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

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Nonylphenolic compounds

\[ \text{H}_9\text{C}_9-(\text{O-CH}_2\text{-CH}_2)_n-\text{OH} \]

(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

\[
\begin{align*}
\text{NP}_n\text{EO} & \xrightarrow{K_1} \text{NP}_2\text{EO} \\
\text{NP}_2\text{EO} & \xrightarrow{K_1'} \text{NP}_1\text{EO} \\
\text{NP}_1\text{EO} & \xrightarrow{K_2} \text{NP}_2\text{EC} \\
\text{NP}_2\text{EC} & \xrightarrow{K_3} \text{NP}_1\text{EC} \\
\text{NP}_1\text{EC} & \xrightarrow{K_3'} 4-\text{NP} \\
4-\text{NP} & \xrightarrow{K_4} \text{Final biodegradation or volatilization} \\
\end{align*}
\]

Oxidation of ethoxylate chain

Increasing toxicity and estrogenic activity

Giger et al. 2009

Non-oxydative

Oxydative

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

Scientific issue

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

**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 m$^3$/s)
- Oise River (95 m$^3$/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, NP$_1$EO and NP$_1$EC
  - semi-quantitative: NP$_n$EO (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

Precursor inputs

K₁, K'₁, K₂, K₃

WWTP
Flow rate
[C] time series

Precursor inputs

OISE RIVER
Flow rate
[C] time series

Precursor inputs

Seine River (hydrodynamic module)

Results

MEULAN
[C] time series
Good fitting of modelled and measured concentrations

Validation of method

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

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

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Concentrations at Meulan by 2050

Dry year

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

**Wet year**

- **ARP_base_2050**
- **reference_2010**

**4-NP**

Concentration (ng/L)

0 50 100 150 200

**NP1_EC**

Concentration (ng/L)

0 50 100 150 200 250 300 350

Significant decreases of concentrations in spring because of the river flooding

[C] < AA-EQS
Concentrations for wet year by 2050 << concentrations found in 2010 at Meulan
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 21st 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 21st century
- AA-EQS could be exceeded downstream of the studied transect \( \Rightarrow \) biodegradation of NP\(_1\)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

\[ [C] = 36,478 \times Q^{-1.1871} \quad R^2 = 0.76 \]

\[ [C] = 19,622 \times Q^{-1.2208} \quad R^2 = 0.75 \]
Annual modelling: 2010

Seine River: Bougival 2010

Concentration (ng/L)

4-NP

NS = 0.83

NP\textsubscript{1}EC

NS = 0.69

Nash-Sutcliffe:

\[
NS = 1 - \left( \frac{\sum (C_{Mes}^\circ - C_{Sim}^\circ)^2}{\sum (C_{Mes}^\circ - C_{Moy}^\circ)^2} \right)
\]

Good fitting

- Validation of boundary conditions

Limit:

- Wet weather urban sources

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Concentrations at Meulan by 2100

Dry year

Concentration (ng/L)

ARP_ref_2100
ARP_opt_2100
Reference_2010

NP
EC

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Analytical protocol

Sample

Filtration
GF/D (2.7 μm) et GF/F (0.45 μm)

Dissolved phase

Extraction surrogate
(NP₁EO-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-NP₁EO)

UPLC-MS-MS

Quantification of: 4-NP, NP₁EO and NP₁EC

Semi-quantitative: NP₁⁻¹⁵EO

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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
Simulation du linéaire de Seine

Significant variability of biodegradation rate constants between sampling campaigns

- July >> September

Influence of biogeochemical conditions of the Seine River

Heteroprophic bacterial biomass ➔ Algal bloom in July

Rate constants ($d^{-1}$)

<table>
<thead>
<tr>
<th></th>
<th>July 2011</th>
<th>September 2011</th>
</tr>
</thead>
<tbody>
<tr>
<td>$K_1 = K'_1$</td>
<td>0.1</td>
<td>0.3</td>
</tr>
<tr>
<td>$K_2$</td>
<td>3.3</td>
<td>0.1</td>
</tr>
<tr>
<td>$K_3$</td>
<td>2.5</td>
<td>0.15</td>
</tr>
</tbody>
</table>

Measured (NP, EC) ProSe
Small scale variabilities

Sampling strategy

<table>
<thead>
<tr>
<th>Sampling site</th>
</tr>
</thead>
<tbody>
<tr>
<td>Seine River</td>
</tr>
<tr>
<td>Conflans-s^t-Honorine</td>
</tr>
<tr>
<td>Left bank</td>
</tr>
<tr>
<td>Middle 1</td>
</tr>
<tr>
<td>Middle 2</td>
</tr>
<tr>
<td>Middle 3</td>
</tr>
<tr>
<td>Right bank</td>
</tr>
</tbody>
</table>

<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>NP_{1}EC</td>
<td>4 %</td>
<td>5 %</td>
<td>6 %</td>
<td>11 %</td>
</tr>
<tr>
<td>NP_{1}EO</td>
<td>14 %</td>
<td>14 %</td>
<td>23 %</td>
<td>37 %</td>
</tr>
</tbody>
</table>

Total variability = spatial variability + temporal variability