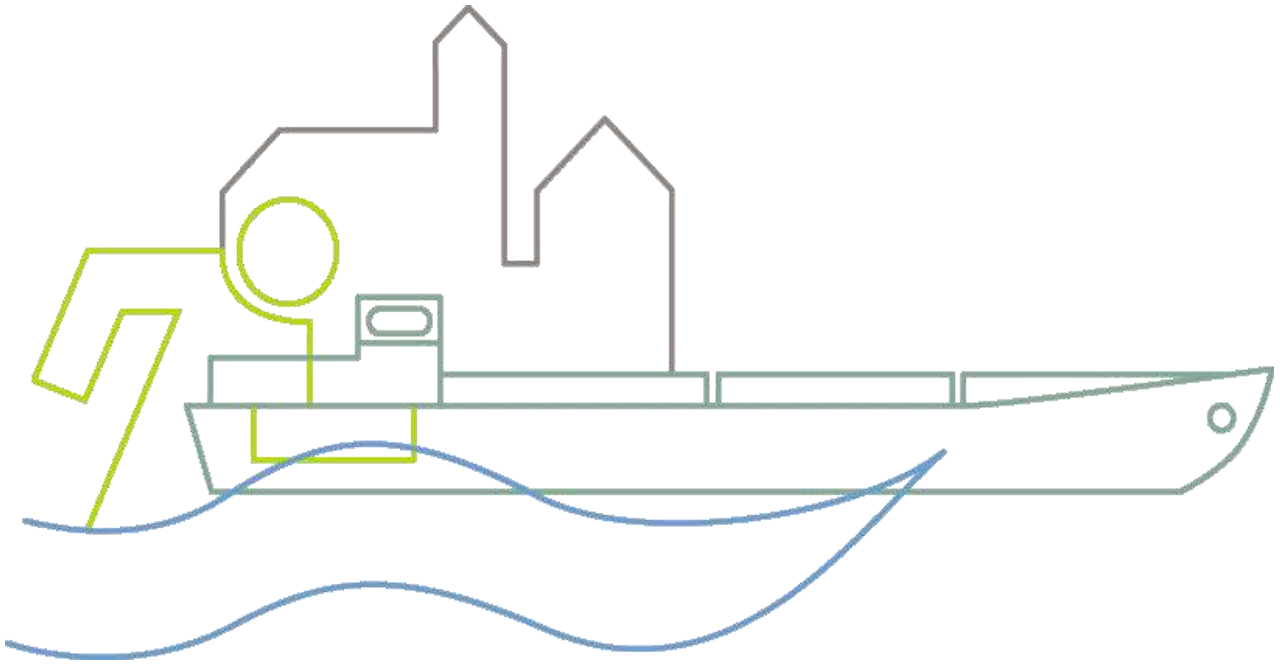
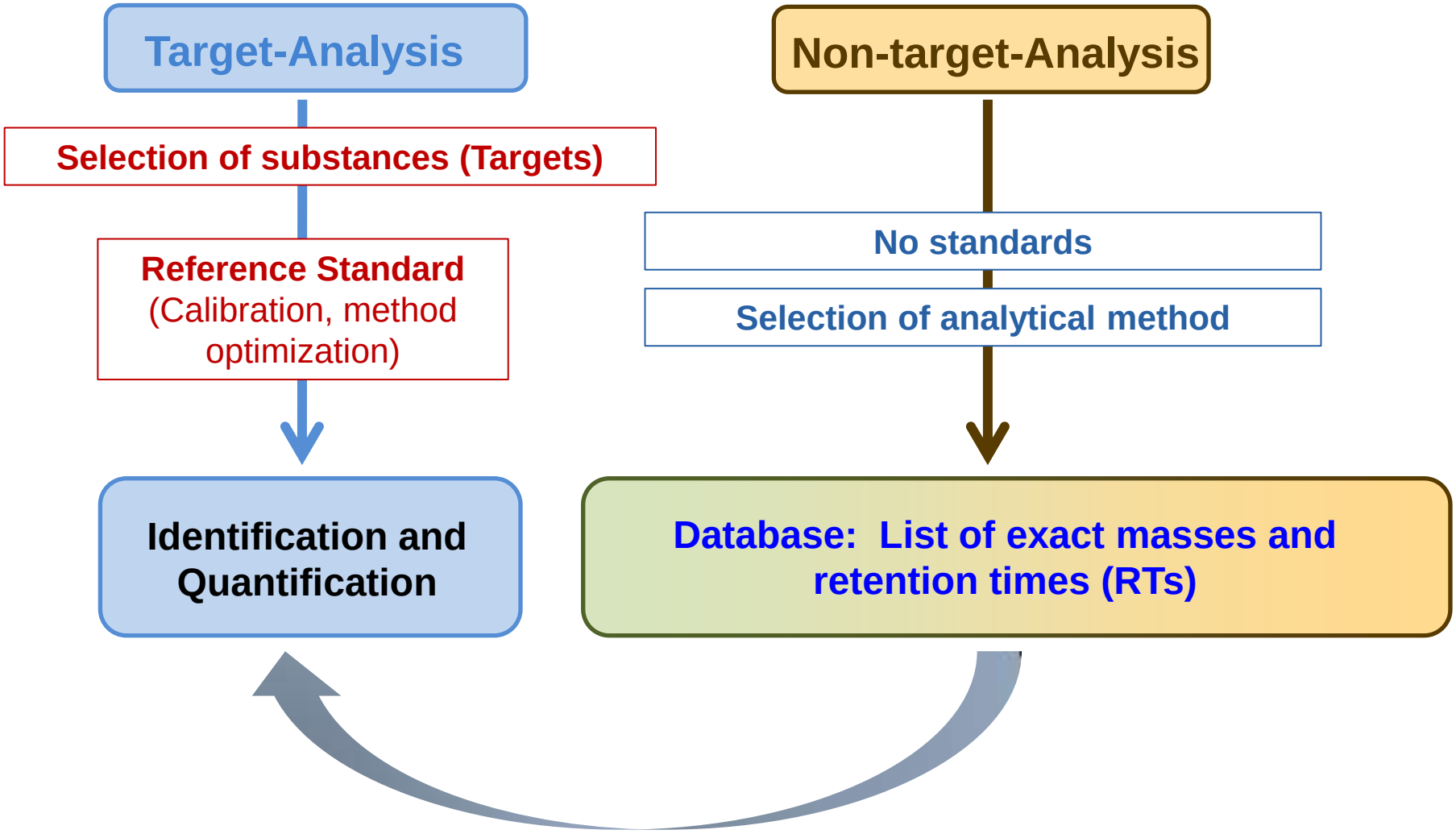


Quaternary phosphonium compounds: new toxic compounds present in sediments and suspended matter

Simon Brand, Uwe Kunkel, Michael Schlüsener, Thomas Ternes
Federal Institute of Hydrology, Koblenz (GER)

11th International SedNet Conference, Dubrovnik
04th April 2019

Target vs. Non-target Analysis

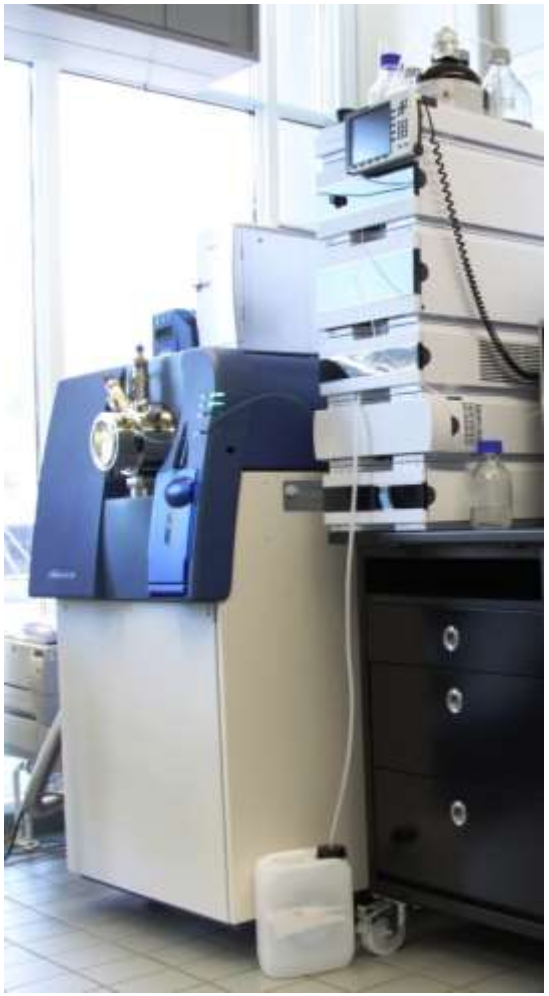


How it all started…

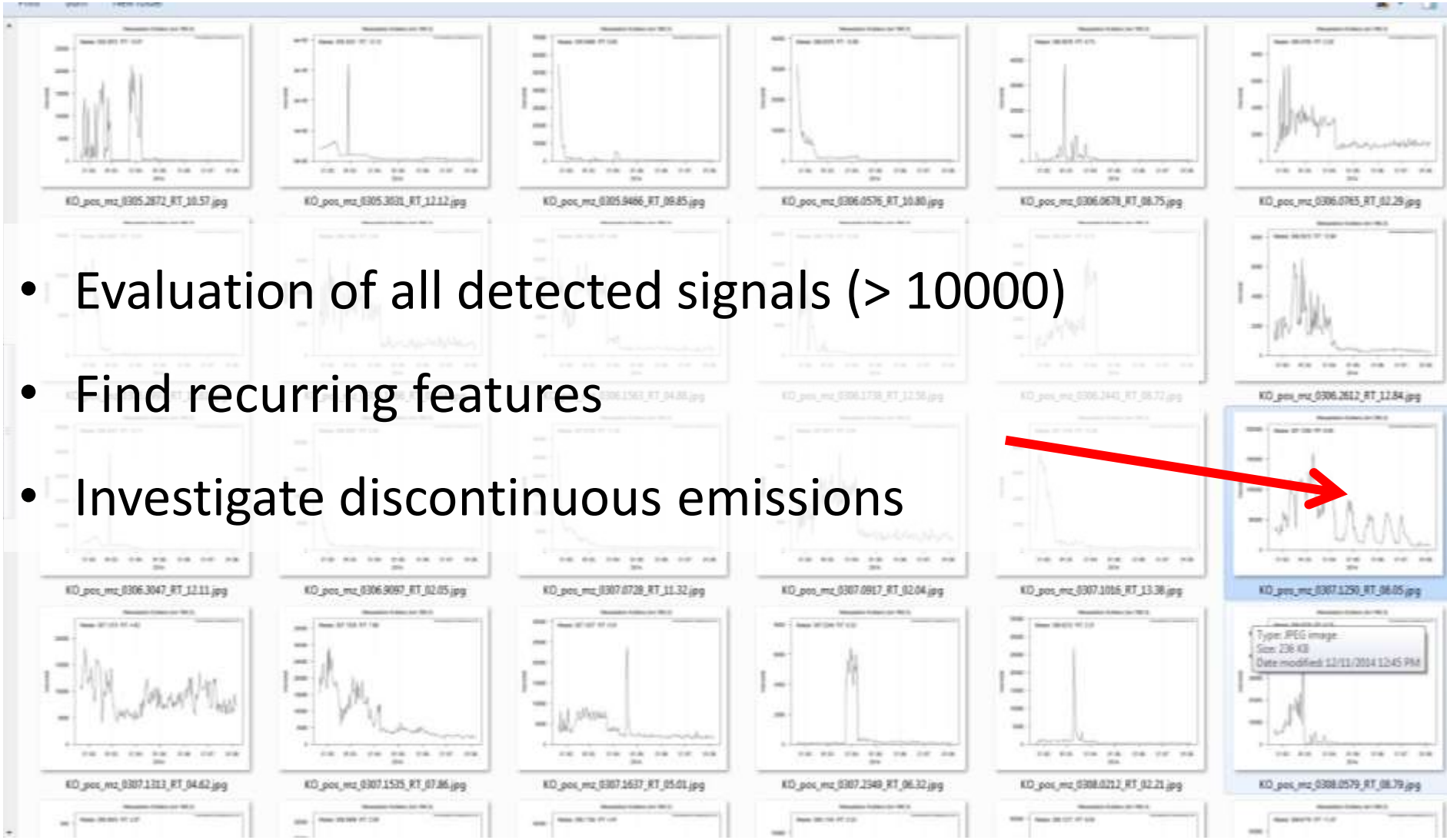
Non-Target Screening in Koblenz:

- 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**



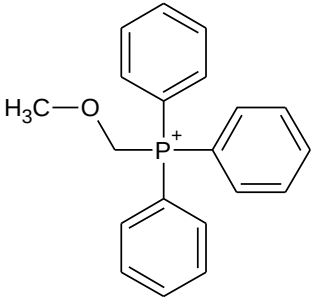
Results: Time trends of features in the Rhine at Koblenz

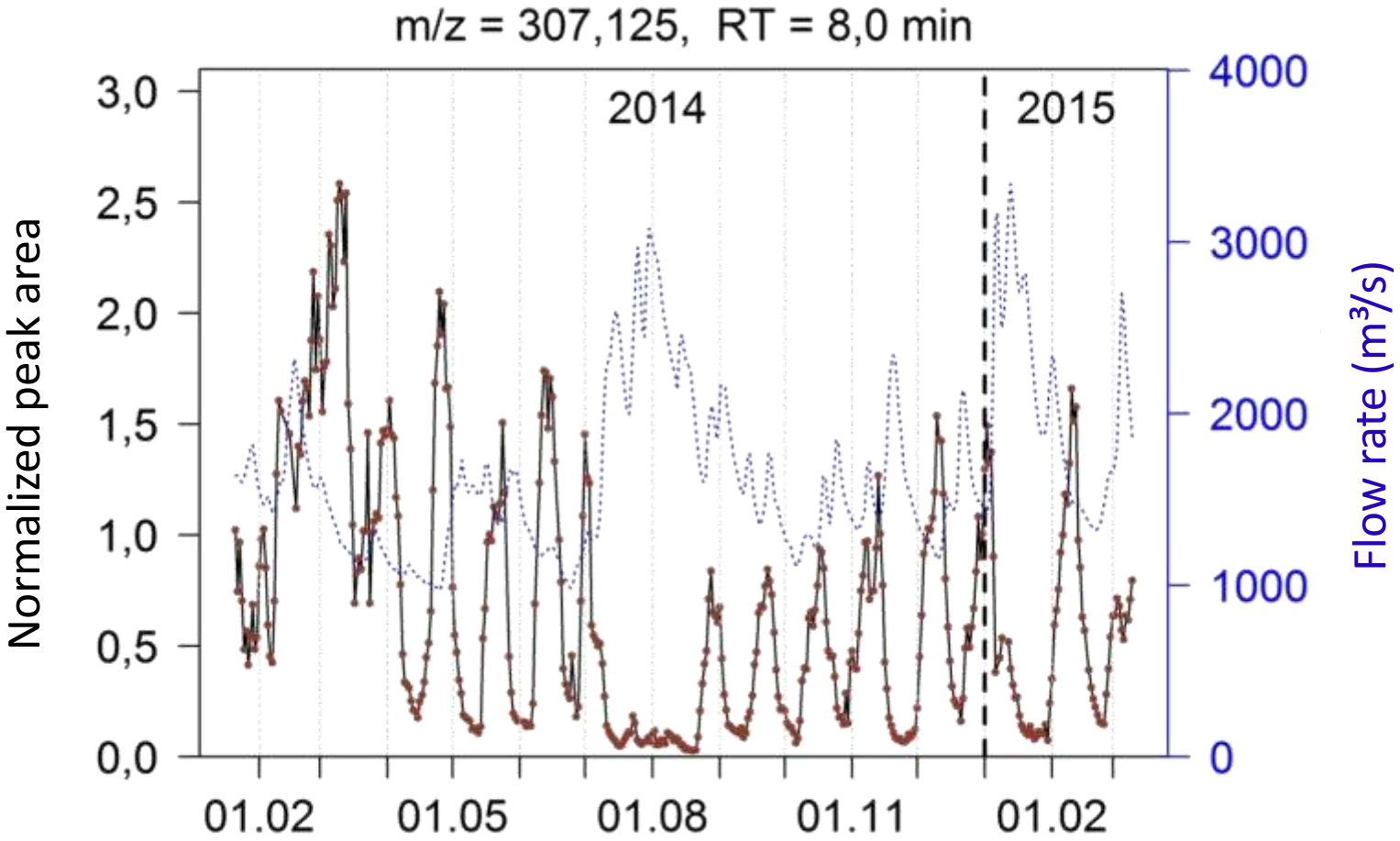


- Evaluation of all detected signals (> 10000)
- Find recurring features
- Investigate discontinuous emissions

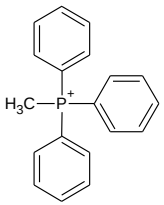
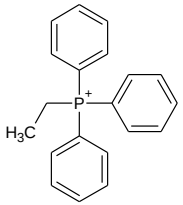
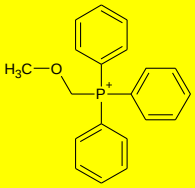
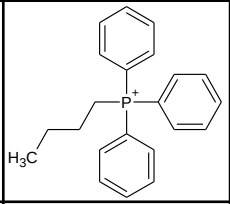
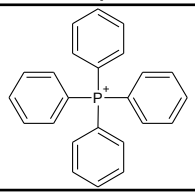
Results: Recurring feature

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



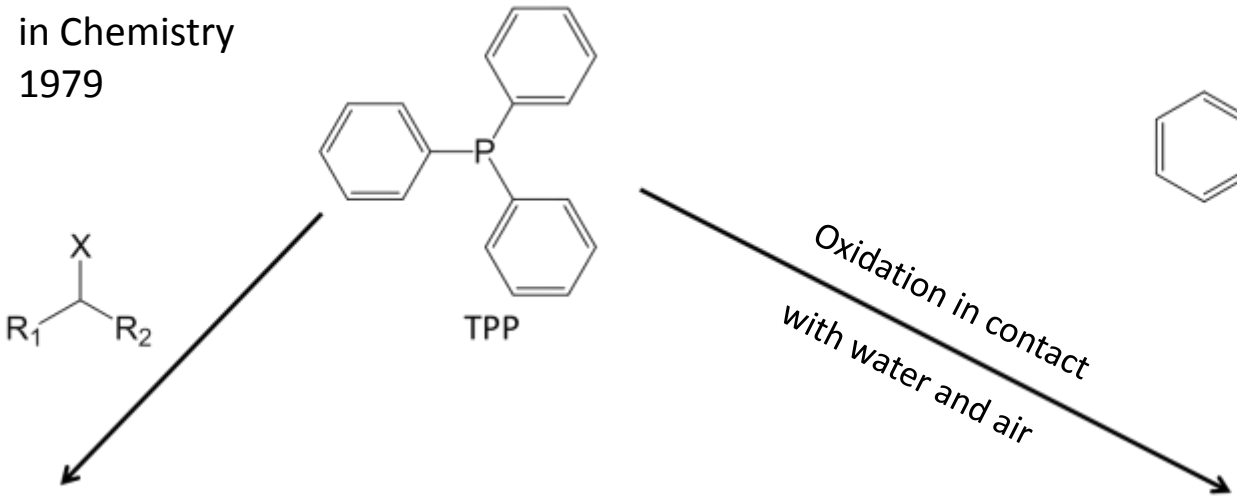


Identification of further quaternary phosphonium compounds (QPC)

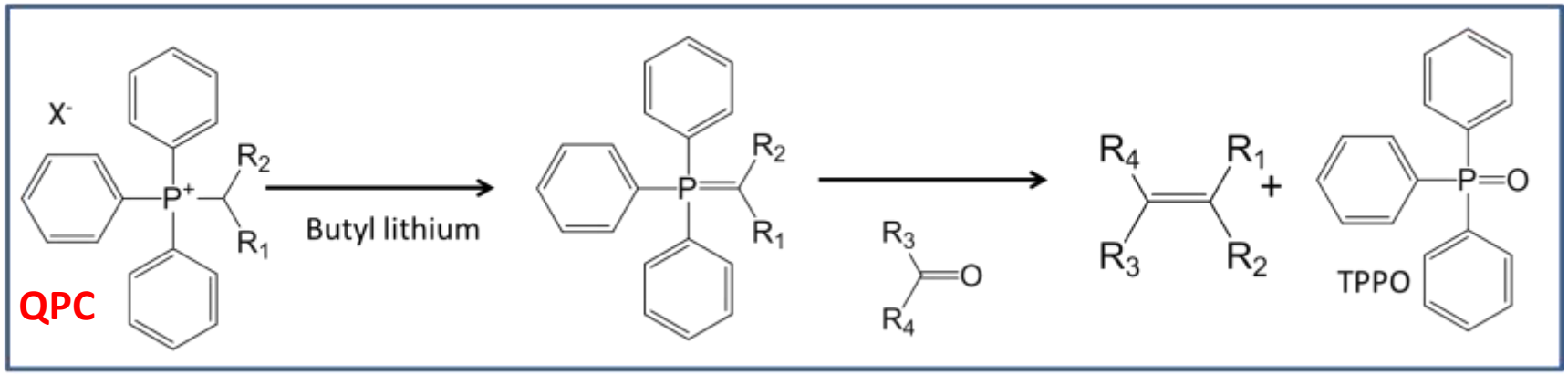
Substance	Formula	Structure	m/z
Methyltriphenyl-phosphonium cation ($Me\text{-}Ph_3P^+$)	$C_{19}H_{18}P^+$		277.1141
Ethyltriphenyl-phosphonium cation ($Et\text{-}Ph_3P^+$)	$C_{20}H_{20}P^+$		291.1297
Methoxymethyl-triphenylphosphoniumcation ($MeOMe\text{-}Ph_3P^+$)	$C_{20}H_{20}OP^+$		307.1246
Butyltriphenyl-phosphonium cation ($Bu\text{-}Ph_3P^+$)	$C_{22}H_{24}P^+$		319.1616
Tetraphenyl-phosphonium cation (Ph_4P^+)	$C_{24}H_{20}P^+$		339.1297

Application of QPCs: Wittig reaction

Nobel Prize
in Chemistry
1979

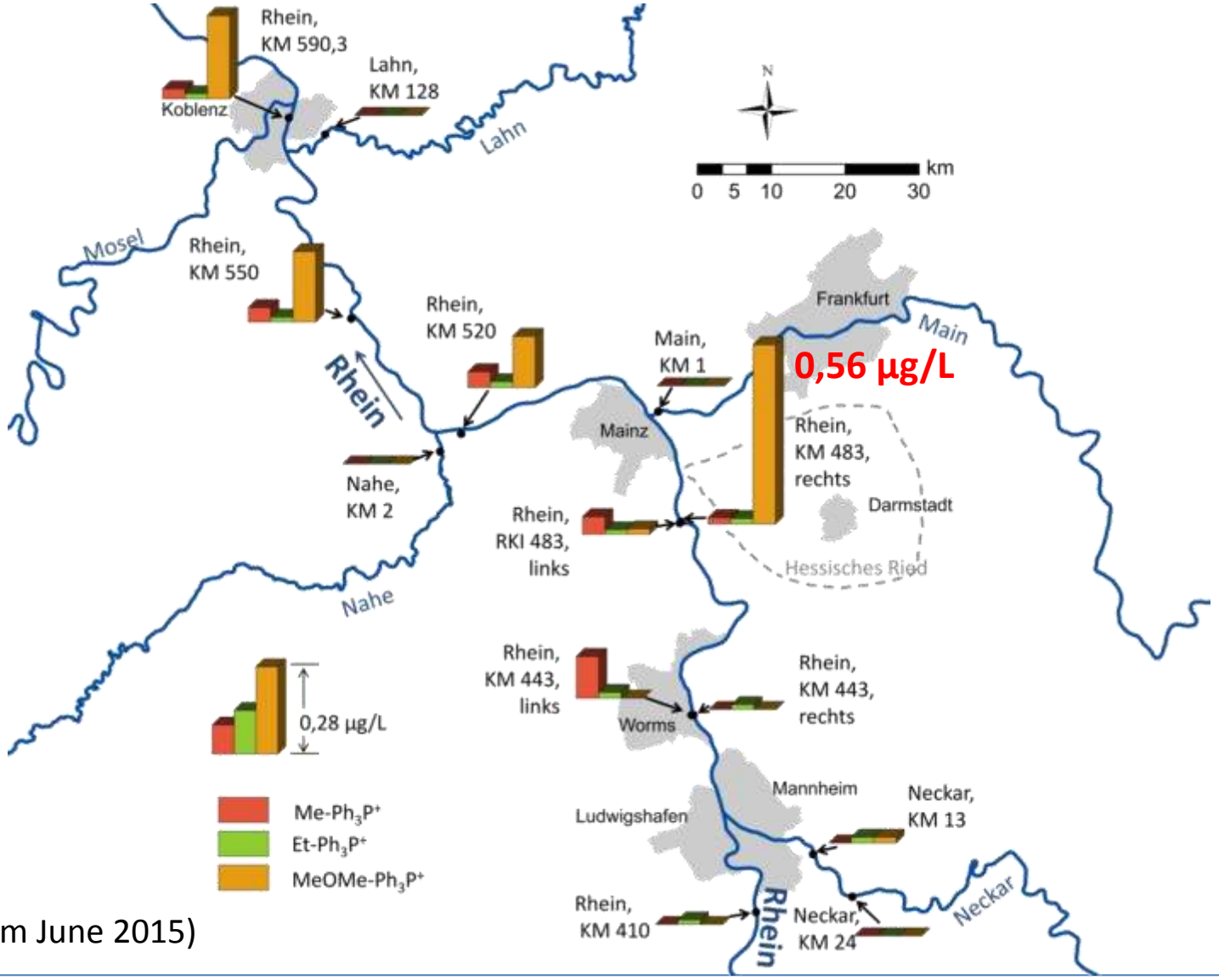


Wittig reaction



a) Wittig reaction: Synthesis of Vitamin A, β-Carotene, …
b) also as phase transfer catalyst

Back to target analysis:

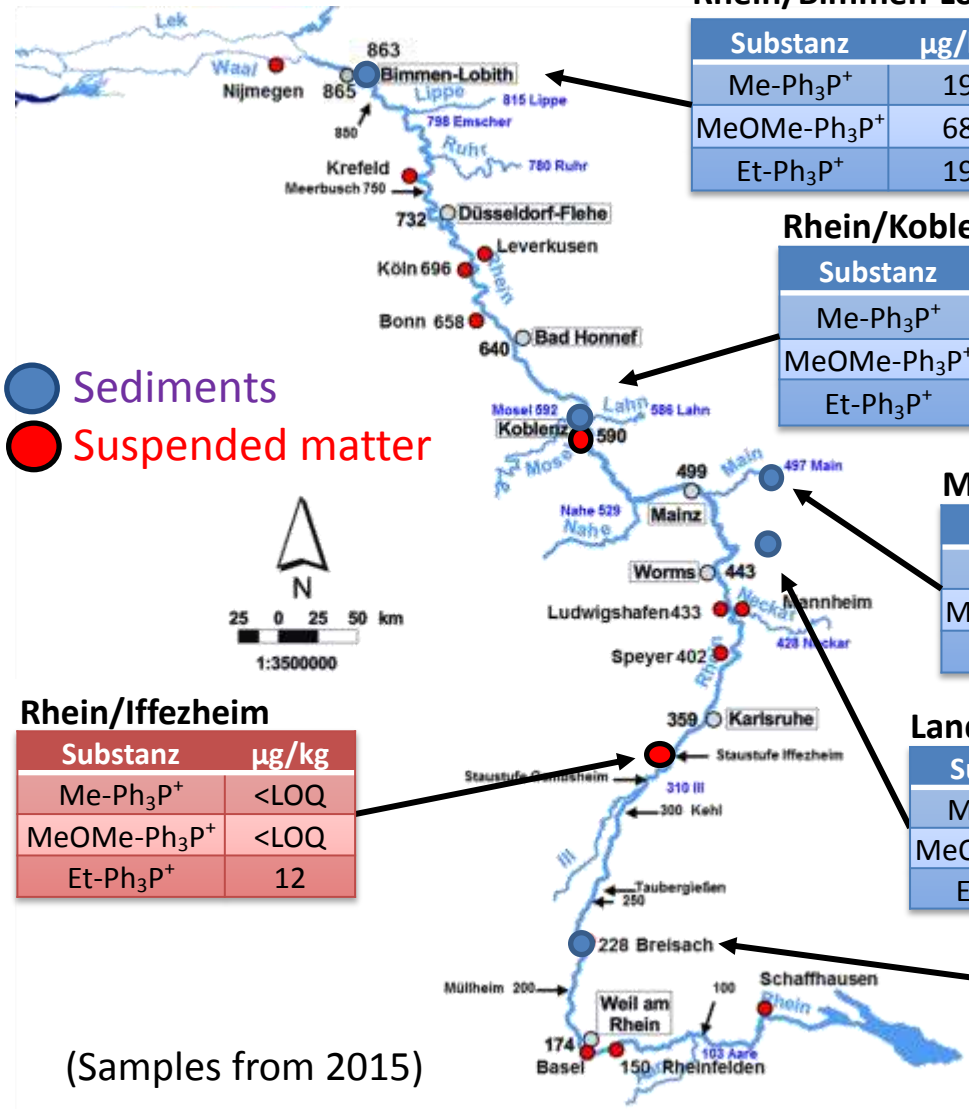


(Samples from June 2015)

Back to target analysis:

Target Method:

- 25 QPCs and derived phosphine oxides
- Longitudinal sampling of sediment (if possible, also suspended matter) at rivers Rhine and Elbe



Sediments

Suspended matter

(Samples from 2015)

Rhein/Bimmen-Lobith

Substanz	µg/kg
Me-Ph_3P^+	19
MeOMe-Ph_3P^+	68
Et-Ph_3P^+	19

Rhein/Koblenz

Substanz	µg/kg
Me-Ph_3P^+	80
MeOMe-Ph_3P^+	**210**
Et-Ph_3P^+	64

Rhein/Koblenz

Substanz	µg/kg
Me-Ph_3P^+	43
MeOMe-Ph_3P^+	**750**
Et-Ph_3P^+	86

Main/Bischofsheim

Substanz	µg/kg
Me-Ph_3P^+	<LOQ
MeOMe-Ph_3P^+	<LOQ
Et-Ph_3P^+	<LOQ

Rhein/Iffezheim

Substanz	µg/kg
Me-Ph_3P^+	<LOQ
MeOMe-Ph_3P^+	<LOQ
Et-Ph_3P^+	12

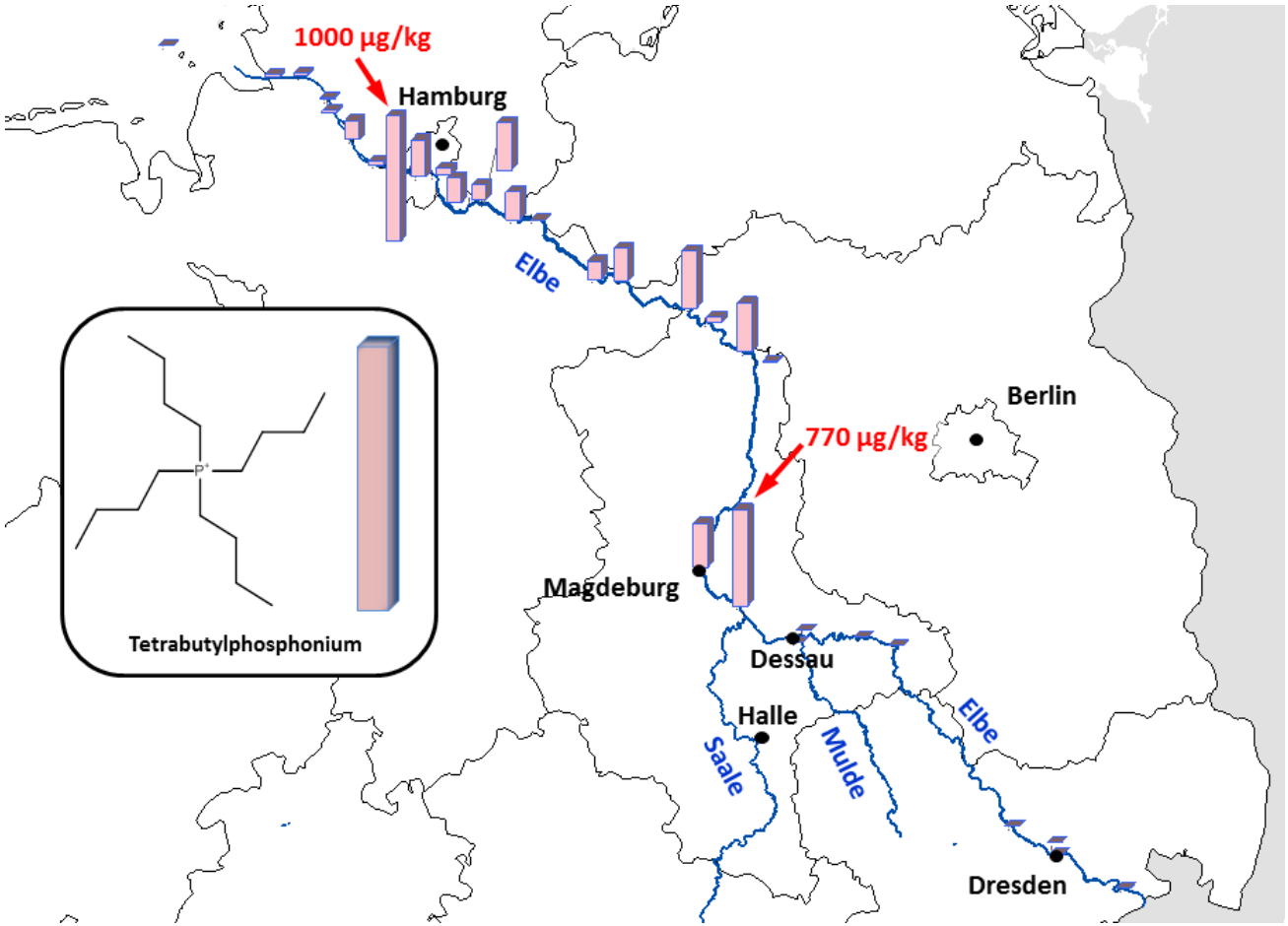
Landgraben/Trebur

Substanz	µg/kg
Me-Ph_3P^+	**560**
MeOMe-Ph_3P^+	**1200**
Et-Ph_3P^+	**190**

Rhein/Breisach

Substanz	µg/kg
Me-Ph_3P^+	<LOQ
MeOMe-Ph_3P^+	<LOQ
Et-Ph_3P^+	85

Back to target analysis:

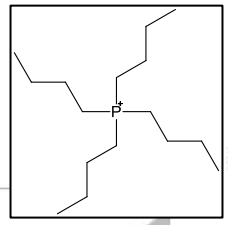


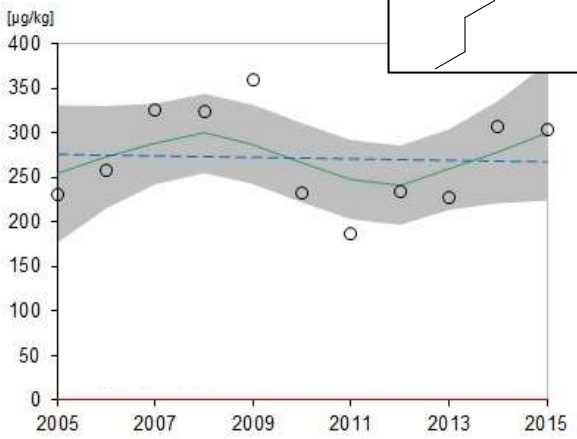
1) Longitudinal sampling gives good idea of the **origin** of the QPC contaminations

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

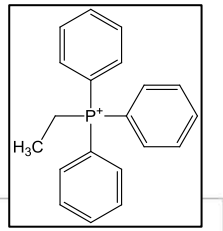
(Samples from 2015)

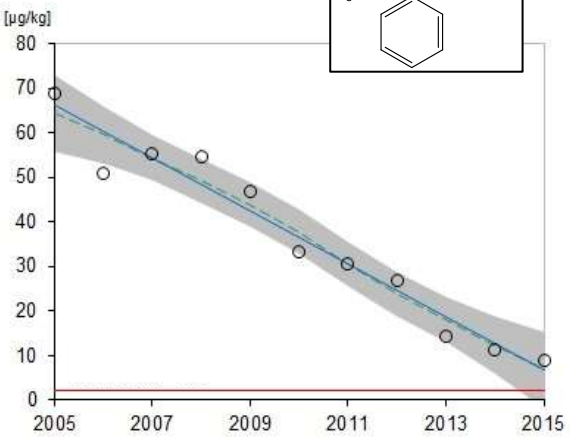
Time Trends:



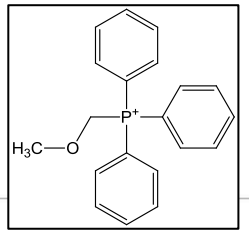


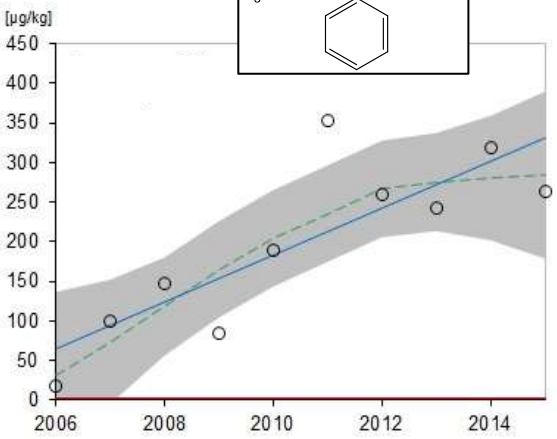
Bu_4P^+
Barby (Elbe)





$Et\text{-}Ph_3P^+$
Blankenese (Tidal Elbe)





$MeOMe\text{-}Ph_3P^+$
Koblenz (Rhein)

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

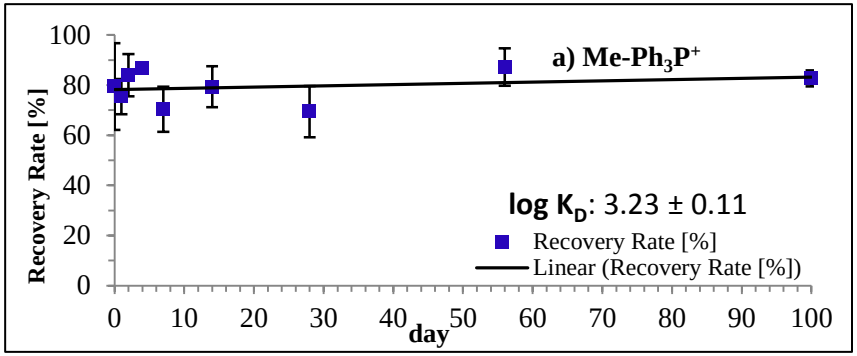
➔ QPCs have been present in the aquatic environment for at least one decade!

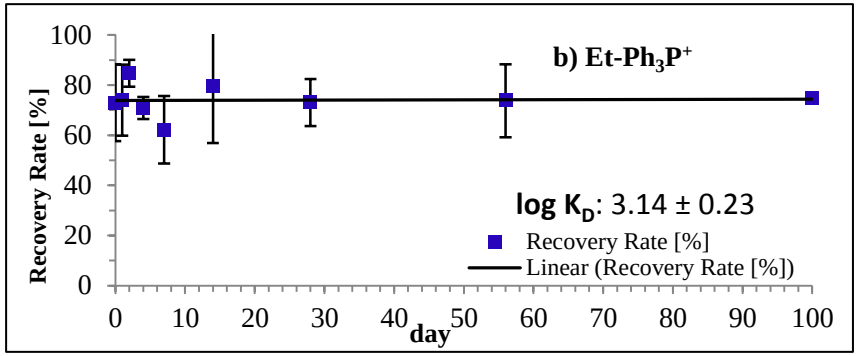
➔ (SM load [t/a] x 10^3 x Concentration [µg/kg]) x 10^{-9} = Annual QPC load [kg/a]

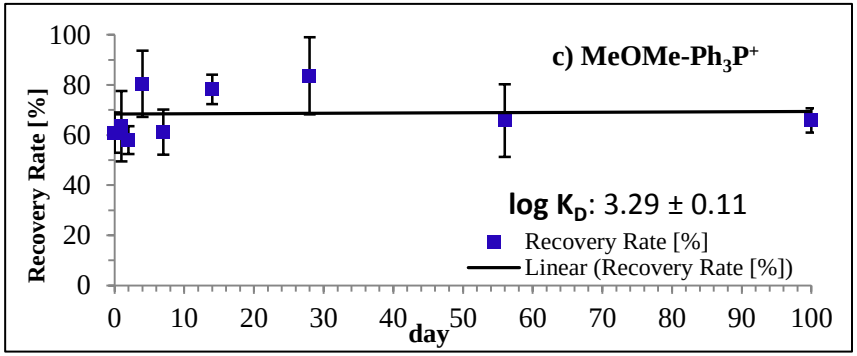
➔ e.g. $MeOMe\text{-}Ph_3P^+$ 2012 in Koblenz: 1 413 116 [t/a] x 260 [µg/kg] x 10^{-6} = **370 kg/a**

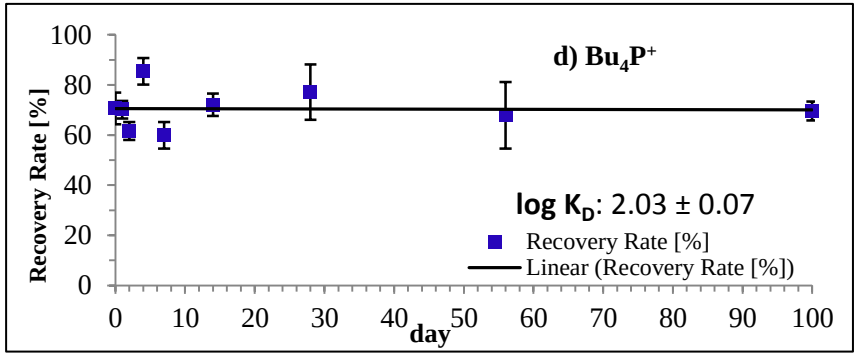
Degradation Experiment:

- Aerobic degradation experiment with four QPCs over 100 days:









- Recovery Rates 70-80%
- Linear trends over 100 days → **no degradation!**
- Recovery in liquid phase significantly lower than in sediment extracts → 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**
  - Ph_4P^+ > Ph_3P^+-R with R=alkyl, Bz > R=Ether/Ester > Bu_4P^+ ; phosphinoxides
- Four substances also showed **genotoxic potential**
  - MeOMe-Ph_3P^+ Cl^-, MeOCarbMe-Ph_3P^+ Br^-, Bu_4P^+ Br^-, **Ph_3PO (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:

- Schlüsener, M. P. et.al., Quaternary Triphenylphosphonium Compounds: A New Class of Environmental Pollutants. *Environ Sci Technol* **2015,** *49* (24), 14282.
- Brand, S. et.al., Quaternary (Triphenyl-) Phosphonium Compounds: Environmental Behavior and Toxicity. *Water Research* **2018**, 136, 207-219.

Acknowledgements

- Financial Support: BMBF/Water JPI, BMU, BMVI
- Working Group & Project Partners

- **… you all for your attention!**

Water JPI

Federal Ministry of Education and Research

Federal Ministry of Transport and Digital Infrastructure

Federal Ministry for the Environment, Nature Conservation and Nuclear Safety

UBA

FRAME