Drug residues removal capacities by surface flow treatment wetlands: pharmaceutical compounds distribution in soil, water and plants compartments

Maximilien NUEL, Julien Laurent, Paul Bois, Dimitri Heintz, Adrien Wanko

a UMR7357/Icube Laboratoire des sciences de l'ingénieur, de l'informatique et de l'imagerie - UdS / CNRS - 2 rue Boussingault 67000 STRASBOURG

b UPR2357/Institut Biologique et Moléculaire des Plantes – UdS / CNRS - 12 Rue du général Zimmer 67084 STRASBOURG
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Context and issues for SFTW around Strasbourg
Context

- **Nuel PhD study**: «Dynamics of pharmaceutical compounds in Surface Flow Treatment Wetland (SFTW)»

- PhD aims:
  - To quantify 81 pharmaceutical compounds from different SFTW compartments (water, plants, soil, invertabrates);
  - To determine long term purifying capacities of 2 full-scale SFTWs (a pond and a vegetated ditch);
  - To optimise the sizing of these systems after a comprehensive understanding of the SFTW hydraulic behavior.

- Are different typologies influence the removal abilities of SFTW?
- Are there pharmaceutical compounds distribution in soil, water and plants compartments?

- Partners: **Water Agency Rhin-Meuse**, Région Alsace, **ICUBE** (UMR7357), **IBMP** (UPR2357), ENGEES, Strasbourg University
Introduction: What is SFTW?

SFTW: 4 main functionalities:

1. Dispersion of releases,
2. Sludge & SS retention,
3. Hydraulic peak attenuation,
4. Additional pollutant mitigation.
Processes and key issues related to SFTW

Processes:
- Infiltration,
- Evapotranspiration,
- Biological degradation
- Nutrients storage by plant,
- Photo-degradation,
- Settling particulate matter,
- ...

Key issues:
- No rule for design.
- What is the relative impact of the above processes on the SFTW good functioning?
- What are their removal abilities for drug compounds?
Aim of this study

Highlight the drug residues removal abilities and their distributions to plants and mud, throughout the sampling sessions in 2 different SFTWs: a pond and a vegetated ditch.

Method

• Regular sampling sessions during two years on 2 different SFTWs: a pond and a vegetative ditch
• 81 pharmaceutical compounds and metabolites scanned and quantified by Ultra Performance Liquid Chromatography coupled to mass spectrometry (UPLC-MSMS)
Materials & method for sampling sessions in SFTW and drug quantification
FALKWILLER
City connected: Falkwiller, Gildwiller & Hecken
Treatment capacity: 1 450 PE
Sewage collection system: wastewater and runoff
Treatment facility: VFCW + SFTW

LUTTER
Two cities connected: Lutter & Raedersdorf
Treatment capacity: 808 PE
Sewage collection system: Wastewater and runoff
Treatment facility: VFCW + SFTW
## Sites presentation

<table>
<thead>
<tr>
<th>Lutter SFTW</th>
<th>Falkwiller SFTW</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Construction</strong></td>
<td>2010</td>
</tr>
<tr>
<td><strong>Reference flow rate</strong></td>
<td>1,080 m³/day</td>
</tr>
<tr>
<td><strong>Plant</strong></td>
<td>Local plants</td>
</tr>
<tr>
<td><strong>Type</strong></td>
<td>Vegetated ditches</td>
</tr>
<tr>
<td><strong>Slope</strong></td>
<td>1 to 1</td>
</tr>
<tr>
<td><strong>deep (cm)</strong></td>
<td>0.3</td>
</tr>
<tr>
<td><strong>Surface (m²)</strong></td>
<td>140</td>
</tr>
<tr>
<td><strong>Volume (m³)</strong></td>
<td>60</td>
</tr>
</tbody>
</table>

### 2009

- **Local plants**: Pond
- **Pond**: 1 to 4
- **Pond depth (cm)**: 0.3 – 0.9
- **Surface**: 750
- **Volume**: 425
- **Expected mechanisms**: Peak attenuation, Sedimentation, Photodegradation, Evaporation, Infiltration

### 2010

- **Local plants**: Plant
- **Type**: Vegetated ditches
- **Slope**: 1 to 1
- **Deep (cm)**: 0.3
- **Surface (m²)**: 140
- **Volume (m³)**: 60
- **Expected mechanisms**: Peak attenuation, Evapotranspiration, Plant uptake, Infiltration
Materials

Weather stations

Ultrasound sensors (inlet & outlet)

Automatic and chilled samplers (inlet & outlet) controlled by the flow rate

Multiparameters probes for: PH, OD, $T^\circ$, redox, Salinity,...

Sample bags, a cooler, laboratory gloves, pruning shears, ...
Sampling strategy

- Sessions every two months during two years

- Samples:
  - Inlet and outlet water => 7 Liters
  - 5 different plant species => 150 g per plant
  - 1 composite mud sample => 100 g

- Data acquired in situ:
  - Weather parameters
  - Inlet and outlet flowrates
  - Inlet and outlet physicochemical parameters (PH, OD, T°, redox, Salinity,...)
Sampling strategy

- Soft rush (Juncus effusus)
- Willow (Salix alba)
- Callitriche (Callitriche palustris)
- Sedge (Carex caryophyllea)
- Yellow flag (Iris pseudacorus)

Lutter SFTW

Falkwiller SFTW
Drug extraction from liquide and solide samples

1. Conditioning

- Drained sludge
- Dried and crushed plants
- Maceration with acetonitrile

2. SPE cartridges concentrate and stock drugs

- Filters
- SPE cartridges
- Eluted by 10 mL of methanol

3. Drug extraction

- Cartridges were eluted by 10 mL of methanol
- Samples were dried and stocked at -80°C

Vacuum pump

Tin vacuum
Drug quantifications: UPLC-MSMS

4. Solubilization

- 400 µL 10% Methanol

5. Detection and quantification

- 30 µL analysed

<table>
<thead>
<tr>
<th>Samples</th>
<th>Drug concentration units</th>
</tr>
</thead>
<tbody>
<tr>
<td>Liquid</td>
<td>µg/L</td>
</tr>
<tr>
<td>Solid (plants &amp; Mud)</td>
<td>pg/g</td>
</tr>
</tbody>
</table>

6. Removal capacities

\[
C = \frac{C_{\text{Inlet}} \cdot V_{\text{Inlet}} - C_{\text{Outlet}} \cdot V_{\text{Outlet}}}{C_{\text{Inlet}} \cdot V_{\text{Inlet}}}
\]

C: Drug concentrations; V: Daily volumes

Thanks to specific drug standard curves
Results on the drug residues removal capacities and drug distributions to plants and mud in SFTWs
**Average drug concentrations in liquid samples**

### Falkwiller SFTW:
- **Inlet**: nb=45
- **Outlet**: nb=43

<table>
<thead>
<tr>
<th>Drug</th>
<th>Concentration (µg/L)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Alpha ethinylestradiol</td>
<td>89</td>
</tr>
<tr>
<td>Tramadol</td>
<td>46</td>
</tr>
<tr>
<td>Estriol</td>
<td>28</td>
</tr>
</tbody>
</table>

### Lutter SFTW:
- **Inlet**: nb=48
- **Outlet**: nb=49

<table>
<thead>
<tr>
<th>Drug</th>
<th>Concentration (µg/L)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Alpha ethinylestradiol</td>
<td>1140</td>
</tr>
<tr>
<td>Tramadol</td>
<td>222</td>
</tr>
<tr>
<td>Theophylline</td>
<td>33</td>
</tr>
</tbody>
</table>

**Biggest average concentrations in water:**
- **Falkwiller**:
  - Alpha ethinylestradiol (89 µg/L)
  - Tramadol (46 µg/L)
  - Estriol (28 µg/L)
- **Lutter**:
  - Alpha ethinylestradiol (1 140 µg/L)
  - Tramadol (222 µg/L)
  - Theophylline (33 µg/L)

**What about their removal efficiencies by the SFTWs??**
Variable drug removal efficiencies

Falkwiller SFTW:

- Tramadol
- Theophylline
- Sotalol
- Paracetamol
- Ofloxacin
- Naproxen
- Lamotrigine
- Ketoprofen
- Gabapentin
- Carbamazepine
- Caffeine
- Bisoprolol
- Sulfamethoxazole
- Metoprolol
- Fenoprofen
- Phloroglucinol
- Levetiracetam
- Telmisartan
- Erythromycin
- Candesartan
- Antorvastatine
- Propafenone
- Omeprazole
- Losartan
- Clindamycin
- Ampicillin
- Trimethoprim
- Ibuprofen
- Esomeprazole
- Quetiapine
- Pantoprazole
- O-Desmethylltramadol
- O-Desmethyllnaproxen
- Mefenamic acid
- Indomethacin
- Diclofenac
- Alpha ethylnerastadiol
- Topiramate
- Sulfadiazine
- Ramipril
- Prednisolone
- Nefopam
- Haloperidol
- Etorol
- Domperidone
- Cefpodoxime proxetil
- Amitriptyline

Lutter SFTW:

- Tramadol
- Theophylline
- Sotalol
- Propafenone
- Paracetamol
- Nefopam
- Ketoprofen
- Fenoprofen
- Carbamazepine
- Caffeine
- Bisoprolol
- Clindamycin
- Trimethoprim
- Sulfamethoxazole
- Mefenamic acid
- Losartan
- Ibuprofen
- Erythromycin
- Diclofenac
- Candesartan
- Estrasol
- Eprosartan
- Topiramate
- Sulfadiazine
- Indomethacin
- Haloperidol
- Gemfibrozil
- Atorvastatin
- Amoxicillin
- Acid clonidric

- 12 (Falkwiller) and 13 (Lutter) compounds were always detected in water samples.

Is there a specific behavior of this compounds in our two different SFTWs?
Drug compounds behavior characterization

Falkwiller SFTW:
- Removal efficiencies ≈ 13%
- Relatively low inlet and high inlet and outlet concentrations

Lutter SFTW:
- High variability and high inlet and outlet concentrations
- Good removal efficiencies ≈ 40%
- High inlet and outlet concentrations (29 and 20 µg/L)

There is different behaviors of the drug compounds due to the SFTW typologies

Are there drugs transfers from the water to the plants??

- High variability and negative removal efficiencies
- Low outlet concentration ≈ 1 µg/L
- Negative removal efficiencies (<100%)

- Outlet concentration ≈ 10 µg/L
Average drug concentrations in plants samples

Falkwiller SFTW

Himalayan balsam (Impatiens glandulifera)

Yellow flag (Iris pseudacorus)

Soft rush (Juncus effusus)

Creeping primrose (Ludwigia peploides)

Willow (Salix alba)

- Willow sample has the biggest number and highest concentrations of drug compound uptake from the water
- It is also the only tree among this plants samples

Are there the same observations for Lutter plants??
Average drug concentrations in plants samples

Lutter SFTW

- Willow shows again good abilities to uptake drug compound from the water
- It is still the only tree among this plants samples

What about the mud stocked in the SFTWs ??
Average drug concentrations in mud

Falkwiller SFTW

Drug number throughout the seasons

- Continuous drug adsorption

Lutter SFTW

Drug number throughout the seasons

- Dynamic accumulation:
  - Release on Winter
  - Accumulation on summer
Drugs distribution to plant and mud

- There is a global transfer and distribution of drug compounds to all of the solid samples.
- Willow plants also allow high uptakes of few compounds.

Low concentrations in all samples

Too high average concentrations
- Alpha ethinylestradiol => Rush
- Ibuprofen=> Sedge
- Mefenamic acid => Willow
- Tramadol => callitriche, iris and willow
CONCLUSION & OUTLOOK

• After wastewater treatment facilities, 86 drug compounds and metabolites were quantified.
• SFTW removal efficiencies were highly variable for each drug compounds.
• There are specific drug compounds transfers from the water to the plants.
• Plants uptakes quantities of drugs are negligible in comparison to outlet drug flow.
• In the pond, the drug adsorption in mud was dynamic and affected by seasonal effects whereas in the vegetated ditch, it was continuous.

Perspectives

Estimate the total mass of drug uptaken by plants and stocked in the mud before potential sludge extractions.
Thanks for your attention

Contact

Maximilien NUEL
mnuel@engees.eu

ICUBE
2 Rue Boussingault
67000 Strasbourg
FRANCE