Determination of selected organophosphorus flame retardants (OPFR) in the Aquatic Environment by LC-MS/MS

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Analysis of Emerging Pollutants

- Pharmaceuticals
  - Human, Veterinary
- Surfactants
  - Anionic – LAS, Nonionic – NPEOs, Cationic – QACs
  - Fluorinated – PFOS, PFOA, etc.
- Naphthalene sulphonic acid
- Natural and synthetic hormones
  - Estrone, estradiol, 17-α-ethinylestradiol, estriol
- Organotin compounds
Analysis of Emerging Pollutants

- Phthalates
- Pesticides (e.g. Pyrethroids)
- Benzotriazoles
- Fragrances (e.g. nitro and polycyclic musks)
- Flame retardants
  - PBDE
  - PFAS
  - OPFRs

Publications to results are available on our homepage www.umweltbundesamt.at

Use of OPFR

- Flame retardant
  - Upholsterer
  - Paints, varnishes
  - (Polyurethane) foams
  - Electronic devices
  - Garment
- Lubricant
- Plasticizer
**OPFR - characteristics**

- Consumption: >40,000 t/year TCPP worldwide
  >5,000 t/year TCEP, TCPP, TDCPP in the EU
- Persistent and stable
- Relatively low capability for bioaccumulation/biomagnification
- Moderate acute toxicity (dependant on the single compound)
  - but acute aquatic toxicity
- Some of them probably carcinogenic to men (especially the chlorinated ones)

**Examples: OPFR**

- Tris-(2-chloroethyl) phosphate (TCEP)
  - CAS: 115-96-8
- Tris (2-butoxyethyl)-phosphat (TBEP)
  - CAS: 78-51-3
Analysis of OPFR

- Water Samples
  - Addition of surrogate standard (TBP-d27)
  - Liquid-Liquid Extraction with dichloromethane
  - Solvent change to acetonitrile

- Sediment Samples
  - Addition of surrogate standard (TBP-d27)
  - US extraction
  - Solvent change to acetonitrile

- Determination by LC-MS/MS

Sediment spiked with 50 ng/g
Wastewater Samples in Austria

- 16 municipal STPs
  - 16 biological treatment
  - 16 nitrogen removal by nitrification
  - 13 nitrogen removal by nitrification/denitrification
  - 14 phosphorus removal
  - P.e.: 460 – 950.000

- Grab samples of the effluents
  - To prove occurrence in the aquatic environment

Mean, Max. and Min. in Austrian effluents

<table>
<thead>
<tr>
<th>Compound</th>
<th>Mean</th>
<th>Max.</th>
<th>Min.</th>
</tr>
</thead>
<tbody>
<tr>
<td>TEP</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>TCEP</td>
<td></td>
<td></td>
<td></td>
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<tr>
<td>TCPP</td>
<td></td>
<td></td>
<td></td>
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<tr>
<td>TPhP</td>
<td></td>
<td></td>
<td></td>
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<tr>
<td>TDCPP</td>
<td></td>
<td></td>
<td></td>
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<tr>
<td>TBP</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>TBEP</td>
<td></td>
<td></td>
<td></td>
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<tr>
<td>TKP</td>
<td></td>
<td></td>
<td></td>
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<tr>
<td>TEHP</td>
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</tbody>
</table>
Conclusions – Wastewater

- TCEP, TCPP and TBEP are the most abundant
- Concentration levels are in the low µg/l
- Comparison to other international studies:

<table>
<thead>
<tr>
<th></th>
<th>Austria (n=16)</th>
<th>W. Europe (n=8)</th>
<th>Germany (n=2)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>mean</td>
<td>mean</td>
<td>mean</td>
</tr>
<tr>
<td>TCEP</td>
<td>0.19</td>
<td>0.2</td>
<td>0.36</td>
</tr>
<tr>
<td>TCPP</td>
<td>0.68</td>
<td>0.6</td>
<td>1.9</td>
</tr>
<tr>
<td>TBEP</td>
<td>0.91</td>
<td></td>
<td>0.42</td>
</tr>
</tbody>
</table>

Reemtsma et al. 2006  Meyer et al. 2004

Influence of STP in the aquatic environment
### Results Effluent – Sediments Danube

<table>
<thead>
<tr>
<th>Effluent Linz</th>
<th>Asten right [µg/kg TM]</th>
<th>Asten left [µg/kg TM]</th>
</tr>
</thead>
<tbody>
<tr>
<td>TEP 120 ng/l</td>
<td>5.7</td>
<td>&lt;3.3</td>
</tr>
<tr>
<td>TCEP 140</td>
<td>13</td>
<td>n.n.</td>
</tr>
<tr>
<td>TCPP 1400</td>
<td>110</td>
<td>7</td>
</tr>
<tr>
<td>TPhP 27</td>
<td>29</td>
<td>&lt;1.3</td>
</tr>
<tr>
<td>TDCPP 1400</td>
<td>n.n.</td>
<td>n.n.</td>
</tr>
<tr>
<td>TBP 420</td>
<td>&lt;11</td>
<td>&lt;11</td>
</tr>
<tr>
<td>TBEp 57</td>
<td>3.4</td>
<td>2.9</td>
</tr>
<tr>
<td>TCP n.n.</td>
<td>8.1</td>
<td>&lt;1.5</td>
</tr>
<tr>
<td>TEHP n.n.</td>
<td>1.7</td>
<td>3.3</td>
</tr>
</tbody>
</table>

### River and sediment monitoring

- **Danube**
  - Two sample points
  - 2nd largest river in Europe
  - 1900 m²/s (Vienna)
- **Schwechat**
  - Influenced by industry and high density population
  - nearby Vienna
  - 7.9 m²/s
- **Liesing**
  - Influenced by industry and high density population
  - nearby Vienna
  - 0.38 m²/s
Danube, Schwechat and Liesing

Liesing
Results – Danube, Schwechat, Liesing

Conclusions

- Max. up to 500 ng/l
- Especially small rivers are contaminated
- Contamination pattern of the river Danube is different – small influence from the STPs
- TCEP, TCPP and TBEP – Liesing, Schwechat
- TBP, TBEP and TCEP – Danube
- no TCP and TEHP
Results - sediment

Conclusions

- Max. up to low mg/kg range
- Only in sediment samples significant differences between the Danube sample points
- Especially small rivers are contaminated
- TCPP, TCEP, TPhP, TBEP and TEHP are the most important ones
- TCP and TEHP in relevant concentration
  - Apparently strong adsorption
  - Sewage sludge might be heavily contaminated
Conclusions

- Due different Kd values, different contamination pattern of aqueous and sediment phase
  - might be important for the fate in STPs
- TCPP, TCP, TEHP and TPhP more in the sediment
- TDCPP, TBP and TBEP more in the water phase
- TCEP and TEP in both phases
Acknowledgement

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