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

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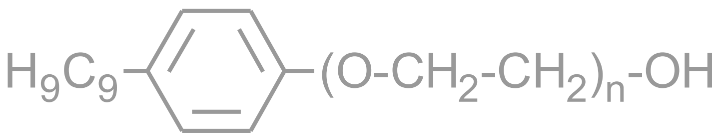
laboratoire eau environnement systemes urbains

Nonylphenolic compounds

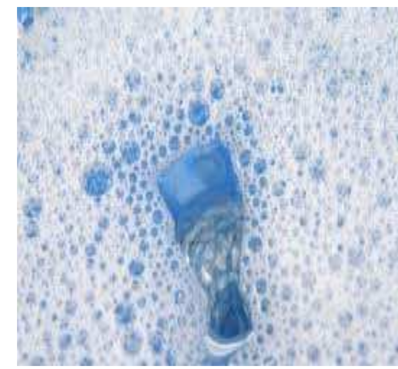


(NPnEO ; n = 1 - 50)

Non ionic surfactants ➔ detergents, wetting agent

World consumption: 500,000 tons in 2000

(Ying *et al.* 2002)



Endocrine disrupting compounds

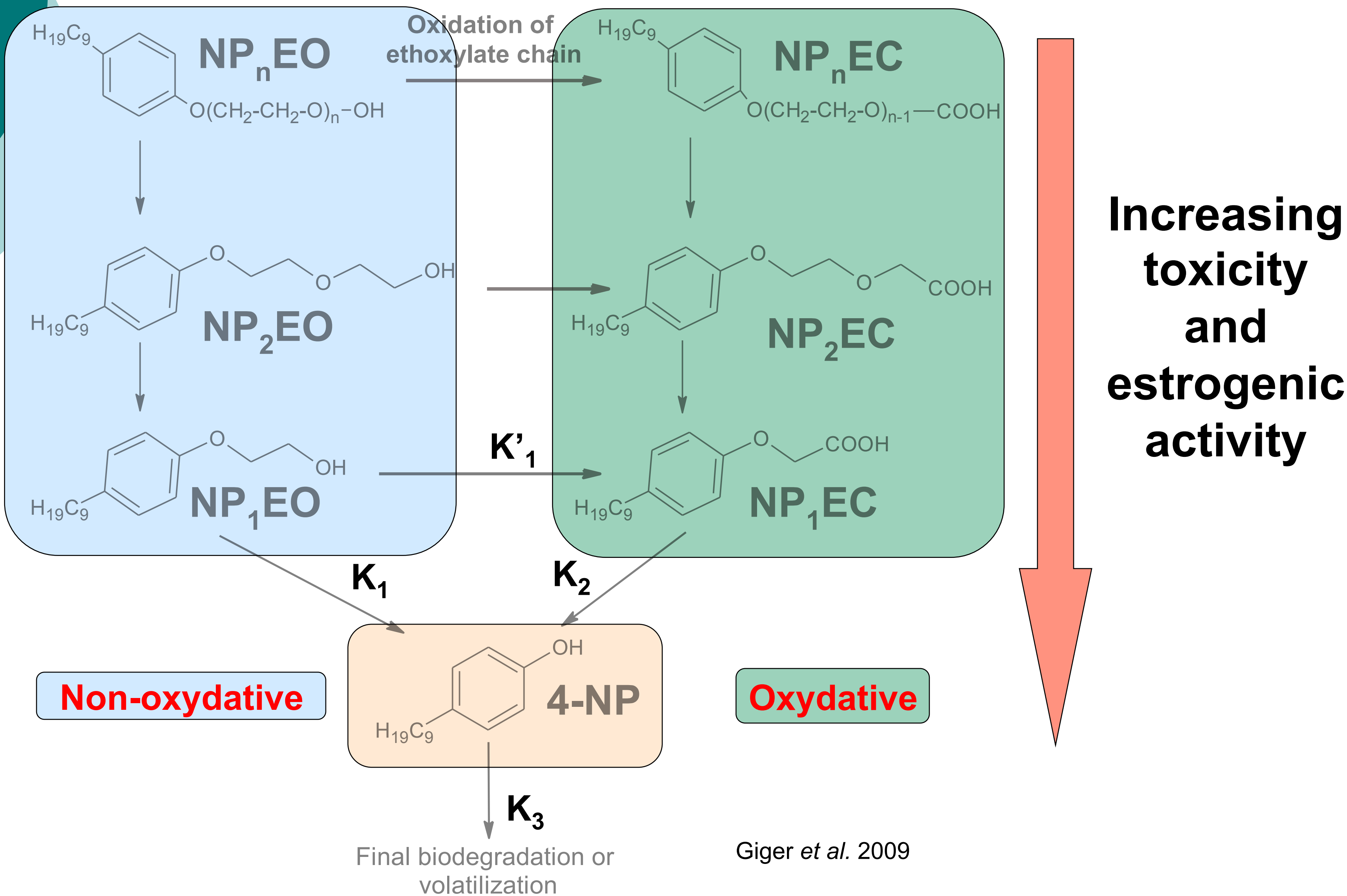
Key role in estrogenic activity of surface water

(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



Giger *et al.* 2009

Scientific issue

➔ NPnEO are **readily biodegradable** in the environment

➔ Production of NP_1EO, NP_1EC and 4-NP

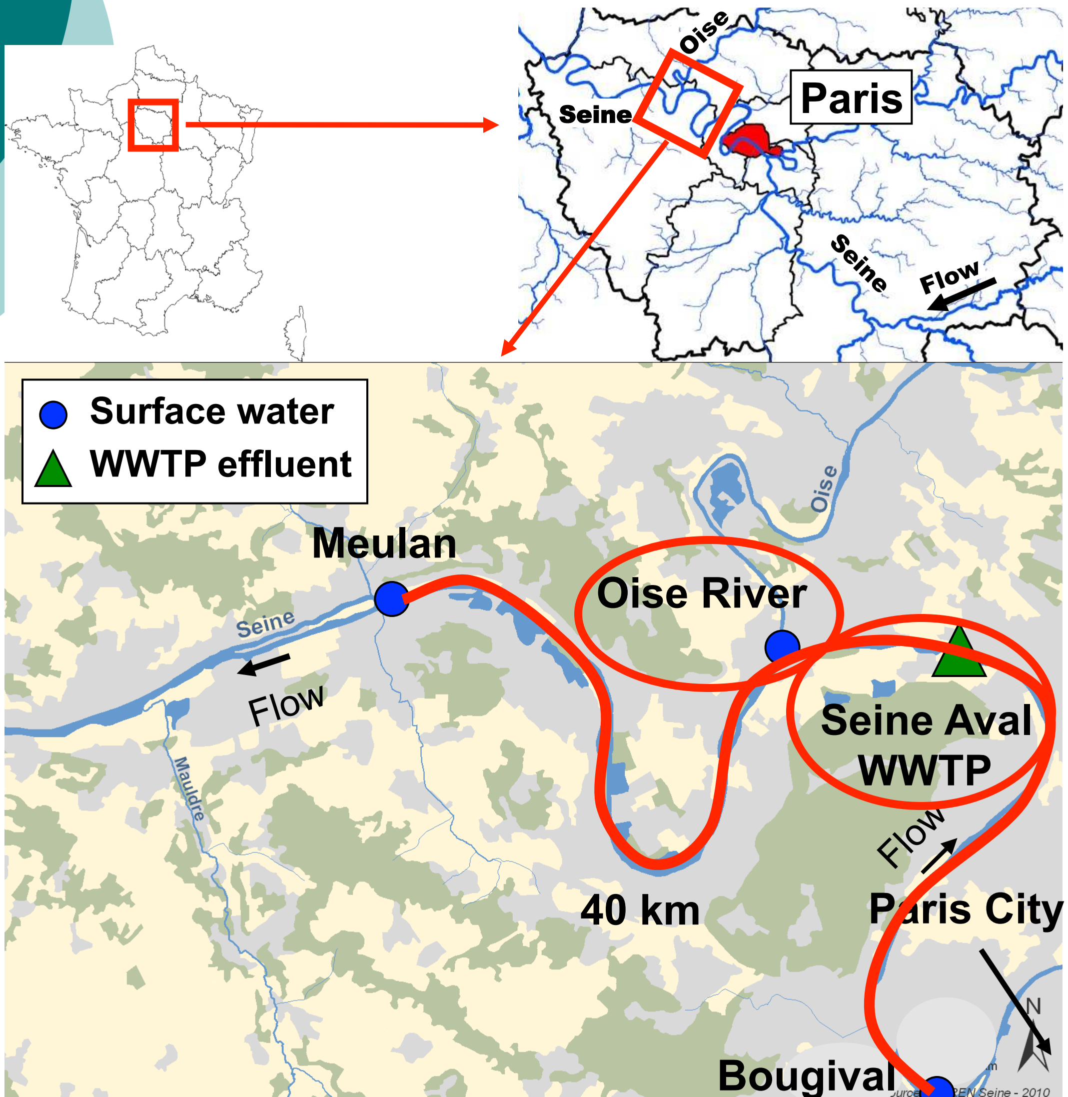
↓

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) 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

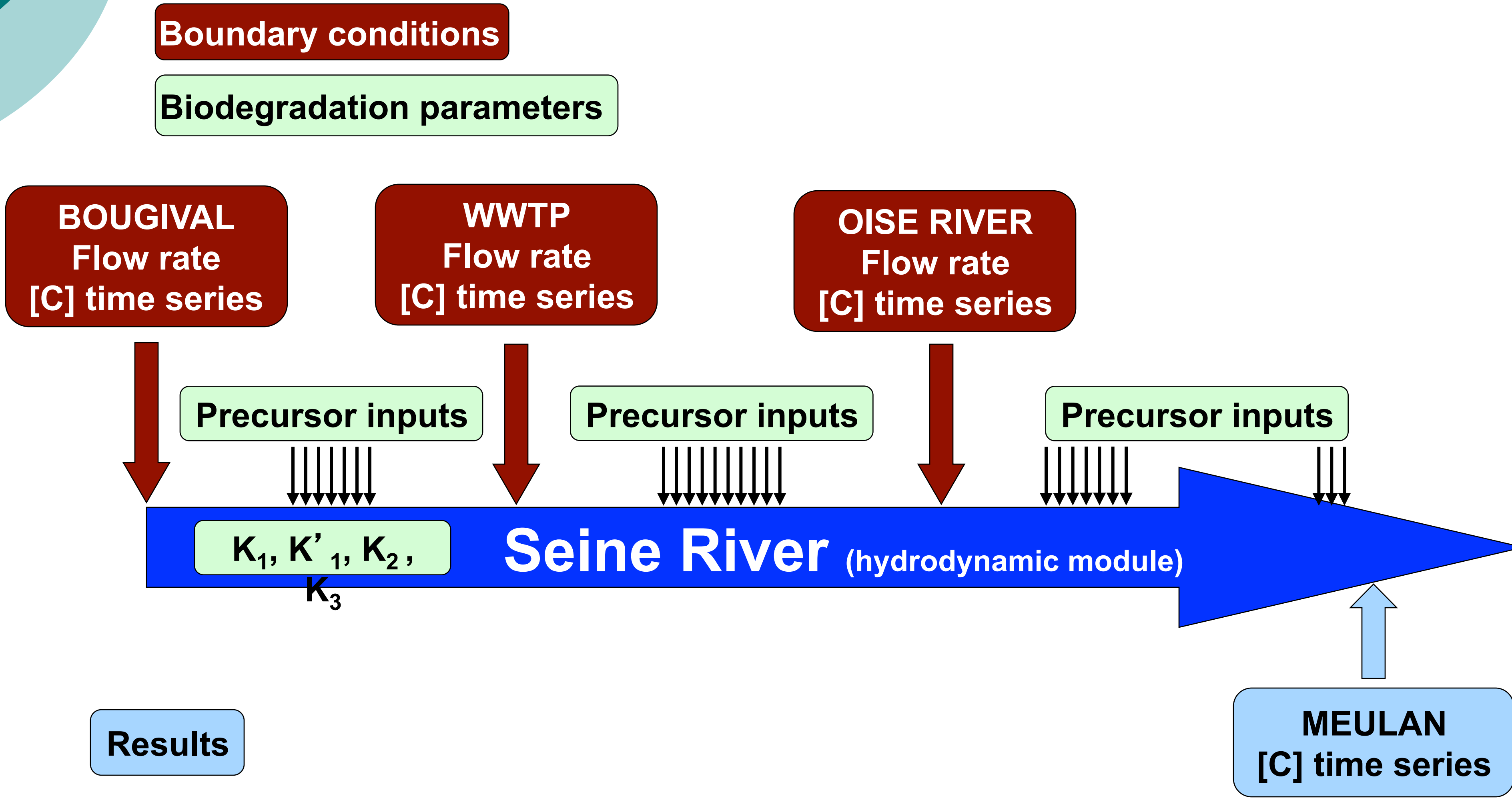
Analysis: UPLC-MS-MS

- **quantification: 4-NP, NP_1EO and NP_1EC**
- **semi-quantitative: NPnEO (n= 1-15)**

Hydro-ecological ProSe model

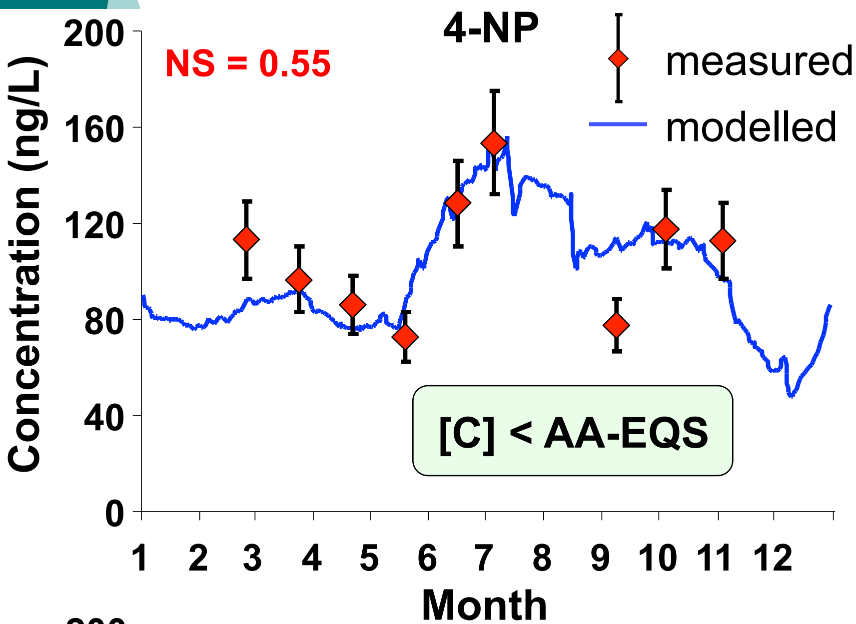
Hydrodynamic module: Shallow water equations

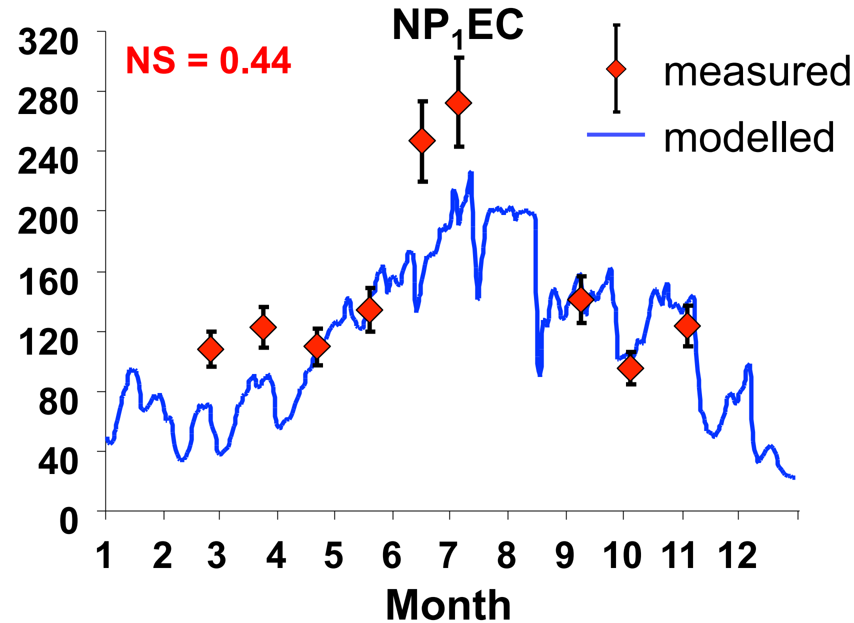
Biogeochemical module: biodegradation of nonylphenolic compounds

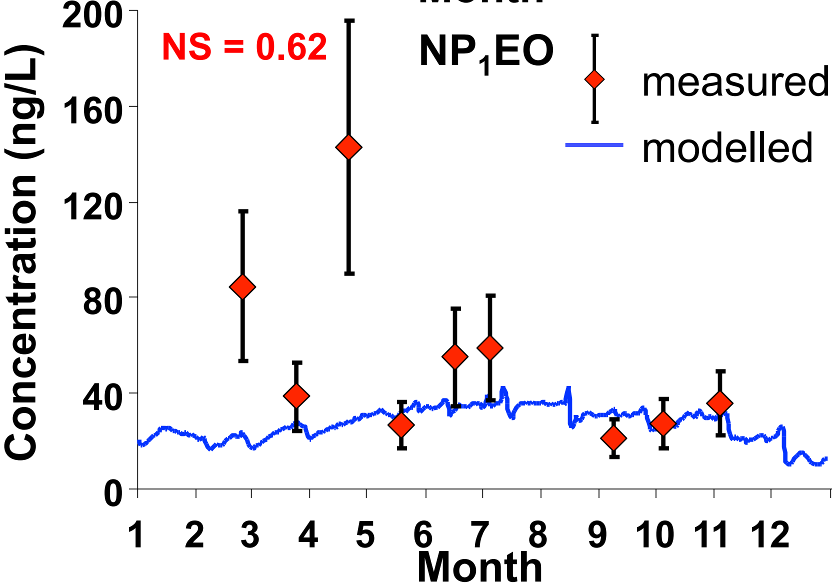


Annual modelling : 2010

Meulan 2010







Good fitting of modelled and measured concentrations

➢ **Validation of method**

Nash-Sutcliffe : $NS = 1 - \left(\frac{\sum \left(C^{\circ}_{Mes} - C^{\circ}_{Sim} \right)^2}{\sum \left(C^{\circ}_{Mes} - C^{\circ}_{Moy} \right)^2} \right)$

Forecast of global change impacts

Assessment of global change scenarios by 2050 and 2100:

Forecast of global change impacts

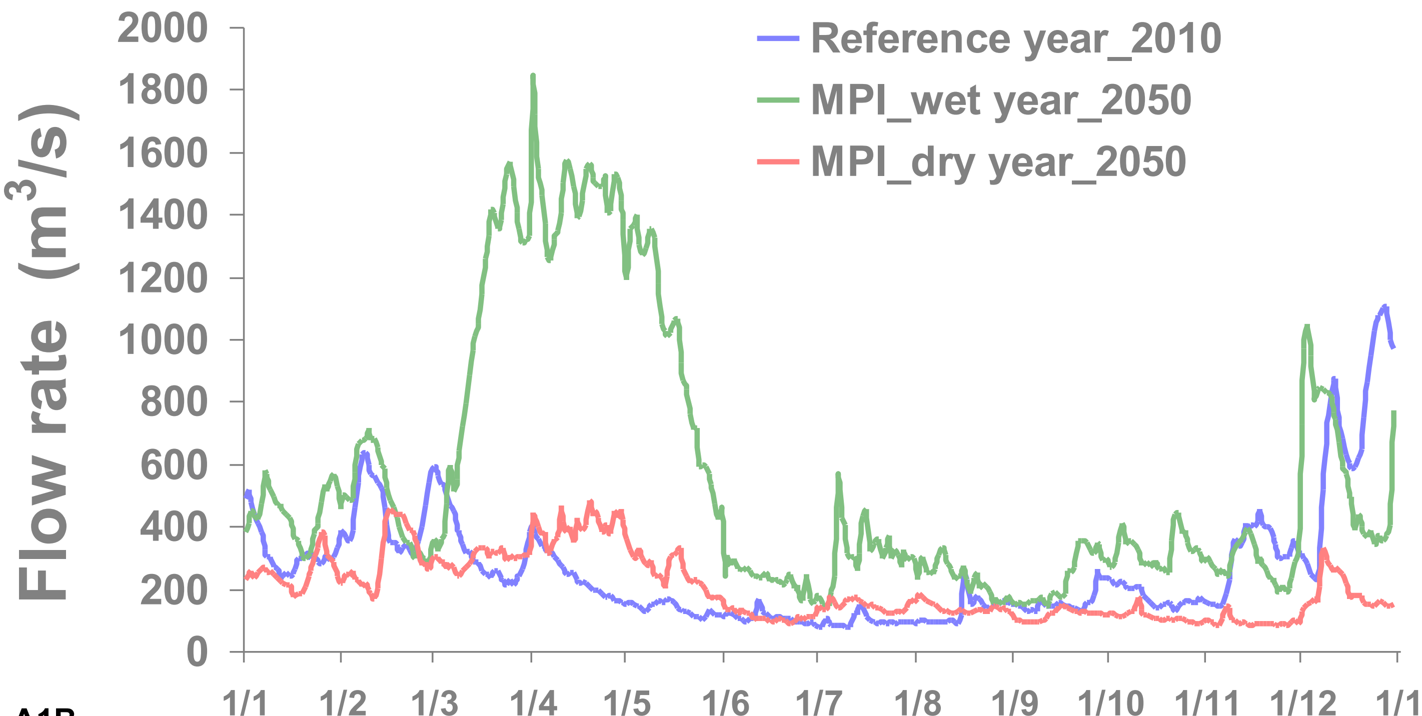
Assessment of global change scenarios by 2050 and 2100:

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

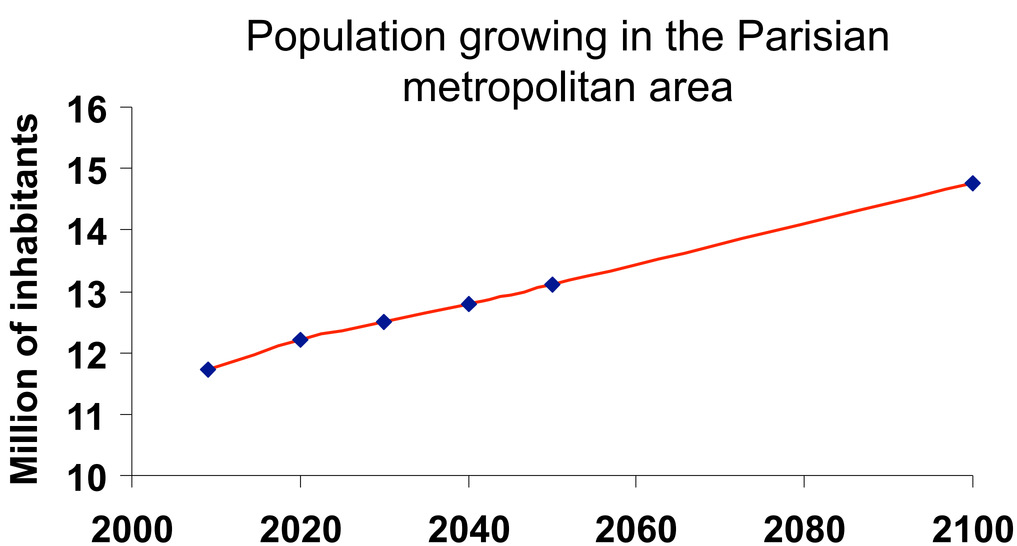
Forecast of global change impacts

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



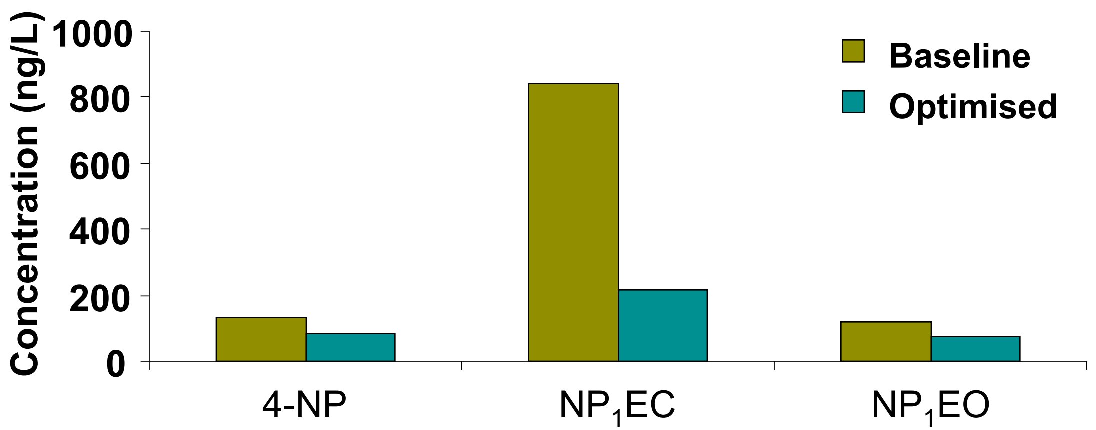
Forecast of global change impacts

Assessment of global change scenarios by 2050 and 2100:

Optimisation of Seine Aval treatment:

Two scenarios :

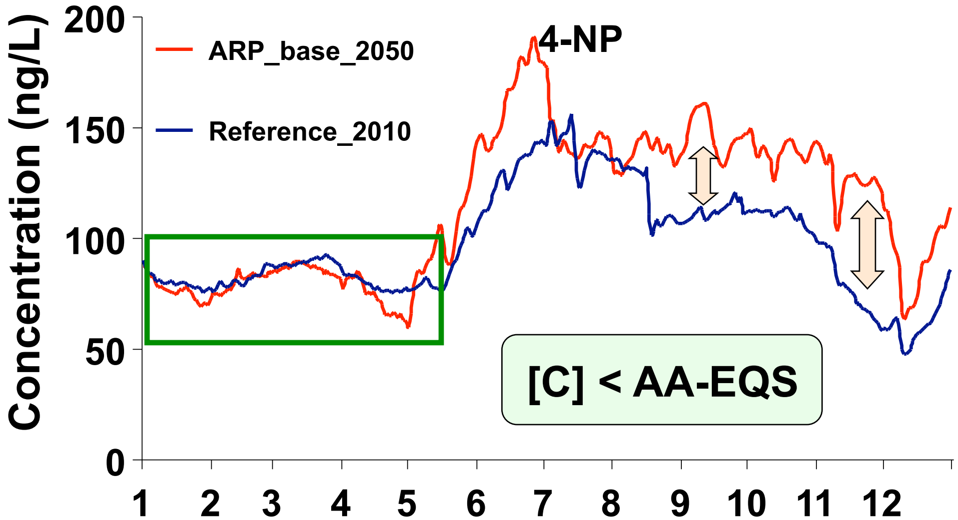
- Baseline (Base) : Seine Aval **non optimised** by 2050
- Optimised (Opt): Seine Aval **optimised** by 2050

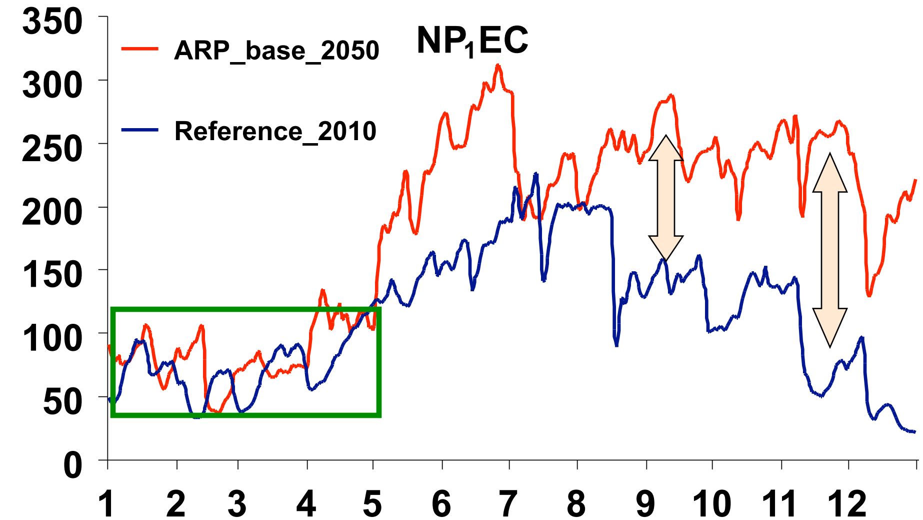


Cladière et al. (2013) ESPR

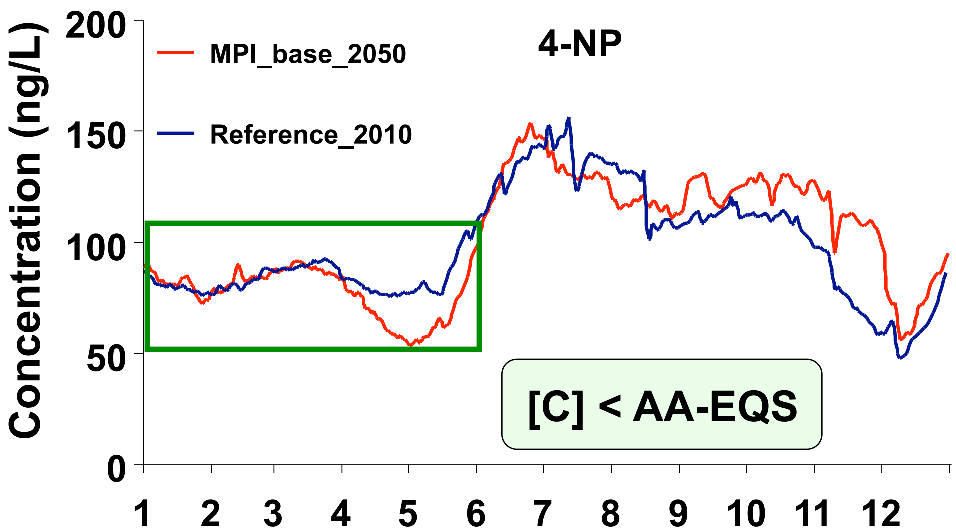
Concentrations at Meulan by 2050

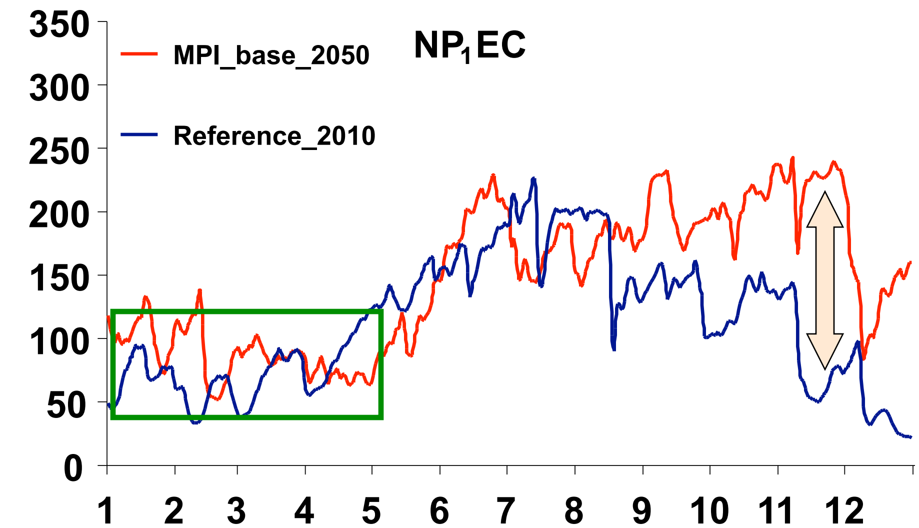
Dry year





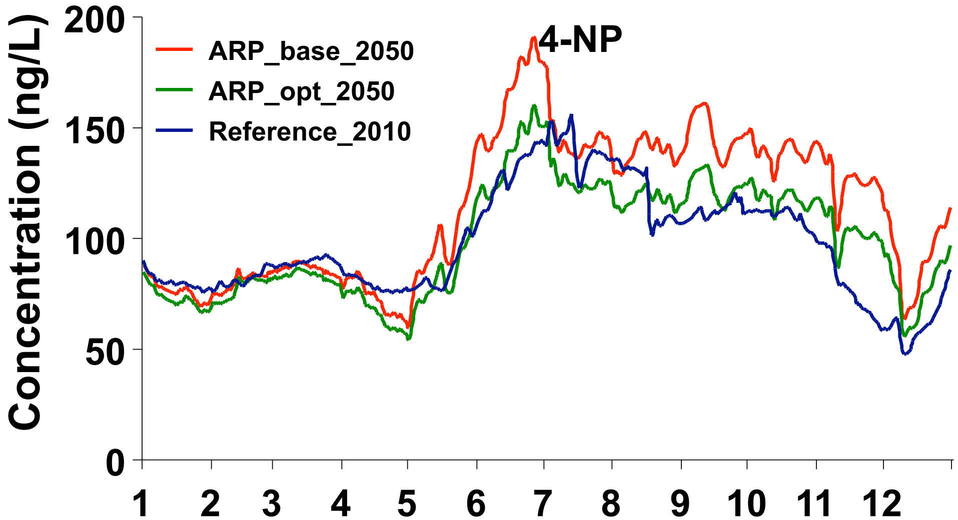
Significant influence of global changes during low-water period (summer, autumn)

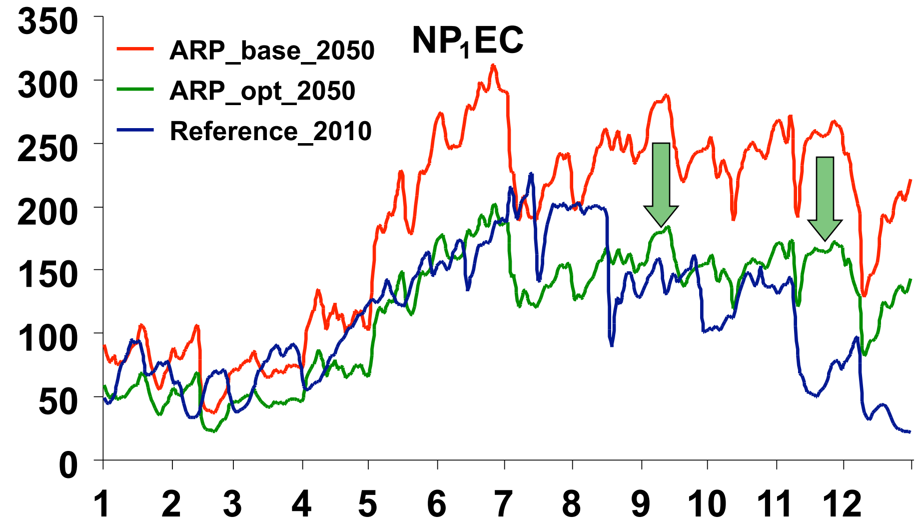




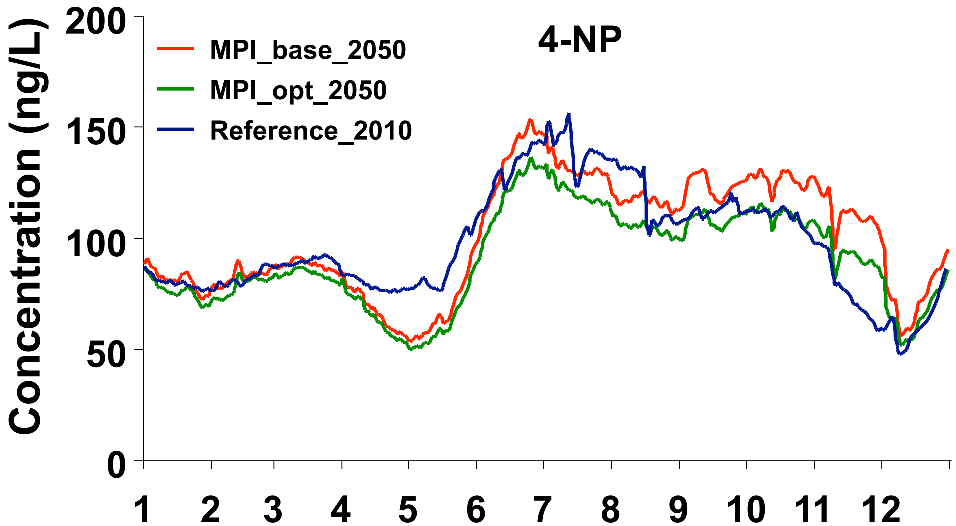
Concentrations at Meulan by 2050

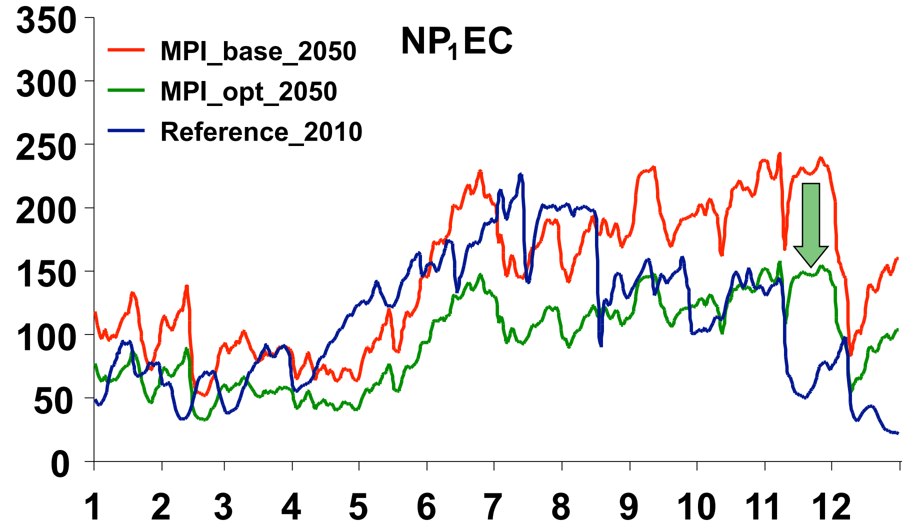
Dry year





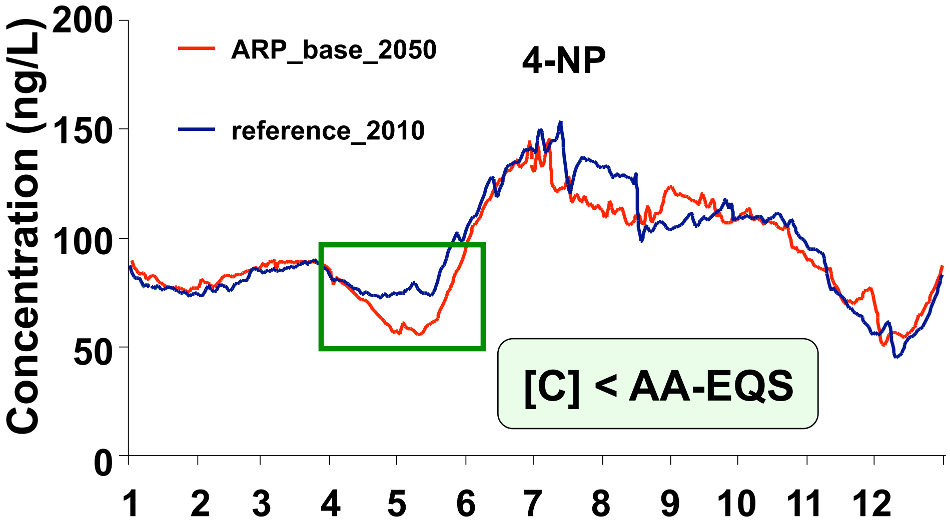
Optimisation of Seine Aval treatment compensate the influence of global changes

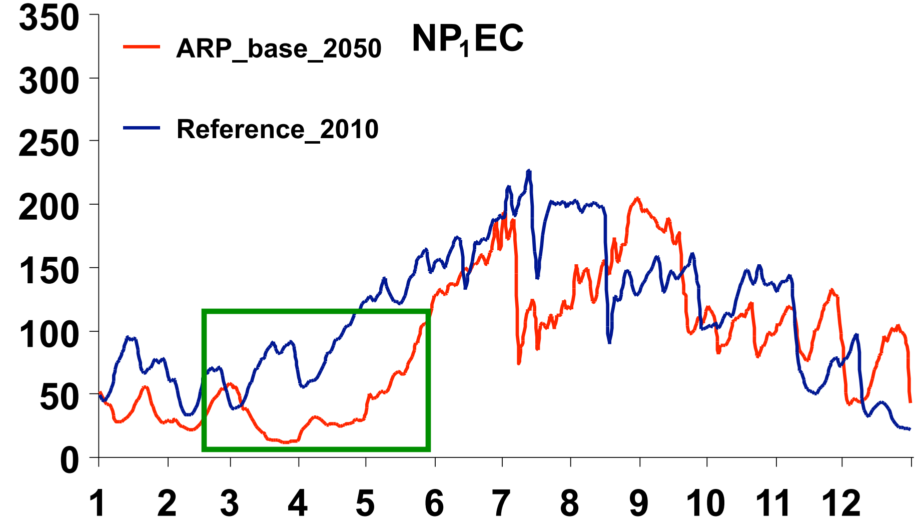




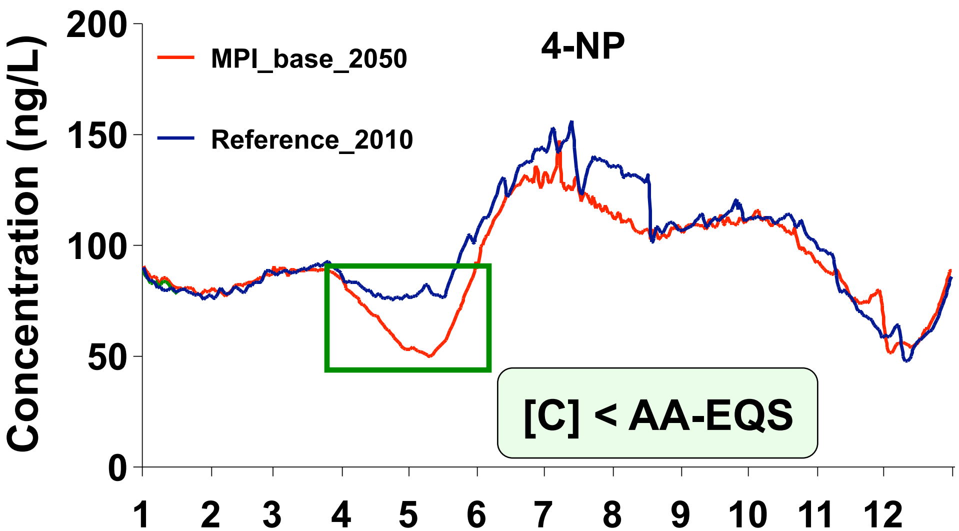
Concentrations at Meulan by 2050

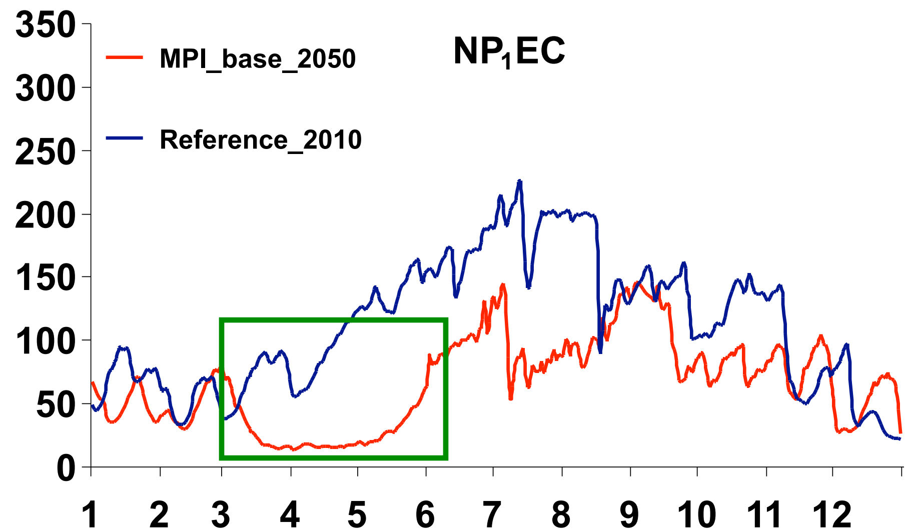
Wet year





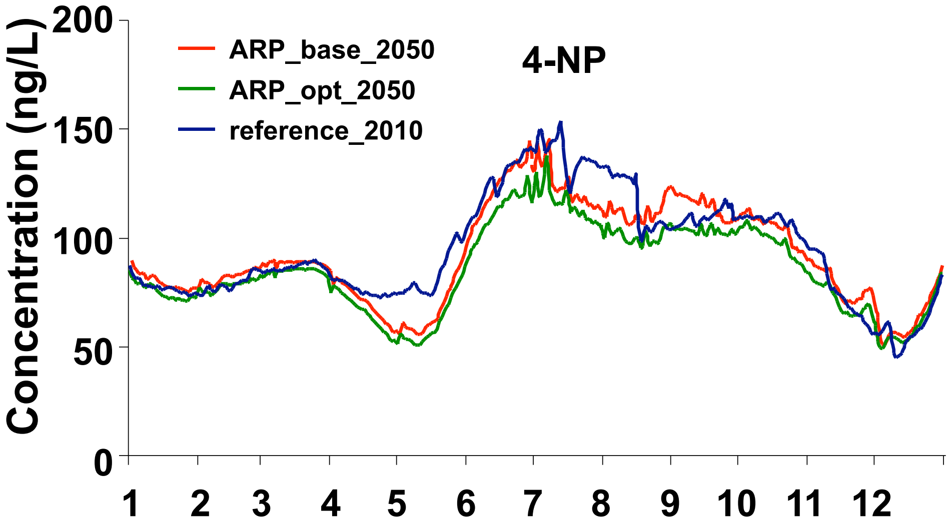
Significant decreases of concentrations in spring because of the river flooding

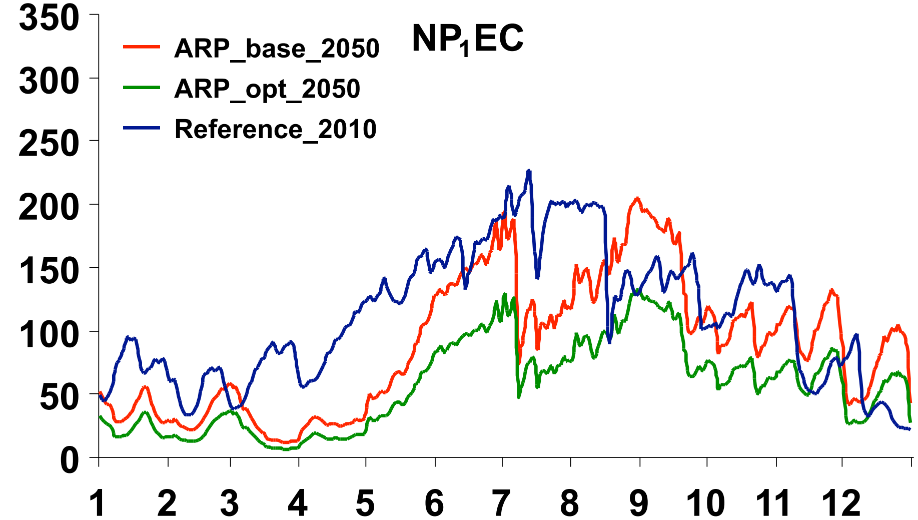




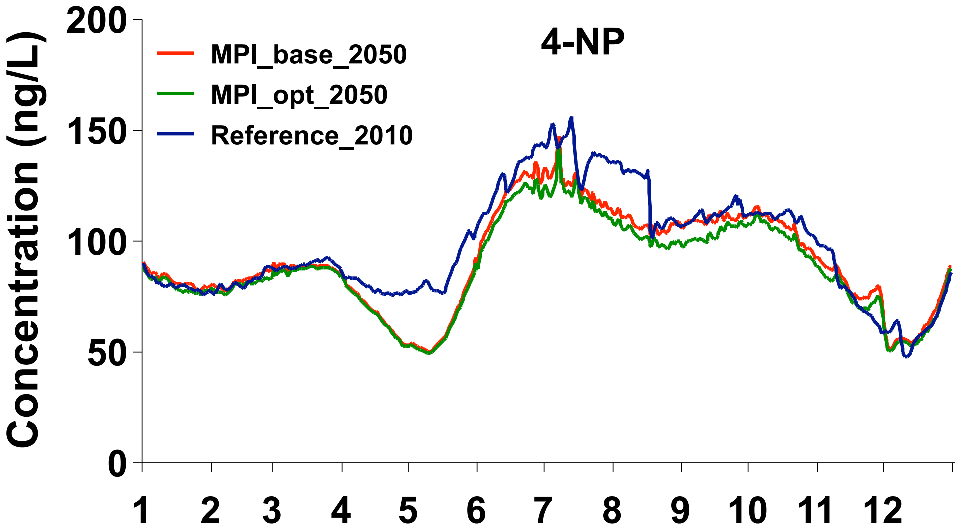
Concentrations at Meulan by 2050

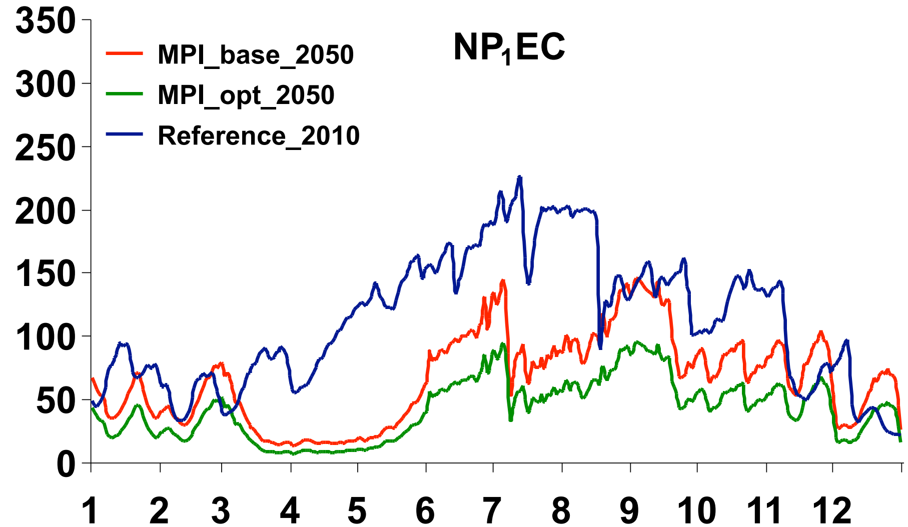
Wet year





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 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 ➔ biodegradation of NP_1EC
- **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

PIREN Seine

leesu

laboratoire eau environnement systemes urbains

MINES ParisTech

Building of Boundary conditions

Daily mean flow

River ➔ National discharge gauging stations

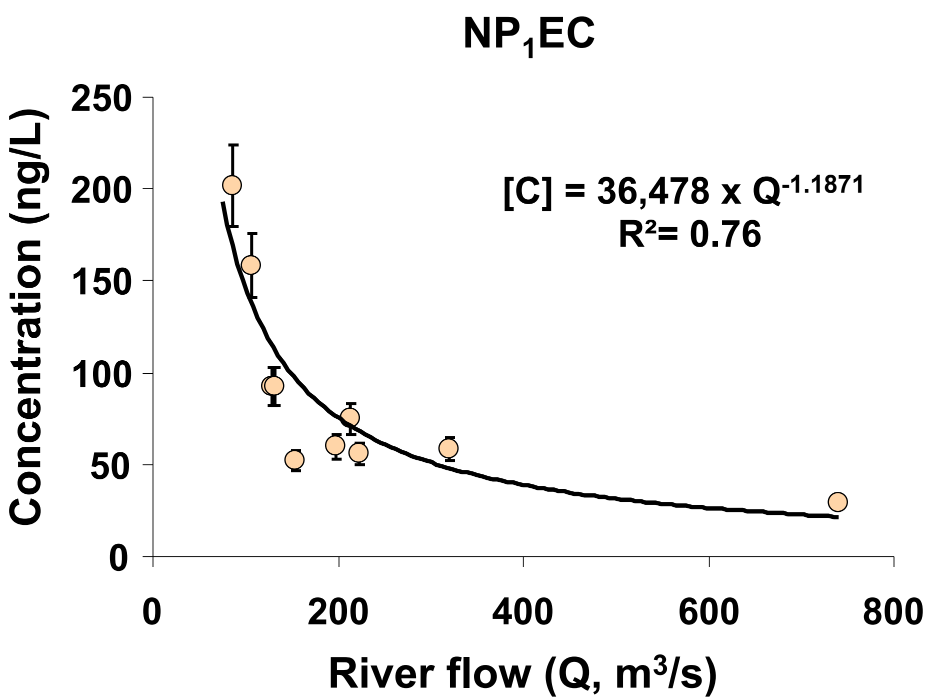
WWTP ➔ Paris public sanitation service (SIAAP)

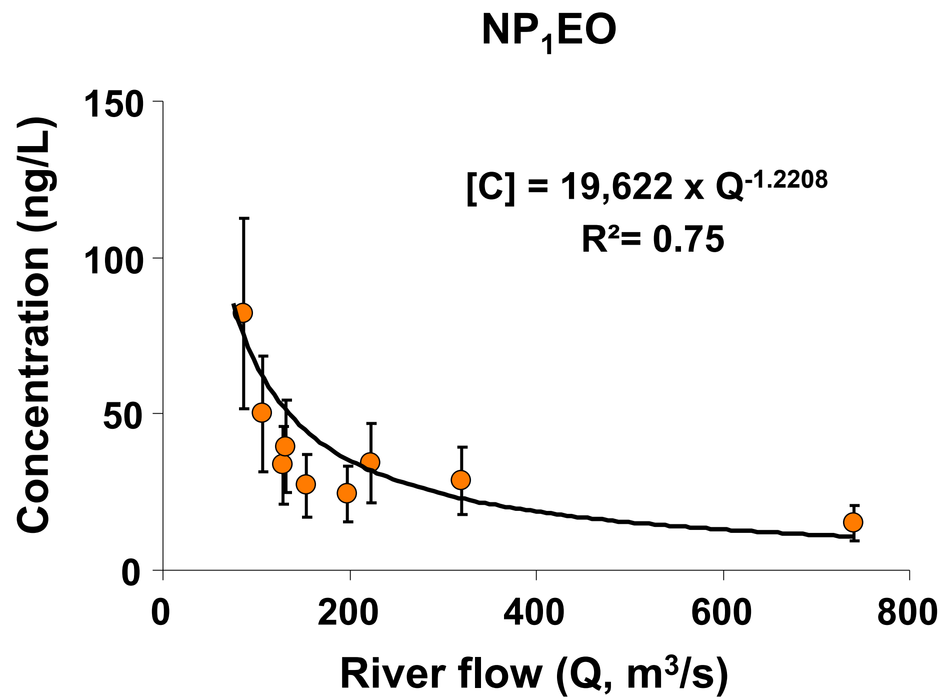
Time series of concentrations

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

WWTP ➔ constant over the year (NP_1EC : 842 ng/L, NP_1EO: 120 ng/L, 4-NP: 133 ng/L)

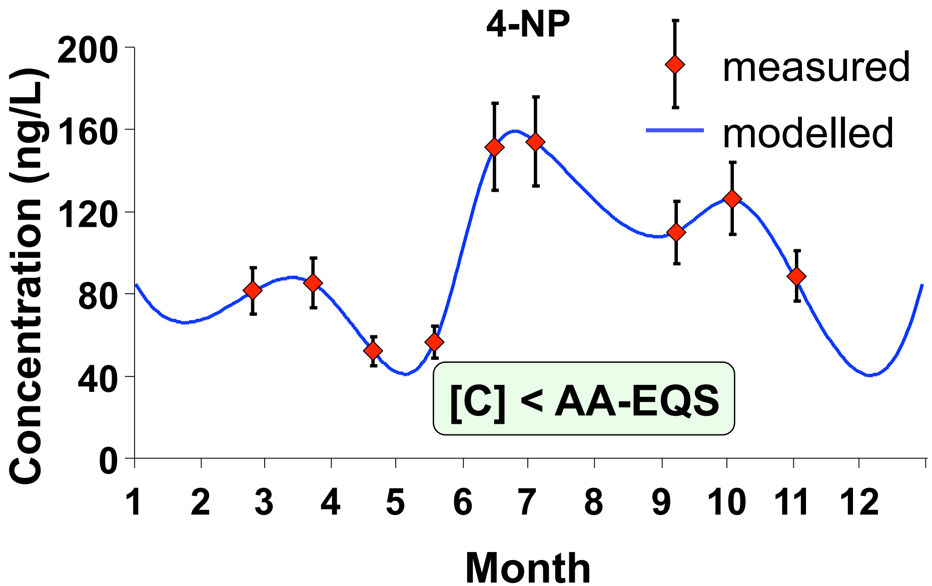
Seine River at Bougival

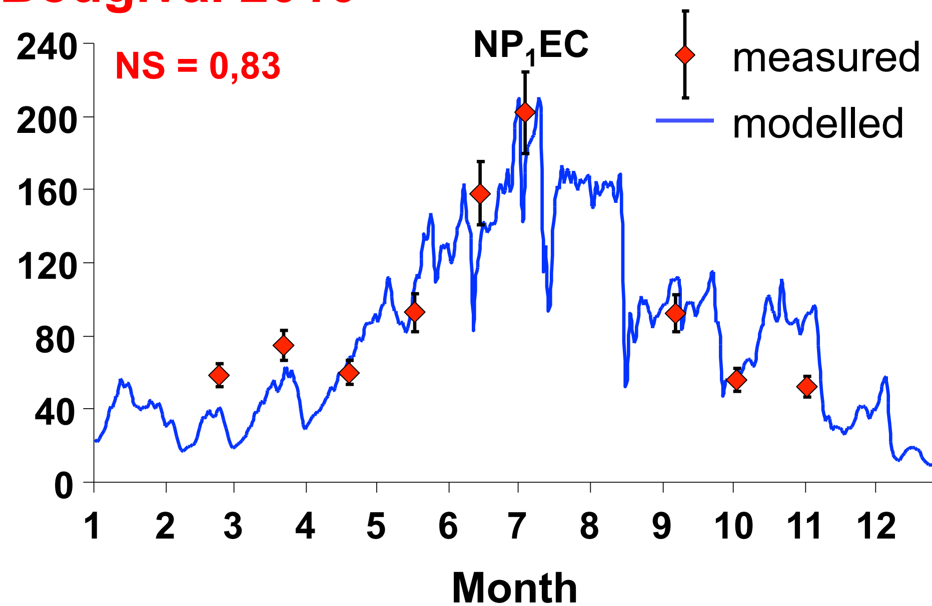


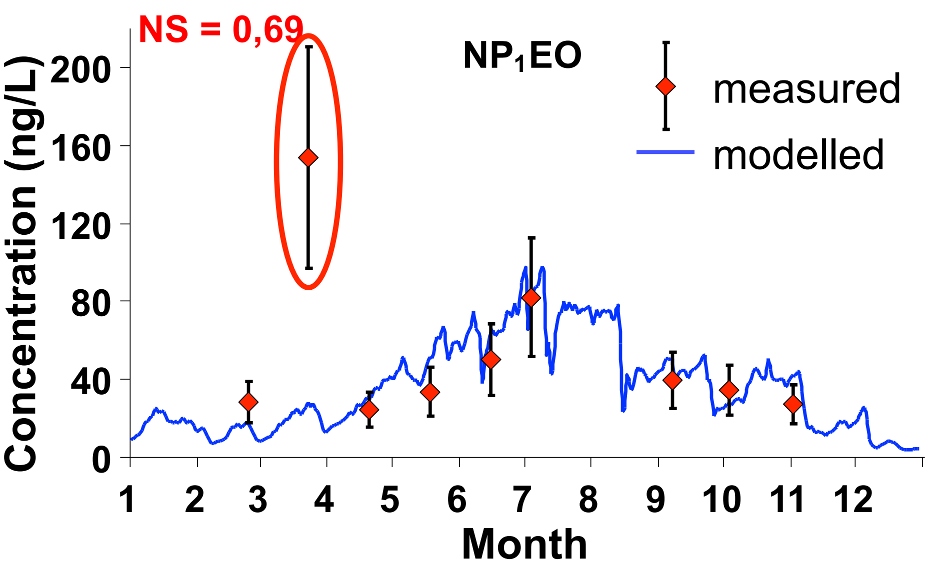


Annual modelling: 2010

Seine River: Bougival 2010







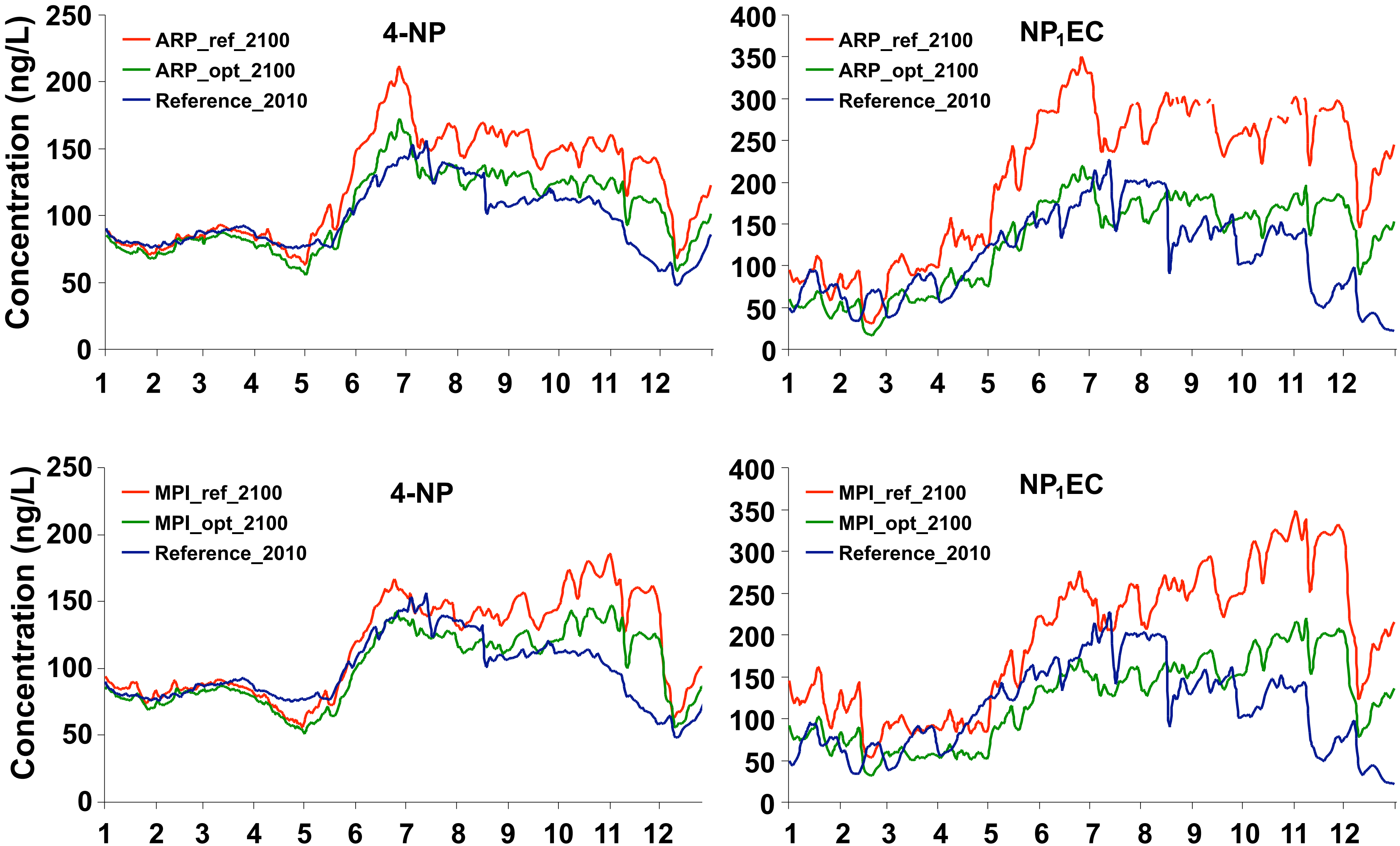
Nash-Sutcliffe : $NS = 1 - \left(\frac{\sum \left(C^{\circ}_{Mes} - C^{\circ}_{Sim} \right)^2}{\sum \left(C^{\circ}_{Mes} - C^{\circ}_{Moy} \right)^2} \right)$

Good fitting
➢ **Validation of boundary conditions**

Limit:
➢ **Wet weather urban sources**

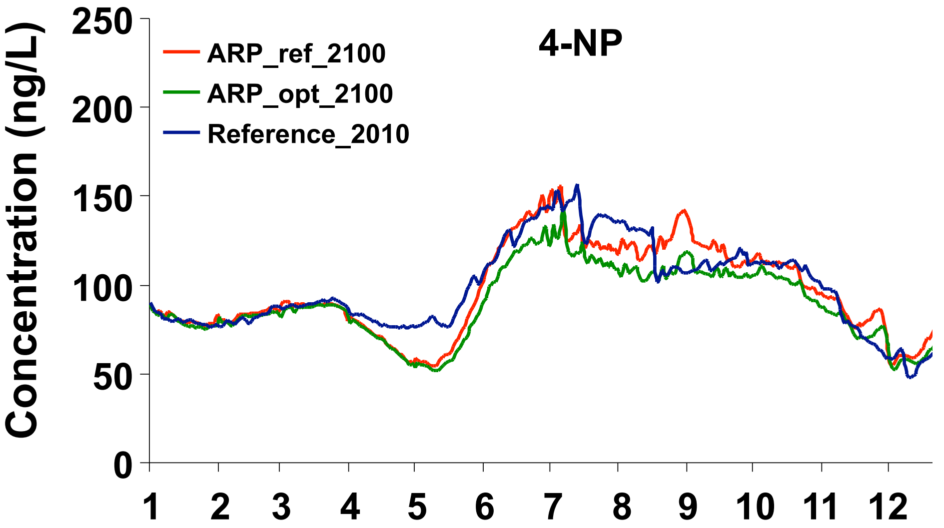
Concentrations at Meulan by 2100

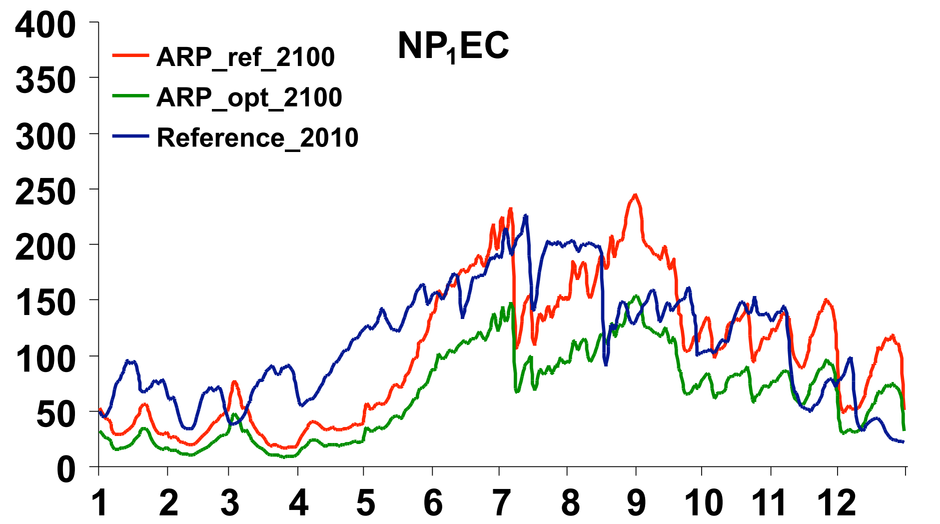
Dry year

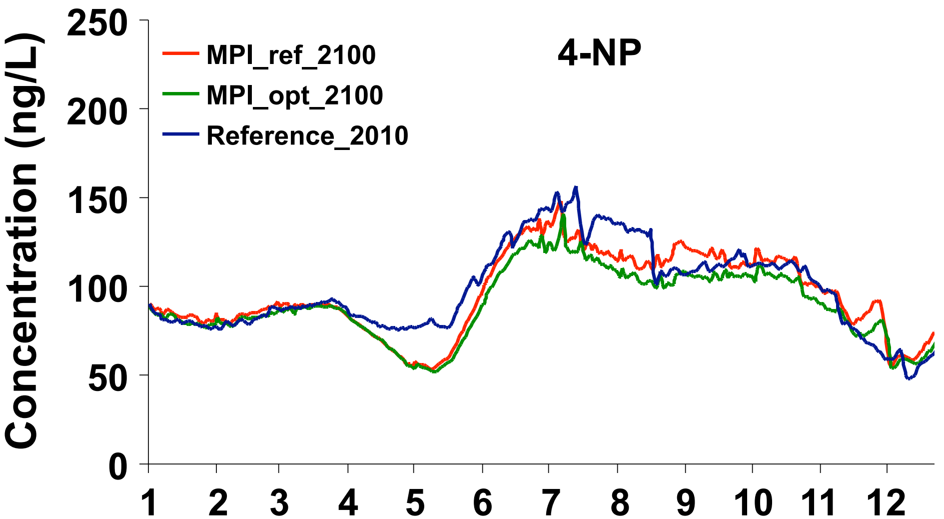


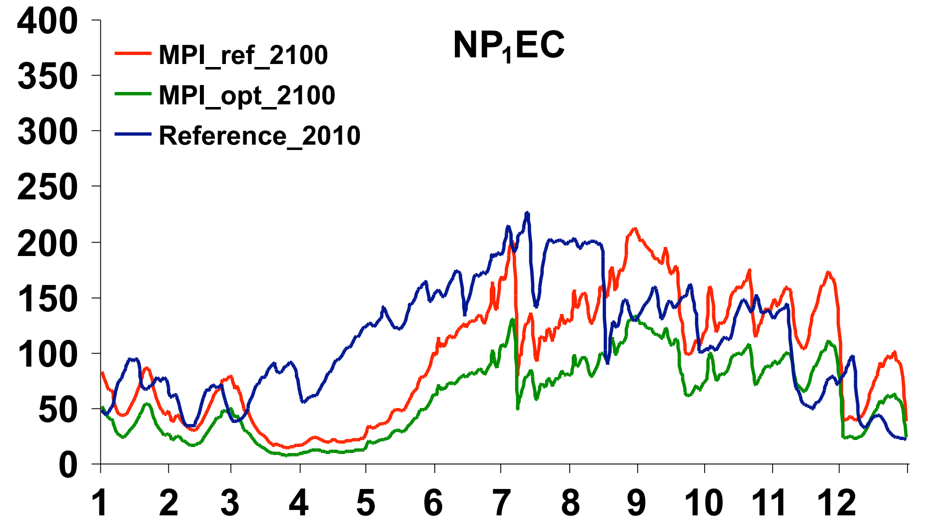
Concentrations at Meulan by 2100

Wet year









Analytical protocol

Sample

Filtration
GF/D (2,7 µm) et GF/F (0,45 µm)

Dissolved phase ← **Extraction surrogate** *(NP_1EO-d2, BPA-d6, OP-d17)*

Extraction (SPE)
OASIS HLB (200 mg/6 ml)
(Gilbert 2011)

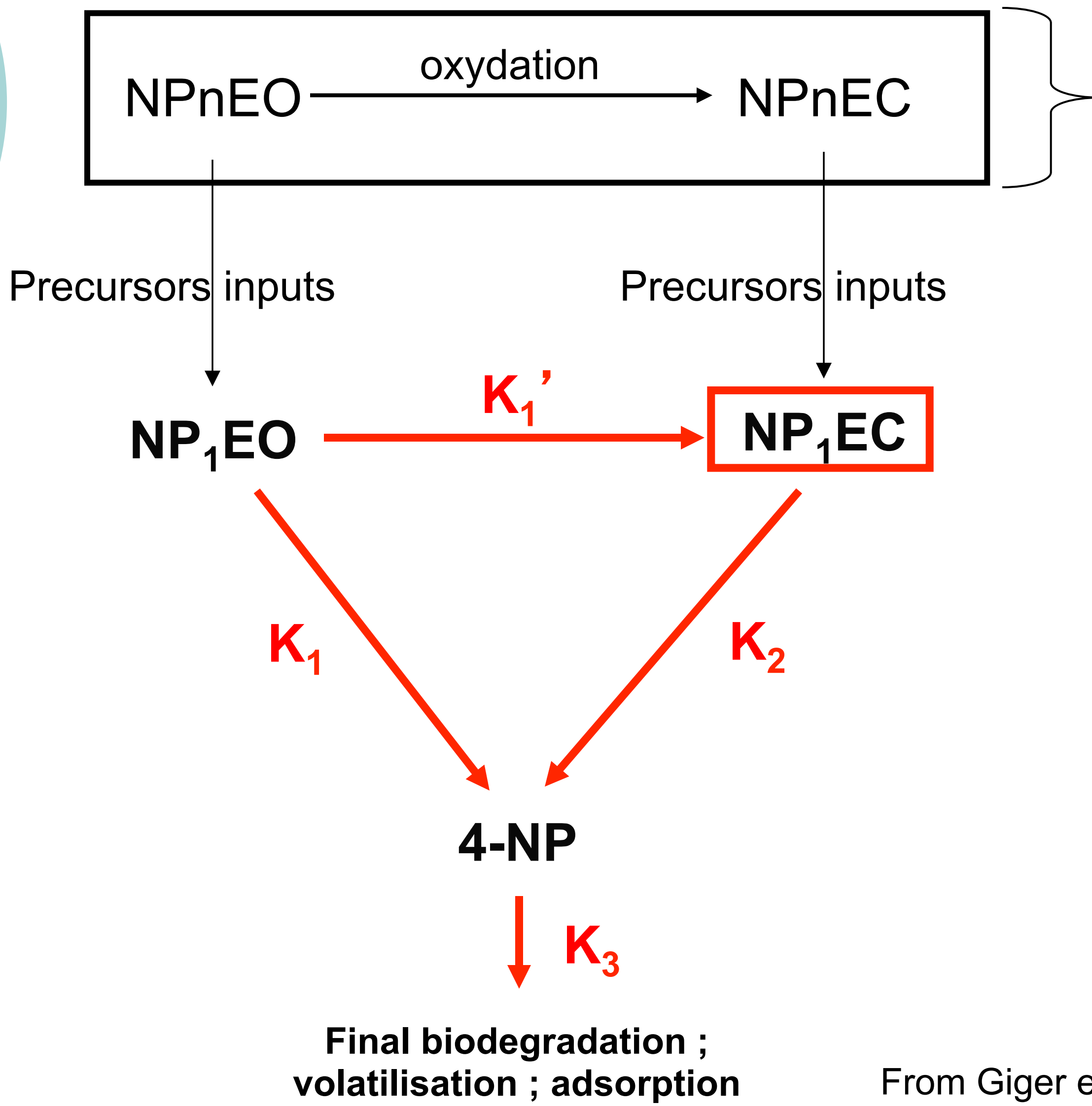
Extract ← **Internal standard** *(BPA-d16, 4-n-NP, 4-n-NP_1EO)*

UPLC-MS-MS

Quantification of: 4-NP, NP_1EO and NP_1EC

Semi-quantitative: $NP_{1-15}EO$

Biodégradation des nonylphénols



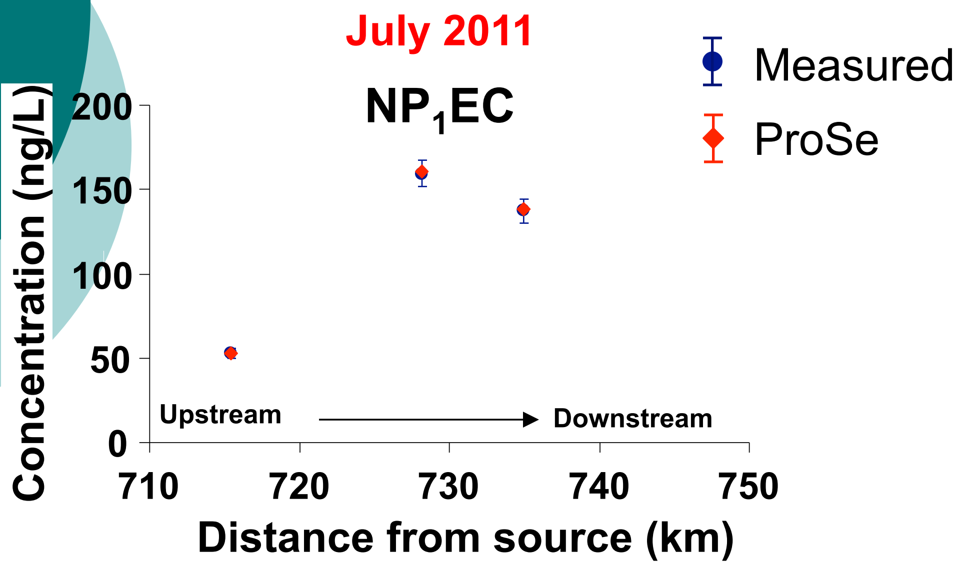
ProSe model : Precursor inputs in the Seine River symbolazing their biodegradation

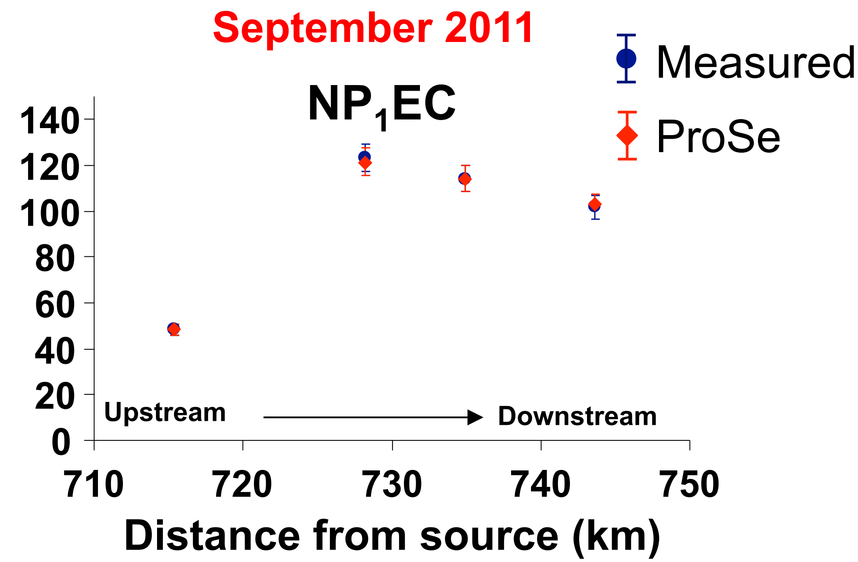
Hypothesis :

- **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

Simulation du linéaire de Seine





Rate constants (d^{-1})	
$K_1 = K'_1$	0.1
K_2	3.3
K_3	2.5

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Rate constants (d^{-1})	
$K_1 = K'_1$	0.3
K_2	0.1
K_3	0.15

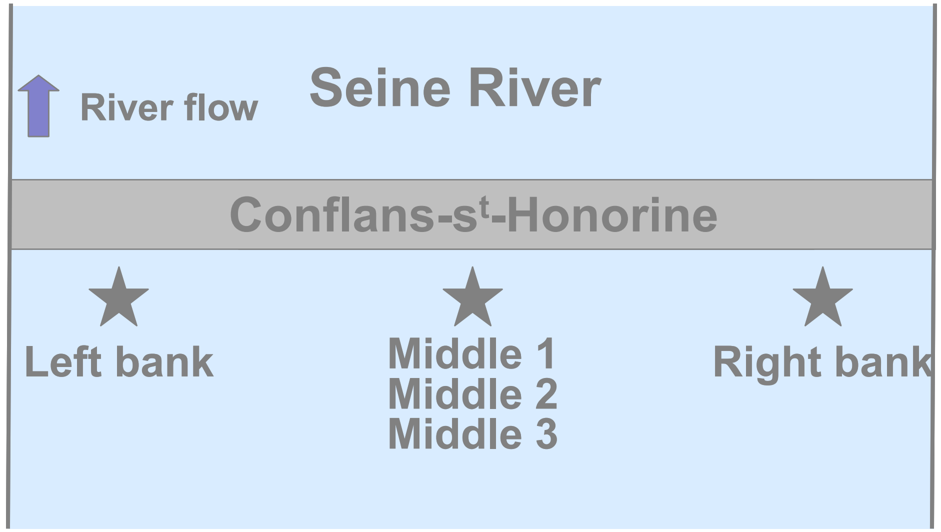
Significant variability of biodegradation rate constants between sampling campagins
➔ July >> September

Influence of biogeochemical conditions of the Seine River

Heteroprophic 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_1EC	4 %	5 %	6 %	**11 %**
NP_1EO	14 %	14 %	23 %	**37 %**

Total variability = spatial variability **+** temporal variability