Micropollutants in sludge deposits of French Vertical Flow Constructed Wetlands treating domestic wastewater

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CWs for domestic wastewater treatment

The most used raw domestic wastewater treatment for small communities in France (< 2000 Population Equivalent)

CONSTRUCTED WETLANDS

Number of constructed wetlands in France*

*Molle, 2012; Bellin, 2016
Functioning of French VFCWs

Wastewater

Biological pretreatment by trickling filter

Surface sludge deposit

P treatment by FeCl₃ injection

PAH
PESTICIDES
ALKYLPHENOLS
PPCPs
Objectives

- Recent interest for the micropollutants
- In constructed wetlands: Many studies focus on 24h input-output balance on the wastewater
Objectives

PRELIMINARY INVESTIGATION

PPCPs

SLUDGE DEPOSIT

Surfactants

Screening in limited number of sludge deposits

Target micropollutants
Characteristics of Pharmaceutical and Personal Care Products

**Betablocker**
- Propranolol
- Atenolol

**Antidepressant**
- Carbamazépine

**Antibiotic**
- Sulfamethaxazole
- Ibuprofen
- Paracetamol
- Salicylic Acid
- Ethinylestradiol
- Ketoprofen
- Diclofenac
- Ciprofloxacine

**Antifongic**
- Econazole
Characteristics of surfactants

- **cationic**
  - Amine Hydrochloride
  - Quaternary ammonium

- **anionic**
  - Alkylsulfates
  - Alkylsulfonates
  - Alkylarylsulfates

- **non-ionic**
  - Hydroxyles
  - Fatty Alcohol

- **ionic**
  - Betains
  - Polypeptides

- **zwitterionic**
  - betaine

**Surfactants**
Description of the selected VFCWs

Domestic wastewater
### Description of the selected VFCWs

<table>
<thead>
<tr>
<th>BAG1</th>
<th>BAY</th>
<th>VER</th>
<th>COR</th>
<th>MAT</th>
</tr>
</thead>
<tbody>
<tr>
<td>![BAG1 Image]</td>
<td>![BAY Image]</td>
<td>![VER Image]</td>
<td>![COR Image]</td>
<td>![MAT Image]</td>
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</tbody>
</table>

<table>
<thead>
<tr>
<th>PROCESS</th>
<th>POPULATION EQUIVALENT</th>
<th>YEAR OF IMPLEMENTATION</th>
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<tr>
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</tr>
<tr>
<td>1100</td>
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<td>2015</td>
</tr>
<tr>
<td></td>
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Protocol for PPCPs and surfactants analyses

**ON THE FIELD**

Winter sampling between January and November 2015

Sampling of a few kg of sludge in the whole depth of the layer from 5-10 spots of first stage surface

Manual extraction of reeds rhizomes and gravels if any

Homogenization of sludge material

**IN THE LAB**

Drying at 35°C then storage at 4°C until analyses
Protocol for PPCPs and surfactants analyses

1. Dried sludge sample
2. Freeze-drying
3. QuEChERS Extraction
4. Special Extraction of ciprofloxacin
5. LC-MS/MS

EXTRACTION

ANALYSIS
Pharmaceuticals and Personal Care Products (PPCPs): Results

SORPTION

SOLUBILITY

BIODEGRADATION

3 major physicochemical properties: pKa; log $K_{ow}$; $K_d$

Similar concentration in the 4 sludge deposits

Antibiotic
Beta-blocker
Antidepressant
Antifungal
Pharmaceuticals and Personal Care Products (PPCPs): Results

Due to the use of these PPCPs for a retirement home?
**Surfactants: Results**

<table>
<thead>
<tr>
<th>Surfactant</th>
<th>Amount (mg.kgDM⁻¹)</th>
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<tbody>
<tr>
<td>BAG1</td>
<td>250</td>
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<tr>
<td>BAY</td>
<td>200</td>
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<tr>
<td>VER</td>
<td>150</td>
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<tr>
<td>COR</td>
<td>100</td>
</tr>
<tr>
<td>Lauryl betaine</td>
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<tr>
<td>Triton x100</td>
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</tr>
<tr>
<td>Sodium 2-ethylhexyl sulfate</td>
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<tr>
<td>Bacolzoazole</td>
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<tr>
<td>Comperlan 100</td>
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<td>Incromine SD</td>
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<td>Stepanquat GA 90</td>
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<tr>
<td>SDS</td>
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<tr>
<td>Lauryl pyridinium</td>
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<tr>
<td>Texapon N 701 S</td>
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<td>LAS C12</td>
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<tr>
<td>LAS C13</td>
<td>50</td>
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**LC-MS/MS**

Anionic surfactants such as [LAS] are concentrated in VER sample and could be linked to the presence of FeOOH (injection of FeCl₃) (Yazid, 2010).
Conclusions & Perspectives

- High concentration in surfactants → Anionic surfactants / Possible nocive effect on microorganisms

- Similar PPCPs concentration in sludge deposits

- Relatively high retention of PPCPs in sludge deposit → Possible influence of the catchment
  - Link of the sludge deposit characteristics and PPCPs characteristics
  - Related the results in sludge deposit to 24h input-output balances
  - Study of pesticides and other micropollutants
THANK YOU FOR YOUR ATTENTION