Quaternary phosphonium compounds: new toxic compounds present in sediments and suspended matter

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Target vs. Non-target Analysis

**Target-Analysis**
- Selection of substances (Targets)
- Reference Standard (Calibration, method optimization)
- Identification and Quantification

**Non-target-Analysis**
- No standards
- Selection of analytical method
- Database: List of exact masses and retention times (RTs)
How it all started…

Non-Target Screening in Koblenz:

• Daily composite sample of the river Rhine (km 590.3) since beginning of 2014

• Analysis of samples via HPLC- QToF-MS (SCIEX TripleTOF 5600/6600)
  ➔ Direct injection of Rhine water samples

• Possibility of retrospective data analysis

• **Goal: Detection of „features“ with different concise time trends**
Results: Time trends of features in the Rhine at Koblenz

- Evaluation of all detected signals (> 10000)
- Find recurring features
- Investigate discontinuous emissions
Results: Recurring feature

Identification:
$C_{20}H_{20}OP^+$; Methoxymethyl-triphenylphosphonium cation

$m/z = 307.125$, $RT = 8.0$ min

Normalized peak area

Flow rate (m³/s)

01.02 01.05 01.08 01.11 01.02
# Identification of further quaternary phosphonium compounds (QPC)

<table>
<thead>
<tr>
<th>Substance</th>
<th>Formula</th>
<th>Structure</th>
<th>m/z</th>
</tr>
</thead>
<tbody>
<tr>
<td>Methyltriphenylphosphonium cation (Me-Ph$_3$P$^+$)</td>
<td>C$<em>{19}$H$</em>{18}$P$^+$</td>
<td><img src="image" alt="Structure" /></td>
<td>277.1141</td>
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<tr>
<td>Ethyltriphenylphosphonium cation (Et-Ph$_3$P$^+$)</td>
<td>C$<em>{20}$H$</em>{20}$P$^+$</td>
<td><img src="image" alt="Structure" /></td>
<td>291.1297</td>
</tr>
<tr>
<td>Methoxymethyltriphenylphosphonium cation (MeOMe-Ph$_3$P$^+$)</td>
<td>C$<em>{20}$H$</em>{20}$OP$^+$</td>
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<tr>
<td>Butyltriphenylphosphonium cation (Bu-Ph$_3$P$^+$)</td>
<td>C$<em>{22}$H$</em>{24}$P$^+$</td>
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</tr>
<tr>
<td>Tetraphenylphosphonium cation (Ph$_4$P$^+$)</td>
<td>C$<em>{24}$H$</em>{20}$P$^+$</td>
<td><img src="image" alt="Structure" /></td>
<td>339.1297</td>
</tr>
</tbody>
</table>
Application of QPCs: Wittig reaction

Nobel Prize in Chemistry 1979

a) Wittig reaction: Synthesis of Vitamin A, β-Carotene, ...
b) also as phase transfer catalyst
Back to target analysis:

(Samples from June 2015)
### Target Method:
- 25 QPCs and derived phosphine oxides
- Longitudinal sampling of sediment (if possible, also suspended matter) at rivers Rhine and Elbe

### Rhein/Bimmen-Lobith
- Me-Ph$_3$P$^+$: 19 µg/kg
- MeOMe-Ph$_3$P$^+$: 68 µg/kg
- Et-Ph$_3$P$^+$: 19 µg/kg

### Rhein/Koblenz
- Me-Ph$_3$P$^+$: 80 µg/kg
- MeOMe-Ph$_3$P$^+$: 210 µg/kg
- Et-Ph$_3$P$^+$: 64 µg/kg

### Rhein/Koblenz
- Me-Ph$_3$P$^+$: 43 µg/kg
- MeOMe-Ph$_3$P$^+$: 750 µg/kg
- Et-Ph$_3$P$^+$: 86 µg/kg

### Main/Bischofsheim
- Me-Ph$_3$P$^+$: <LOQ
- MeOMe-Ph$_3$P$^+$: <LOQ
- Et-Ph$_3$P$^+$: <LOQ

### Landgraben/Trebur
- Me-Ph$_3$P$^+$: 560 µg/kg
- MeOMe-Ph$_3$P$^+$: 1200 µg/kg
- Et-Ph$_3$P$^+$: 190 µg/kg

### Rhein/Breisach
- Me-Ph$_3$P$^+$: <LOQ
- MeOMe-Ph$_3$P$^+$: <LOQ
- Et-Ph$_3$P$^+$: 85 µg/kg

(Samples from 2015)
Back to target analysis:

1) Longitudinal sampling gives good idea of the origin of the QPC contaminations.

2) Tidal amplitude may move contaminated sediments upstream to originally unexpected sites.
   → „Tidal Pumping“

(Samples from 2015)
Time Trends:

- Freeze-dried annual composite suspended matter samples, provide by the German Environmental Specimen Bank

\[ \text{QPCs have been present in the aquatic environment for at least one decade!} \]

\[ (\text{SM load [t/a]} \times 10^3 \times \text{Concentration [µg/kg]}) \times 10^{-9} = \text{Annual QPC load [kg/a]} \]

\[ \text{e.g. MeOMe-Ph}_3\text{P}^+ \text{ 2012 in Koblenz: 1 413 116 [t/a]} \times 260 [\text{µg/kg}] \times 10^{-6} = 370 \text{ kg/a} \]
Degradation Experiment:

- Aerobic degradation experiment with four QPCs over 100 days:

  a) Me-Ph$_3$P$^+$
  \[ \log K_D: 3.23 \pm 0.11 \]

  b) Et-Ph$_3$P$^+$
  \[ \log K_D: 3.14 \pm 0.23 \]

  c) MeOMe-Ph$_3$P$^+$
  \[ \log K_D: 3.29 \pm 0.11 \]

  d) Bu$_4$P$^+$
  \[ \log K_D: 2.03 \pm 0.07 \]

- Recovery Rates 70-80%
- Linear trends over 100 days \( \rightarrow \) no degradation!
- Recovery in liquid phase significantly lower than in sediment extracts \( \rightarrow \) high $K_D$ values, good sorption onto sediment/suspended matter!
Toxicity:

- The following tests were performed with 13 QPCs:
  - Determination of ROS (reactive oxygen species), determination of cytotoxicity, AMES-Test, induction of micronuclei

- (Nearly) all QPCs exhibited cytotoxicity
  - $\text{Ph}_4\text{P}^+ > \text{Ph}_3\text{P}^+\text{-R}$ with $\text{R}=\text{alkyl}$, $\text{Bz} > \text{R}=\text{Ether/Ester} > \text{Bu}_4\text{P}^+$; phosphinoxides

- Four substances also showed genotoxic potential
  - $\text{MeOMe-Ph}_3\text{P}^+ \text{Cl}^-$, $\text{MeOCarbMe-Ph}_3\text{P}^+\text{Br}^-$, $\text{Bu}_4\text{P}^+\text{Br}^-$, $\text{Ph}_3\text{PO (TPPO)}$

- Keep in Mind: as intermediates in chemical synthesis they are not covered by any product regulation!
Conclusion:

- With the help of (retrospective) **non-target analysis**, new emerging contaminants can be identified.
- **Quaternary phosphonium compounds (QPCs)** were identified as anthropogenic contaminants in German rivers.
- QPCs **adsorb** very well onto sediment and suspended matter; concentrations of up to 1200 µg/kg (Rhein catchment area) or 1000 µg/kg (Tidal Elbe) have been detected.
- QPCs are **persistent** and have been present for at least one decade in the aquatic environment.
- QPCs show **cytotoxicity** and some exhibit even **genotoxic potential**, which emphasizes the need for an emission regulation of these compounds.

**Publications:**
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• ... you all for your attention!