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Nicolas Flipo, Florence Habets, Bruno Tassin

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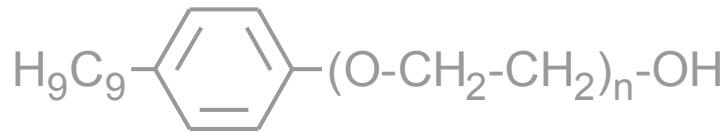
# Assessing the impact of global change in aquatic ecosystems: Modelling the fate of nonylphenolic compounds in the Seine River

Mathieu Cladière<sup>1</sup>, Céline Bonhomme<sup>1</sup>, Lauriane Vilmin<sup>2</sup>,  
Johnny Gasperi<sup>1</sup>, Nicolas Flipo<sup>2</sup>, Florence habets<sup>2</sup>  
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<sup>2</sup> Centre de Géosciences, Ecole des Mines ParisTech

# Nonylphenolic compounds



(NPnEO ; n = 1 - 50)

Non ionic surfactants → 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)

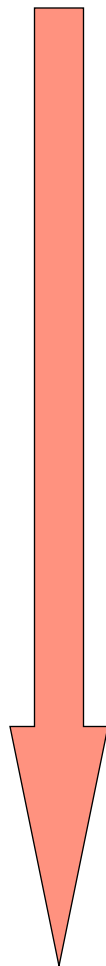
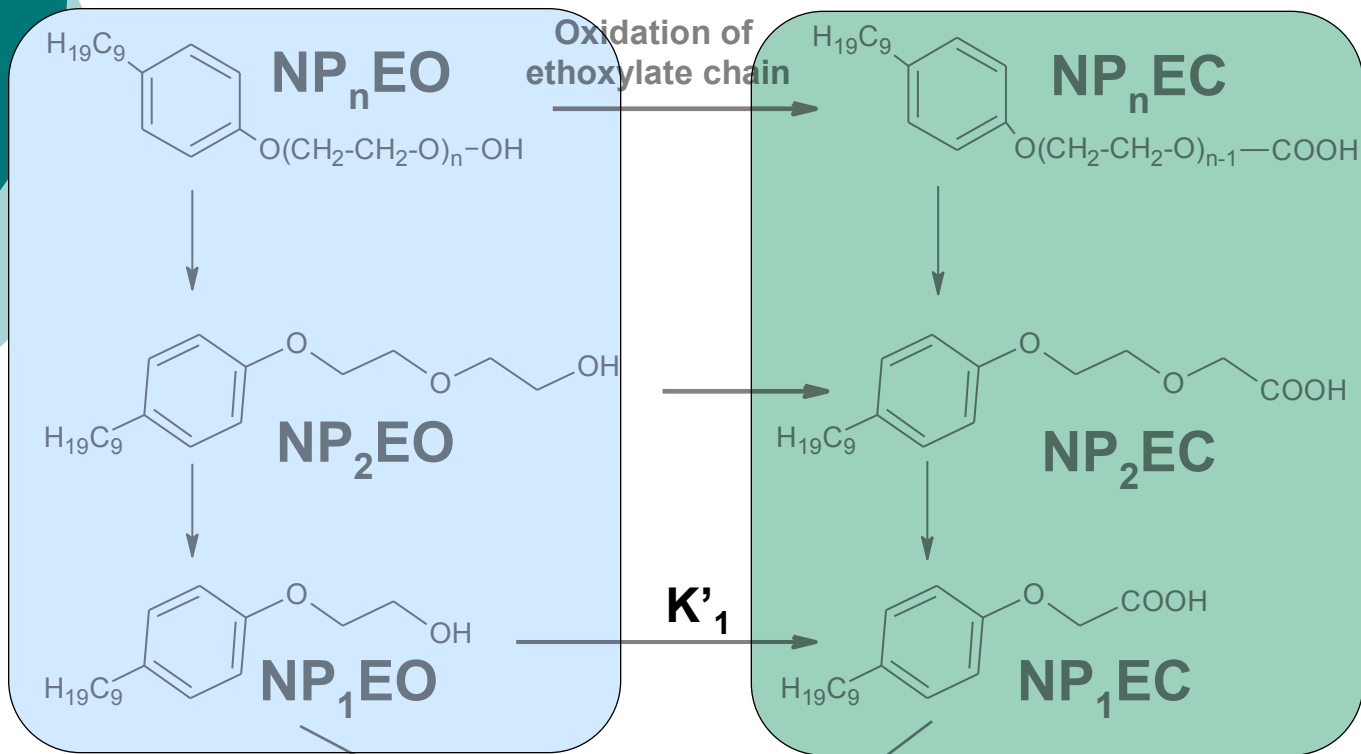


European legislation: Directive 2000/60/EC and 2008/105/EC

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



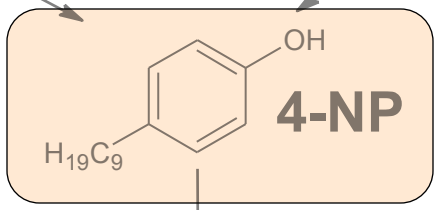
# Simplified biodegradation of NPnEO



**Increasing toxicity and estrogenic activity**

**Non-oxydative**

**Oxydative**



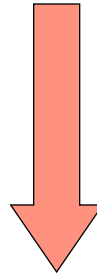
**K<sub>3</sub>**  
 Final biodegradation or volatilization

Giger et al. 2009

# Scientific issue

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- NPnEO are **readily biodegradable** in the environment
- Production of NP<sub>1</sub>EO, NP<sub>1</sub>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)
2. **Modelling concentrations for a reference year (2010)**
3. **Building scenarios for the middle (2050) and late (2100) 21<sup>st</sup> 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<sup>3</sup>/s)

➤ Oise River (95 m<sup>3</sup>/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<sub>1</sub>EO and NP<sub>1</sub>EC

➤ 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

Precursor inputs

Precursor inputs

Precursor inputs

$K_1, K'_1, K_2,$

$K_3$

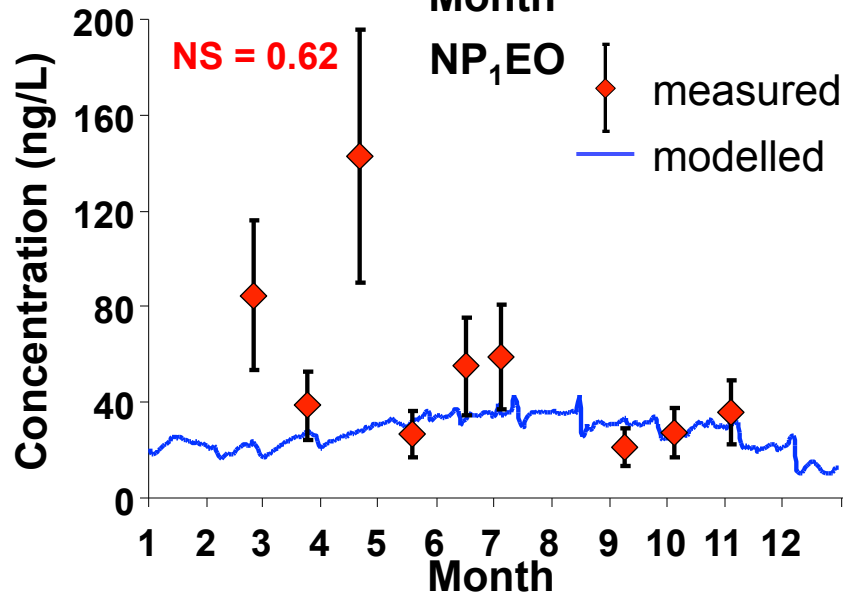
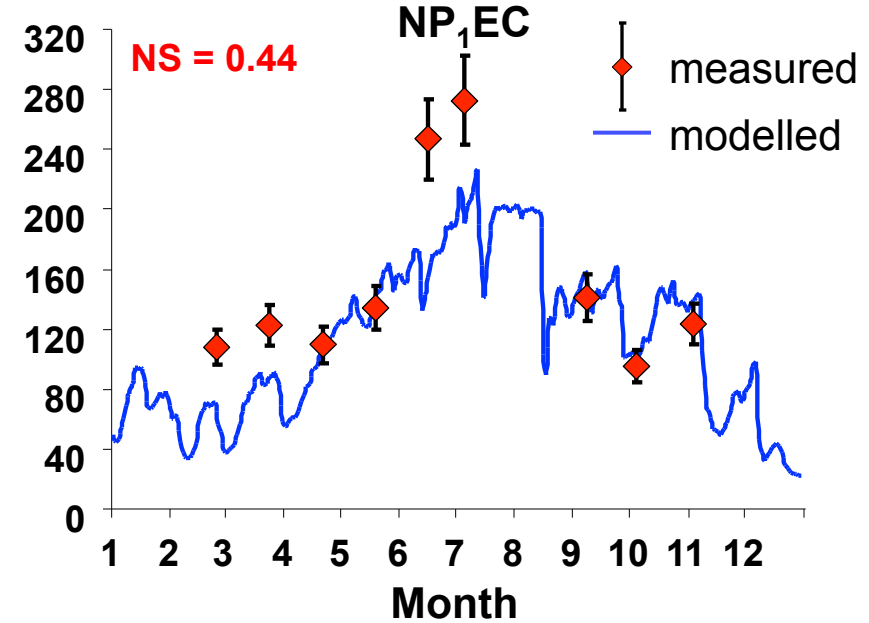
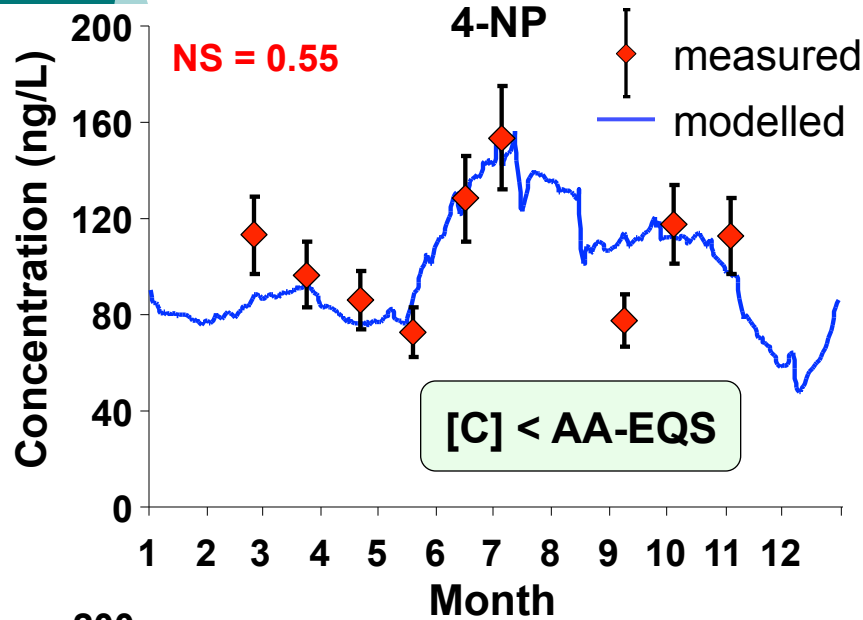
Seine River (hydrodynamic module)

Results

MEULAN  
[C] time series

# Annual modelling : 2010

## Meulan 2010



Good fitting of modelled and measured concentrations

➤ **Validation of method**

**Nash-Sutcliffe :**

$$NS = 1 - \frac{\sum (C_{Mes}^{\circ} - C_{Sim}^{\circ})^2}{\sum (C_{Mes}^{\circ} - C_{Moy}^{\circ})^2}$$





# Forecast of global change impacts

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**Assessment of global change scenarios by 2050 and 2100:**

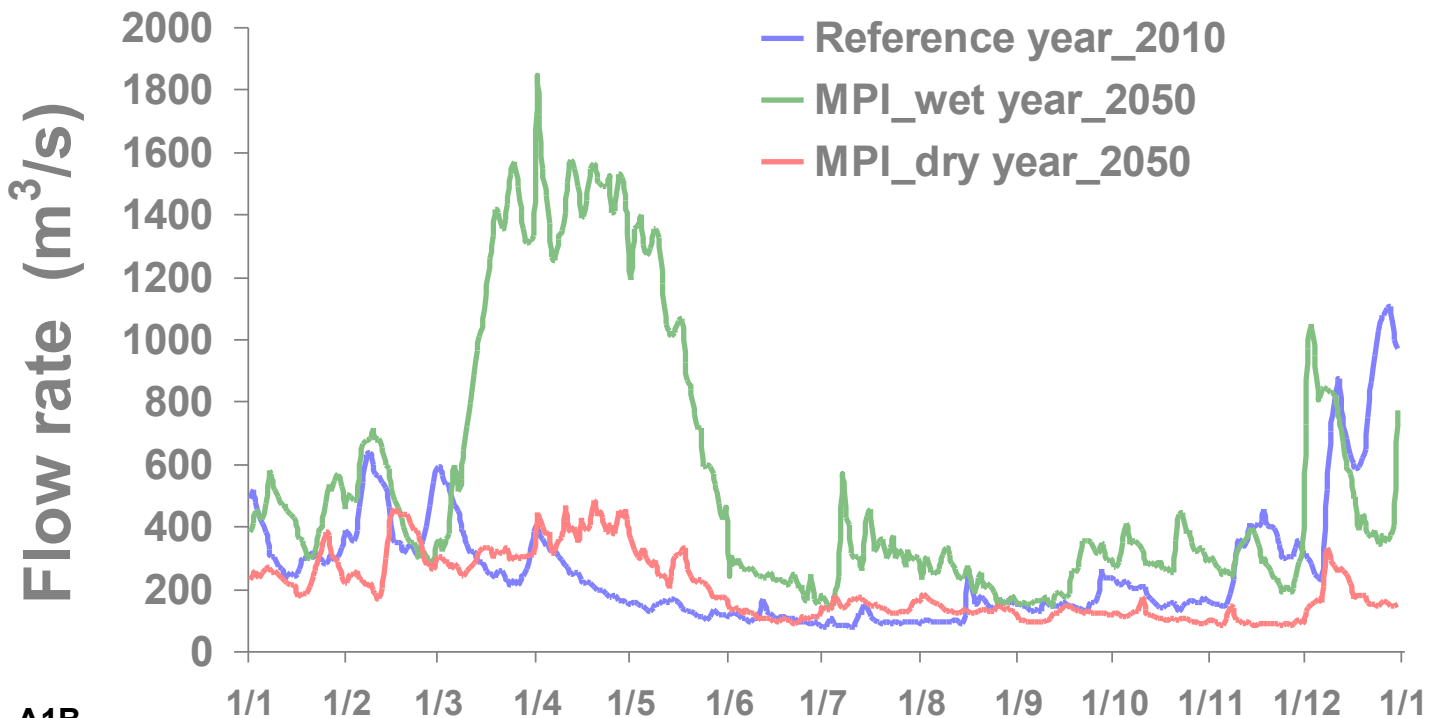
# Forecast of global change impacts

## 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

# Forecast of global change impacts

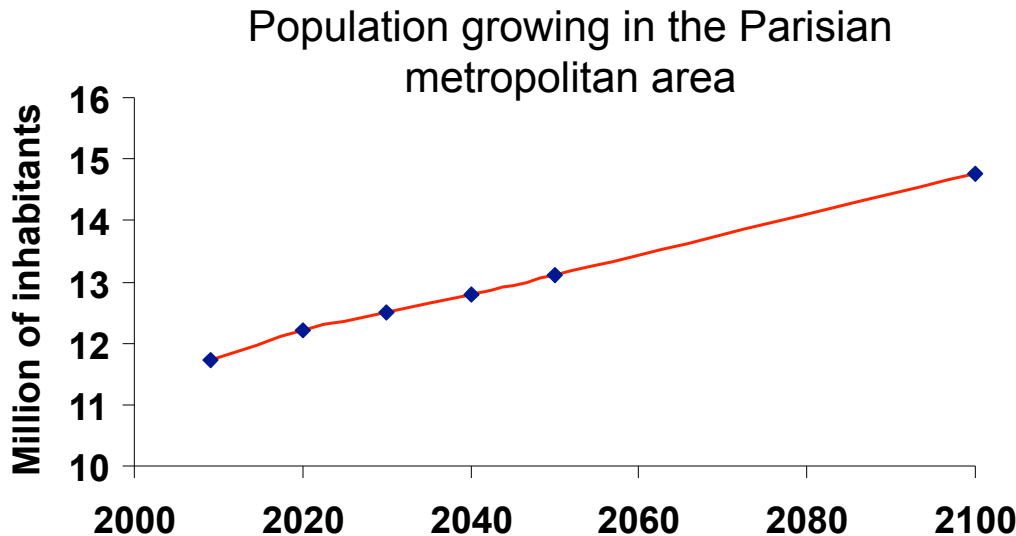
## Assessment of global change scenarios by 2050 and 2100:

### Population growing:

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

➤ + **12 %** by 2050 and + **26 %** by 2100

➤ Seine Aval WWTP: 19 m<sup>3</sup>/s in 2010, **22.6 m<sup>3</sup>/s** by 2050 and **24.3 m<sup>3</sup>/s** by 2100



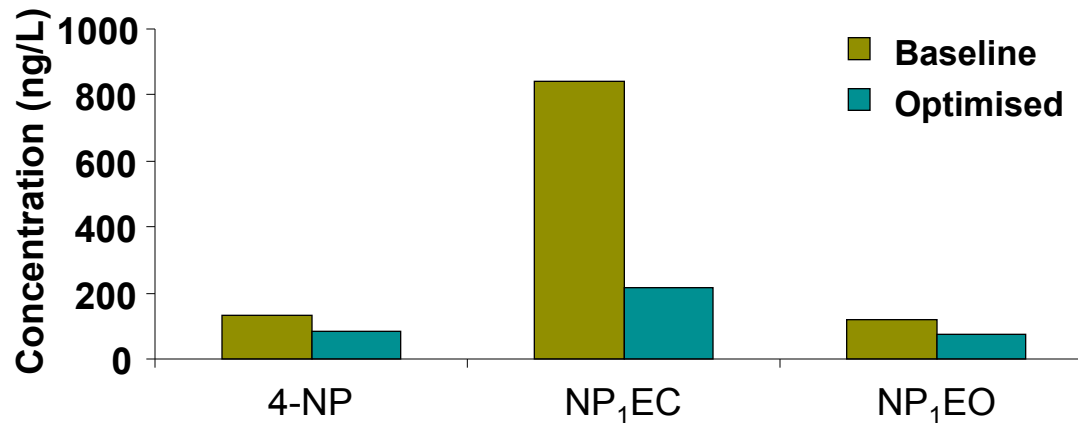
# Forecast of global change impacts

## Assessment of global change scenarios by 2050 and 2100:

### Optimisation of Seine Aval treatment:

Two scenarios :

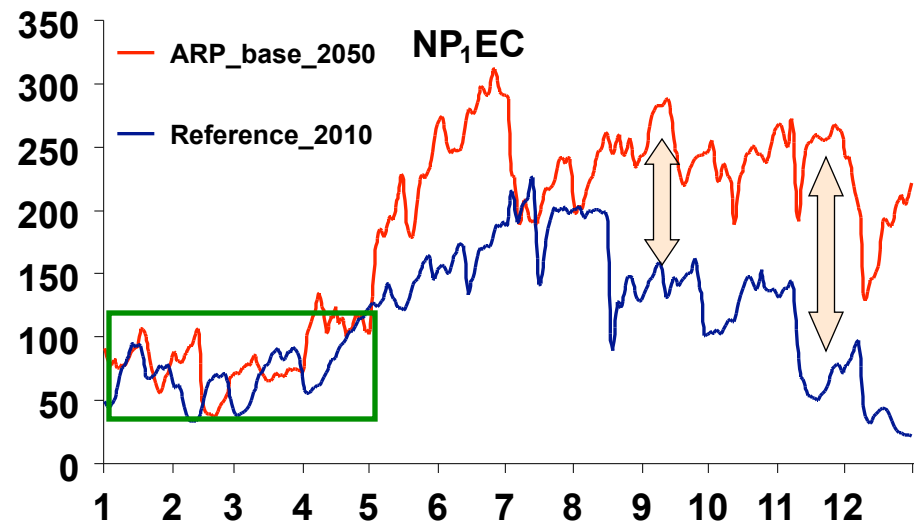
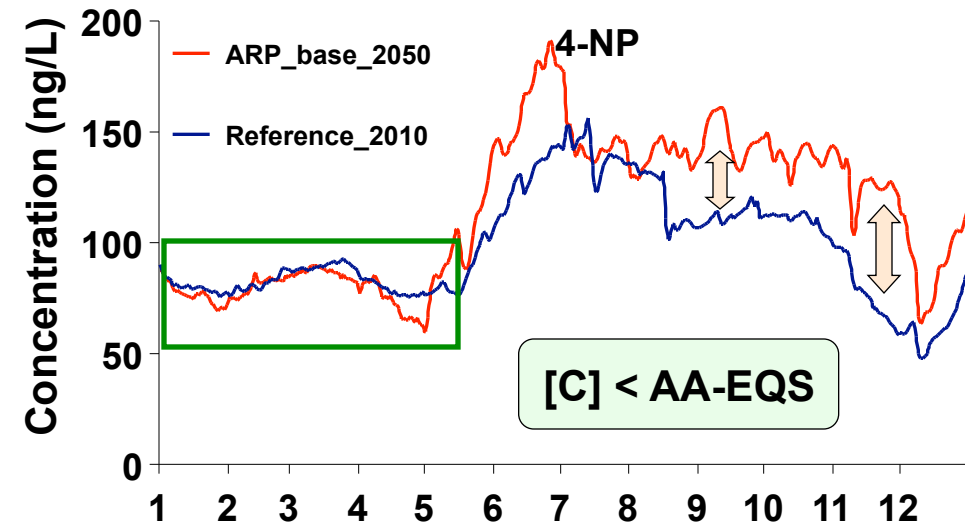
- Baseline (Base) : Seine Aval **non optimised** by 2050
- Optimised (Opt): Seine Aval **optimised** by 2050



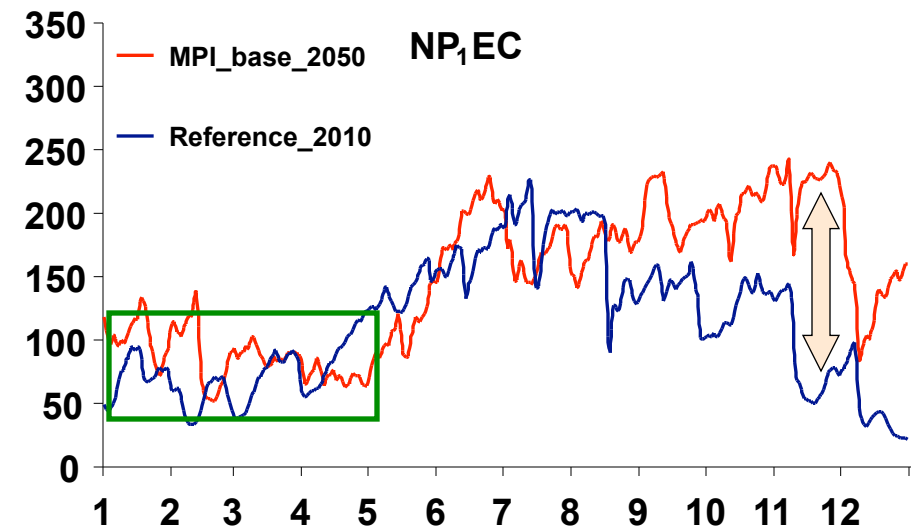
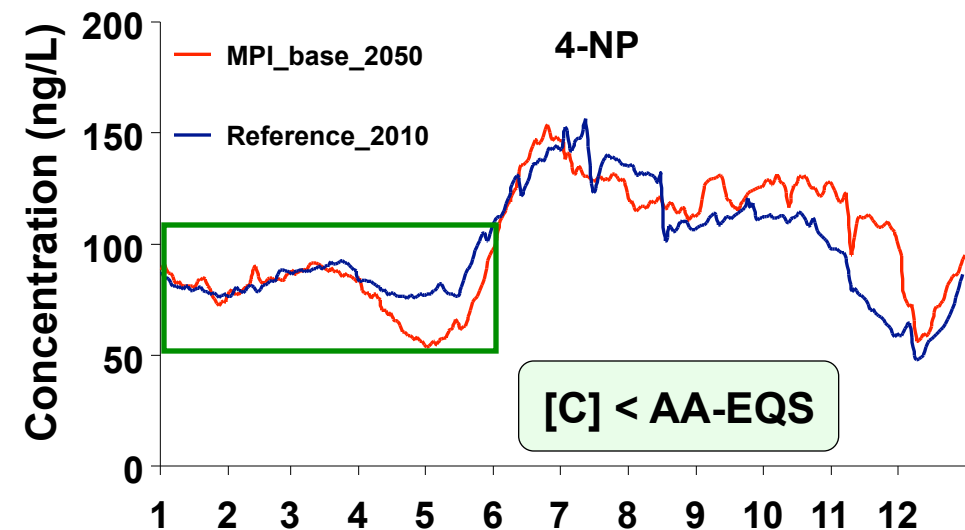
Cladière et al. (2013) ESPR

# Concentrations at Meulan by 2050

## Dry year

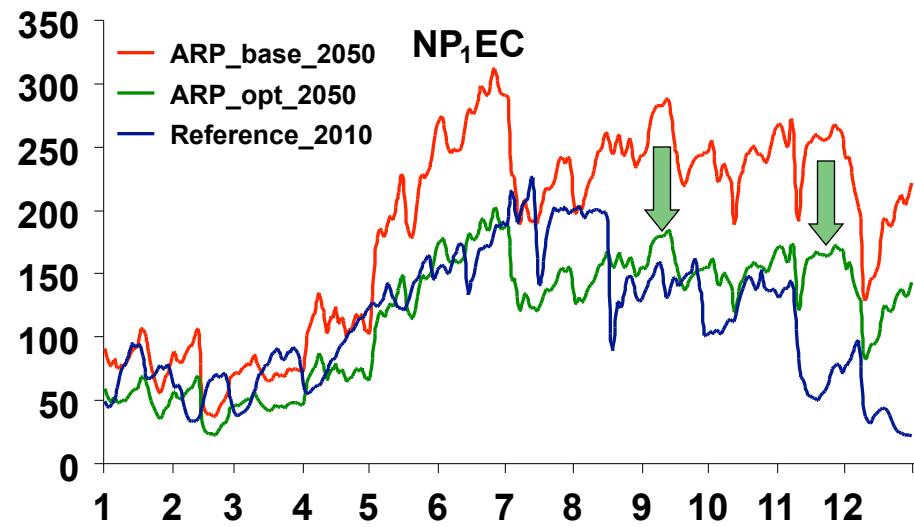
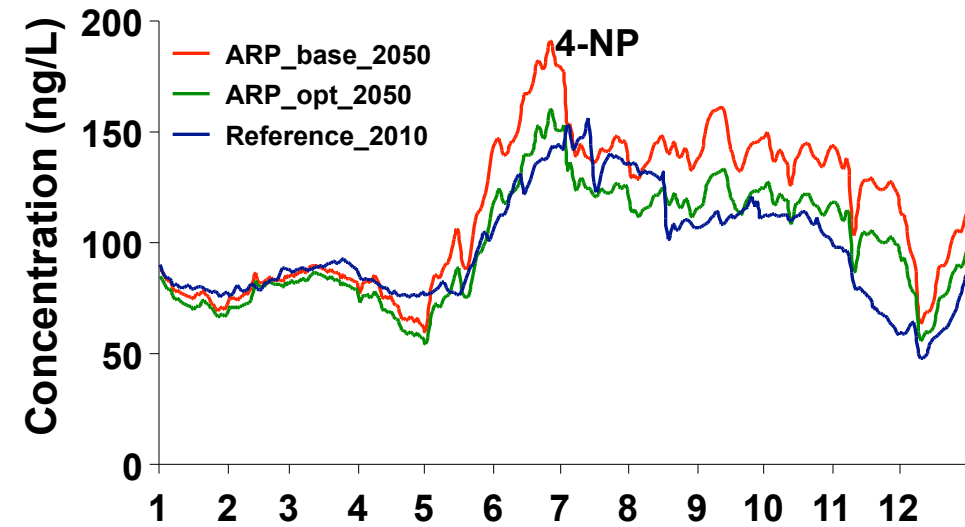


Significant influence of global changes during low-water period (summer, autumn)

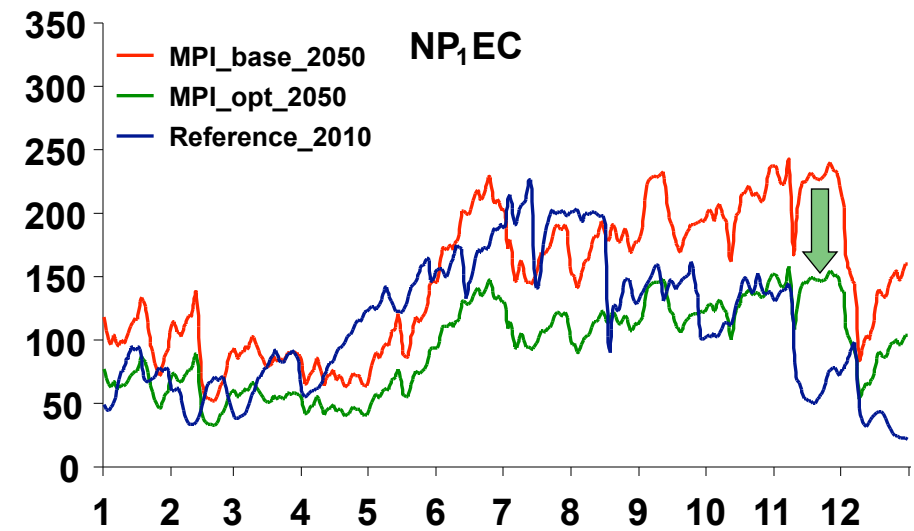
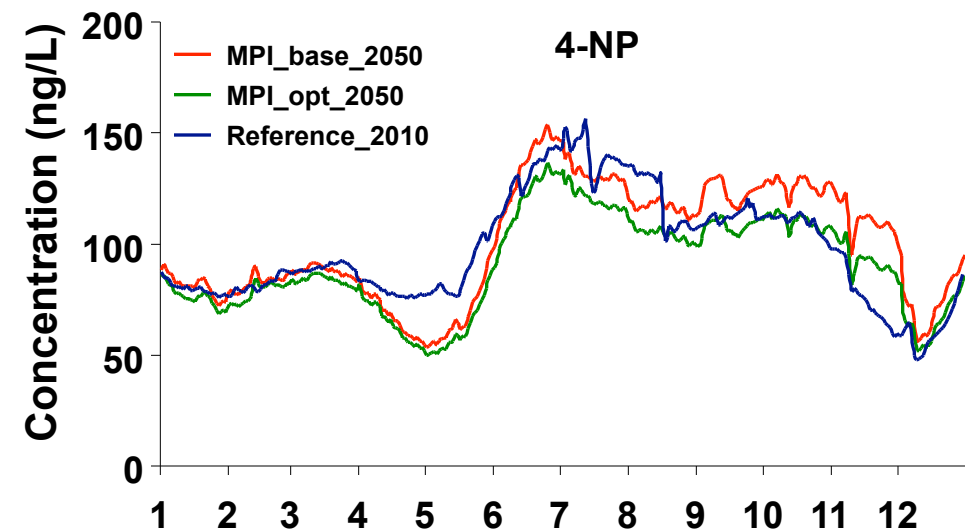


# Concentrations at Meulan by 2050

Dry year

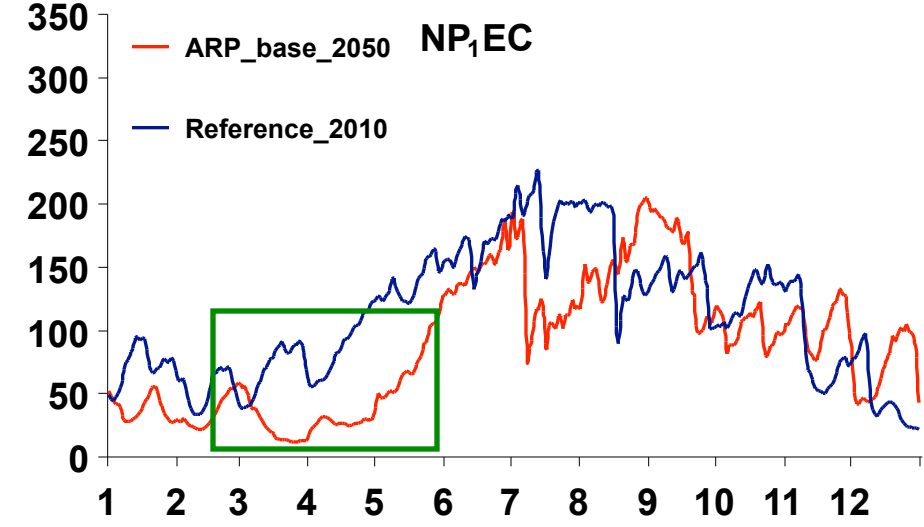
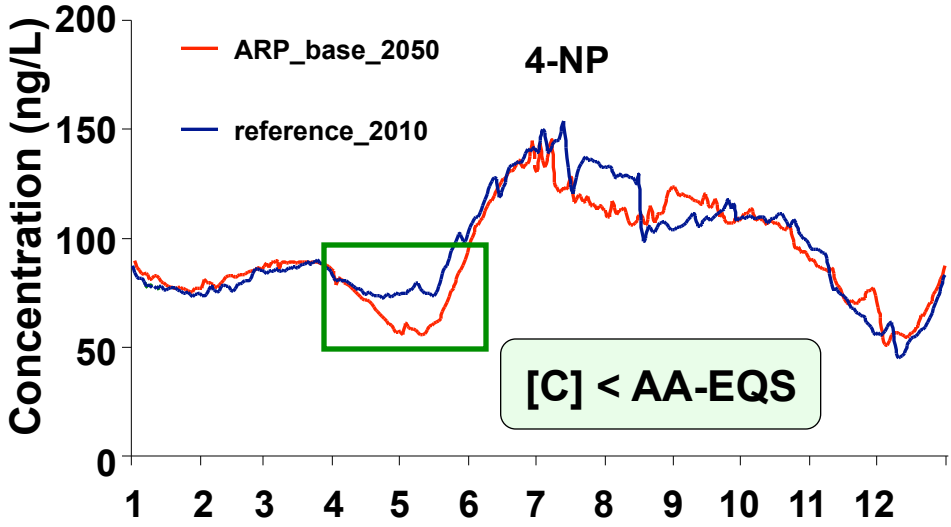


Optimisation of Seine Aval treatment compensate the influence of global changes

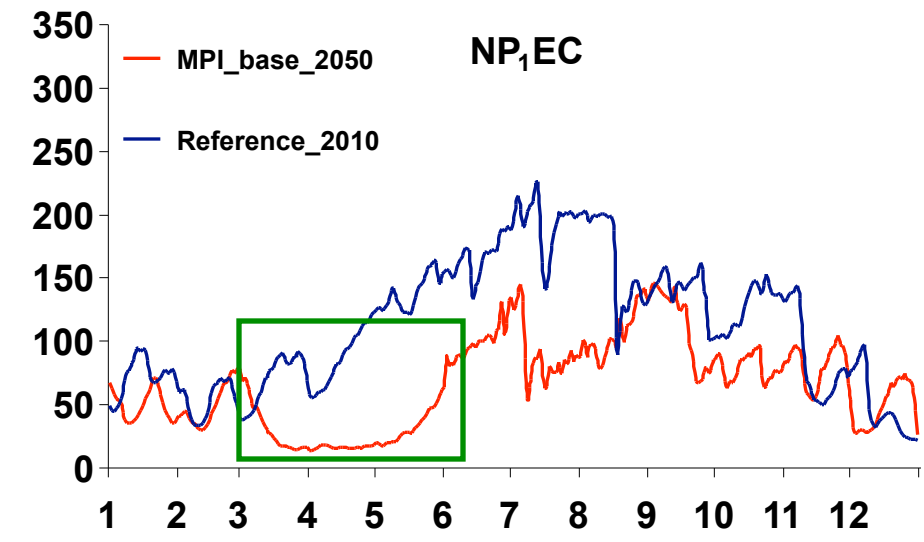
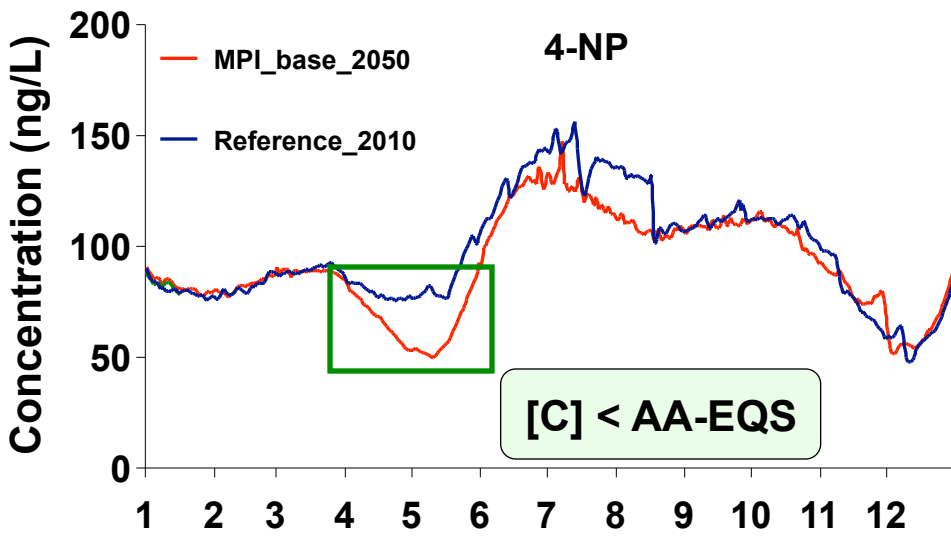


# Concentrations at Meulan by 2050

Wet year

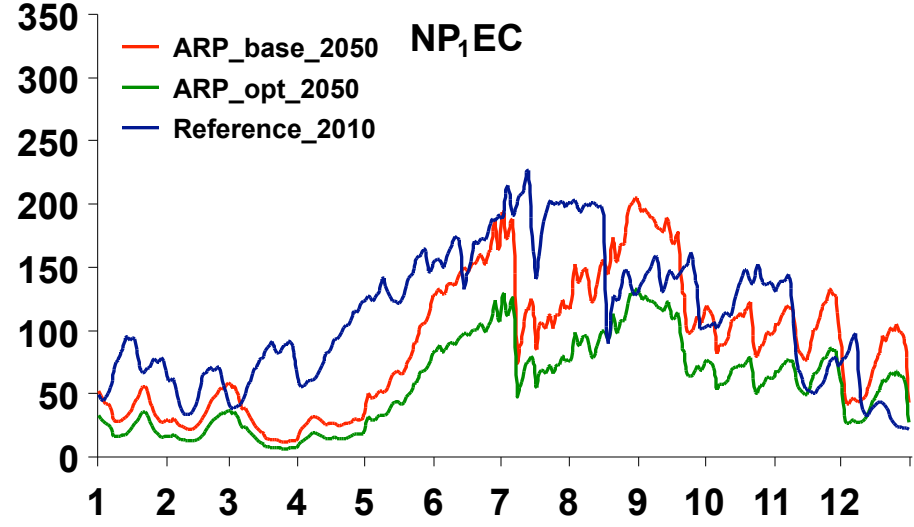
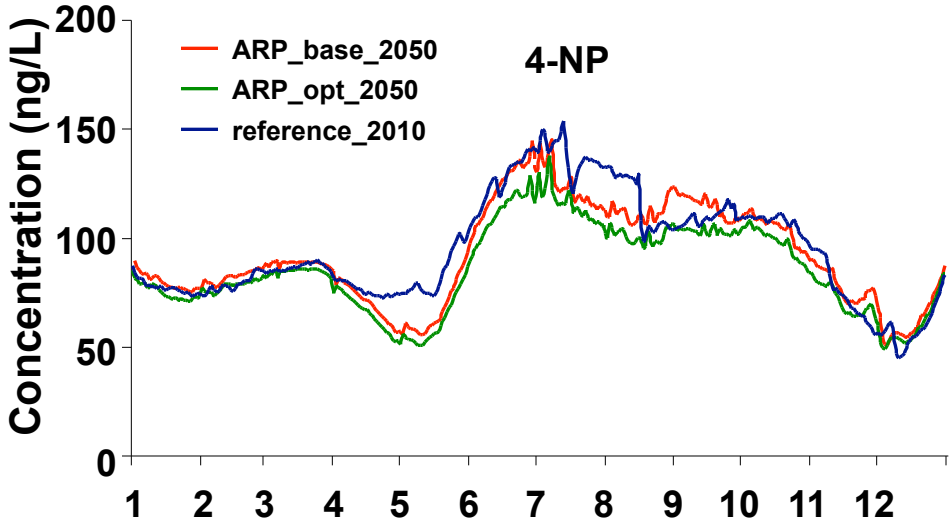


Significant decreases of concentrations in spring because of the river flooding

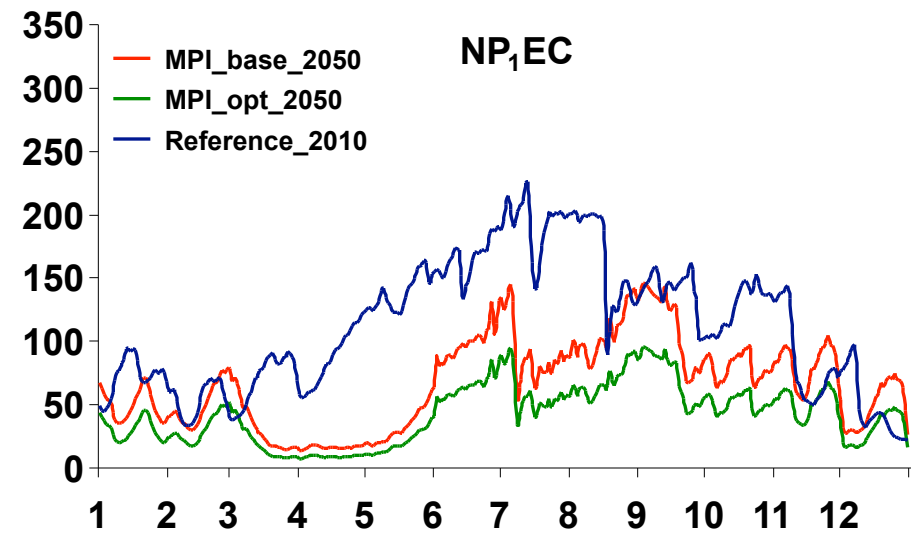
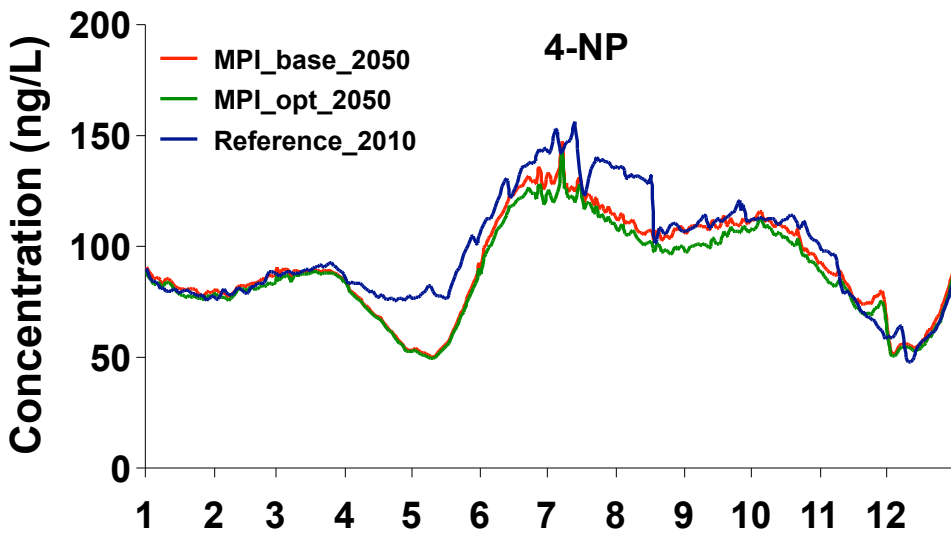


# Concentrations at Meulan by 2050

Wet year



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 21<sup>st</sup> 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<sup>st</sup> century
- AA-EQS **could be exceeded** downstream of the studied transect → biodegradation of NP<sub>1</sub>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

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## 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 21<sup>st</sup> 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

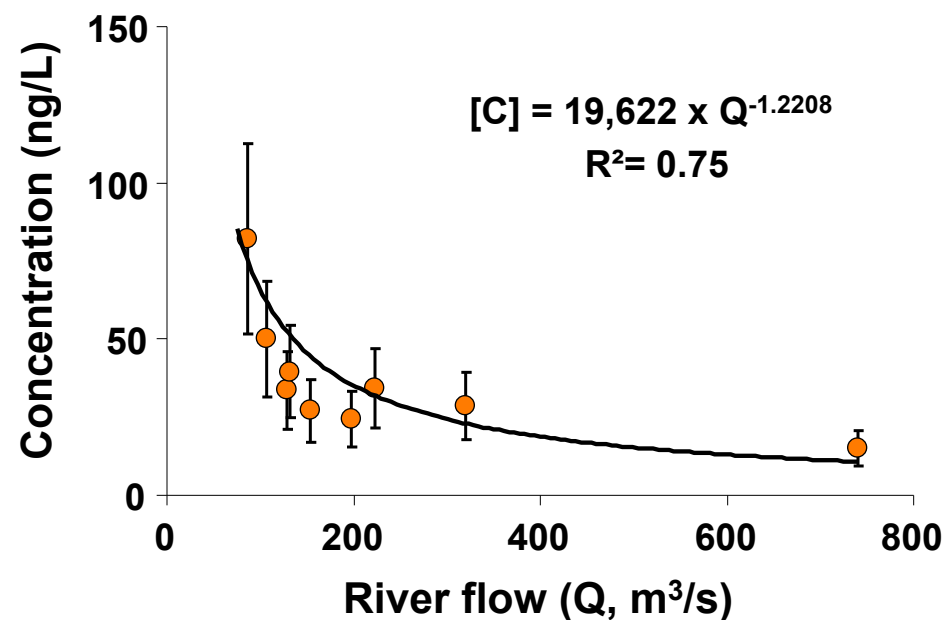
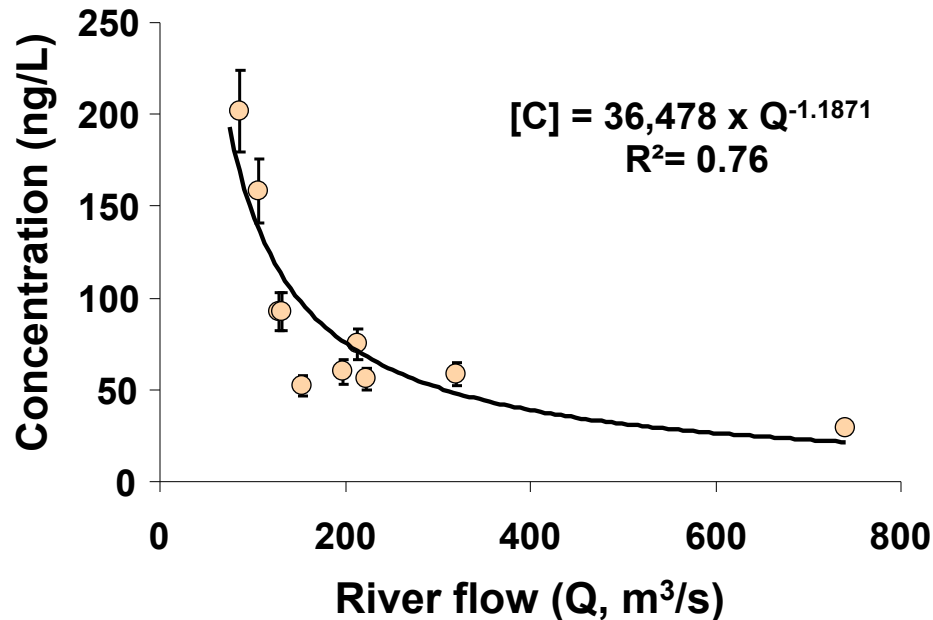
River → Relationship between concentrations and river flow (except for 4-NP)

WWTP → constant over the year (NP<sub>1</sub>EC : 842 ng/L, NP<sub>1</sub>EO: 120 ng/L, 4-NP: 133 ng/L)

## Seine River at Bougival

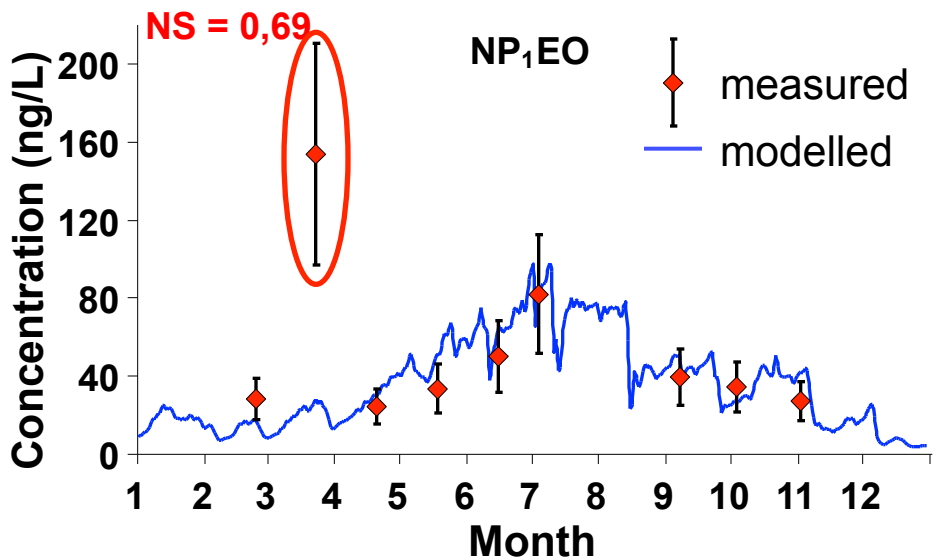
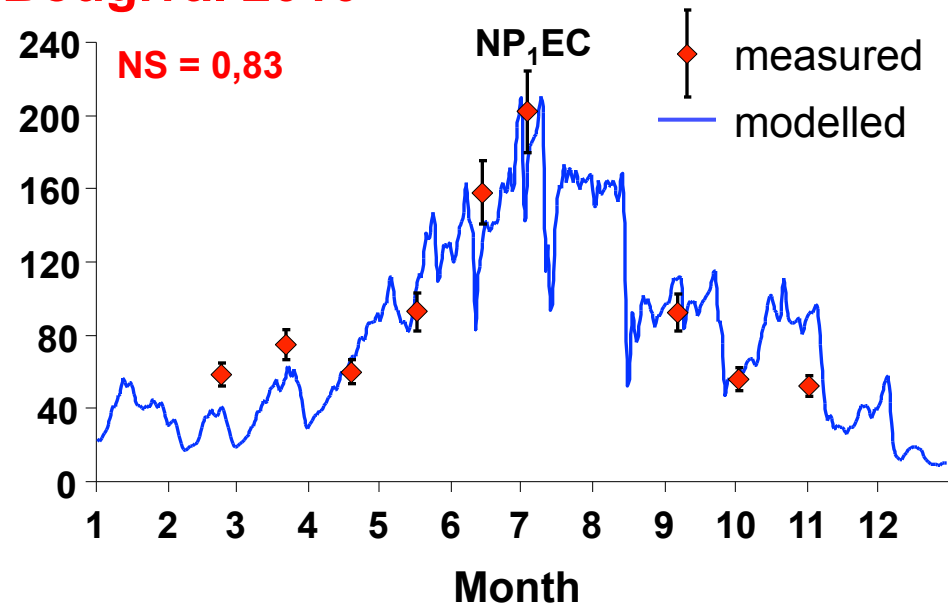
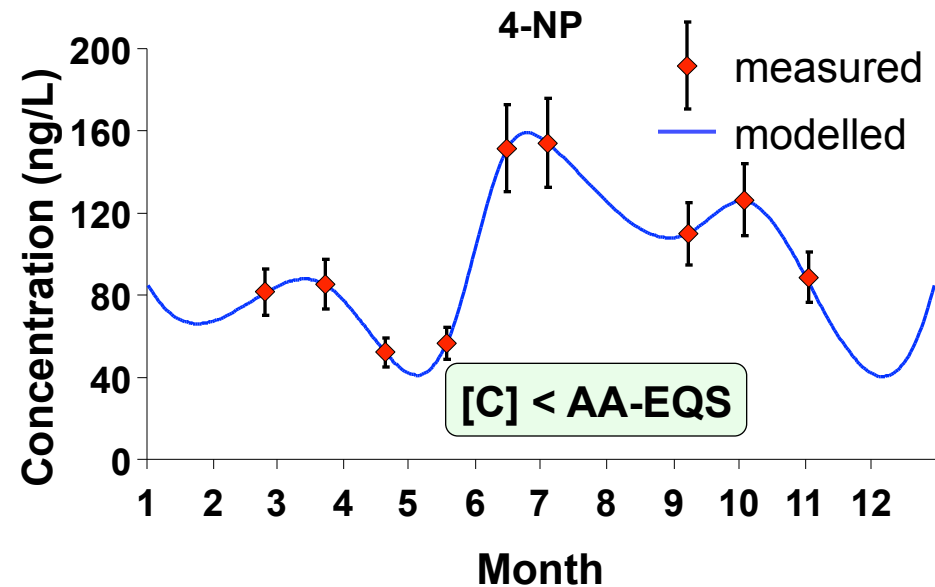
NP<sub>1</sub>EC

NP<sub>1</sub>EO



# Annual modelling: 2010

## Seine River: Bougival 2010



**Nash-Sutcliffe :**

$$NS = 1 - \frac{\sum (C_{Mes}^{\circ} - C_{Sim}^{\circ})^2}{\sum (C_{Mes}^{\circ} - C_{Moy}^{\circ})^2}$$

Good fitting

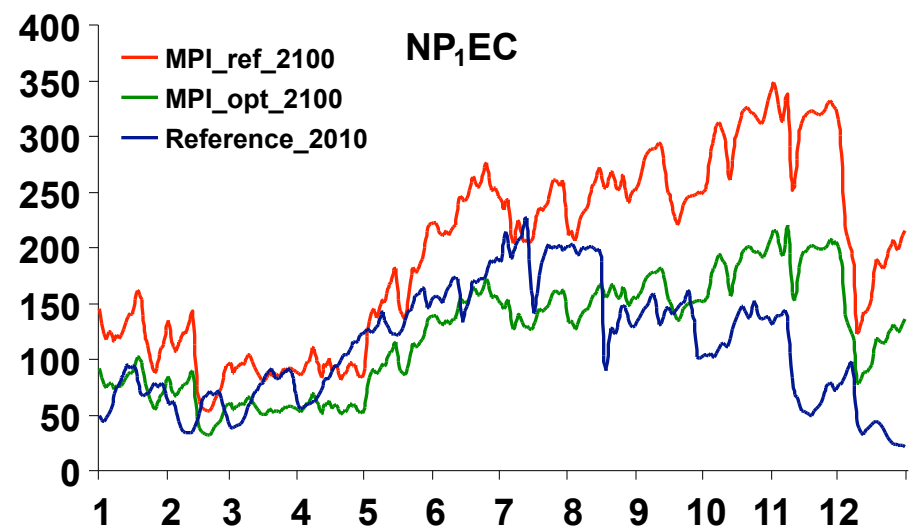
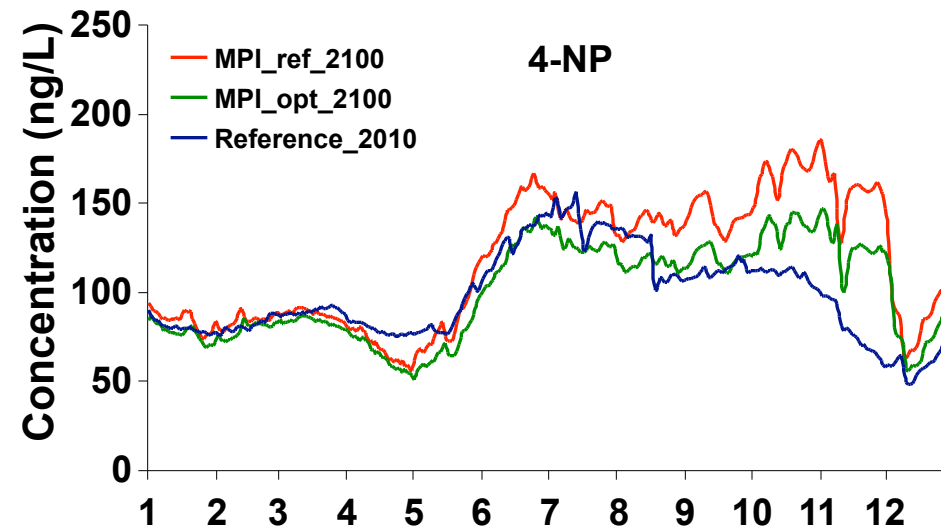
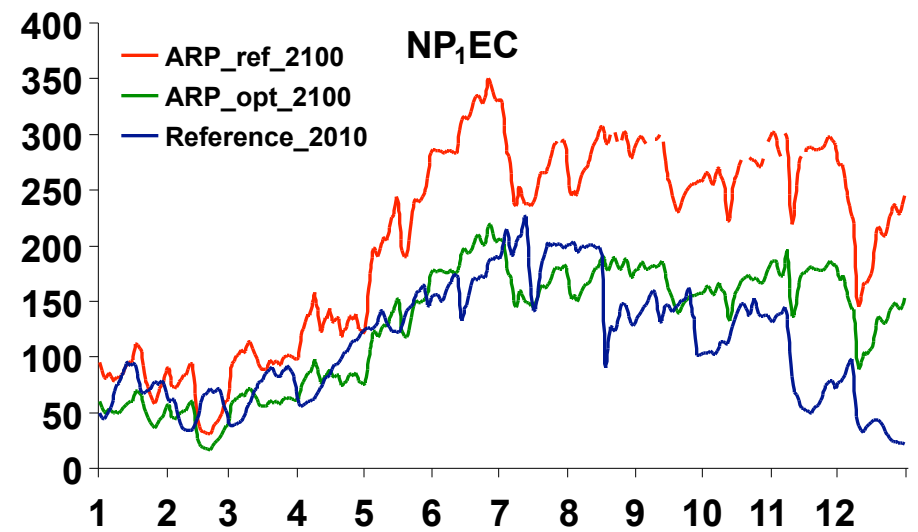
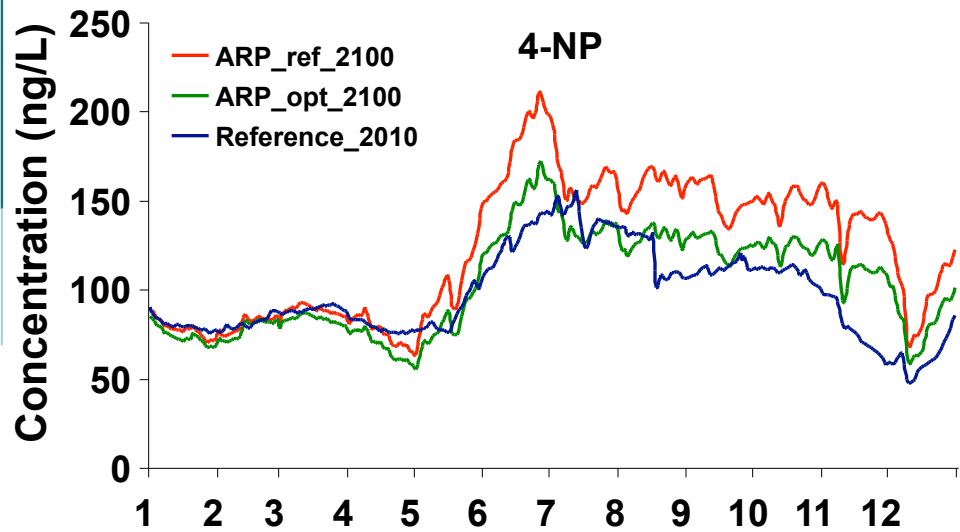
➤ **Validation of boundary conditions**

Limit:

➤ **Wet weather urban sources**

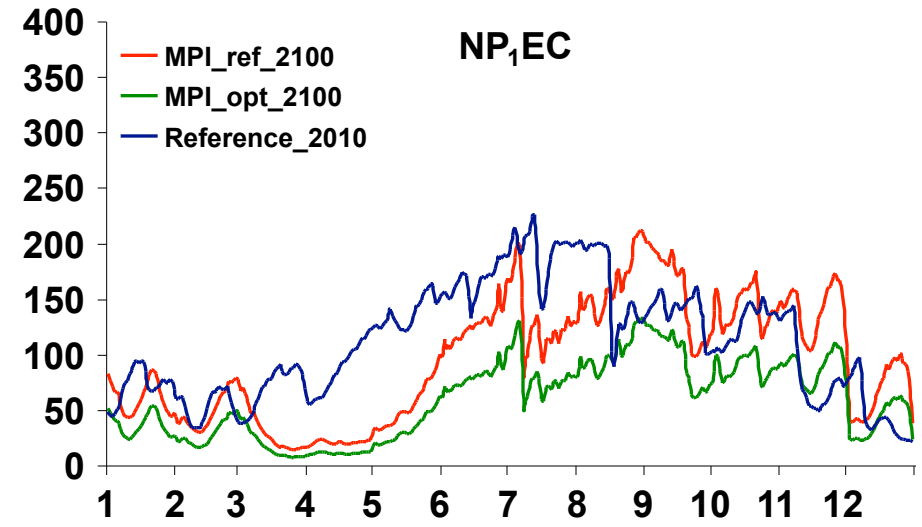
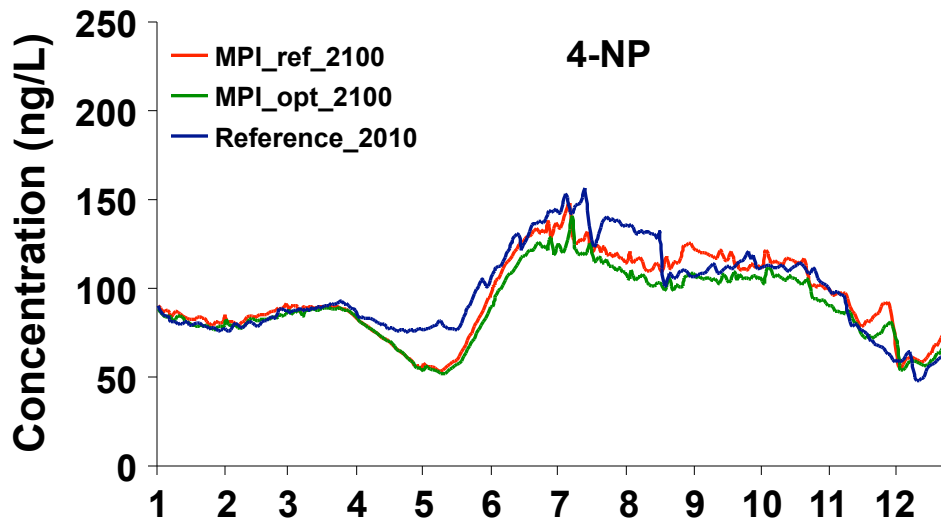
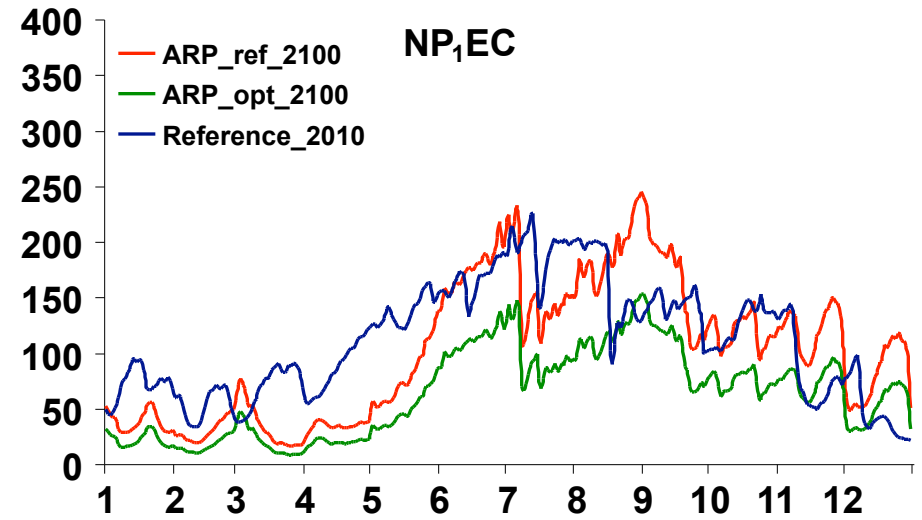
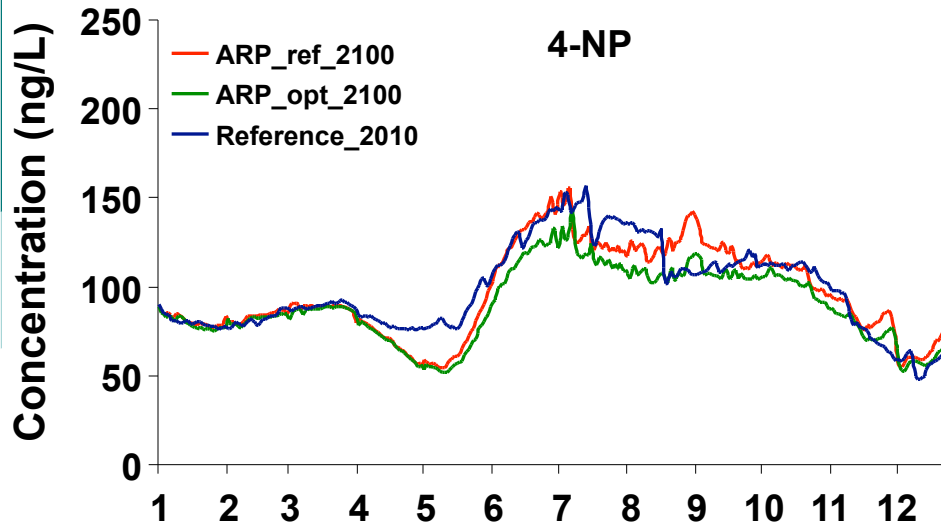
# Concentrations at Meulan by 2100

Dry year

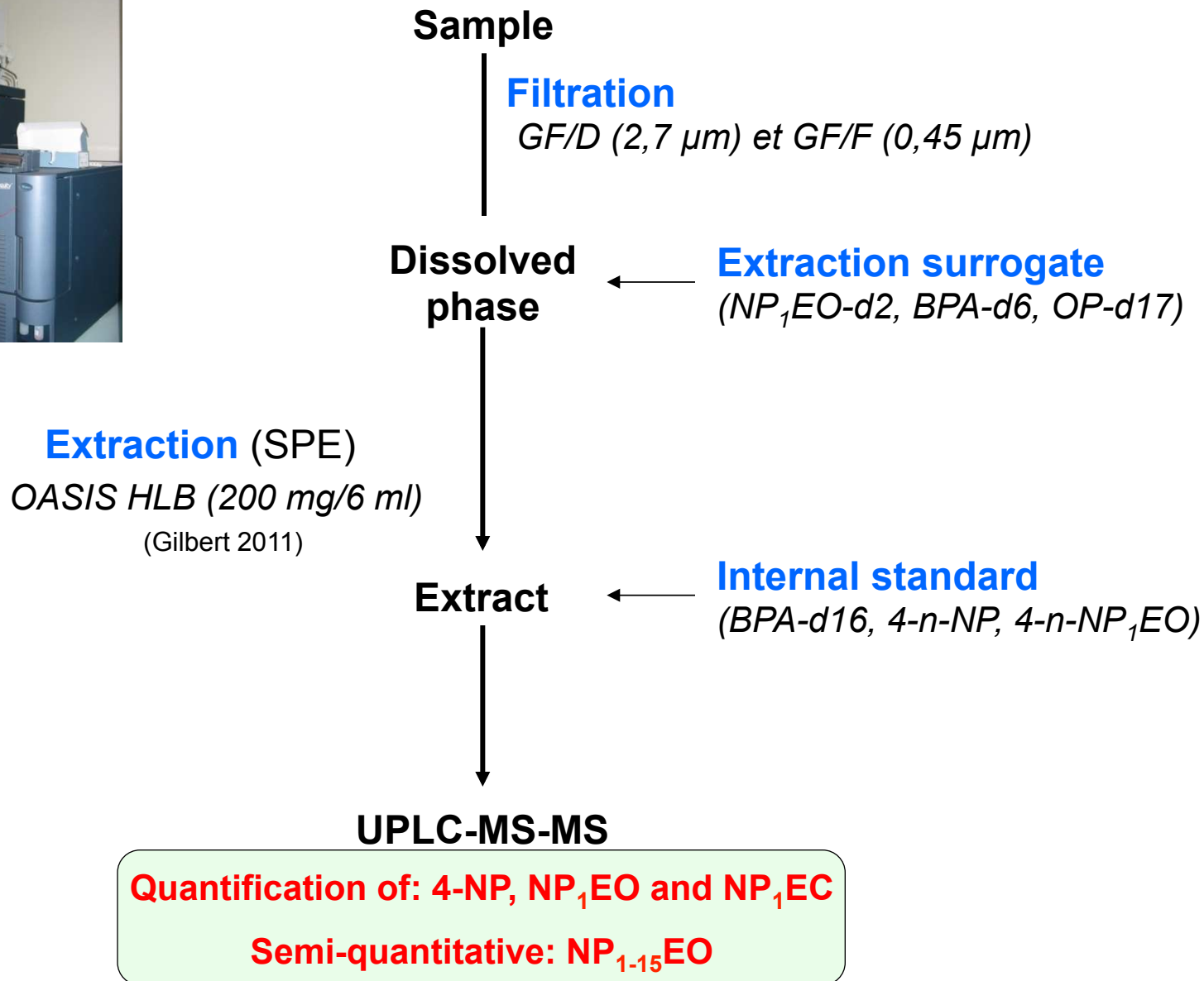


# Concentrations at Meulan by 2100

Wet year

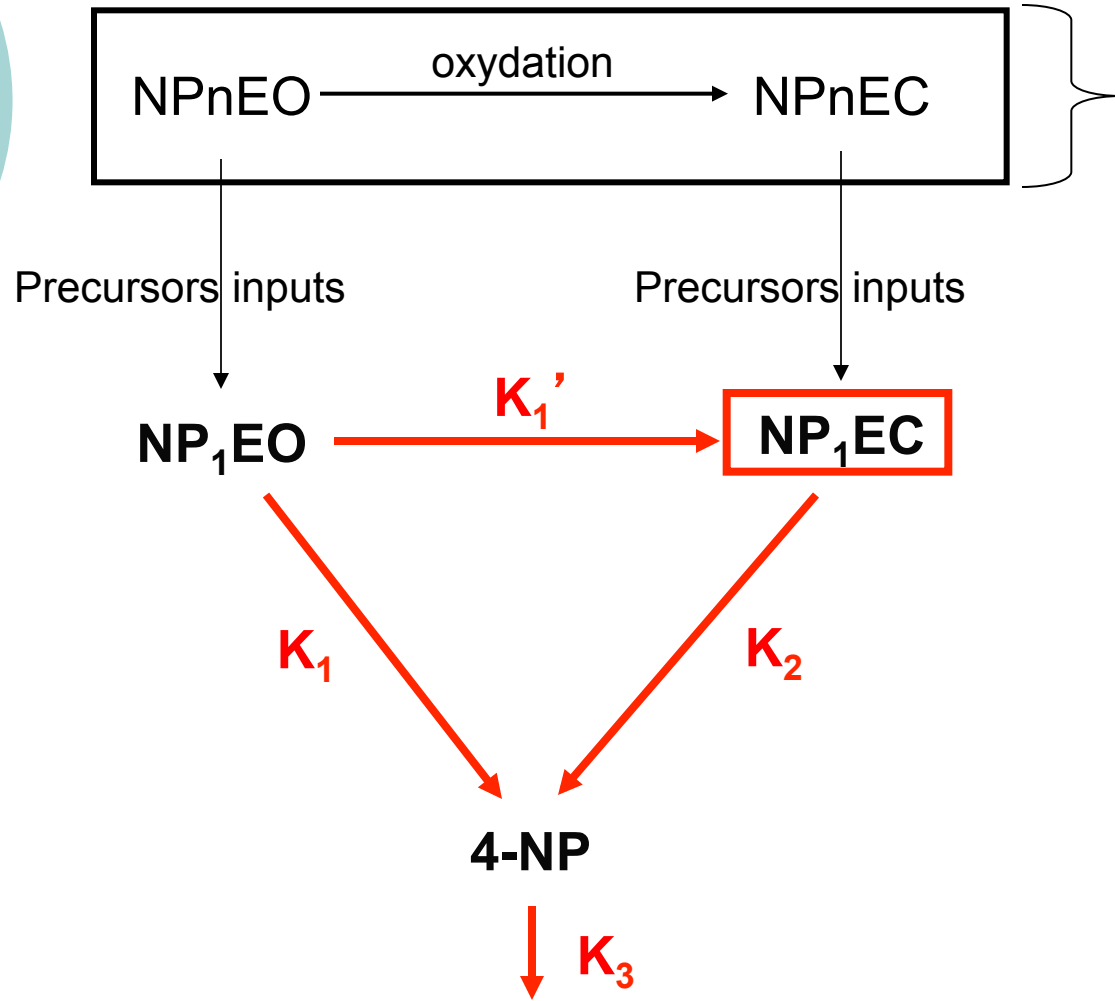


# Analytical protocol





# Biodégradation des nonylphénols



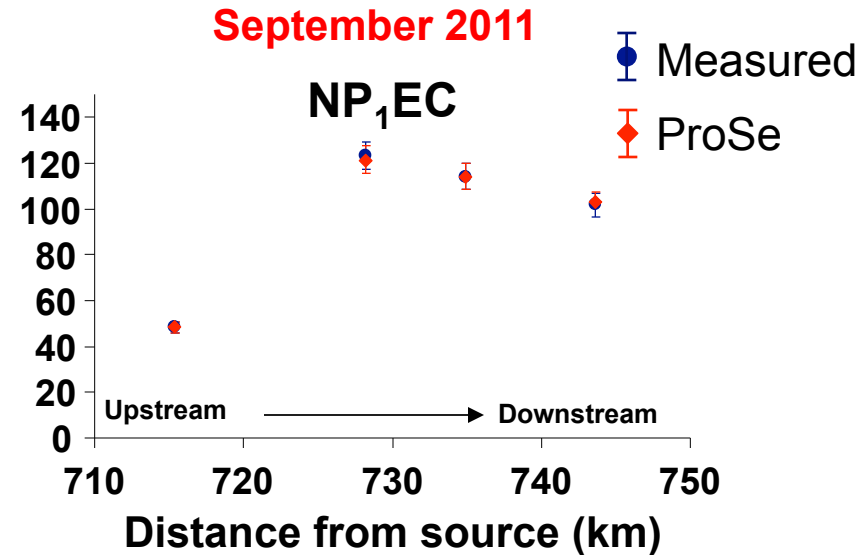
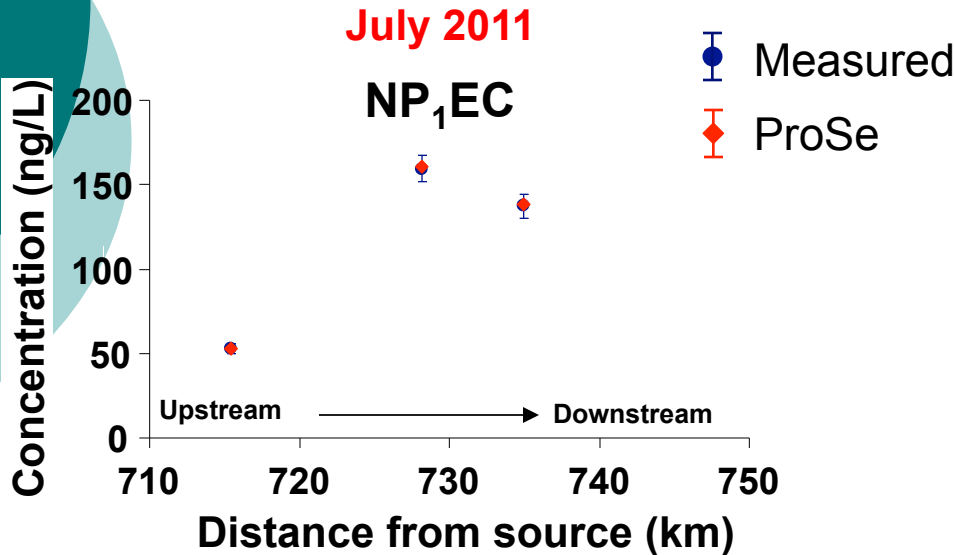
**ProSe model** : Precursor inputs in the Seine River symbolizing their biodegradation

- 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)

Final biodegradation ;  
volatilisation ; adsorption

From Giger et al. 2009

# Simulation du linéaire de Seine



Rate constants (d <sup>-1</sup> )	
$K_1 = K'_1$	0.1
$K_2$	3.3
$K_3$	2.5

<  
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Rate constants (d <sup>-1</sup> )	
$K_1 = K'_1$	0.3
$K_2$	0.1
$K_3$	0.15

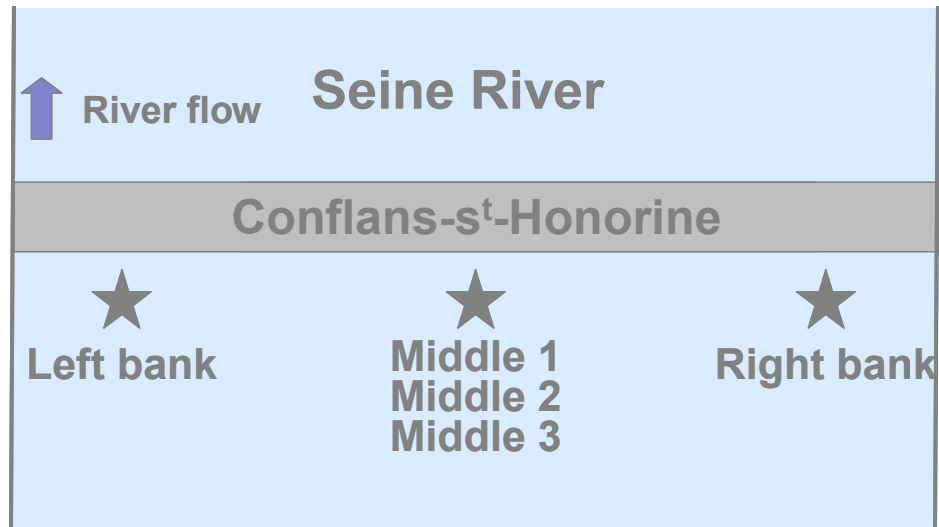
**Significant variability of biodegradation rate constants between sampling campaigns**  
**→ July >> September**

**Influence of biogeochemical conditions of the Seine River**

**Heterotrophic bacterial biomass → Algal bloom in July**

# Small scale variabilities

## Sampling strategy



## Résultats

Compound	Analytical repeatability	Spatial variability	Temporal variability	Total variability
4-NP	7 %	7 %	7 %	14 %
NP <sub>1</sub> EC	4 %	5 %	6 %	11 %
NP <sub>1</sub> EO	14 %	14 %	23 %	37 %

Total variability = spatial variability + temporal variability