synthetic river water to perform a river die-away experiment (closer to *in-situ* conditions) and found biodegradation rate constants ranging from 0.04 d^{-1} to 0.10 d^{-1} for NP_9EO and from 0.08 to 0.09 d^{-1} for 4-NP. The difficulty to assess the NPnEO concentrations and their biodegradation relies in the fact that there is a lack of commercial pure reference standards which can be used for a reliable

analysis, and that various commercial mixtures exist with different chain lengths according to their use (Ayorinde *et al.*, 1999).

To date, only one study focuses on the determination of *in-situ* attenuation rate constants of NPnEO and 4-NP based on a hydrodynamic and biogeochemical model (Jonkers *et al.*, 2005). However, these attenuation rate constants have to be confirmed since:

i) *In-situ* biodegradation was determined in estuarine saline water. Authors suggest that biodegradation may significantly change in freshwater;

ii) The knowledge of biodegradation pathways has been updated; NP_1EC is now recognized as a biodegradation precursor of 4-NP (Montgomery-Brown *et al.*, 2008; Giger *et al.*, 2009).

Thus, it is crucial to assess the *in-situ* biodegradation of short chain nonylphenol and 4-NP in surface water in order to evaluate their environmental fate and their impact on aquatic wildlife surrounding heavily urbanized area such as the Seine River downstream of Paris, France.

A global project on modelling NPnEO was launched in 2009. The first part aims at evaluating the attenuation rate constants; the second aims at modelling the fate of nonylphenolic compounds at the annual scale in order to validate the parameters calibrated in the first part and forecast future profiles of the Seine River. This study deals with the first part of the NPnEO modelling project, while the second part is handled in a companion paper with the simulation of annual time series of NPnEO and 4-NP concentrations for a reference year (2010) in the Seine River. At last, a forecast of nonylphenolic compound concentrations in the Seine River is attempted for the 21^{st} century according to global changes scenarios (Cladière *et al.*, 2013a).

Therefore the goal of this first part is to determine the *in-situ* attenuation rate constants of 4-NP, NP_1EC and NP_1EO in the Seine River. To achieve this goal, two sampling campaigns are carried out and the data are used to calibrate a hydro-ecological model implemented for the Seine River. A special attention has been paid to the small scale spatial and temporal variabilities of the concentrations which are firstly *in-situ* assessed and then used in the model calibration procedure. Finally, the sensitivity analysis of the model to the biodegradation parameters is performed based on an approach “one factor at a time” (OFAT).

The calibrated parameters are then validated in the companion paper according to 11 monthly sampling campaigns carried out in 2010 at 3 sites on the Seine River and the Oise River as well as the effluent of the largest WWTP of the Parisian Metropolitan Area (Cladière *et al.* 2013a).

2. Materials and methods

2.1. Study site

This study focuses on the Seine River, downstream of Paris City (annual average flow in Paris = 300 m^3/s, 120 m^3/s in summer). The investigated transect of the Seine River is 28 km long from Maisons-Laffite to Triel-sur-Seine (Fig.1).

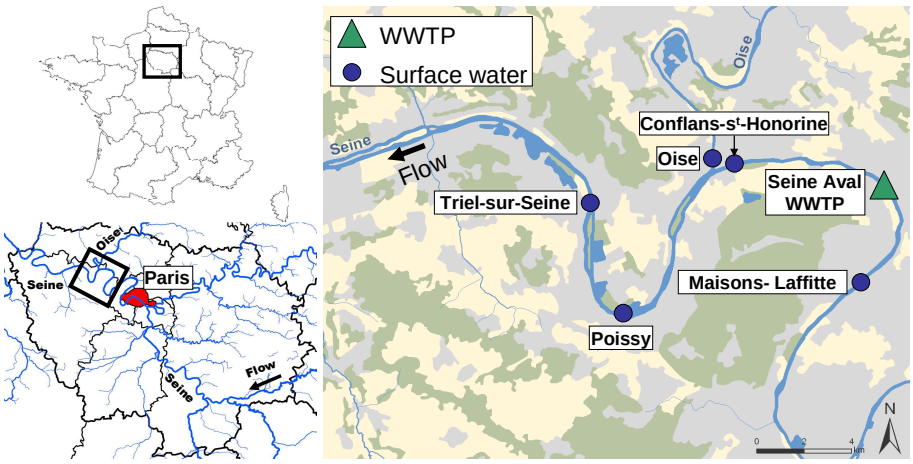

Fig. 1 Investigated transect of the Seine River (28 km-long) downstream of Paris and sampling sites

Four sampling sites are considered along this transect (Maisons-Laffite, Conflans-st-Honorine, Poissy and Triel-sur-Seine) and two for the effluents of Seine Aval Waste Water Treatment Plant (WWTP) and the Oise River (Fig.1).

This transect is selected based on two major criteria. First, there are only two significant tributaries in the Seine River between Maisons-Laffite and Triel-sur-Seine, i.e. the effluents of Seine Aval WWTP and the Oise River (Fig.1). The Seine Aval WWTP is the biggest treatment plant of the Parisian Metropolitan Area and treats approximately 1,666,000 m^3 per day (70 % of Parisian wastewater) with an average effluent flow of 19 m^3/s. The Oise River is one of the largest tributaries of the Seine River with an average discharge flow of 95 m^3/s (30 m^3/s in summer). These two inflows account for 30 % to 40 % of the Seine River flow at Triel-sur-Seine during low-flow conditions. The small number of lateral inflows along this transect simplifies the determination of the boundary conditions for the modelling procedure. The second criterion is the distance between Maisons-Laffite and Triel-Sur-Seine. According to the average Seine River velocity (≈ 0.15 m/s) during low-flow conditions (< 150 m^3/s), the transit time along this transect is approximately 60 h. This duration is similar to the half-lives of 4-NP and NPnEO found in the literature: between 2 and 7 days (Staples et al., 2001; Jonkers et al., 2005).

2.2. Sampling campaigns

Two sampling campaigns were carried out in July and September 2011. These campaigns are designed to acquire data for the calibration of the ProSe model and the assessment of attenuation rate constants of nonylphenolic compounds in the Seine River. The timing of the sampling is estimated according to the Seine River flow velocity in order to collect samples in the same water volume from Maisons-Laffitte to Triel-sur-Seine (Lagrangian approach). The Seine River velocity is simulated using the hydrodynamic module of the ProSe model (see section 2.3), with measured upstream boundary conditions (national discharge gauging station located in Paris City). The description of the sampling campaigns (kilometre points, hours of sampling and flows) are provided in Table 1. The sampling campaigns were exclusively carried out under dry weather conditions in order to ensure that the Seine Aval WWTP and the Oise River are the sole lateral inflows (no wet weather sources). Due to an unexpected rain event, the July campaign was stopped at Poissy (45 h).

Table 1 Sampling campaign description for July 2011 and September 2011.

Sampling points	Kilometre point (km)	July 2011 (Tw = 21°C) Hours of sampling	Flow (m^3/s)	September 2011 (Tw = 19°C) Hours of sampling	Flow (m^3/s)
Maisons-Laffitte	715.4	10/07 8:42	72	29/09 8:00	97
Seine Aval (WWTP)	720.1	10/07 19:24	16	29/09 15:30	18
Conflans-s^t-Honorine	728.2	11/07 16:30	88	30/09 7:00	115
Oise River	728.7	11/07 17:06	32	30/09 7:30	28
Poissy	734.9	12/07 5:35	120	30/09 19:00	143
Triel-sur-Seine	743.6	*	-	01/10 18 :50	143
Total sampling time		45 h		59 h	

*: The July sampling campaign was stopped at Poissy due to a rain event. Tw = water temperature

Samples are collected from bridges in the middle of the river with 2 L glass bottles. The analytical protocol is described in details by Cladière *et al.*, (2013b). Briefly, the water samples are filtered through a 0.45 µm porosity glass fiber filter (GF/F, Whatmann). Only the dissolved phase is kept and analyzed as the suspended particles account approximately for 5 % of total concentrations of NP_1EO, NP_1EC and 4-NP within the Seine River (Cladiere *et al.*, 2010). After a spiking with a surrogate mixture (octylphenol-d17, NP_1EO-d2), 250 mL of dissolved phase is extracted by solid phase extraction on OASIS® HLB cartridges (200 mg/6 mL; Waters©). Finally, the extracts are analyzed by means of an ultra-performance liquid chromatography coupled to a tandem mass spectrometer (UPLC-MS-MS; Waters©) using an internal standard mixture (linear compounds: 4-nNP, nNP_1EO and nNP_2EC). Based on this analytical protocol, the concentrations of 4-NP, NP_1EC and NP_1EO are quantified for surface water and WWTP effluents. Given that no pure standard is commercially available for NP_3EO to $NP_{15}EO$, only semi-quantitative analyses are performed for these compounds. A semi-quantitative

analysis does not provide the real value of compound concentration but a concentration equivalent value proportional to the real concentration (the factor is not known because of the lack of pure standard). For each *n* (from 3 to 15), dividing the NP*n*EO peak area by the peak area of the relative internal standard nNP_1EO give the concentration equivalent of the NP*n*EO. These concentration equivalent values enable comparisons from one site to another but not between compounds (e.g. the factor of proportionality of NP_3EO is different from that of $NP_{15}EO$).

2.3. Modelling tool: the ProSe model

The hydrodynamic and biogeochemical model ProSe was firstly developed to simulate the impacts of human activities on nitrogenous and phosphorous pollutions in the Seine River and its tributaries (Even *et al.*, 1998; Flipo *et al.*, 2007; Even *et al.*, 2007). All mathematical equations used by the ProSe model to simulate the river flowing, pollutant advection and other biogeochemical parameters are provided by Even *et al.* (1998). For this study the biogeochemical module is updated to take into account the biodegradation pathways of NPnEO following Giger *et al.*, (2009) scheme (Fig. 2).

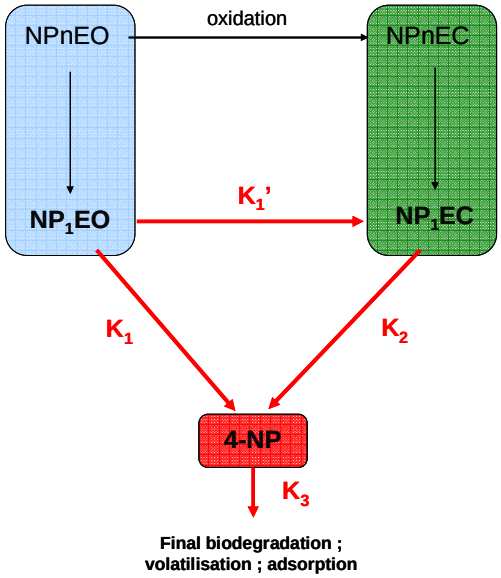

Fig. 2 Fate schema of nonylphenolic compounds in a well oxygenated surface water. The attenuation rate constant K_1, K_1', K_2 and K_3 are determined by the ProSe model. The biodegradation of NPnEO and NPnEC is introduced in the ProSe model as precursor inputs of NP_1EO and NP_1EC along the Seine River.

In the Figure 2, the attenuation rate constants K_1, K_1' and K_2 only represent the biodegradation of NP_1EO or NP_1EC into their products (NP_1EC or 4-NP). On the contrary, K_3 represent the global attenuation of 4-NP due to biodegradation, volatilisation and adsorption onto particles.

Assuming first-order kinetics (Jonkers *et al.*, 2003; Jurado *et al.*, 2009), the attenuation rate constants K_1, K_1', K_2 and K_3 are calibrated using a trial-error procedure to optimise the matching of the modelled longitudinal profiles of 4-NP, NP_1EO and NP_1EC with the measured ones. Jonkers *et al.* (2005) suggest, during the sensitivity analysis of their model, that the sorption onto particles have a very limited influence on the fate of nonylphenolic compounds in estuarine water. Indeed, set sorption to 0 or multiply their optimum value by 5 lead to small variations of NP_1EO and NP_1EC dissolved concentrations. In addition, Cladiere *et al.* (2010) showed that the particulate concentrations of nonylphenolic compounds account for less than 5% of the total concentration. Therefore, the sorption onto particles of NP_1EO and NP_1EC has been considered as negligible. Similarly to Jonkers *et al.* (2005), the water-air exchange of the nonylphenolic compounds (except for 4-NP) has been considered as insignificant due to very low Henry's constants (e.g. NP_1EO and $NP_2EO \approx 0.0003$ $Pa.m^3/mole$).

Consequently, three equations are implemented in the biogeochemical module of the ProSe model:

$$\frac{d[NP_1EO]}{dt} = -K_1\,[NP_1EO] - K_1'\,[NP_1EO] + precursor\ inputs \qquad \textbf{Equation 1}$$

$$\frac{d[NP_1EC]}{dt} = +K_1'\,[NP_1EO] - K_2\,[NP_1EC] + precursor\ inputs \qquad \textbf{Equation 2}$$

$$\frac{d[4-NP]}{dt} = +K_1\,[NP_1EO] + K_2\,[NP_1EC] - K_3\,[4-NP] \qquad \textbf{Equation 3}$$

Due to the lack of suitable information for NP_1EO degradation and in order to reduce the number of parameters to calibrate, we assume that the oxidation and the biodegradation of NP_1EO are equal ($K_1 = K_1$'). Moreover, data on long chain nonylphenol ethoxylates are scarce and their attenuation rate constants are not determined. The semi-quantitative analyses reveal that the effluent of Seine Aval WWTP is from 2 (NP_3EO) to 11 (NP_8EO) times more concentrated than the upstream of the Seine River. In addition, by comparing the concentration equivalents found at Poissy to the expected ones (combining of Conflans-s^t-Honorine and the Oise River), discrepancies of -39 % (NP_3EO) to -64 % (NP_8EO) are noticed. These discrepancies give evidence of the disappearance of these compounds in the Seine River due to biodegradation processes. In order to take into account the biodegradation of long chain ethoxylates within the Seine River, "precursor inputs" terms are considered in the ProSe model scheme as linear sources, also being calibrated during the calibration process (Equations 1 and 2). Based on the disappearance of long chain nonylphenol ethoxylate along the Seine River (revealed by semi-quantitative analyses), the precursor inputs are assumed to decrease along the simulated transect. The highest precursor inputs are estimated close to the Seine Aval discharge and decrease until Triel-sur-Seine following natural logarithm shape representative of first-order kinetics. These precursor inputs take into account the appearing of

NP_1EC or NP_1EO along the studied transect due to the biodegradation of long chain compounds and they are expressed in nanogram per litter of water and per day (ng/L/d).

The scheme in Fig. 3 shows the layout and input parameters of the model. In the ProSe model, it is necessary to define the boundary conditions such as the upstream river flow (national discharge gauging station) and the upstream compound concentrations [C] (field measurements). The attenuation rate constants and precursor inputs are calibrated according to the concentrations at Conflans-S^t-Honorine, Poissy and Triel-sur-Seine.

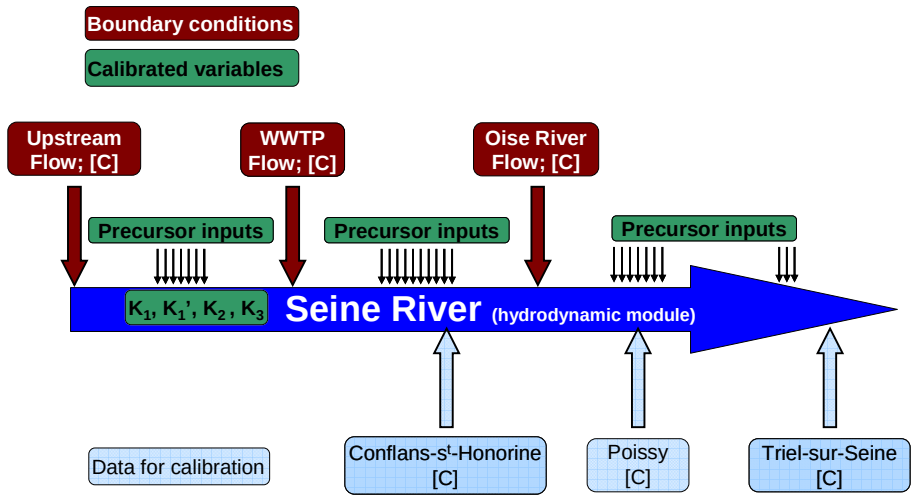

Fig. 3 Scheme of the ProSe model and the required input parameters. ([C] =concentrations of 4 NP, NP_1EO and NP_1EC in ng/L)

2.4. Sampling strategy for determining small scale spatial and temporal variabilities

Small scale variabilities are crucial since they have a direct impact on the calibration process and the assessment of the attenuation rate constants (Beven, 2010). The spatial and temporal variabilities of 4-NP, NP_1EC and NP_1EO concentrations are assessed at Conflans-s^t-Honorine (during September campaign) as depicted in Fig. 4 and are assumed to be representative of variabilities along the whole Seine River transect.

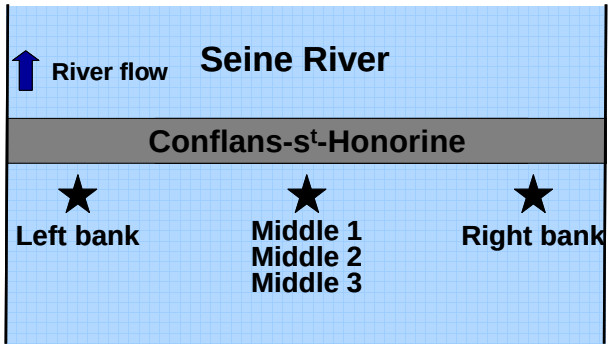

Fig. 4 Sampling strategy to determine the small scale variabilities of concentrations. The sampling points are indicated by stars. Middle 1, 2 and 3 were sampled with an interval of 10 minutes.

For the assessment of the spatial variability, samplings are performed simultaneously at the left bank, in the middle and the right bank of the Seine River, while two additional samples in the middle are collected with a 10-min interval to assess the temporal variability. The relative standard deviations (%RSD) are used to assess the spatial (Left bank, Middle and Right bank) and temporal (Middle 1, 2 and 3) variabilities. The analytical repeatability is assessed by means of multiple extractions and UPLC-MS-MS analyses and the results are provided by Cladière *et al.*, (2013b) (4-NP: 7 % , NP_1EC: 4 % and NP_1EO: 14 %).

3. Results

3.1. Small scale variabilities

Table 2 exhibits the concentrations of 4-NP, NP_1EC and NP_1EO within the Seine River as well as small scale spatial and temporal variabilities.

Table 2 Concentrations (ng/L) of left bank, middle and right bank of the Seine River and small scale variabilities

	Dissolved concentrations (ng/L)						Small scale variabilities (%)**		
	Spatial variability			Temporal variability					
	Left bank	Middle (average*)	Right bank	Middle 1	Middle 2	Middle 3	Spatial	Temporal	Total
4-NP	55	57	63	58	57	57	7	7	14
NP_1EC	129	123	118	125	128	115	5	6	11
NP_1EO	10	9	11	11	7	10	14	23	37

*The concentrations for Middle used for the spatial variability are the averages of Middle 1, 2 and 3. **The spatial and temporal variabilities are determined by the relative standard deviation of samples (%RDS). The total variabilities are calculated by the sum of spatial and temporal variabilites (we assume that analytical uncertainties are included in spatial and temporal variabilities).

The concentrations of 4-NP and NP_1EC found in the Seine River (≈ 100 ng/L) are far higher than their limits of quantification (4-NP: 24.5 ng/L; NP_1EC: 1.7 ng/L) except for NP_1EO (NP_1EO: 9.8 ng/L). The repeatability is taken into account in the assessment of spatial and temporal variabilities by selecting the highest value between the relative standard deviation of samples and the analytical repeatability. The small scale variabilities (sum of spatial and temporal) of 4-NP, NP_1EC and NP_1EO concentrations in the Seine River reach respectively 14 %,

11 % and 37 %. These results provide quantification errors due to the sampling protocol, which are usually not reported in most of articles dealing with pollutants in receiving surface water.

The sampling strategy is thus applicable to 4-NP and NP_1EC measurements, but is less accurate for NP_1EO. Therefore, the variabilities on Seine River profiles are plotted as error bars for the measured concentrations. In addition, the variabilities on boundary conditions are considered on the modelled profiles.

3.2. Attenuation rate constants

The concentrations of 4-NP, NP_1EC and NP_1EO found in the Seine and Oise Rivers and the effluents of Seine Aval WWTP as well as the biogeochemical parameters (water temperature, dissolved organic carbon (DOC), dissolved oxygen and pH) are exhibited in Table 3. All concentrations found during July and September sampling campaigns are consistent with the literature and previous results found in the Seine River (Jonkers *et al.*, 2009; Loos *et al.*, 2010; Cladière *et al.*, 2013b). The concentrations found during July in the Seine River are higher than those found during September, mainly due to the significant higher concentrations of Seine Aval WWTP and the Oise River (Table 3). Whatever the sampling campaign, no exceedance of the European Quality Standard (300 ng/L) is observed along the 28 km transect of the Seine River even downstream of Seine Aval WWTP.

Table 3 Biogeochemical parameters and nonylphenolic compound concentrations measured in July and September sampling campaigns

	July					September					
Parameters*	Upstream	Seine Aval WWTP	Conflans-st-Honorine	Oise river	Poissy	Upstream	Seine Aval WWTP	Conflans-st-Honorine	Oise river	Poisy	Triel-sur-Seine
Flow (m^3/s)	72	17	89	32	121	97	18	115	28	143	143
Tw (°C)	20.8	20.9	22.2	21.4	21.0	19.3	ND	19.1	17.5	20.8	ND
σ (µS/cm)	600	1195	693	690	699	612	720	635	739	666	ND
pH	8.0	ND**	7.5	7.8	7.6	7.6	ND	7.6	8.0	7.6	ND
O_2 (mg/L)	4.9	ND	4.0	5.0	ND	ND	ND	9.3	11.3	7.7	ND
DOC (mg/L)	2.95	11.60	4.08	2.74	3.83	2.84	8.97	3.74	3.32	3.37	3.63
4-NP (ng/L)	102	320	201	138	143	53	136	57	35	45	70
NP_1EC (ng/L)	52	751	159	66	137	49	616	123	76	114	102
NP_1EO (ng/L)	19	80	35	17	30	19	43	9	20	11	14

*σ: conductivity, O_2: dissolved oxygen, DOC: dissolved organic carbon. **ND: not determined.

Before calibrating the attenuation rate constants in the Seine River, a first simulation is performed considering nonylphenolic compounds as a conservative tracer for July and September campaigns. Results (data not shown) underscore that the modelled trends do not fit the observed ones indicating that only physical processes (transport and lateral inflows) do not explain the fate of 4-NP, NP_1EC and NP_1EO along the Seine River.

Attenuation rate constants and precursor inputs are, thereafter, calibrated (Fig 5). In parallel, small scale variability intervals are used to assess uncertainties around the optimal values of attenuation rate constants.

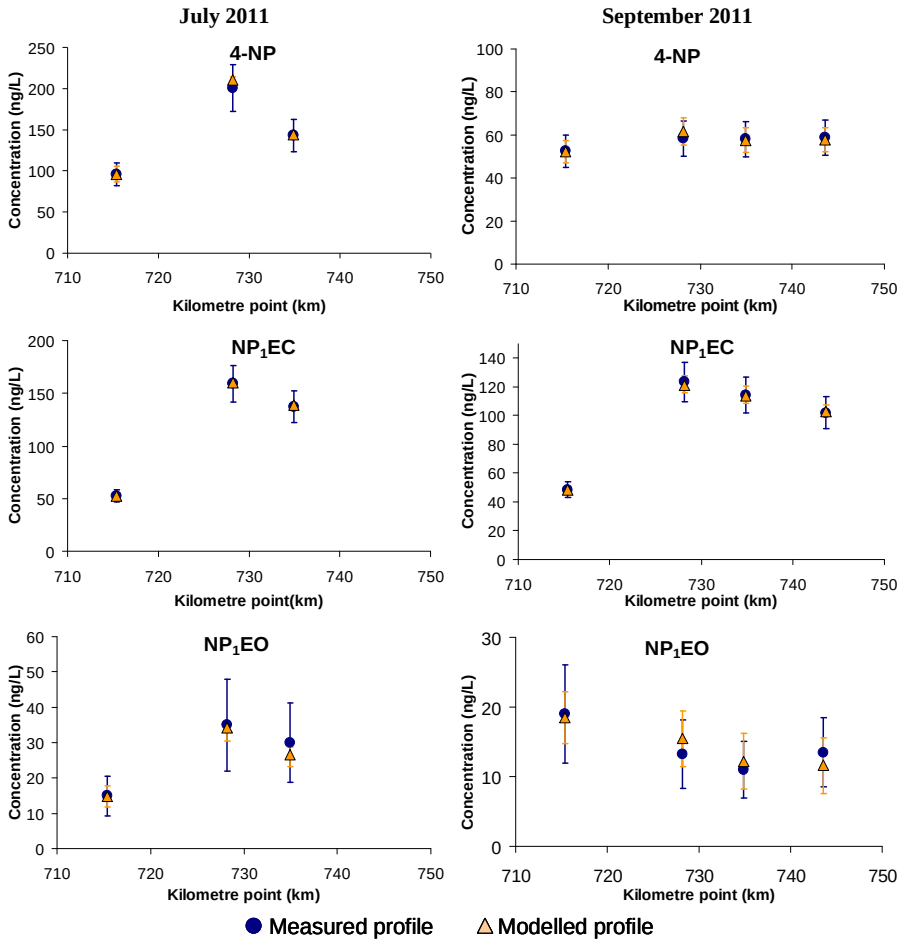

Fig. 5 Modelled (optimised rate constants) and actual profiles of 4-NP, NP_1EC and NP_1EO concentrations in the Seine River. The points exhibited are Maisons-Laffite (715.4 km), Conflans-st-Honorine (728.2 km), Poissy (734.9 km) and Triel-sur-Seine (743.6 km). The y error bars represented on the actual profile indicate the total variabilities linked to in-situ sampling while they represent the uncertainties attached to boundary conditions on modelled profile

Table 4 shows the minimum, optimal and maximum attenuation rate constants as well as precursor inputs for July and September sampling campaigns.

Table 4 Attenuation rate constants (d^{-1}) and precursor inputs (ng/L/d)

	Attenuation rate constants (d^{-1})			Precursor inputs (ng/L/d)	
	$K_1 = K_1'$ min - opt - max	K_2 min - opt - max	K_3 min - opt - max	NP_1EC min - max	NP_1EO min - max
July 2011	0.05 - 0.10 - 0.15	3.14 - 3.30 - 3.47	2.38 - 2.50 - 2.75	3.44 - 7.84	0.06 - 0.4
September 2011	0.29 - 0.30 - 0.33	0.08 - 0.10 - 0.14	0.09 - 0.15 - 0.19	0.01 - 0.3	0.04 - 0.4
Jonkers *et al.*, 2005 (estuary)	0.060 - 0.089	0.019 - 0.020	0.024 - 0.043	-	-
Jonkers *et al.*, 2005 (estimation river)	0.18 - 0.21	0.048 - 0.159	0.072 - 0.21	-	-
Staples *et al.*, 2001 (laboratory)	0.065	0.099	0.076 - 0.092	-	-

Min and max values were assessed according to the small scale variabilities. Optimised values (opt) enable the best fit between simulated and observed profiles.

For July, Table 4 discloses high values for K_2 (3.14 to 3.47 d^{-1}) and K_3 (2.38 to 2.75 d^{-1}). These rate constants are far higher than those reported by Jonkers *et al.,* (2005) in the Rhine estuary and Staples *et al.,* (2001) in laboratory batch reactor (Table 4). In parallel, the precursor inputs were estimated between 7.84 ng/L/d and 3.44 ng/L/d for NP_1EC and between 0.4 ng/L/d and 0.06 ng/L/d for NP_1EO. In the case of NP_1EC, the total precursor flux along the Seine River transect (33.6 g/d) accounts for 10 % of the upstream load (370 g/d) and only for 2.4 % of the Seine Aval input (1,480 g/d) which means that they are not main sources of NP_1EC and NP_1EO into the Seine River. However, the precursors inputs are crucial in the fate of NP_1EC and NP_1EO since neglect them during the calibration process does not allow a good fit between modelled and observed profiles.

Calibration parameters for the September campaign are much lower (Table 4). Mean values of K_2 and K_3 are respectively 17 and 33 times lower than those estimated for the July campaign. In parallel, the maximum precursor inputs for NP_1EC drops by a factor 26. The decreases of K_2, K_3 and NP_1EC precursor inputs suggest that the aerobic biodegradation was significantly higher in July compared to September. Moreover, the rate constants estimated in September are consistent with the literature (Jonkers *et al.,* 2005; Staples *et al.,* 2001).

The July and September sampling campaigns enable to calibrate of attenuation rate constants but not to validate them. Validation of the parameter sets is done at the annual scale based on 11 monthly sampling campaigns performed at the Maisons-Laffitte, Seine Aval WWTP effluent, the Oise River and Meulan (downstream Triel-sur-Seine). The validation is provided in the companion paper: “Modelling the fate of nonylphenolic compounds in the Seine River - part 2: assessing the impact of global change on daily concentrations” (Cladière *et al.* 2013a).

4. Discussion

4.1. Influence of biogeochemical conditions of the Seine River

In order to understand the significant differences between July and September, the biogeochemical conditions of the Seine River are examined (e.g. temperature, pH, chlorophyll a, dissolved O_2, Seine River flow). Manzano *et al.,* (1999) highlight the impact of temperature on biodegradation rates of nonylphenolic compounds and report that the higher the temperature, the higher the biodegradation rate. Water temperature is similar in July (21°C) and September (20°C) and cannot explain such differences of the attenuation rate constants. Furthermore, pH, conductivity, meteorological and hydrological conditions of the Seine River were quite similar during both campaigns.

Chlorophyll a concentrations are continuously monitored in the middle of the considered transect and exhibit high values (up to 20 µg/L representative of an algal bloom in the Seine River) one week before the July sampling campaign (data not shown). On the contrary, during September, low concentrations of chlorophyll a (≈ 5 µg/L) are noticed.

The link between an algal bloom and the growth of heterotrophic bacteria has been reported by Kisand and Noges, (1998) in lake Vortsjarv (Estonia) and by Hygum *et al.,* (1997) for laboratory experiments. Both studies reported a significant increase of the bacteria growth during the decline of an algal bloom. The high activity of heterotrophic bacteria is also visible on dissolved O_2 since the concentrations measured in July are close to 4 mg/L and saturation about 75 % while in September the concentration are far higher at 9 mg/L and saturation at 100 % (Table 3). Based on this conclusion, the decline of the algal bloom during the July campaign favours the increase of heterotrophic bacterial biomass, and consequently enhances the biodegradation of organic matters such as nonylphenolic compounds since Corvini *et al.,* (2006) reported that various environmental bacteria species can biodegrade them. Thus, in July the half-life times of 4-NP and NP_1EC vary between 5 and 7 hours, while in September they are longer and reach 7 days. The half-life time of NP_1EO remains constant in July and September and is close to 2 days.

Finally, the differences between July and September campaigns suggest that the bacterial biomass of the Seine River influences the oxidative biodegradation of NPnEO (K_2, K_3, NP_1EC precursors inputs), especially after an algal bloom. The first-order kinetic approach used in this study seems reliable to describe a punctual state of biodegradation in the Seine River (constant bacterial biomass) but does not take into account the variabilities generated by the fluctuation of bacterial biomass. In order to clarify the impacts of heterotrophic bacteria on

nonylphenolic compounds biodegradation, further studies should focus on coupling the modelling of NPnEO biodegradation and bacterial biomass using biogeochemical models such as ProSe.

In contrast, the non oxidative biodegradation of NPnEO is not impacted by the heterotrophic bacterial biomass of the Seine River since the attenuation rate constants of NP_1EO do not significantly evolve and the NP_1EO precursor inputs remain constant between both campaigns. However, this result must be considered carefully according to the lower confidence on NP_1EO concentration profiles (small scale variability = 37 % and concentrations close to the quantification limit).

4.2. Sensitivity analysis

In order to assess the significance of each process in the biodegradation pathway, a sensitivity analysis is performed using an approach "one factor at a time" (OFAT) (Félix and Xanthoulis, 2005). Input parameters of the model are modified by -10 % and +10 % around its optimised value one after the other. The effect of each modification is analyzed on the outputs by the means of a sensitivity index (SI, Equation 4).

$$SI = \frac{\frac{O_{Test} - O_{Opt}}{O_{mean}}}{\frac{I_{Test} - I_{Opt}}{I_{mean}}} \qquad \text{Equation 4}$$

Where

SI is the sensitivity index;

I_{Opt} is the optimised value of input;

I_{Test} is the tested value of input (+10 % or -10 %);

I_{mean} is the mean of I_{opt} and I_{Test};

O_{Test} and O_{Opt} are the outputs respectively related to I_{Test} and I_{Opt};

O_{mean} is the mean of O_{Test} and O_{opt}.

The sensitivity index weights the impacts of input parameters such as attenuation rate constants or precursor inputs on model outputs (concentrations of 4-NP, NP_1EC and NP_1EO at Conflans-s^t-Honorine, Poissy and Triel-sur-Seine). A positive SI means that input and outputs vary in a similar way while a negative SI means that inputs and outputs vary inversely. In addition, the higher the absolute value of SI, the higher the impact of input parameter on the considered output. The sensitivity indexes of nonylphenolic compound concentrations in the Seine River towards attenuation rate constants (SI_{K1}, $SI_{K1'}$, SI_{K2} and SI_{K3}) and precursor inputs (SI_{NP1EO}, SI_{NP1EC})

are shown in Fig. 6. During this study, an increase or a decrease of the considered inputs give similar results of sensitivity and hence results are compiled in Fig.6.

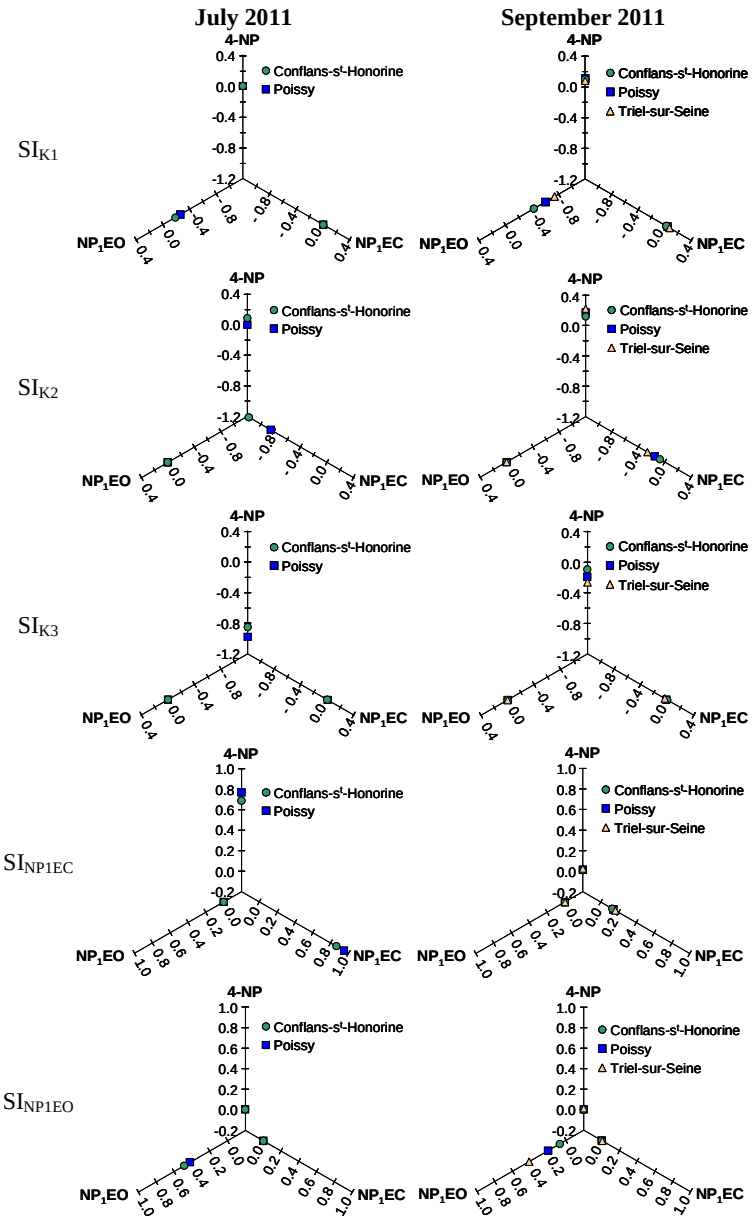

Fig. 6 Sensitivity indexes of simulated concentrations of 4-NP, NP_1EO and NP_1EC at Conflans-st-Honorine, Poissy and Triel-sur-Seine towards attenuation rate constants and precursor inputs

Whatever the sampling campaign, $SI_{K1(K1')}$, SI_{K2} and SI_{K3} are negative meaning that an increase of attenuation rate constants leads to a decrease of modelled concentrations. As underscored in the Fig.6, the sensitivity indexes of biodegradation processes in July and September are not similar confirming that campaigns occur in different conditions.

In July, high values of SI_{K2} (varying from -0.8 - to -1.2) and SI_{K3} (ranging from -0.8 to -1.0) are noticed for NP_1EC and 4-NP concentrations. On the contrary, the SI_{K1} (from -0.18 to -0.26) for NP_1EO concentrations is

smaller but still significant. In September, the SI_{K2} and SI_{K3} are smaller (around -0.25 for NP_1EC and 4-NP concentrations). This observation confirms that the aerobic biodegradation process is important in July while its significance is lower in September. These results corroborate the hypothesis of an enhanced aerobic biodegradation at the end of an algal bloom. A similar conclusion is highlighted for SI_{NP1EC} between July ($SI_{NP1EC} \approx 1$) and September ($SI_{NP1EC} \approx 0.2$).

Despite a significant role of K_2 to determine NP_1EC concentrations, it has a very limited impact on 4-NP concentrations (biodegradation product), as confirmed by the SI_{K2} for 4-NP concentrations (0.09 in July and September). A similar result is noticed for $SI_{K1(K1')}$ for NP_1EC or 4-NP concentrations ($\approx$ 0.007). As a conclusion, according to these sensitivity indexes, a variation of attenuation rate constants K_1 and K_2 has a weak influence on 4-NP concentrations along the simulated transect and points out the need to extend the scale of modelling (spatial and temporal) to better understand the impact of biodegradation processes.

5. Conclusions

This study assesses the *in-situ* attenuation rate constants of 4-NP, NP_1EC and NP_1EO within surface water in a heavily urbanized area such as Paris. Based on a coupling between sampling campaigns and hydraulic and biogeochemical simulations, this study provides the first real case study of the environmental fate of 4-NP, NP_1EC and NP_1EO in freshwater. This study is of prime interest since it proves the possibility to simulate the fate of readily biodegradable pollutants such as 4-NP and its precursors within surface water. Based on the toxicity of these compounds, the assessment of their environmental fate is a key issue to understand their persistence and their possible impacts on aquatic wildlife. Results highlight a strong temporal variability of rate constants between July and September campaigns. While the rate constants evaluated for July are higher than 1 d^{-1} and NP_1EC precursor inputs higher than 344 ng/L/d, the rate constants and precursor inputs assessed for September are smaller ($K \approx 0.1\ d^{-1}$ and precursors inputs $\approx$ 2 ng/L/d) but consistent with the literature. The variability of rate constants seems to be linked to the heterotrophic bacterial biomass and highlights that the first-order kinetic approach used in this study is reliable to describe punctual conditions of the Seine River (with a constant bacterial biomass) but not to describe the complexity of biogeochemical processes at larger temporal scale. Consequently, the coupling between attenuation rate constants and bacterial biomass should be more intensively investigated to definitely validate the impact of biogeochemical conditions of surface water on biodegradation of nonylphenolic compounds.

The sensitivity analysis of the ProSe model points out that the aerobic biodegradation processes are important inputs for the ProSe model and reinforces the hypothesis of the large influence of the biogeochemical conditions of the Seine River. However, this sensitivity analysis also highlights that biodegradation processes are not a key input for 4-NP fate along the 28 km transect, and points out the need to lengthen the transect in order to confirm or contradict this last conclusion at the basin scale.

In order to validate the modelling parameter values, the attenuation rate constants assessed during both sampling campaigns will be applied to simulate daily of concentrations of 4-NP, NP_1EC and NP_1EO for 2010 and compared to monthly sampling campaigns. To this end, 11 sampling campaigns were carried out from February to December 2010 at Maisons-Laffite, Seine Aval WWTP effluent, the Oise River, and Meulan (downstream of Triel-sur-Seine).

At last, the impact of global changes (global warming, population growth, optimisation of WWTP) on daily concentrations will be studied for the middle and the late 21st century. This is presented in a companion paper entitled: "Modelling the fate of nonylphenolic compounds in the Seine River - part 2: assessing the impact of global change on daily concentrations" (Cladière *et al.*, 2013a).

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