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Assessing the impact of global change in aquatic ecosystems: Modelling the fate of nonylphenolic compounds in the Seine River

Mathieu Cladière¹, Céline Bonhomme¹, Lauriane Vilmin², Johnny Gasperi¹, Nicolas Flipo², Florence habets² and Bruno Tassin¹.

¹ LEESU (UMR MA102), UPEC, UPEMLV, ENPC, AgroParisTech.
² Centre de Géosciences, Ecole des Mines ParisTech
Nonylphenolic compounds

\[ \text{NPnEO} \; (n = 1 - 50) \]

Non ionic surfactants \( \rightarrow \) detergents, wetting agent

World consumption: 500,000 tons in 2000

(Ying et al. 2002)

Endocrine disrupting compounds

Key role in estrogenic activity of surface water

(Marcial et al. 2003 ; Fernet et al. 2003 et Jugan et al. 2009)

European legislation: Directive 2000/60/EC and 2008/105/EC

- 4-nonylphenol (4-NP)
- Environmental quality standard (EQS)
  - Annual average value (AA-EQS): 300 ng/L
Simplified biodegradation of NPnEO

Non-oxydative

Oxydative

Increasing toxicity and estrogenic activity

Giger et al. 2009

Final biodegradation or volatilization

K_1

K_2

K_3

NP_{n EO} → NP_{2 EO} → NP_{1 EO} → 4-NP → NP_{1 EC} → NP_{2 EC} → NP_{n EC}

Oxidation of ethoxylate chain

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Scientific issue

- NPnEO are **readily biodegradable** in the environment
- Production of NP$_1$EO, NP$_1$EC and 4-NP

How simulate annual time series of concentrations of nonylphenolic compounds in surface water?

Methodology

1. Assessing the *in-situ* biodegradation rate constants (see poster)
3. Building scenarios for the middle (2050) and late (2100) 21st century
Site and sampling campaigns

Study site:
Seine River downstream of Paris, France
40 km transect from Bougival to Meulan
2 lateral inflows:
- Seine Aval WWTP (19 m³/s)
- Oise River (95 m³/s)

Sampling campaigns:
11 monthly sampling campaigns
From Feb. 2010 to Feb. 2011

Analysis protocol:
Extraction: Solid Phase Extraction
Analysis: UPLC-MS-MS
- quantification: 4-NP, NP₁EO and NP₁EC
- semi-quantitative: NPnEO (n= 1-15)
Hydro-ecological ProSe model

Hydrodynamic module: Shallow water equations
Biogeochemical module: biodegradation of nonylphenolic compounds

Boundary conditions
Biodegradation parameters

BOUGIVAL
Flow rate
[C] time series

WWTP
Flow rate
[C] time series

OISE RIVER
Flow rate
[C] time series

Seine River (hydrodynamic module)

Precursor inputs

K₁, K’₁, K₂, K₃

Results

MEULAN
[C] time series

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Annual modelling : 2010

Meulan 2010

Good fitting of modelled and measured concentrations

Validation of method

Nash-Sutcliffe : 

\[
NS = 1 - \frac{\sum (C_{\text{Mes}} - C_{\text{Sim}})^2}{\sum (C_{\text{Mes}} - C_{\text{Moy}})^2}
\]
Forecast of global change impacts

Assessment of global change scenarios by 2050 and 2100:
Forecast of global change impacts

Assessment of global change scenarios by 2050 and 2100:

Climate changes:
RExHySS project ➔ Impact of climate changes on the Seine River basin
2 extreme projections: APR* et MPI** (rainfall, evapotransp., temperature)

Seine River flow rate by 2050 for a dry and wet year (MPI)

*: ARP_CONT_A1B
**: MPI_ECHAM5_A1B

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Forecast of global change impacts

Assessment of global change scenarios by 2050 and 2100:

Population growing:

Data from National Institute of Statistic and Economic Studies (INSEE):

- +12% by 2050 and +26% by 2100
- Seine Aval WWTP: 19 m$^3$/s in 2010, 22.6 m$^3$/s by 2050 and 24.3 m$^3$/s by 2100

Population growing in the Parisian metropolitan area

![Graph showing population growth from 2000 to 2100 with data points indicating an increase over time.](image)
Forecast of global change impacts

Assessment of global change scenarios by 2050 and 2100:

Optimisation of Seine Aval treatment:
Two scenarios:
- Baseline (Base): Seine Aval non optimised by 2050
- Optimised (Opt): Seine Aval optimised by 2050

Cladière et al. (2013) ESPR
Concentrations at Meulan by 2050

Dry year

- 4-NP
- NP

ARP_base_2050 vs. Reference_2010

MPI_base_2050 vs. Reference_2010

Significant influence of global changes during low-water period (summer, autumn)

[C] < AA-EQS
Concentrations at Meulan by 2050

Dry year

Optimisation of Seine Aval treatment compensate the influence of global changes
Concentrations at Meulan by 2050

Significant decreases of concentrations in spring because of the river flooding
Concentrations at Meulan by 2050

Concentrations for wet year by 2050 << concentrations found in 2010 at Meulan

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Conclusions

First study coupling analytical chemistry and a hydro-ecological model for assessing annual concentrations of pollutants in river water

Modelling for 2010:
- Efficient method to assess concentrations of nonylphenolic compounds in Seine River
- The AA-EQS of 4-NP is not exceeded in the Seine River downstream of Paris

Forecast for the 21\textsuperscript{st} century:
- Similar trends are found for 2050 and 2100 but more pronounced for 2100

Dry years:
- Low water periods are a key issue for the 21\textsuperscript{st} century
- AA-EQS could be exceeded downstream of the studied transect \(\rightarrow\) biodegradation of NP\textsubscript{1}EC
- Optimisation of wastewater treatment is a good solution to compensate low-water influence

Wet years:
River flooding lead to significant decreases of concentrations during spring (April, May)
Outlooks

Method limits for annual modelling:

- Include wet *weather urban sources* for annual modelling
- Include the *variability* of concentrations of *Seine Aval effluent*
- Introduce a *variability* of *biodegradation* according to the *microbial biomass* (poster)

Forecast for the 21st century:

- **Mature** our scenarios (land use, reuse of treated water, new technologies, NPnEO uses…)
- **Extend** the simulated transect from Paris to the estuary (see impact of biodegradation)
- Consider the *increase of water temperature* on biodegradation of compounds
Thank you for your attention

Acknowledgment

Paris public sanitation service (SIAAP)

Especially for:

Vincent Rocher

Céline Briand
Building of Boundary conditions

Daily mean flow
River ➔ National discharge gauging stations
WWTP ➔ Paris public sanitation service (SIAAP)

Time series of concentrations
River ➔ Relationship between concentrations and river flow (except for 4-NP)
WWTP ➔ constant over the year (NP$_1$EC : 842 ng/L, NP$_1$EO: 120 ng/L, 4-NP: 133 ng/L)

Seine River at Bougival

NP$_1$EC

$[C] = 36,478 \times Q^{-1.1871}$

$R^2 = 0.76$

NP$_1$EO

$[C] = 19,622 \times Q^{-1.2208}$

$R^2 = 0.75$
Good fitting

Validation of boundary conditions

Limit:

Wet weather urban sources

Annual modelling: 2010

Seine River: Bougival 2010

Nash-Sutcliffe: \[ NS = 1 - \frac{\sum (C_{Mes} - C_{Sim})^2}{\sum (C_{Mes} - C_{Moy})^2} \]

Good fitting

Validation of boundary conditions
Concentrations at Meulan by 2100

Dry year

Concentration (ng/L)

ARP_ref_2100
ARP_opt_2100
Reference_2010

4-NP

NP1EC

MPI_ref_2100
MPI_opt_2100
Reference_2010

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Concentrations at Meulan by 2100

Wet year

Concentration (ng/L)

ARP_ref_2100
ARP_opt_2100
Reference_2010

NP_EC

4-NP

NP_EC

4-NP

Concentration (ng/L)

ARP_ref_2100
ARP_opt_2100
Reference_2010

MPI_ref_2100
MPI_opt_2100
Reference_2010

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Analytical protocol

Sample

Filtration

GF/D (2,7 µm) et GF/F (0,45 µm)

Dissolved phase

Extraction surrogate

(NP$_1$EO-d2, BPA-d6, OP-d17)

Extraction (SPE)

OASIS HLB (200 mg/6 ml)

(Gilbert 2011)

Extract

Internal standard

(BPA-d16, 4-n-NP, 4-n-NP$_1$EO)

UPLC-MS-MS

Quantification of: 4-NP, NP$_1$EO and NP$_1$EC

Semi-quantitative: NP$_{1-15}$EO
Biodégradation des nonylphénols

**ProSe model** : Precursor inputs in the Seine River symbolazing their biodegradation

**Hypothesis** :
- First order kinetics
- $K_1' = K_1$
- $NP_1EO$ et $NP_1EC$ : no volatilisation (Jonkers et al. 2005)
- $NP_1EO$ et $NP_1EC$ : no adsorption onto particles (Jonkers et al. 2005)

From Giger et al. 2009

**Final biodegradation** ; volatilisation ; adsorption

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Influence of biogeochemical conditions of the Seine River

Heteroprophic bacterial biomass ➔ Algal bloom in July

Significant variability of biodegradation rate constants between sampling campaigns ➔ July >> September
Small scale variabilities

Sampling strategy

Résultats

<table>
<thead>
<tr>
<th>Compound</th>
<th>Analytical repeatability</th>
<th>Spatial variability</th>
<th>Temporal variability</th>
<th>Total variability</th>
</tr>
</thead>
<tbody>
<tr>
<td>4-NP</td>
<td>7 %</td>
<td>7 %</td>
<td>7 %</td>
<td>14 %</td>
</tr>
<tr>
<td>NP₁EC</td>
<td>4 %</td>
<td>5 %</td>
<td>6 %</td>
<td>11 %</td>
</tr>
<tr>
<td>NP₁EO</td>
<td>14 %</td>
<td>14 %</td>
<td>23 %</td>
<td>37 %</td>
</tr>
</tbody>
</table>

Total variability = spatial variability + temporal variability