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Modelling the fate of nonylphenolic compounds in the Seine River - part 2: assessing the impact of global change on daily concentrations

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This study aims at modelling the daily concentrations of nonylphenolic compounds such as 4-nonylphenol (4-NP), nonylphenol monoethoxylate (NP_1EO) and nonylphenoxy acetic acid (NP_1EC) within the Seine River downstream of Paris City over a year, firstly in the present state (year 2010) and for years 2050 and 2100 in order to assess the consequences of global change on the fate of nonylphenolic compounds in the Seine river.

Concentrations were first simulated for the year 2010 and compared to monthly measured values downstream of Paris. To achieve this goal, the hydrodynamic and biogeochemical model, ProSe, was updated to simulate the fate of 4-NP, NP_1EO and NP_1EC. The Seine upstream and Oise Rivers (tributaries of the Seine River) concentrations are estimated according to concentrations - flow relationships. For Seine Aval wastewater treatment plan (SA-WWTP), the concentrations are considered constant and the median values of 11 campaigns are used. The biodegradation kinetics of 4-NP, NP_1EO and NP_1EC in the Seine River were deduced from the results of the companion paper. The Nash-Sutcliffe coefficient indicates a good efficiency to simulate the concentrations of 4-NP, NP_1EC and NP_1EO over an entire year.

Eight scenarios were built to forecast the impacts of global warming (flow decrease), population growth (SA-WWTP flow increase) and optimisation of wastewater treatment (improvement of the quality of effluents) on annual concentrations of 4-NP, NP_1EO and NP_1EC at Meulan by 2050 and 2100. As a result, global warming and population growth may increase the concentrations of 4-NP, NP_1EC and NP_1EO, especially during low-flow conditions, while the optimisation of wastewater treatment is an efficient solution to balance the global change by reducing WWTP outflows.

Keywords: Nonylphenol; nonylphenol ethoxylate; endocrine disrupting compounds; global change;

1. Introduction

Climate change at the scale of Europe is expected to increase the frequency of extreme events such as dry periods or storms (Christensen *et al.,* 2007). These extreme events have significant influence on river flow rates such as long low-water periods or river flooding (Habets *et al.*, 2013). In addition to climate change, population growth and economic development of urbanized area are forecasted by the 21st century (De Biasi, 2010). Combining both aspects suggest that the European cities will likely put a higher pressure on receiving surface water during the 21st century than at the end of 20th century.

Global change on European river basins may lead to a disruption of the biogeochemical status of river as already predicted for nitrogen and phosphorus concentrations (Andersen *et al.*, 2006; Hadjikakou *et al.,* 2011; Wilson and Weng, 2011). Despite the significant concern no study deals with the modelling of the global change influence on endocrine disruptor concentrations in surface water. Among the endocrine disruptors, nonylphenol ethoxylates NPnEO and especially 4-nonylphenol (4-NP) hold an important place due to their widespread presence all over the world (Ahel *et al.,* 1994; Vethaak *et al.,* 2005; Bergé *et al.*, 2012) and their proved toxicity. 4-NP mainly originates from the biodegradation of non-ionic surfactants nonylphenol polyethoxylate (NPnEO) through anaerobic (John and White, 1998) or aerobic (Jonkers *et al.*, 2001) processes. NPnEO are used in a large range of domestic and industrial detergents, as emulsifier or wetting agents with a world annual consumption of 500,000 tons in 2000 (Ying *et al.,* 2002). The fate of NPnEO in the environment is a important issue since their biodegradation products (nonylphenol monoethoxylate - NP_1EO - nonylphenol acetic acid - NP_1EC - and 4-NP) are recognized as being more toxic and estrogenic than the longer NPnEO (Soto *et al.*, 1991). Jugan *et al.*, (2009) reported that the 4-NP significantly contributes to the estrogenic activities found in surface water. Based on the toxicity of 4-NP on the aquatic wildlife, it has been added to the 33 priority pollutants of the Water Framework Directive 2000/60/EC (European Commission, 2000). The European directive 2008/105/EC (European Commission, 2008) fixed its annual average environmental quality standard (AA-EQS) within surface water at 300 ng/L.

The occurrence and fate of endocrine disrupting compounds such as 4-NP in river water are of concern for aquatic wildlife as well as regarding the capacity of European cities to provide safe drinkable freshwater to their residents. Therefore decision makers need reliable information to select the most efficient solutions to reach or maintain the good ecological status of water bodies as defined by the Water Framework Directive, in the upcoming years and decades. This issue is more crucial for the largest European cities such as London, Moscow or Paris since they are built in basins of very small rivers.

A modelling project was intended in 2010 to assess the long-term fate of nonylphenolic compounds in the Seine River was carried out in order to forecast the impacts of global change on the Parisian Metropolitan Area and it describes in two successive papers. Beyond studied compounds, this modelling project also attempts to give guidelines and methodology for fate modelling of other pollutants included in the list of priority pollutants (European Commission, 2000) or for emerging pollutants with close behaviours as regards their sources, transfer and biodegradability in surface water.

The first step, performed in a companion paper (Cladière *et al.,* 2014), aimed at setting up an efficient model by determining the *in-situ* attenuation rate constants of 4-NP, NP_1EC and NP_1EO within the Seine River. This first part provides relevant information on attenuation constant rates and reveals that the calibrated parameters vary significantly according to the biogeochemical conditions of the Seine River. Two parameter sets have been calculated from July and September 2011 campaigns and need to be tested over longer periods of time.

In this paper, this model is firstly validated over a complete year (2010) by comparing results to data collected monthly at different locations on the Seine River catchment. Then, the impact of global change in the Seine River basin on daily concentrations of nonylphenolic compounds is assessed over one year in the middle (2045 - 2055) and the late (2090 - 2100) 21st century. Two aspects of the global change are considered: i) the climate change (based on two contrasted projections), ii) the growth of the Parisian population and iii) the wastewater treatment optimisation in the Parisian largest plant.

2. Material and methods

2.1. Studying sites

This study focuses on the Seine River basin and especially the Parisian Metropolitan Area. Nowadays, the Paris City puts a strong anthropic pressure on the Seine River by a combination of important volume of treated water (≈ 30 m^3/s generated by 12 millions of inhabitants) discharged in the Seine River which has a low mean annual flow (300 m^3/s). The Seine River transect considered in this study is located downstream of Paris City and is 40 km long from Bougival to Meulan (Fig.1) to ensure that the downstream point included all Parisian discharges. This transect is selected because of the presence of two major hydro-ecological discontinuities: the confluence with the Oise River (annual mean flow = 110 m^3/s) and the outflow of Seine Aval wastewater treatment plant (SA-WWTP) (annual mean flow = 19.3 m^3/s) which are the only lateral inflows during dry weather periods.

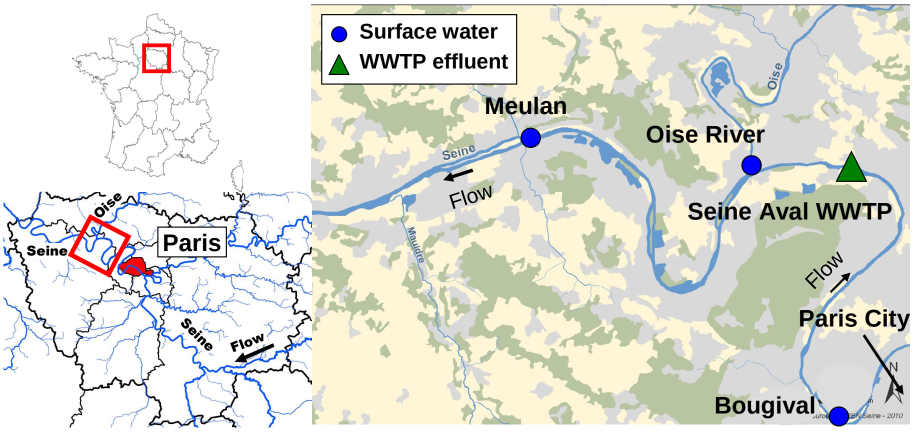

Fig. 1 Simulated transect downstream of Paris City and sampling sites

Annual and seasonal variabilities of 4-NP, NP_1EC and NP_1EO concentrations in the Seine River were examined during eleven monthly sampling campaigns. Samples were collected for surface water and SA-WWTP effluent from February 2010 to February 2011. The surface waters were manually sampled at Bougival (upstream point), and at Meulan (downstream point) for the transect and in the Oise River at its confluence with the Seine River and SA-WWTP effluents for the tributaries, in 2L amber glass bottles (Fig.1). These four sampling points provide all boundary conditions required to simulate this transect. The analytical procedure, including sample preparations and analyses (liquid chromatography coupled to a tandem mass spectrometry, UPLC-MS-MS), is described in details by Cladière *et al.*, (2013b). This method enables the quantification of 4-NP, NP_1EC and NP_1EO concentrations in the dissolved phase of water samples.

2.2. Modelling tool: ProSe model

The hydrodynamic and biogeochemical ProSe model was firstly developed to simulate the impacts of human activities on the carbon, nitrogen, and phosphorus cycles in the Seine River and its tributaries (Even *et al.*, 1998; Flipo *et al.*, 2004; Flipo *et al.*, 2007). For this study the biogeochemical module is updated to take into account the biodegradation pathways of NPnEO lastly updated in the literature by Giger *et al.*, (2009). The conceptual scheme of the modelling attempt and the input parameters needed to simulate daily concentrations of nonylphenolic compounds at Meulan are depicted in the Fig. 2.

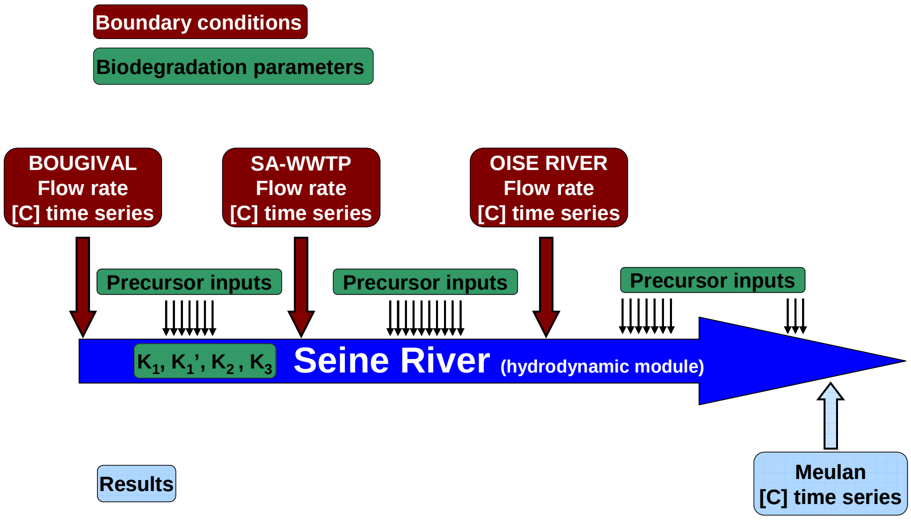

Fig. 2 Conceptual scheme of the modelling approach and the required inputs parameters. [C]: concentrations of 4-NP, NP_1EC and NP_1EO

As previously explained in the companion paper (Cladière *et al.*, 2014), the nonylphenol polyethoxylate biodegradation scheme (Giger et al., 2009) and two sampling campaigns are used to determine biodegradation parameters. The attenuation rate constants K_1, K_1' and K_2 represent the biotransformation of NP_1EO and NP_1EC into their products (NP_1EC or NP) while K_3 represents the global disappearance of 4-NP from the dissolved phase and takes into account biodegradation, volatilisation and sorption onto particles without possibility to differentiate the processes (Cladière *et al.* 2014). Jonkers *et al.* (2005) reported for NP_1EO and NP_1EC that their concentrations are relatively insensitive toward sorption. Based on this result and considering the fact that we focused on dissolved concentration as Jonkers *et al.* (2005), we decide to neglect sorption onto particles for NP_1EO and NP_1EC. In addition, the water-air exchange for nonylphenolic compounds (NP_1EO and NP_1EC) has been considered as insignificant due to very low Henry's constants (e.g. NP_1EO and NP_2EO ≈ 0.0003 Pa.m^3/mole). The precursor inputs in ng/L/d correspond to the appearance of NP_1EC and NP_1EO due to the biodegradation of long chain precursors (nonylphenol polyethoxylates: NPnEO and nonylphenoxy polyethoxy acetic acids: NPnEC).

The biodegradation parameters have been calibrated according to two sampling campaigns carried out in July and September 2011. The biodegradation parameters, summarised in Table 1, are significantly higher in July than in September 2011. This discrepancy may be linked to an enhanced microbial activities in July due to an algal bloom (Chlorophyll a > 20 µg/L) while in September no disturbance of biogeochemical status of the Seine River is found (Chlorophyll a < 5 µg/L) (Cladière *et al.*, 2014).

Table 1 Biodegradation parameters (rate constants in d^{-1} and precursor inputs in ng/L/d) assessed in the Seine River

	Attenuation rate constants (d^{-1})			Precursor inputs (ng/L/d)	
	$K_1 = K_1'$ (NP_1EO) min - opt - max	K_2 (NP_1EC) min - opt - max	K_3 (4-NP) 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

K_x = attenuation rate constant. Biodegradation scheme is provided in the companion paper.

2.3. Determination of model efficiency

The efficiency of an annual simulation is evaluated by calculation of the Nash-Sutcliffe coefficient (Nash and Sutcliffe, 1970) (NS, Equation 1)

$$NS = 1 - \left(\frac{\sum \left(C^{\circ}_{Mes} - C^{\circ}_{Sim} \right)^2}{\sum \left(C^{\circ}_{Mes} - C^{\circ}_{Avg} \right)^2} \right) \qquad \textbf{Equation 1}$$

Where:

NS is the Nash-Sutcliffe efficiency coefficient

$C°_{Mes}$ is the measured concentration

$C°_{Sim}$ is the simulated concentration

$C°_{Avg}$ is the average value of measured concentrations

The NS can range from - ∞ to 1. A positive NS coefficient means that the model gives more accurate prediction than the average value of measured concentrations. The higher the value, the better the model. Commonly, a model could be considered as accurate if NS is higher than 0.4 (Nash and Sutcliffe, 1970).

2.4. Boundary conditions for 2010

2.4.1. Calculation methods for daily concentrations of boundary conditions

The boundary conditions such as flow rates and concentrations of nonylphenolic compounds (at Bougival, SA-WWTP and Oise River) are calculated on a daily basis. The river flow rates are extracted from national discharge gauging stations (supplementary data, Fig. S1) and the SA-WWTP flow rate is provided by the Paris public sanitation service. Concentrations of nonylphenolic compounds measured at Bougival, the Oise River, Seine Aval WWTP and Meulan as well as biogeochemical parameters are available in the supplementary material Table S1.

Concentration-flow relationships [C] = a x Q^{-b}, where [C] is the concentration and Q the river flow rate were adjusted for year 2010 to the monthly sampling campaigns, for NP_1EC and NP_1EO at Bougival (Fig.3) and for the NP_1EC in the Oise River (supplementary data, Fig. S2).

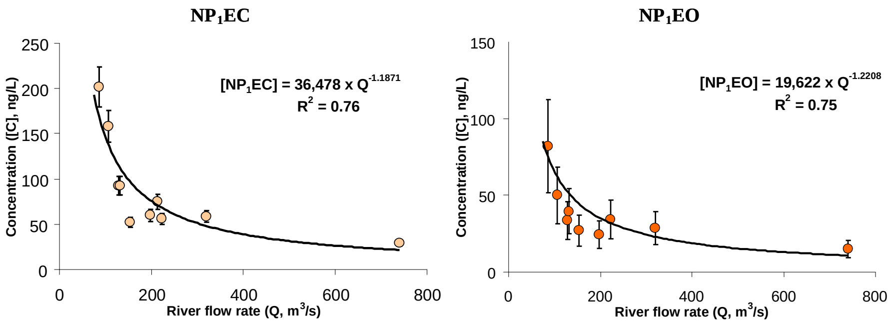

Fig. 3 Relationships between NP_1EC and NP_1EO concentrations and Seine River flow at Bougival

The coefficients of determination (R^2), higher than 0.75 and a p value < 0.05, suggest that these relations are robust enough to estimate daily concentrations. The concentrations - flow relationship of 4-NP and NP_1EO in the Oise River are based on linear correlations between fluxes (g/d) and river flow rate (Fig. S2). No concentration - flow relationship exists for 4-NP at Bougival and a polynomial interpolation of concentrations between two sampling campaigns has been used. The empirical correlations between concentrations and river flows are not designed to explain all processes involved in the fate of nonylphenolic compound but are intended to simplify building of daily concentrations in the Seine River.

Concerning SA-WWTP effluent quality and flow, no seasonal variation is observed. Flow rates (19.3 m^3/s) and concentrations are, therefore, considered as constant and equal to their median values (n = 11, 4-NP: 133 ng/L; NP_1EC: 842 ng/L and NP_1EO: 120 ng/L).

2.4.2. Upstream daily concentrations in 2010

Based on the relationships between flow rate and compound concentrations, daily concentrations of 4-NP, NP_1EC and NP_1EO are built at Bougival and downstream the Oise River. These concentrations are compared to the measured ones at Bougival (Fig. 4) and downstream the Oise River (Fig. S3 in the supplementary data).

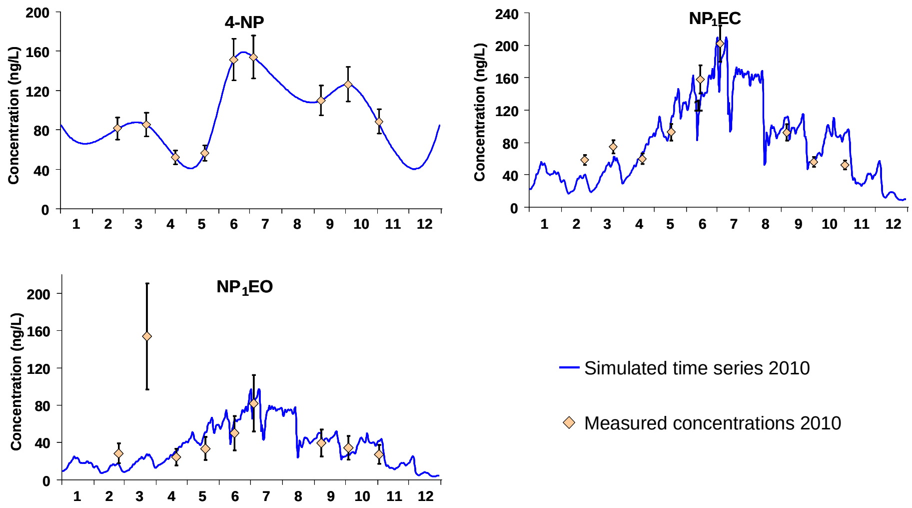

Fig. 4 Daily concentrations of 4 NP, NP_1EC and NP1EO at Bougival in the Seine River in 2010 versus measured concentrations

Modelled concentrations match concentrations measured at Bougival, except for the March campaign (23 March 2010), where large combined sewer overflows occurred (1,000,000 m^3), (Fig. 4).

The NS for the estimated boundary conditions are exhibited in Table 2.

Table 2 Nash-Sutcliffe efficiency coefficients for boundary conditions

Site	Simulation type	4-NP	NP_1EC	NP_1EO
Bougival	Boundary condition building	1,00	0,83	0,69
Oise	Boundary condition building	0,03	0,78	0,61

The NS for NP_1EC and NP_1EO at Bougival and the Oise River are higher than 0.60, validate the methodology used to define the model inputs. Concerning the 4-NP; for Bougival (NS = 1) by construction while the result for the Oise River shows the low efficiency of our approach (NS = 0.03).

2.5. Scenarios of global change and boundary conditions for 2050 and 2100

Different projections of global changes in the Seine River basin are built for the middle and the late 21st century to assess their role on the evolution of concentrations in surface water. Three main drivers are considered for the building of scenario: i) climate change, ii) growth of the Parisian population, iii) wastewater treatment optimisation at SA-WWTP.

Currently no reliable information is available concerning the evolution of the European consumption of nonylphenolic compounds in the future, and especially during the 21st century. However a decrease of consumption could be expected as a result of the European legislation on these compounds (Directive 2003/53/EC) and the availability of substitutes (U.S EPA, 2012). Forecasting the impacts of consumption decrease of nonylphenolic compounds is a hard task due to their miscellaneous uses such as urban uses (industrial wetting agent, detergent) and agricultural uses (pesticides). Actually, decrease of consumption would influence concentrations of the upstream part of river basins (commonly used for agriculture) as well as urban discharges. Given the impossibility of currently modelling the impacts of consumption decrease of nonylphenolic compounds on the upstream part of the Seine River basin, their consumption is considered as constant during the 21st century and this study will focus on the impacts of climate change, growth of the Parisian population and wastewater treatment optimisation.

Climate projections from CMIP3 (Coupled Model Intercomparison Project Phase 3) over Europe presents important variability (Christensen *et al.*, 2007). In order to limit the number of simulations, two of these climate projections downscaled by a weather typing approach (Boé *et al.*, 2009), which give contrasted results on the Seine River flow rate (Habets *et al.*, 2013), are used. They are the ARP_CONT_A1B (ARP) and MPI_ECHAM5_A1B (MPI) and use the SRES-A1B gas emission scenario for the 21st century (Randall *et al.*, 2007). ARP projects important decrease of rainfall by 2050 (-13.7 %) and 2100 (-21.8 %) while MPI projects less pronounced decrease (2050: +0.1 % and 2100: -6.9 %). Both models are in accordance with increases of potential evaporation and air temperature by 2050 and 2100 (supplementary data, Table S2).

The impacts of climate change on Seine and Oise River flows are estimated by the hydrogeological model MODCOU in the framework of the REXHYSS project (Habets *et al.*, 2013) using these two downscaled climate projections (ARP and MPI). Thus, two projections of the monthly river flow rates are available for three different periods, the reference decade (2000 - 2010), the middle (2045 - 2055) and the late 21st century (2090 - 2100). The anomalies of river flow rates induced by climate change are calculated for every month by dividing the flow rates predicted in 2045 - 2050 or 2090 - 2100 by those simulated for the reference decade (2000 - 2010). The ratios, thereby calculated, are exhibited in Table 3.

Table 3 Impact of the climate change scenario ARP and MPI on the Seine River flow at Bougival and the Oise River flow

	Seine River					Oise River				
	Reference	ARP		MPI		Reference	ARP		MPI	
	2000-2010	2045-2055	2090-2100	2045-2055	2090-2100	2000-2010	2045-2055	2090-2100	2045-2055	2090-2100
	Flow (m^3/s)	Anomalies ratio	Anomalies ratio	Anomalies ratio	Anomalies ratio	Flow (m^3/s)	Anomalies ratio	Anomalies ratio	Anomalies ratio	Anomalies ratio
January	515	1.0	1.0	0.7	0.6	179	0.9	1.0	0.9	0.7
February	487	1.1	1.3	0.8	0.8	175	1.1	1.4	0.9	0.9
March	433	1.3	1.0	1.0	1.1	154	1.2	1.0	1.0	1.0
April	338	0.8	0.7	1.4	1.1	127	0.8	0.7	1.2	1.0
May	239	0.5	0.5	1.2	0.7	88	0.6	0.5	1.0	0.7
June	153	0.6	0.5	1.0	0.8	64	0.6	0.5	1.0	0.7
July	144	0.8	0.6	1.1	0.7	51	0.7	0.6	1.1	0.7
August	126	0.7	0.5	1.1	0.7	39	0.6	0.6	1.0	0.7
September	146	0.6	0.6	0.8	0.6	41	0.6	0.6	0.9	0.7
October	211	0.6	0.6	0.8	0.4	50	0.7	0.6	0.8	0.5
November	314	0.7	0.6	0.9	0.5	81	0.7	0.7	0.9	0.6
December	439	0.8	0.7	1.2	0.9	148	0.7	0.7	1.1	0.9

According to these anomalies, daily river flows can be estimated for one dry year or one wet year in the decades 2045 - 2055 or 2090 - 2100. The present day proxy of a dry year is based on the year 2005 which had a pronounced low-water period (from June to October 2005) and the present day proxy of the wet year is 2001 which had a significant river flooding during spring. Thus, for instance; a dry year (wet year) in the middle and late 21st century is estimated to have the daily river flow rate of 2005 (2001) corrected by the monthly ratios calculated (Table 3). The Seine and Oise River flow rates predicted for a dry and a wet year in 2045 - 2050 and 2090 - 2100 are shown in Fig. S4 (supplementary data).

The estimate of the Parisian population growth by 2050 was provided by the French National Institute of Statistics and Economic Studies (INSEE). By 2050, the Parisian population should reach between 11 millions (low hypothesis) and 15 millions (high hypothesis) of inhabitants with a median hypothesis of 13 millions of inhabitants, which means an increase of 11.7 % compared to 2009 (De Biasi, 2010). No study focuses on the Parisian population growth by 2100; however by linear extrapolation of the median hypothesis for 2050 the population could be estimated about 14.7 millions of inhabitants (+26 % compared with 2009). Assuming that the water consumption per capita remains constant during the 21st century, the growth of the Parisian population leads to an increase of wastewater volume treated daily. Therefore, the SA-WWTP flow rate is estimated at 22.6 m^3/s in 2050 and 24.3 m^3/s in 2100 (2010 flow rate: 19.3 m^3/s).

Finally, the optimisation of wastewater treatment of SA-WWTP is also taken into account. Currently this WWTP uses activated sludge coupled to a single stage biofiltration. In the upcoming years, the treatment will be optimised by implementing essentially a three stage biofiltration. Consequently, two scenarios for SA-WWTP are simulated: 1) the wastewater treatment remains similar (baseline scenario) and 2) the wastewater treatment is optimised (optimised scenario). For the first scenario, SA-WWTP effluent concentrations in 2010 (4-NP: 133 ng/L, NP_1EC: 842 ng/L and NP_1EO: 120 ng/L) are considered. For the second scenario, concentrations found at the most efficient WWTP in 2010 in Paris Metropolitan Area, where the three stage biofiltration is already implemented, are applied (4-NP: 85 ng/L, NP_1EC: 214 ng/L et NP_1EO: 74 ng/L) (Cladière *et al.*, 2013b). All scenarios considered, are summarised in the Table 4. They are similar for a dry and a wet year in 2050 and 2100.

Table 4 **Description of changes considered for one dry or wet year in periods 2050 and 2100 and their corresponding name**

Year	Climate change model	Population growth	Seine Aval WWTP	Name of scenario
2050	ARP_CONT_A1B	+ 11.7 %	Baseline scenario	ARP_base_2050
2050	ARP_CONT_A1B	+ 11.7 %	Optimised scenario	ARP_opt_2050
2050	MPI_ECHAM5_A1B	+ 11.7 %	Baseline scenario	MPI_base_2050
2050	MPI_ECHAM5_A1B	+ 11.7 %	Optimised scenario	MPI_opt_2050
2100	ARP_CONT_A1B	+ 26 %	Baseline scenario	ARP_base_2100
2100	ARP_CONT_A1B	+ 26 %	Optimised scenario	ARP_opt_2100
2100	MPI_ECHAM5_A1B	+ 26 %	Baseline scenario	MPI_base_2100
2100	MPI_ECHAM5_A1B	+ 26 %	Optimised scenario	MPI_opt_2100

3. Results and discussion

3.1. Modelling of daily concentrations at Meulan over the reference year 2010

Based on the boundary conditions and the biodegradation parameters (July and September), daily concentrations of 4-NP, NP_1EC and NP_1EO are modelled at Meulan and compared with the monthly sampling campaigns in order to test the robustness of both biodegradation sets (July and September).

The simulation using the September biodegradation parameters are displayed in Fig.5 while simulations using the July biodegradation parameters are shown in Fig. S5 (supplementary data). With July parameters, the simulated concentrations are far lower than the measured concentrations, likely due to the high attenuation rate constants (about 1 d^{-1}), and the seasonal cycle of concentrations is not reproduced (Fig. S5). The negative values of NS (Table 5) confirm the inefficiency of these parameters to simulate concentrations at the annual scale and reinforce the hypothesis of the disruption of the biogeochemical status of the Seine River in July 2011 (Cladière *et al.*, 2014).

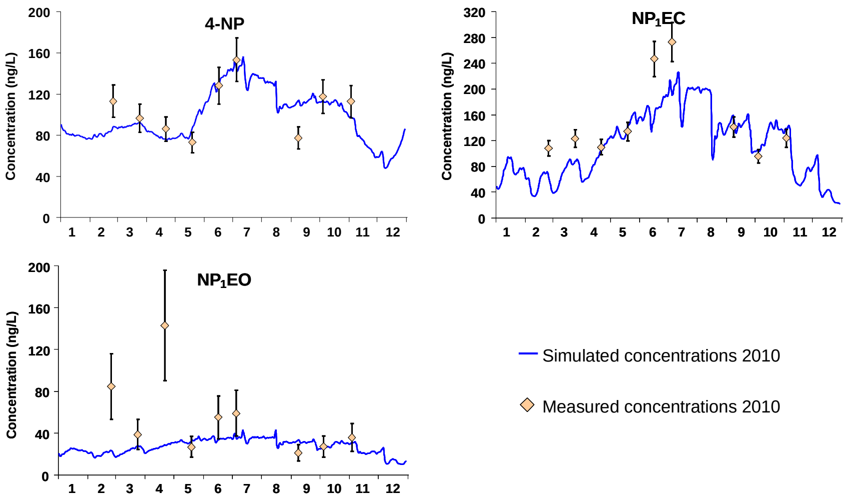

Fig. 5 Simulated concentrations of 4 NP, NP_1EC and NP_1EO at Meulan using the Prose model (September parameter set) versus measured concentrations

As exhibited in Fig. 5 the simulated concentrations modelled by coupling the boundary conditions and the September biodegradation parameters, are close to the measured concentrations and reproduce the annual variation of concentrations of 4-NP, NP_1EC and to a lesser extend NP_1EO (previously underlined by Cladière *et al.*, (2013b).

Table 5 Nash-Sutcliffe efficiency coefficients for annual modelling at Meulan

Site	Simulation type	4-NP	NP_1EC	NP_1EO
Meulan	ProSe modelling (July constants)	-0,25	-1,64	-0,44
Meulan	ProSe modelling (September constants)	0,55	0,44	0,61

The NS determined for this simulation range from 0.44 for NP_1EC to 0.61 for NP_1EO (Table 5) and suggest that the model, using September biodegradation parameters is efficient to predict annual concentrations in the Seine River at Meulan.

Moreover, the 4-NP AA-EQS (300 ng/L) is never exceeded in the Seine River at Meulan downstream of all urban discharges. This observation likely results from the low concentrations in SA-WWTP effluent (133 ng/L) and the biodegradation occurring within the Seine River.

This modelling approach has, however, three possibility of improvement for modelling of daily concentrations of nonylphenolic compounds. First, this study focuses on dry weather conditions which represent the most important part of the year but cause punctual underestimations of NP_1EO concentrations at Bougival and Meulan. Indeed, combined sewer overflows may constitute significant alkylphenol inputs into the Seine River during wet weather conditions (Cladière *et al.*, 2013b). Second, SA–WWTP effluent is assumed to remain constant all over the year which is not entirely representative since variabilities of concentrations are observed from a campaign to another. Finally, the biodegradation parameters remain constant in the model over the year, while the water temperature variability between summer and winter (± 10°C) may affect the biodegradation constant rates (Manzano et al., 1999). Moreover, the results between July and September 2011 highlight discrepancies according to the biogeochemical status of the Seine River (Cladière *et al., 2014*). However, despite these deficiencies, the current simulations are satisfying to predict the annual concentrations of 4-NP, NP_1EC and NP_1EO in the Seine River. Therefore, in the context of the parsimony of our approach, these deficiencies are not determining for modelling the daily concentrations of nonylphenolic compounds in the Seine River and could be neglected.

3.2. Forecasted concentrations in the middle of 21st century (2045 - 2055)

The 4-NP and NP_1EC concentrations were simulated at Meulan for one dry or wet year in the decade 2045 - 2055 (Fig. 6). NP_1EO concentrations are not discuss because of their significant variability (± 37 %) pointed out in (Cladière *et al.*, 2014). In addition, the increase of air temperature by 2050 (+ 2 K) or 2100 (+ 3 K) (probably lower for water temperature) is not considered since the variability intra-annual in 2010 (± 10 K) seems not influence the modelling of the fate of nonylphenolic compounds in the Seine River.

The forecasted concentrations for the middle of the 21st century are compared with the ones of 2010 hereafter.

3.2.1. Dry year

As underscored by the scenario ARP_base_2050 and MPI_base_2050 during one dry year (Fig. 6), the long low-water period has a significant influence on NP_1EC concentrations and to a lesser extent on 4-NP concentrations. Without optimisation of Seine Aval WWTP (baseline scenario), the concentrations of NP_1EC reach 300 ng/L in July and exceed 250 ng/L from June to December according to the ARP_base_2050 scenario (against 200 ng/L for MPI_base_2050). Although the current concentrations are about 150 ng/L, it may become a concern in the future if the SA-WWTP does not improve its efficiency.

4-NP concentrations reach a maximum of 180 ng/L (ARP_base_2050) and are generally below 150 ng/L. Despite climate change and growth of the Parisian population, the AA-EQS of 300 ng/L is not exceeded. However, the high concentration of NP_1EC (which can be biodegraded into 4-NP) at Meulan suggests a risk of exceeding the AA-EQS downstream, in the Seine River estuary.

The optimisation of SA-WWTP (scenarios ARP_opt_2050 and MPI_opt_2050), could compensate the effect of global change on the Seine River basin by 2050. The Fig. 6 points out significant decreases of NP_1EC concentrations during the low-water period. Decreases of concentrations are also noticeable for 4-NP. Finally, thanks to the optimisation of SA-WWTP, NP_1EC and 4-NP concentrations during a dry year in the decade 2045 - 2055 remain lower or close to those simulated for 2010 meaning that the quality of the Seine River may be preserved.

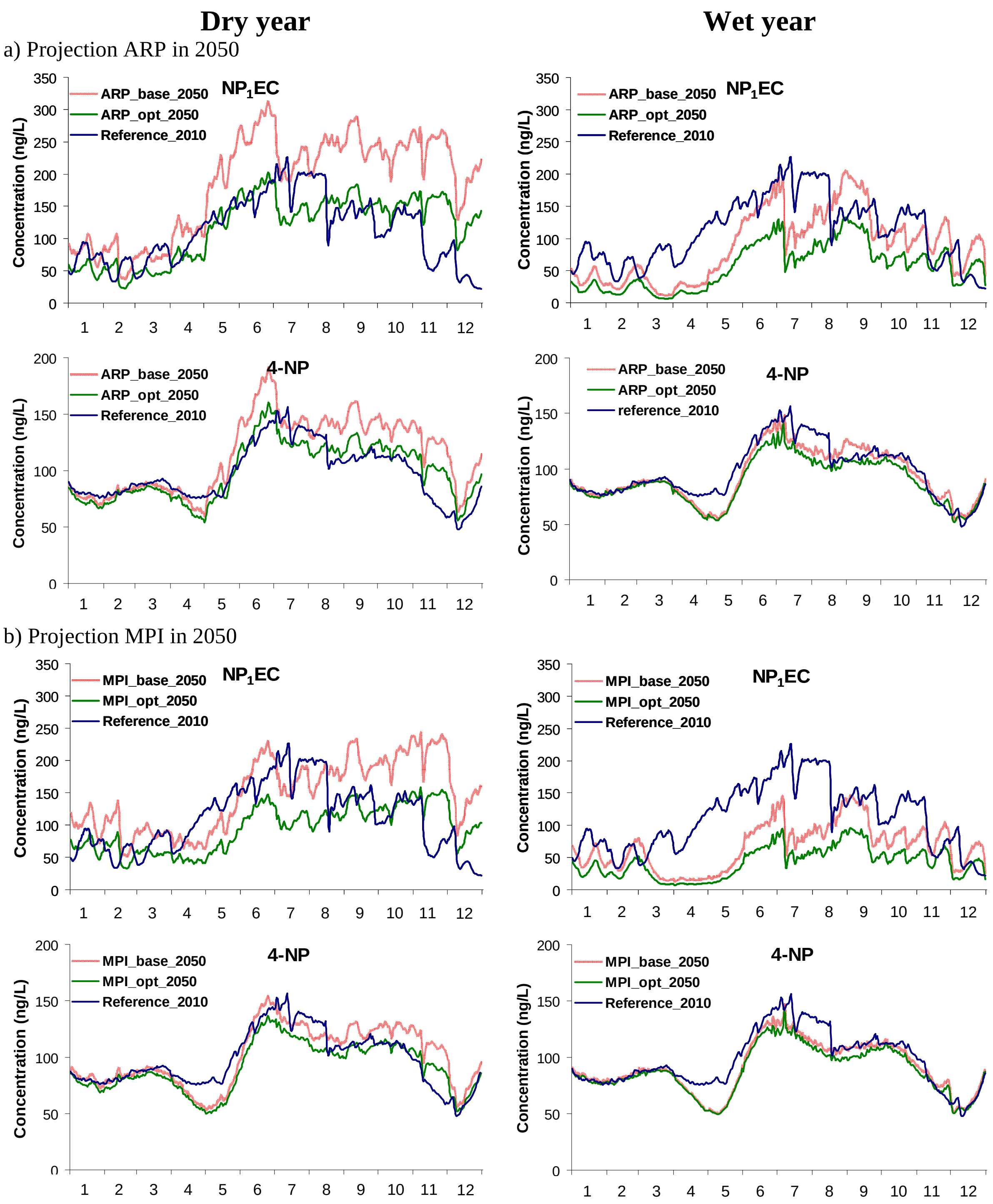

Fig. 6 Forecasted concentrations of 4 NP and NP_1EC for one dry and wet year in the decade 2045 - 2055

3.2.2. Wet year

Fig. 6 shows that during one wet year in the decade 2045 - 2055 the concentrations of NP_1EC and 4-NP are not higher than concentrations simulated for 2010, even without optimisation of SA-WWTP.

Both ARP and MPI scenarios predict similar drops of 4-NP and NP_1EC concentrations during Seine River flooding (from March to May). The decreases of concentrations are more significant for the MPI projection

(NP_1EC < 20 ng/L from 18th March to 6th May) than for the ARP projection (NP_1EC < 20 ng/L from 15th March to 1st April). However, the wet weather urban sources, which may play a significant role during a wet year, are not taken into account in this forecast. The concentrations of nonylphenolic compounds predicted during the river flooding are, therefore, likely underestimated. This has to be confirmed or contradicted by further studies.

At last, the optimisation of SA-WWTP has a smaller influence during a wet year than a dry year (Fig.6), mainly explained by effluent dilution factor during a wet year (about 37) against a dry year (about 11).

3.3. Forecasted concentrations in the late 21st century (2090 - 2100)

4-NP and NP_1EC concentrations at Meulan are simulated for one dry or wet year in the decade 2090 - 2100 (Fig. 7).

3.3.1. Dry year

The observations are similar to 2050 but the trends are reinforced especially at the end of autumn (November). Indeed, without optimisation of SA-WWTP, the ARP_base_2100 scenario projects that the NP_1EC concentrations may reach 350 ng/L in July and exceed 250 ng/L during 7 months. For MPI_base_2100 scenario, the highest concentration (350 ng/L) is reached in November and the concentrations exceed 300 ng/L from October to December. To a lesser extent, similar observations are noticeable for 4-NP concentrations. Despite the long low-water period forecasted for a dry year by 2100, no exceedance of the current AA-EQS is pointed out for both baseline scenarios. However, like for 2050, the NP_1EC concentration is of concern for downstream stations due to biodegradation processes.

As previously observed for 2050, the optimisation of SA-WWTP may counterbalance the impacts of climate change coupled to the growth of the Parisian population from January to October (ARP and MPI projections). During this period the concentrations of 4-NP and NP_1EC are close to those simulated for 2010. Nevertheless, despite the significant decrease of 4-NP and NP_1EC concentrations due to SA-WTTP optimisation, the latter may exceed concentrations of 2010 from October to December. These differences are likely due to the long low-water period (June to December).

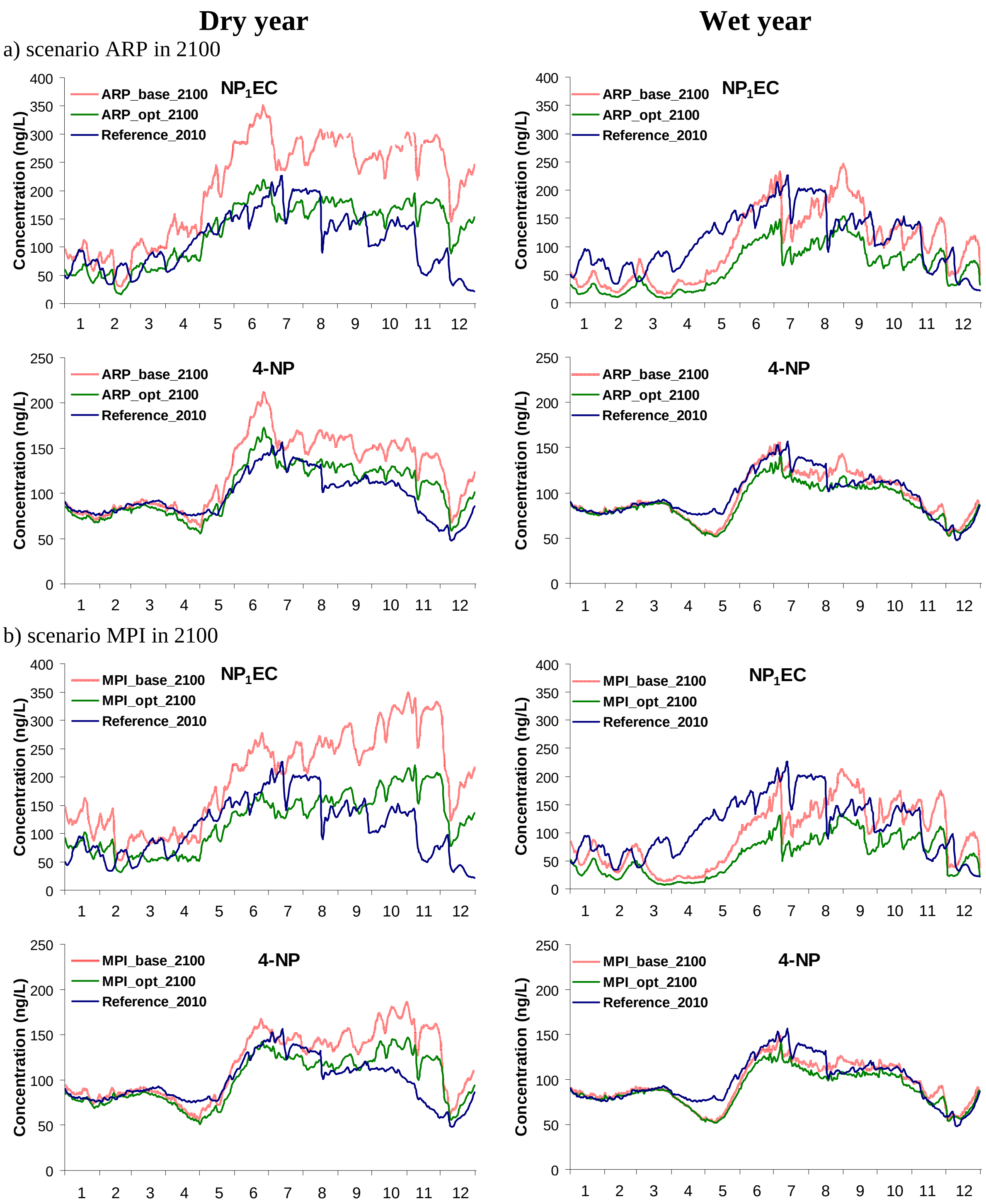

Fig. 7 Forecasted concentrations of 4 NP and NP_1EC for one dry or wet year in the decade 2090 - 2100

3.3.2. Wet year

For a wet year by 2100, only slightly higher concentrations of 4-NP and NP_1EC during the low-water period are observed compared with 2050. However, considering the analytical variabilities (±14 % for 4-NP and ±11 % for NP_1EC) these concentrations are close to those simulated for 2010. The Seine River flood has similar effects on 4-NP and NP_1EC concentrations during spring leading to very low concentrations (NP_1EC < 20 ng/L).

4. Conclusions

A global project of modelling the fate of nonylphenolic compounds in river water was launched in 2010 with the objectives to determine *in-situ* attenuation rate constants and to apply them to simulate their annual behaviour for present and upcoming years (Cladière *et al.,* (2014) and this paper).

In pursuit of the first part paper, this study aimed at testing the biodegradation parameters and at using them to forecast the fate of nonylphenolic compounds in the Seine River in the middle and the late 21st century.

In a first step, the modelling of annual concentrations of 4-NP, NP_1EC and NP_1EO at Meulan in the Seine River reveals that the biodegradation parameters calibrated in September 2011 have been validated for the year 2010 and can be used to forecast the fate of nonylphenolic compounds in the middle and the late 21st century.

For the first time, this study provides relevant results on the fate of micropollutants in river water with regard to global change. In this study, climate change, the growth of the Parisian population and the optimisation of Seine Aval wastewater treatment plant for the middle (2050) and the late (2100) 21st century were considered.

The first forecasts by 2050 and 2100 underscore the key impact of low-water periods on NP_1EC and 4-NP concentrations downstream of Paris City. These longer and more pronounced low water periods (according to the climate change projections ARP_CONT_A1B and MPI_ ECHAM5_A1B) combined with the growth of the Parisian population, could lead to significant concentration increases in autumn. Wastewater treatment optimisation (currently in progress for SA-WWTP) appears to be an efficient solution to limit the impacts of population growth and low-water periods by 2050 and to a lesser extent by 2100.

Although the assessed changes are the most important expected on the Seine River basin, the parsimony of our approach leads to disregard others significant factors such as evolution of nonylphenolic compound consumption or the intra-annual variability of concentrations because of the scarcity of reliable information. In addition, all annual simulations are performed under dry weather conditions and do not considered the wet weather urban sources. Thus, the concentrations forecasted for the 21st century could be punctually underestimated since combined sewer overflows and urban runoff are significant sources of nonylphenolic compounds in the Seine River during storm events, as previously demonstrated for 2010 by Cladière *et al.,* (2013b).

Ultimately, the two parts of this study highlight that the coupling between analytical chemistry, biogeochemical modelling is, despite its limits, a key tool to understand and forecast the fate of nonylphenolic compounds in surface waters and the influence of global change. This study gives the first guidelines and considerations for forecasting the fate of pollutants in surface water during the 21st century. Therefore, this kind of approach could be applied to other pollutants such as priority pollutants (European Commission, 2000) or emerging pollutants.

Moreover, this study could support the implementation of the Water Framework Directive and its daughter Directives in surface water in the upcoming years and decades.

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