Ability of polymeric membranes to take into account pollution peaks: Exposure to continuous and discontinuous PAH pollution in pilot river

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Since several years, the Leesu is interested in using polymeric membranes as passive samplers for hydrophobic compounds. The use of single absorbing material is considered as:
- More resistant
- More adjustable (polymere, size...)
- More straightforward in determining constants

Polymeric membranes have already been used in laboratory and in environmental studies (Booij et al., 2002; Rusina et al., 2007; Yates et al., 2007; ......)
It is conventionally recognized that passive samplers allow the quantification of **time-weighted average concentrations** (TWA)

- Large variations of concentrations over time?
- Pollution peaks?

**Integrative sampler = time-weighted average concentration**
Context

- It is conventionally recognized that passive samplers allow the quantification of **time-weighted average concentrations (TWA)**
  - Large variations of concentrations over time?
  - Pollution peaks?

- **Emestox** project funded by ANR:
  - LPTC, Leesu, Irstea, LRSAE, Ifremer, Total
  - Passive samplers for chemical substance monitoring and associated toxicity assessment in water and industrial effluents
    - Optimisation and comparison of different passive samplers (SPMD, POCIS, polymeric membranes...)
    - Assessment of the performances of each tool
Aims of this presentation

(i) to show if polymeric membranes are reliable to quantify micropollutants in the receiving environment by comparing: - the actual exposure concentration
  - the mean concentration estimated by the sampler

(ii) to understand how polymeric membranes assimilate a concentration that varies over time
Materiel and Methods
Materiel and Methods

- Membrane preparation and analysis
  - LDPE (28 cm * 2 cm * 50 µm) and PDMS (15 cm * 2 cm * 500 µm)

Clean up heptane / ethylacetate → Clean up ultrapure water → Spiking with PRC methanol / water → Clean up ultrapure water

2 lab blanks

Exposure

2 field blanks

Dialysis heptane / ethylacetate

GC/MS analysis
Materiel and Methods

- Calcul of available water concentration
  - First order kinetic model

\[
C_w = \frac{C_s}{K_{sw}} \left(1 - \exp\left[-\frac{R_{field} t}{K_{sw} V_s}ight]\right)
\]
Materiel and Methods

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\[ C_W = \frac{C_s}{K_{SW}} \left[ 1 - \exp \left( - \frac{R_{field} K_{comp} t}{K_{SW} V_s} \right) \right] \]

- Lab calibration: simultaneous monitoring of adsorption and desorption in closed pilot

Cf. poster IPSW 2013 Lorgeoux et al.
Materiel and Methods

- Calcul of available water concentration
  - First order kinetic model
    \[
    C_w = \frac{C_s}{1 - \exp\left(-\frac{R_{s\text{comp}}^\text{field} \cdot t}{K_{sw} V_s}\right)}
    \]

- Lab calibration: simultaneous monitoring of adsorption and desorption in closed pilot

- Correction of R_s in situ
  - Desorption of PRC
    \[
    k_{ePRC}^{\text{field}} = -\frac{\ln(C_{PRC}(t)/C_{PRC}(0))}{t}
    \]

- Correction of R_s
  \[
  \frac{R_{s\text{PRC}}^\text{field}}{R_{s\text{comp}}^\text{field}} = \frac{R_{s\text{PRC}}^\text{lab}}{R_{s\text{comp}}^\text{lab}}
  \]

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Materiel and Methods

- Exposure conditions
  - Artificial streams developed in Lacq bypassing the river Gave (TOTAL)
    - Length: 40 m, height: 20-30 cm, speed: 2 cm.s⁻¹
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    ○ Length: 40 m, height: 20-30 cm, speed: 2 cm.s⁻¹
  ● Injection of anthracene, chrysene and benzo[a]pyrene
    ○ EQS level and 1/3 of EQS level
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  - 3 scenarii
    - **Chronic pollution**: continuous injection

![Chronic pollution](image-url)
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    - Chronic pollution: continuous injection
    - Accidental pollution: injection of PAHs in the river during the first 3 days of the 21-day exposure
    - Discontinuous pollution: injection of PAHs during 3 periods of 3 days separated by 4 days
Results and discussion
Chronic pollution: continuous injection

- PRC desorption in LDPE

- Desorption of PRC over time in a first order kinetics
- Equilibrium is not reached after 21 days
- The speed of the kinetics decreases with the hydrophobicity of the compounds

**Anthracene D10** chosen as PRC to correct kinetic parameters

=> losses >30 % for each time
Chronic pollution: continuous injection

○ Compound adsorption in LDPE

- **Anthracene**
  - EQS
  - 1/3 EQS
  - PAH accumulation: First order kinetics

- **Chrysene**
  - EQS
  - 1/3 EQS
  - Equilibrium seems to be reached for LMW substances

- **Benzo[a]pyrene**
  - EQS
  - 1/3 EQS
  - Accumulated quantities are 3 times higher for EQS than for 1/3 EQS
Chronic pollution: continuous injection

- Dissolved (--) concentration

![Graphs showing dissolved concentrations of Anthracene, Benzo[a]pyrene, and Chrysene over time (d) with EQS and 1/3 EQS levels.](image-url)
Chronic pollution: continuous injection

- Dissolved (---) concentration vs. LDPE available (●▲) concentration -

**Anthracene**
- Relatively constant concentrations over time
- Ratio $\text{EQS}/(1/3\text{EQS}) = 3 \pm 0.3$
  
**Chrysene**
  
**Benzo[a]pyrene**
  
But
- Low decrease at $t = 21$ days => equilibrium?
Chronic pollution: continuous injection

- Dissolved (---) concentration vs. LDPE available (▲) concentration - Percentage of labile fraction

- Relatively constant concentrations over time
- Ratio $\text{EQS}/(1/3\text{EQS}) = 3 \pm 0.3$

But

- Low decrease at $t = 21$ days => equilibrium?
- Overestimation of labile fraction

- LDPE is reliable to integrate chronic pollution
- Need to adjust the calibration
Accidental pollution: 3 days injection

- Integrated average dissolved concentration (▲)

![Anthracene](image1)

![Chrysene](image2)

![Benzo[a]pyrene](image3)
Accidental pollution: 3 days injection

- Integrated average dissolved concentration (---) vs. LDPE available (●) concentration

- Concentration peak observed at the 7th day
- Decrease during the last 14 days
Accidental pollution: 3 days injection

- Integrated average dissolved concentration (---) vs. LDPE available (●) concentration - Percentage of labile fraction

- Concentration peak observed at the 7th day
- Decrease during the last 14 days

- Chrysene, benzo[a]pyrene: Same percentage of labile fraction at t=7 and 21 days
- Anthracene: Disappearance of contamination at the 21st day => low molecular weight

- LDPE is reliable to integrate accidental pollution for HMW substances
- For LMW substances: no memory of the contamination after 14 days
Discontinuous pollution: 3*3 days injection

- Integrated average dissolved concentration (△) vs. LDPE available (●) concentration.

- Increase of concentrations after injection
- Decrease of concentrations without injection
Discontinuous pollution: 3*3 days injection

- Integrated average dissolved concentration (●) vs. LDPE available (△) concentration - Percentage of labile fraction

- Increase of concentrations after injection
- Decrease of concentrations without injection

- Percentage of labile fraction: constant over time => Successful integration of the discontinuous pollution

- LDPE is reliable to integrate discontinuous pollution
- Overestimation of the labile fraction for HMW substances: need to adjust calibration
LDPE/PDMS comparison (1)
Exchanges are slower in the PDMS. Equilibrium is reached more quickly for LDPE.
LDPE/PDMS comparison (2)

- Discontinuous scenario

**LDPE**

**Anthracene**

- Graph showing concentration (C) in ng/L over time (d) ranging from 0 to 25 days.

**Benzo[a]pyrene**

- Graph showing concentration (C) in ng/L over time (d) ranging from 0 to 25 days.

**PDMS**

**Anthracene**

- Graph showing concentration (C) in ng/L over time (d) ranging from 0 to 25 days.

**Benzo[a]pyrene**

- Graph showing concentration (C) in ng/L over time (d) ranging from 0 to 25 days.
Comparison of the different scenarios

LDPE-TWA at 21 days

- TWA dissolved conc.
- Continuous at NQE
- Continuous at 1/3 NQE*3
- Accidental at NQE
- Discontinuous at NQE
- Discontinuous at 1/3 NQE*3

Low molecular compounds: Underestimation of pollution peaks, no memory of the contamination after 14 days
Comparison of the different scenarios

LDPE-TWA at 21 days

Low molecular compounds: Underestimation of pollution peaks, no memory of the contamination after 14 days

High molecular compounds: Overestimation in the case of alternating contamination / no contamination
Comparison of the different scenarios

Similar results have been highlighted in PDMS and LDPE
Comparison of the different scenarios

PDMS-TWA at 21 days

Similar results have been highlighted in PDMS and LDPE

After 21 days of exposure, membranes are available to give an evaluation of TWA concentration
- Underestimation for LMW compounds: case of a short pollution peak
- Overestimation for HMW compounds: case of discontinuous pollution
Conclusion and outlook
Conclusion

LDPE and PDMS membranes are **reliable to quantify micropollutants** in the receiving environment:
- The use of PRC allows the correction of exposure conditions
- Good correspondence between dissolved and membrane-available measures
- Calibration to optimize

LDPE and PDMS membranes **integrate time-variation** of concentrations:
- Pollution peaks just for HMW compounds
- Discontinuous pollution

**Underestimation** of pollution peaks: no memory of the contamination after 14 days for LMW compounds
**Small overestimation** in the case of alternating contamination / no contamination for HMW compounds

Membrane-available fraction is not stable
Stability of injection, SS, DOM? Correction of PRCs?
Outlooks

- Understanding and improving the **calibration**

- **Modeling** the theoretical behaviour of membranes
  - Compare with measures

- Investigating the validity of the model in **presence of interfering**: Other scenarios have been tested
  - Injection of a **mixture of substances** (PAH, pesticides, AP...)
  - Injection of an **industrial effluent**

- The same work has been done for **alkylphenols**
  - Kinetics are too fast in LDPE
  - Promising results in PDMS
Thank you for your attention

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