Discharge of endocrine disrupting chemicals by combined sewer overflows into receiving waters: case-study of the Paris conurbation

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Alkylphenols and bisphenol A

\[ \text{Bisphenol A (BPA)} \]

\[ \begin{array}{c}
\text{H}_3\text{C} & \text{CH}_3 \\
\text{HO} & \text{OH} \\
\end{array} \]

4-4’- dihydroxy-2,2- diphenylpropane

**Uses**: monomer in the manufacture of polycarbonate plastics (water bottles, baby bottles); epoxy resins (food contact lacquers: cans, tin cans).

**World annual consumption**: 450 000 t/year *(Vanderberg 2007)*

\[ \text{Alkylphenols (APs)} \]

\[ R(\text{O-CH}_2\text{-CH}_2)_n\text{-OH} \]

**Uses**: non-ionic surfactants, detergents, industrial wetting agents or emulsifiers.

\( R = 9 \)
Nonyl- 80 %

\( R = 8 \)
Octyl- 20 %

**World annual consumption**: 500 000 t/year *(Ying 2002)*
# Studied compounds

<table>
<thead>
<tr>
<th>Structures</th>
<th>Nomenclatures</th>
<th>Names</th>
</tr>
</thead>
<tbody>
<tr>
<td><img src="image1.png" alt="Structure 1" /></td>
<td>NP&lt;sub&gt;2&lt;/sub&gt;EO</td>
<td>Nonylphenol diethoxylate</td>
</tr>
<tr>
<td><img src="image2.png" alt="Structure 2" /></td>
<td>NP&lt;sub&gt;1&lt;/sub&gt;EO</td>
<td>Nonylphenol monoethoxylate</td>
</tr>
<tr>
<td><img src="image3.png" alt="Structure 3" /></td>
<td>NP</td>
<td>Nonylphenol</td>
</tr>
<tr>
<td><img src="image4.png" alt="Structure 4" /></td>
<td>NP&lt;sub&gt;1&lt;/sub&gt;EC</td>
<td>Nonylphenol acetic acid</td>
</tr>
<tr>
<td><img src="image5.png" alt="Structure 5" /></td>
<td>OP&lt;sub&gt;2&lt;/sub&gt;EO</td>
<td>Octylphenol diethoxylate</td>
</tr>
<tr>
<td><img src="image6.png" alt="Structure 6" /></td>
<td>OP&lt;sub&gt;1&lt;/sub&gt;EO</td>
<td>Octylphenol monoethoxylate</td>
</tr>
<tr>
<td><img src="image7.png" alt="Structure 7" /></td>
<td>OP</td>
<td>Octylphenol</td>
</tr>
<tr>
<td><img src="image8.png" alt="Structure 8" /></td>
<td>BPA</td>
<td>Bisphenol A</td>
</tr>
</tbody>
</table>
Interest of studying BPA and APs?

Compounds ubiquitous in environment (Uguz et al. 2003)

Toxicity ➔ NP, OP and BPA have estrogenic effects on wildlife
Endocrine disrupting chemicals (EDC) (Correa-Reyes et al. 2007)

Disruptions on wildlife:
Deformity (gills, liver, kidneys) Rosy barb (Battcharaya et al. 2008)
Reproductive toxicity: male mice (El-dakdoki and Helal 2007)
Embryo development: Daphnia magna (Zhang et al. 2002)
Combined sewerage systems

Dry weather periods
- Wastewater
  - Wastewater treatment plants
  - Seine River

Wet weather periods
- Stormwater
- Wastewater
  - Combined sewer overflows (CSO)
  - Combined sewage
  - Wastewater treatment plants
  - Seine River
Objectives

- Evaluate the concentrations of APs and BPA in CSO

- Comparison of loads discharge at the scale of an event
  - Against daily wastewater treatment plant loads
  - Against daily exported loads by the Seine River

- Comparison of loads discharge at the scale of a year
  - Against annual wastewater treatment plant loads
  - Against annual exported loads by the Seine River
Clichy outfall

Sampling:
250 ml every 5 min
Total duration: 3h

Source: DDP SIAAP
### Sampling campaigns

<table>
<thead>
<tr>
<th>Sampling campaigns</th>
<th>Discharged volumes (m³)</th>
<th>Conductivities (µS.cm⁻¹)</th>
<th>% wastewater</th>
</tr>
</thead>
<tbody>
<tr>
<td>16/06/2010</td>
<td>34,000</td>
<td>449</td>
<td>39</td>
</tr>
<tr>
<td>12/07/2010</td>
<td>580,000</td>
<td>284</td>
<td>20</td>
</tr>
<tr>
<td>14/07/2010</td>
<td>1,000,000</td>
<td>201</td>
<td>11</td>
</tr>
<tr>
<td>08/09/2010</td>
<td>38,000</td>
<td>380</td>
<td>31</td>
</tr>
<tr>
<td>24/06/2010</td>
<td>279,000</td>
<td>260</td>
<td>18</td>
</tr>
<tr>
<td>26/06/2010</td>
<td>144,000</td>
<td>346</td>
<td>27</td>
</tr>
<tr>
<td>08/11/2010</td>
<td>42,000</td>
<td>451</td>
<td>39</td>
</tr>
<tr>
<td>09/11/2010</td>
<td>286,000</td>
<td>374</td>
<td>30</td>
</tr>
</tbody>
</table>

**Discharged volumes (m³/5min)**

**Duration of CSO (hh:mm)**

**Discharged volumes (10³ m³)**

Legend:

- *69 %*: 2005-2010
- *26 %*: < 150
- *5 %*: 150 < x < 400
- *x > 400*
Analytical procedure

**Combined water**

**Filtration**
- GF/D (2.7 µm)
- GF/F (0.45 µm)

**Extraction (SPE)**
- OASIS HLB (200 mg/6ml)

**Particulate**

**Freeze dry**
- Alpha 1-2 LDplus

**Extraction**
- Microwave: Multiwave 3000

**Purification**
- SPE cartridge OASIS HLB

**UPLC-MS-MS**
- Internal standard
  - (BPA-d16, 4-n-NP, 4-n-NP1EO)

**Calliper:** AutoTrace SPE

**Anton Paar:** Multiwave 3000

**Waters:** UPLC-MS-MS

09/06/2011  WWW-YES-2011 – Cladière et al.
**Results: Total concentrations**

Huge concentrations of BPA: 917 – 2,098 ng.l\(^{-1}\); WWTP effluents: 47 ng.l\(^{-1}\)

Literature (wastewater): 226 – 12,000 ng.l\(^{-1}\)

Mean concentration: 1,410 ng.l\(^{-1}\) ± 437 ng.l\(^{-1}\) ± 31 %
Results: Total concentrations

Mean concentration CSO ≈ WWTP effluent concentration

CSOs: low NP₁EC : 207 – 572 ng.l⁻¹ ; WWTP effluents : 1,454 ng.l⁻¹

Mean concentration : 2,260 ng.l⁻¹ ± 740 ng.l⁻¹ ± 33 %
CSO loads vs. WWTP loads

CSO loads vs. daily loads $\Sigma$ WWTP (5 WWTPs $\Rightarrow$ 8 million inhabitant equivalent)

CSO loads = sum of loads of all CSO outfalls of the Greater Paris

**Loads of BPA:**
- Small $\Rightarrow$ 2 times higher than WWTP loads
- Medium $\Rightarrow$ 4 times higher than WWTP
- High $\Rightarrow$ 13 times higher than WWTP

CSOs could be important sources of BPA within receiving waters at the scale of the event

**Loads of APs:**
- Small – medium – high : < 50 % of WWTP loads

CSOs do not appear as important sources of APs within receiving waters at the scale of the event
CSO loads vs. Seine River loads

CSO loads vs. daily exported loads by the Seine River (dry weather)

Loads of BPA:
- Small ➔ Exported loads are 20 % higher
- Medium ➔ Exported loads are 40 % higher
- High ➔ Exported loads can double

CSOs may play a key role for exported loads of BPA by the Seine River during wet weather periods

Loads of APs:
- Small – medium – high : ≤ 20 % of exported loads by the Seine River

CSOs do not play an important role for exported loads of APs by the Seine River during wet weather periods
First assessment of annual loads

CSO annual loads \(\rightarrow\) estimation thanks to total volumes discharged from 2005 to 2010

WWTP annual loads \(\rightarrow\) estimation thanks to 5 monthly sampling campaigns: 2010-2011

Seine River loads \(\rightarrow\) estimation thanks to 10 monthly sampling campaigns: 2010

<table>
<thead>
<tr>
<th></th>
<th>(\Sigma) Paris outfalls</th>
<th>(\Sigma) WWTP effluents</th>
<th>Seine River</th>
<th>% (\Sigma) Paris outfalls</th>
<th>% (\Sigma) WWTP effluents</th>
</tr>
</thead>
<tbody>
<tr>
<td>Volume ((m^3.y^{-1}))</td>
<td>14,443,482</td>
<td>772,705,000</td>
<td>9,486,374,400</td>
<td>0.2</td>
<td>8.1</td>
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<tr>
<td>BPA</td>
<td>17.3</td>
<td>33</td>
<td>468</td>
<td>3.7</td>
<td>7.1</td>
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<tr>
<td>4-t-OP</td>
<td>0.9</td>
<td>28</td>
<td>101</td>
<td>0.9</td>
<td>27.6</td>
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<tr>
<td>OP(_1)EO</td>
<td>0.9</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>OP(_2)EO</td>
<td>0.2</td>
<td>33</td>
<td>29</td>
<td>0.8</td>
<td>115.4</td>
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<td>4-NP</td>
<td>9.8</td>
<td>251</td>
<td>777</td>
<td>1.3</td>
<td>32.3</td>
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<tr>
<td>NP(_1)EC</td>
<td>4.0</td>
<td>923</td>
<td>1,007</td>
<td>0.4</td>
<td>91.7</td>
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<tr>
<td>NP(_1)EO</td>
<td>4.4</td>
<td>344</td>
<td>469</td>
<td>1.0</td>
<td>76.6</td>
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<tr>
<td>NP(_2)EO</td>
<td>2.9</td>
<td>501</td>
<td>449</td>
<td>0.5</td>
<td>106.8</td>
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<tr>
<td>Sum APEOs</td>
<td>22.8</td>
<td>2,080</td>
<td>2,831</td>
<td>0.8</td>
<td>73.5</td>
</tr>
</tbody>
</table>

Loads: kg/year

At the scale of a year \(\rightarrow\) CSOs are not relevant sources of BPA and APs within Seine River
Conclusions and outlooks

Conclusions:

High concentrations of BPA (1,410 ng.l\(^{-1}\)) within CSO

Concentrations of APs in CSOs similar to WWTP effluents

At the scale of an event: CSOs could play a key role for BPA loads but not for APs

At the scale of a year: CSOs are not relevant sources of BPA and APs within Seine River

Outlooks:

Improve our estimation of CSO loads and exported loads by modeling (PROSE)

Improve our understanding of the influence of CSO on exported loads (particulate loads)

Evaluate the proportion of contamination owed to wastewater or runoff for each event
Thank you for your attention

Acknowledgement:
SIAAP and Paris Municipality: Providing sampling site, and volumes discharged from 2005 to 2010
LEESU: Florent Leroy, Mohamed Saad and Alexandre Segor for their technical assistances

Source: DDP SIAAP
BPA ➔ 92 % in dissolved phase

NP, NPEO ➔ highly present in particulate phase (mean 39%), except NP₁EC (4%)
Simplified NPnEO biodegradation

Anaerobic biodegradation pathway

Aerobic biodegradation pathway

Terminal oxidation of the polyethoxy chain

Fast

Slow

Unknown mechanisms

Very slow

Lente

Ipsa-substitution, only under aerobic conditions

Mineralization (Giger et al 2009)