Impact of pharmaceuticals discharges on the receiving environment: a two years monitoring results

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TRACES Group
Technology and Research in Analytical Chemistry for Environment, health and their interactionS

Laure Wiest, Alexandre Bergé, Robert Baudot and Emmanuelle Vulliet
The SIPIBEL Site

- In 2012, opening of a new hospital: the Alps-Léman Hospital Center (CHAL)
- WW discharged into the Arve river
The SIPIBEL Site

• A field observatory
  • Seven sampling sites
  • 130 parameters

• Research actions
  • Pollutant flows
  • Treatment
  • Risk
  • Sociology
The SIPIBEL Observatory

450 beds

30,000 habitants

www.sipibel.org
The SIPIBEL Observatory

• **Physico-chemistry**
  • 5-day biochemical oxygen demand (BOD$_5$), chemical oxygen demand (COD), conductivity, dissolved organic carbon (DOC), pH, total suspended solids (TSS), total phosphorus (TP), phosphates (PO$_4^{3-}$), kjenahl nitrogen (TKN), ammonium (NH$_4^+$), adsorbable organic halogen (AOX)

• **Emerging compounds**
  • Pharmaceuticals

• **Microbiology**
  • Bacterial resistance to antibiotics

• **Bioassays**
  • Microalgae, microcrustacean
  • Endocrine disruptor
## Pharmaceuticals Selection

- A list of 62 compounds
  - Hospital consumption
  - Domestic consumption
  - PBT Index

- A list of 35 compounds
  - Analytical feasibility

- A list of 15 compounds
  - Economical feasibility

<table>
<thead>
<tr>
<th>MOLECULE CONSOMME CHAL</th>
<th>DOSABLE / EAU DOSABLE / ORGANISMES</th>
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<tr>
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<td>7 ATÉNOLOL</td>
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<tr>
<td>9 AZTREONAM</td>
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<td>59 TELITHROMYCINE</td>
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<td>62 VANCOMYCINE</td>
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Pharmaceuticals List

**Analgesic**
- Paracetamol
- Salicylic Acid

**Anti-inflammatory**
- Ketoprofen
- Diclofenac
- Ibuprofen

**Beta-blocker**
- Atenolol
- Propranolol

**Anti-fungal**: Econazole

**Hormone**: Ethinylestradiol

**Anti-convulsant**: Carbamazepine

**Antibiotic**
- Sulfamethoxazole
- Ciprofloxacin
- Aztreonam
- Meropenem
- Vancomycin
Analytical Method Sensitivity

Wastewater

Surface water
Raw wastewater

Domestic vs Hospital
Domestic Wastewater

Detection frequency

- Diclofenac
- Propranolol
- Carbamazepine
- Atenolol
- Sulfamethoxazole
- Ibuprofen
- Ketoprofen
- Ciprofloxacin
- Paracetamol
- Econazole (particular phase)

Concentration (μg/L)

Not detected:
- Ethinylestradiol
- Meropenem
- Aztreonam
- Vancomycin
Hospital Wastewater

Detection frequency

Diclofenac
Propranolol
Carbamazepine

Atenolol
Salicylic acid
Ibuprofen

Sulfamethoxazole
Ketoprofen

Ciprofloxacin
Paracetamol

Vancomycin

Econazole (particular phase)

> 70 %

30 à 70 %

Concentration (μg/L)

Not detected:
* Ethinylestradiol
* Meropenem
* Aztreonam
Raw WW: Concentrations

Concentrations (µg/L)

- Ketoprofen
- Ciprofloxacin
- Sulfamethoxazole
- Vancomycin

Domestic
Hospital

EWA 18th International Symposium - 2016/06/01
Raw WW: Flows

Concentrations (μg/L)

Flow (g/day)

Domestic
4800 m³/d

Hospital
130 m³/d

Ketoprofen
Ciprofloxacin
Sulfamethoxazole
Vancomycin

Flow (g/day)
Raw WW: Variability

Sulfamethoxazole - Hospital

Sulfamethoxazole - Domestic

Flow (kg/day)

EWA 18th International Symposium - 2016/06/01
### Raw WW: Metabolites

**Diclofenac (DCF)**
- DCF COH
- DCF lactam
- DCF CH₂OH
- CPAB
- Oxindole
- DCF 4’OH
- DCF 5’OH
- DCF carboxylic acid
- DCF glucuronide

**Sulfamethoxazole (SMX)**
- SMX N-acetylated
- SMX glucuronide
- SMX iso
Raw WW: Metabolites

**Diclofenac (DCF)**
- DCF COH
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- DCF CH$_2$OH
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- DCF carboxylic acid
- DCF glucuronide

**Sulfamethoxazole (SMX)**
- SMX N-acetylated
- SMX glucuronide
- SMX iso
Wastewater treatment
Treated Wastewater

Detection frequency

> 70%

Paracetamol
Ibuprofen
Diclofenac
Ketoprofen
Atenolol
Propranolol
Carbamazepine
Sulfamethoxazole

30 à 70 %

Ciprofloxacin
Econazole

Not detected:
* Ethinylestradiol
* Meropenem
* Aztreonam
* Vancomycin
Treated WW: Flows

Flow (g/day)

- Paracetamol
- Ketoprofen
- Diclofenac
- Ibuprofen
- Atenolol
- Propranolol
- Carbamazepine
- Ciprofloxacin
- Sulfamethoxazole
Removal efficiency

Removal (%)

- Domestic
- Hospital

Removal efficiency for various medications:

- Paracetamol
- Salicylic acid
- Ketoprofen
- Diclofenac
- Ibuprofen
- Atenolol
- Propranolol
- Carbamazepine
- Ciprofloxacin
- Sulfamethoxazole
Removal efficiency: variability

Domestic WW Treatment

Diclofenac

Ibuprofen
Removal efficiency: variability

Hospital WW Treatment

Diclofenac
Ibuprofen
Surface water
Arve Upstream

Detection Frequency (%)

Propranolol
Sulfamethoxazole
Salicylic acid
Econazole
Ciprofloxacin
Diclofenac
Carbamazepine
Ketoprofen
Ibuprofen
Atenolol
Paracetamol

Not detected:
* Ethinylestradiol
* Hospital antibiotics

Concentration (ng/L)
Arve Downstream
Arve: a ressource for Human consumption

Groundwater surface

France-Switzerland border

SIPIBEL Observatory

France-Switzerland border
Arve: a ressource for Human consumption

- **Sulfamethoxazole (6/7)**, quantified (5/7) between 1.8 et 2.6 ng/L (LOQ: 1.7)
- **Salicylic Acid (3/7)**
- **Sulfamethoxazole (6/6)**, quantified (6/6) between 1.9 and 2.8 ng/L
- **Salicylic Acid (3/6)**
- **Carbamazepine (5/6)** quantified (4/6) between 0.5 et 1.7 ng/L (LOQ: 0.3)
- **Sulfamethoxazole (3/7)**
- **Paracetamol (3/7)**
Conclusions
And Perspectives....
Conclusions

- **Large scale of time and space consolidated data**
  - Raw and treated Wastewater, Surface water and groundwater
  - Two years monitoring

- **Hospital vs Domestic Wastewaters**
  - Hospital > Domestic in terms of concentrations
  - Hospital < Domestic in terms of flows

- **Mean removal efficiencies >50 %**
  - except Diclofenac and Carbamazepine

- **Surface water and groundwater contamination in the ng/L range**
Perspectives

- Evolution of the list of Pharmaceuticals
- Activated sludge analysis
- Statistical correlation between parameters

- Perspectives of the SIPIBEL observatory
  - Survey of Pharmaceuticals until at least 2018
  - New projects?
Acknowledgments

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  www.isa-lyon.fr

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