Contamination of various types of Parisian sewage sludge by a wide range of priority and emerging micropollutants

Romain MAILLER¹,², Johnny GASPERI¹, Dominique PATUREAU³, Emmanuelle VULLIET⁴, Steven DESHAYES¹,⁵, Sabrina GUERIN², Régis MOILLERON¹, Ghassan CHEBBO¹, Vincent ROCHER²

¹LEESU, Université Paris-Est, Créteil
²SIAAP, DDP, Colombes
³LBE, INRA, Narbonne
⁴ISA, CNRS, Villeurbanne
⁵LCPP, Paris
• Hydrophobic and adsorbable compounds removed from wastewater by sorption to sludges (Mailler et al. 2013; Choubert et al. 2012; Clara et al. 2007)

→ Presence of micropollutants in sewage sludge

• > 50% of treated sludge (DM) is landfilled in Europe (Kelessidis and Stasinakis 2012)

• European Directive about sludge management (86/278/CEE) only concerns some metals and PAHs

→ What about others micropollutants?
Scientific and operational issues:

• Contamination of Parisian sewage sludges

• Fate during sludge treatments (centrifugation, digestion, thermal drying, press filtration)

• What about centrifuged and condensed waters?
The studied WWTPs

**Seine Centre**
- 240,000 m³/day
  - Raw sludge (RS) → Centrifuged water → Centrifugation → Incineration → Smoke treatment
  - RS: raw sludge
  - CS: centrifuged sludge
  - DS: digested sludge
  - TS: dried sludge
  - SC: sludge cake

**Seine Aval**
- 1,700,000 m³/day
  - Raw sludge (RS) → Biogas → Digestion → Thickening → Press filtration → Landfarming
  - RS: raw sludge
  - DS: digested sludge
  - TS: dried sludge
  - SC: sludge cake

**Seine Grésillons**
- 300,000 m³/day
  - Raw sludge (RS) → Polymer → Buffer tank → Centrifugation → Thermal drying → Condensed water
  - RS: raw sludge
  - CS: centrifuged sludge
  - TS: dried sludge

n = number of campaigns performed.
The analytical procedure

• 5 types of sludges: raw, centrifuged, digested, thermally dried and sludge cake

• 7 sampling campaigns (2013 – 2014)

• Punctual sampling

• 71 priority and emerging pollutants:
  - Pharmaceuticals and hormones
  - Perfluorinated acids
  - Alkylphenols
  - LAS
  - PCBs and PAHs
  - Phthalates

• 5 laboratories involved
Results of the study

Occurrence of emerging pollutants in sludge

< 50% for some pharmaceuticals

> 75% for fluoroquinolones, phthalates, alkylphenols, LAS, PAHs and PCBs
Results of the study

Contamination of sewage sludge (1/2)

For fluoroquinolones up to 200 mg/kg DM

For most pharmaceuticals 10 – 500 µg/kg DM
Results of the study

Contamination of sewage sludge (2/2)

Very high contents for DEHP and LAS

LAS > DEHP ≈ Fluoroquinolones > Alkylphenols ≈ Phthalates > Pharmaceuticals ≈ PAHs ≈ PCBs ≈ perfluorinated acids ≈ hormones

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Results of the study

Evolution during sludge treatment (1/4)

Decrease/stability of contents in sludge + decrease of the mass flow

⇒ Decrease of the fluoroquinolone fluxes by sludge treatments

RS: raw sludge
CS: centrifuged
DS: digested
TS: dried
SC: sludge cake

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Results of the study

Evolution during sludge treatment (2/4)

Increase of contents in sludge + decrease of the mass flow
→ assessment of pollutant fluxes (next step)

RS: raw sludge
CS: centrifuged
DS: digested
TS: dried
SC: sludge cake

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Results of the study

Evolution during sludge treatment (3/4)

RS: raw sludge
CS: centrifuged
DS: digested
TS: dried
SC: sludge cake

Content (µg/kg DM)

Acetaminophen
Tramadol
Estrone
Estriol

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Results of the study

Evolution during sludge treatment (4/4)

<table>
<thead>
<tr>
<th>Content (μg/kg DM)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Σ PAHs</td>
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<tr>
<td>Σ PCBs</td>
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<tr>
<td>PFOS</td>
</tr>
</tbody>
</table>

RS: raw sludge
CS: centrifuged
DS: digested
TS: dried
SC: sludge cake

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Results of the study

The issue of centrifuged and condensed waters

- Centrifugation and thermal drying remove water from sludge and water reinjected to WWTP influents

Average of 3 campaigns

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Conclusions

What is the contamination of Parisian sewage sludge by priority and emerging pollutants?

• High occurrence (> 75%) for LAS, phthalates, fluoroquinolones, PAHs, PCBs, alkylphenols, acetaminophen and tramadol

• LAS > DEHP ≈ Fluoroquinolones > Alkylphenols ≈ Phthalates > Pharmaceuticals ≈ PAHs ≈ PCBs ≈ perfluorinated acids ≈ hormones

• The micropollutant pattern is relatively stable in all types of sludge
**Conclusions**

### Emerging pollutants pattern of Parisian sewage sludges

<table>
<thead>
<tr>
<th>&lt;LD</th>
<th>1</th>
<th>10</th>
<th>$10^2$</th>
<th>$10^3$</th>
<th>$10^4$</th>
<th>$10^5$</th>
<th>$10^6$</th>
<th>μg/kg MS</th>
</tr>
</thead>
<tbody>
<tr>
<td><em>Pesticides</em></td>
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<td>VOCs</td>
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<tr>
<td>Benzene derivatives</td>
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<tr>
<td>C10-C13 chloroalkanes</td>
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<tr>
<td>Chlorophenols</td>
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<td></td>
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<tr>
<td>Metals</td>
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</tbody>
</table>

**Organotins**

- OP
- OP_{12}EO
- NP_{2}EO
- BDE 209

**Benzene derivatives**

- DEP
- DnBP

**C10-C13 chloroalkanes**

- 4-NP
- NP_{1}EO
- DEHP

**Chlorophenols**

- PFOA
- PFOS
- PAHs
- PCBs
- Tributylphosphate

--- Fluoroquinolones---

---LAS-----

**References**

Mailler et al. 2014 – Priority and emerging pollutants in sewage sludge and fate during sludge treatment. Waste Management, 34, 1217-26

Conclusions

What is the contamination of Parisian sewage sludge by priority and emerging pollutants?

• Increase of content during treatment for PCBs, PAHs, LAS, DEHP, hormones and alkylphenols \(\Rightarrow\) sludge cakes are the most concentrated

• This trend is not observed for pharmaceuticals and perfluorinated acids

• Presence of most micropollutants in centrifuged and condensed waters \(\Rightarrow\) transfer from sludge to water
This study

• Calculation of fluxes by pollutants and by process,

• Removal of micropollutants by anaerobic digestion and thermal drying,

• Mass balances by process and by WWTP,

⇒ Publication in preparation

Future study

• What about centrifuged and condensed waters treatment?

• What about emerging pollutants with growing concern: PCPs, artificial sweeteners, benzotriazole, iodinated X-ray agents, surfactants, etc.?
Thank you for your attention!

romain.mailler@siaap.fr
gasperi@u-pec.fr

Mailler et al. 2014 – Priority and emerging pollutants in sewage sludge and fate during sludge treatment. Waste Management, 34, 1217-26
Flux removals observed in this study (1/2)

<table>
<thead>
<tr>
<th>Substance</th>
<th>Digestion</th>
<th>Thermal drying</th>
</tr>
</thead>
<tbody>
<tr>
<td>Acetaminophen</td>
<td>68 ± 35%</td>
<td>21 ± 25%</td>
</tr>
<tr>
<td>Carbamazepine</td>
<td>66 ± 39%</td>
<td>44 ± 40%</td>
</tr>
<tr>
<td>Propranolol</td>
<td>88 ± 25%</td>
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<tr>
<td>Sulfamethoxazole</td>
<td>76 ± 33%</td>
<td></td>
</tr>
<tr>
<td>Lidocaine</td>
<td>90 ± 21%</td>
<td></td>
</tr>
<tr>
<td>Tramadol</td>
<td>98 ± 4%</td>
<td>-48 ± 100%</td>
</tr>
<tr>
<td>Domperidone</td>
<td>99 ± 1%</td>
<td></td>
</tr>
<tr>
<td>Ciprofloxacin</td>
<td>43 ± 17%</td>
<td>51 ± 36%</td>
</tr>
<tr>
<td>Norfloxacin</td>
<td>43 ± 36%</td>
<td>32 ± 37%</td>
</tr>
<tr>
<td>Ofloxacin</td>
<td>49 ± 28%</td>
<td>35 ± 43%</td>
</tr>
<tr>
<td>Estrone</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Estriol</td>
<td></td>
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</tr>
</tbody>
</table>

Removal of DM by digestion = 40 ± 6%
Removal of VM by digestion = 54 ± 5%
Flux removals observed in this study (2/2)

<table>
<thead>
<tr>
<th>Substance</th>
<th>Digestion</th>
<th>Thermal drying</th>
</tr>
</thead>
<tbody>
<tr>
<td>PFOA</td>
<td>57 ± 8%</td>
<td>93 ± 7%</td>
</tr>
<tr>
<td>PFOS</td>
<td>77 ± 8%</td>
<td>45 ± 54%</td>
</tr>
<tr>
<td>∑ LAS</td>
<td>15 ± 22%</td>
<td>15 ± 19%</td>
</tr>
<tr>
<td>∑ 14 PAHs</td>
<td>-9 ± 23%</td>
<td>16 ± 13%</td>
</tr>
<tr>
<td>∑ 20 PCBs</td>
<td>11 ± 27%</td>
<td>26 ± 31%</td>
</tr>
<tr>
<td>4-NP</td>
<td>-54 ± 36%</td>
<td>22 ± 10%</td>
</tr>
<tr>
<td>NP₂EO</td>
<td>32 ± 19%</td>
<td>38 ± 29%</td>
</tr>
<tr>
<td>t-OP</td>
<td>-23 ± 37%</td>
<td>43 ± 12%</td>
</tr>
<tr>
<td>DEHP</td>
<td>33 ± 42%</td>
<td>-140 ± 108%</td>
</tr>
<tr>
<td>BBP</td>
<td>43 ± 14%</td>
<td>-142 ± 71%</td>
</tr>
</tbody>
</table>

Removal of DM by digestion = 40 ± 6%
Removal of VM by digestion = 54 ± 5%
Efficiency of anaerobic digestion

Mailler et al. 2014 – Priority and emerging pollutants in sewage sludge and fate during sludge treatment. Waste Management, 34, 1217-26
Efficiency of centrifugation and thermal drying

Mailler et al. 2014 – Priority and emerging pollutants in sewage sludge and fate during sludge treatment. Waste Management, 34, 1217-26
Historical evolution of sludge cakes contamination

Mailler et al. 2014 – Priority and emerging pollutants in sewage sludge and fate during sludge treatment. Waste Management, 34, 1217-26