Trinkwasserrelevanz von chlorierten Organophosphaten (Flammschutzmittel)

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Target compounds

- **TCEP**
  - Tris(2-chloroethyl) phosphate

- **TCPP – Isomer 1**
  - Tris(2-chloro-1-methylethyl) phosphate

- **TDCP**
  - Tris(1,3-dichloro-2-propyl) phosphate

- **TBEP**
  - Tris(2-butoxyethyl) phosphate

- **TnBP**
  - Tri-n-butyl phosphate

- **TiBP**
  - Tri-iso-butyl phosphate
### Use and toxicology

<table>
<thead>
<tr>
<th>Name</th>
<th>Usage</th>
<th>Toxicology</th>
</tr>
</thead>
<tbody>
<tr>
<td>TiBP</td>
<td>Lubricant, plasticizer, concrete (pore size regulation)</td>
<td>-</td>
</tr>
<tr>
<td>TnBP</td>
<td>Solvent for cellulose esters, lacquers, natural gums; plasticizer for plastics and vinyl resins; antifoam agent for concrete and hydraulic fluids</td>
<td>Neurotoxic</td>
</tr>
<tr>
<td>TCEP</td>
<td>Flame-retardant (mostly polyurethane foam) → Phased out due to toxicity issues</td>
<td>Carcinogen</td>
</tr>
<tr>
<td>TCPP</td>
<td>Flame-retardant (mostly polyurethane foam)</td>
<td>Possible carcinogen</td>
</tr>
<tr>
<td>TDCP</td>
<td>Flame-retardant (mostly polyurethane foam), textiles, diverse → Used for specialties only</td>
<td>Carcinogen</td>
</tr>
<tr>
<td>TBEP</td>
<td>Plasticizer (rubber and plastics), floor polish</td>
<td>-</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Property</th>
<th>TCEP</th>
<th>TCPP</th>
<th>TDCP</th>
</tr>
</thead>
<tbody>
<tr>
<td>Henry's law constant (at 25 °C)</td>
<td>$4.155 \times 10^{-5}$ Pa m³ mol⁻¹</td>
<td>$3.96 \times 10^{-4}$ Pa m³ mol⁻¹</td>
<td>$1.24 \times 10^{-4}$ Pa m³ mol⁻¹</td>
</tr>
<tr>
<td>Vapor pressure (at 25 °C)</td>
<td>$1.14 \times 10^{-3}$ Pa</td>
<td>$1.4 \times 10^{-3}$ Pa</td>
<td>$5.6 \times 10^{-6}$ Pa</td>
</tr>
<tr>
<td>Log $K_{ow}$</td>
<td>1.78</td>
<td>$2.68 \pm 0.36$</td>
<td>$3.69 \pm 0.36$</td>
</tr>
<tr>
<td>Water solubility (at 20 °C)</td>
<td>$7820$ mg L⁻¹</td>
<td>$1080$ mg L⁻¹</td>
<td>$18.1$ mg L⁻¹</td>
</tr>
<tr>
<td>Hydrolysis (pH = 7)</td>
<td>$t \frac{1}{2} = &gt;1$ a</td>
<td>$t \frac{1}{2} = &gt;1$ a</td>
<td>$t \frac{1}{2} = &gt;1$ a</td>
</tr>
<tr>
<td>Photodegradation in the atmosphere (5 * 10⁵ OH mL⁻¹)</td>
<td>$t \frac{1}{2} = 17.5$ h</td>
<td>$t \frac{1}{2} = 8.6$ h</td>
<td>$t \frac{1}{2} = 21.3$ h</td>
</tr>
</tbody>
</table>
„Given the low levels of releases, the relatively low volatility and moderate solubility and adsorption coefficient of TCPP, together with its short predicted atmospheric half-life for degradation by hydroxyl radicals, it is not expected that exposure via the atmosphere will be significant.“

Konsequenz: Ein diffuser Eintrag von TCPP über den Niederschlag in die Gewässer ist nicht zu erwarten
Motivation and aims

- Atmospheric transport of organophosphates after their release (urban agglomeration, traffic)
- Detection of organophosphates in precipitation
- Dry and wet deposition as an entry-pathway of organophosphates in surface waters

Laniewski et al. (1998), Marklund et al. (2005), Bacaloni et al. (2008)

- Atmospheric washout of organophosphates by precipitation
- Temporal variation of organophosphate concentrations in precipitation, storm water holding tanks, urban and rural lentic surface waters
- Photodegradation of organophosphates in lakes
- Occurrence and distribution of organophosphates in groundwater
TCCP in rivers and creeks of Hessisches Ried
Sampling area and location of the sampling points

(Quednow, 2008)
Seasonal Variation of TCPP and HHCB concentrations in Rivers of Hessisches Ried
Sampling time: 2003-2006 (n= 175)

(Quednow, 2008)
Distribution of TCPP (ng/L) in Ruhr, Möhne and Lenne

Andresen et al, Sci Total Environ, 2004
Konzentrationen (ng/L) verschiedener Organophosphate im Rhein an der Rheingütestation in Worms, Messzeitraum Nov. 2007 - Jan. 2008, n = 147

Diplomarbeit Frömmel (2008)
**Sampling sites**

**Urban and rural lakes:**

Frankfurt am Main  
→ 06/08 – 05/09, **83 samples**
Eifel  
→ 06/07 – 03/09, **60 samples**
Thuringian Forest / Hessian Rhoen  
→ 10/09, **8 samples**

**Groundwater:**

Monte Scherbelino (Frankfurt/M.)  
→ 02/09 – 04/09, **11 samples**
Hessian Ried  
→ 04/09 – 07/09, **25 samples**
Oderbruch (Brandenburg)  
→ 10/09, **26 samples**
Hesse / Rhineland-Palatinate  
→ 04/09 – 09/09, **10 samples**

Regnery et al. Water Res. (2010), 44, 4097-4104
Sampling sites

Precipitation (rain and snow):

Frankfurt am Main (Riedberg campus)
→ 11/07 – 04/09, 90 samples
Mount Kleiner Feldberg (Taunus)
→ 11/07 – 01/09, 29 samples
Bekond (nearby Mosel River)
→ 12/07 – 03/09, 48 samples
Mount Schmuecke (Thuringian Forest)
→ 12/07 – 04/08, 11/08 – 03/09, 55 samples
Mount Wasserkuppe (Hessian Rhoen)
→ 01/08 – 03/08, 11/08 – 02/09, 33 samples

Storm water holding tank (SWHT):

Frankfurt am Main (Kätcheslachpark)
→ 05/08 – 04/09, 42 samples
Bekond (IRT)
→ spot sampling, 10 samples

Clean-Soil Air Water (2009), 37, 334-342
High concentration variations of some compounds in precipitation

No significant seasonal trend

No correlations of organophosphate concentrations with ambient air temperature, rainfall or global radiation

No concentration differences in urban precipitation (TiBP, TnBP) by comparison of summer and winter months

Regnery et al., Chemosphere (2010), 78, 958-964
Chlorinated organophosphates

- Monthly averaged concentrations:
  - TCPP: 199 – 2670 ng L\(^{-1}\)
  - TCEP: 38 – 230 ng L\(^{-1}\)
  - TDCP: LOD – 36 ng L\(^{-1}\)

- Accumulation of these compounds in storm water holding tanks
- High TCPP concentrations
- No seasonal trend
- Mobilization by means of storm water runoff (buildings)

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Chemosphere (2010), 78, 958-964
## Results (precipitation and SWHTs)

Concentrations of organophosphates (ng L$^{-1}$) in precipitation and storm water holding tank (SWHT) samples

<table>
<thead>
<tr>
<th></th>
<th>Frankfurt am Main</th>
<th></th>
<th>Bekond</th>
<th></th>
<th>Kl. Feldberg</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Precipitation</td>
<td>SWHT</td>
<td>Precipitation</td>
<td>SWHT</td>
<td>Precipitation</td>
</tr>
<tr>
<td>[ng L$^{-1}$]</td>
<td>n = 90</td>
<td>n = 42</td>
<td>n = 48</td>
<td>n = 10</td>
<td>n = 29</td>
</tr>
<tr>
<td>TCEP</td>
<td>71 (10-485)</td>
<td>77 (33-275)</td>
<td>12 (&lt;LOD-127)</td>
<td>78 (23-131)</td>
<td>40 (11-390)</td>
</tr>
<tr>
<td>TCPP$^b$</td>
<td>403 (32-3562)</td>
<td>880 (16-5791)</td>
<td>134 (5-1214)</td>
<td>410 (197-4847)</td>
<td>57 (&lt;LOD-1154)</td>
</tr>
<tr>
<td>TDCP</td>
<td>5 (&lt;LOD-532)</td>
<td>13 (&lt;LOD-73)</td>
<td>7 (&lt;LOD-87)</td>
<td>11 (&lt;LOD-36)</td>
<td>16 (&lt;LOD-497)</td>
</tr>
<tr>
<td>TBEP</td>
<td>21 (&lt;LOD-505)</td>
<td>77 (&lt;LOD-1616)</td>
<td>&lt;LOD (&lt;LOD-205)</td>
<td>36 (&lt;LOD-77)</td>
<td>17 (&lt;LOD-242)</td>
</tr>
<tr>
<td>TiBP</td>
<td>106 (&lt;LOD-1410)</td>
<td>117 (2-1478)</td>
<td>14 (&lt;LOD-160)</td>
<td>359 (32-826)</td>
<td>41 (&lt;LOD-424)</td>
</tr>
<tr>
<td>TnBP</td>
<td>108 (&lt;LOD-1679)</td>
<td>57 (4-417)</td>
<td>16 (&lt;LOD-110)</td>
<td>138 (13-347)</td>
<td>64 (&lt;LOD-458)</td>
</tr>
</tbody>
</table>

$^a$ Median (minimum-maximum)

$^b$ Sum of two isomers; Tris(2-chloro-1-methylethyl) phosphate, CAS 13674-84-5; bis(1-chloro-2-propyl)-2-chloropropyl phosphate, CAS 76025-08-06.

LOD = Limit of detection

Regnery et al., Chemosphere (2010), 78, 958-964
## Results (groundwater)

### A Infiltration via precipitation → Hessian Ried
- TCEP: 40% (n = 10) < LOQ, Max. c = 24 ng L\(^{-1}\)
- TCPP: 30% (n = 10) < LOQ, Max. c = 6 ng L\(^{-1}\)
- TBEP: 20% (n = 10) < LOQ, Max. c = < LOQ
- TiBP: 20% (n = 10) < LOQ, Max. c = 7 ng L\(^{-1}\)

### B Riverbank filtration → Hessian Ried
- TCEP: 67% (n = 15) 7 ng L\(^{-1}\), Max. c = 148 ng L\(^{-1}\)
- TCPP: 74% (n = 15) 38 ng L\(^{-1}\), Max. c = 1795 ng L\(^{-1}\)
- TDCP: 20% (n = 15) < LOQ, Max. c = < LOQ
- TBEP: 40% (n = 15) < LOQ, Max. c = 1813 ng L\(^{-1}\)
- TiBP: 67% (n = 15) 5 ng L\(^{-1}\), Max. c = 105 ng L\(^{-1}\)
- TnBP: 67% (n = 15) 5 ng L\(^{-1}\), Max. c = 51 ng L\(^{-1}\)

### C Polluted landfill site → Monte Scherbelino
- TCEP: 91% (n = 11) 141 ng L\(^{-1}\), Max. c = 318 ng L\(^{-1}\)
- TCPP: 91% (n = 11) 191 ng L\(^{-1}\), Max. c = 343 ng L\(^{-1}\)
- TDCP: 55% (n = 11) < LOQ, Max. c = 45 ng L\(^{-1}\)
- TBEP: 9% (n = 11) < LOQ, Max. c = 199 ng L\(^{-1}\)
- TiBP: 100% (n = 11) 92 ng L\(^{-1}\), Max. c = 697 ng L\(^{-1}\)
- TnBP: 100% (n = 11) 90 ng L\(^{-1}\), Max. c = 213 ng L\(^{-1}\)

http://groundwater.sdsu.edu

J. Environ. Monit., DOI:10.1039/C0EM00419G
Conclusions

- „Short- and mid-range“ transport of organophosphates in atmosphere

- High organophosphate concentrations in precipitation at urban sites

- Precipitation as an all-season entry-pathway for organophosphates into surface waters of urban and rural areas

- High variability but no seasonal trends of chlorinated organophosphates in precipitation, storm water runoff, and lakes

- Accumulation of organophosphates in storm water holding tanks → potential danger of groundwater contamination

- EU risk assessment (TCPP) is wrong with respect to the neglected exposure of TCPP via the atmosphere

- Risk of drinking water supply when bank filtration is used without activated carbon filtration
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