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. Pyrethroides)
- Benzotriazoles
- Fragances (e.g. nitro and polycyclic musks)
- Flame retartands
  - PBDE
  - PFAS
  - OPFRs

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

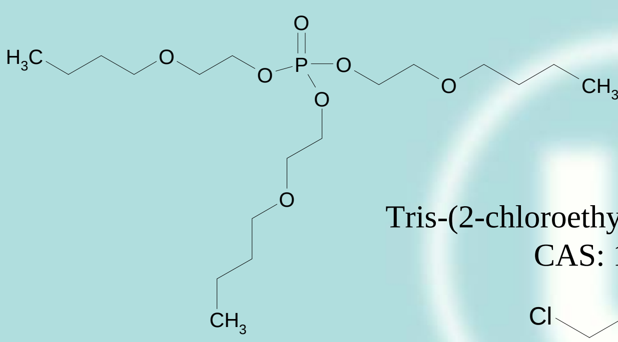
Use of OPFR

- Flame retardant
  - Upholsterer
  - Paints, varnishes
  - (Polyurethane) foams
  - Electronic devices
  - garment
- lubricant
- plasticizer

OPFR - characteristics

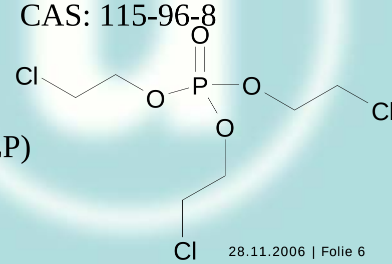
- Consumption: >40.000 t/year TCPP worldwide >5.000 t/year TCEP, TCPP, TDCPP in the EU
- Persistent and stable
- Relatively low capability for bioaccumulation/biomagnification
- moderate acute toxicity (dependant on the single compound)
  - but acute aquatic toxicity
- Some of them probably carcinogenic to men (especially the chlorinated ones)

Examples: OPFR



Tris (2-butoxyethyl)-phosphat (TBEP)
CAS: 78-51-3

Tris-(2-chloroethyl) phosphate (TCEP)
CAS: 115-96-8



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

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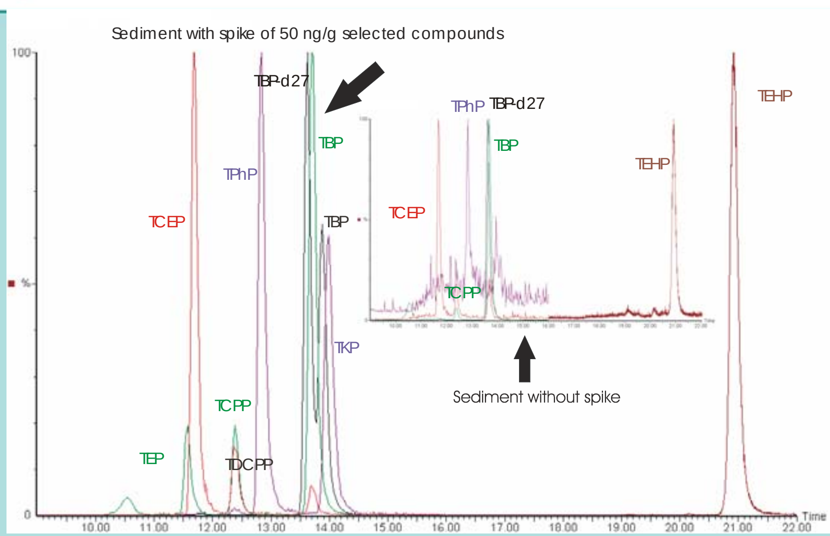
Sediment spiked with 50 ng/g



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Wastewater Samples in Austria

- 16 municipial 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 occurence in the aquatic environment

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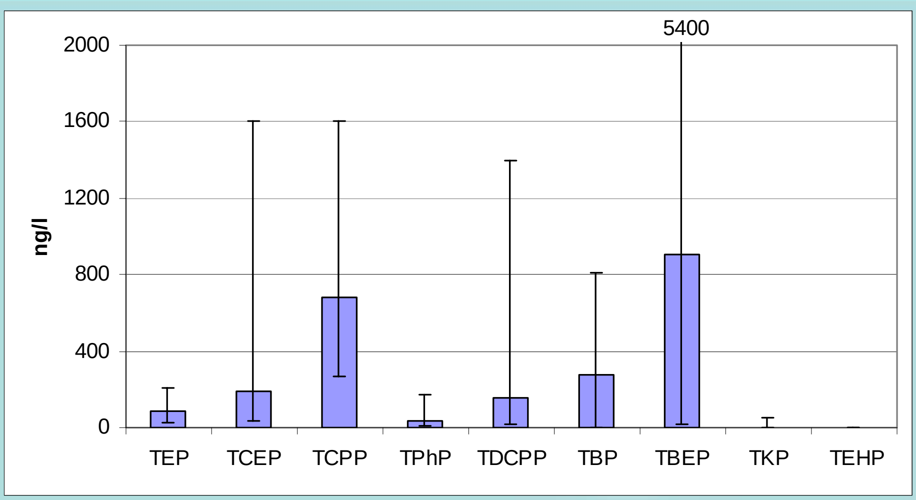
Mean, Max. and Min. in Austrian effluents



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Conclusions – Wastewater

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

	Austria (n=16) mean	W. Europe (n=8) mean	Germany (n=2) mean
TCEP	0,19	0,2	0,36
TCPP	0,68	0,6	1,9
TBEP	0,91		0,42
		Reemtsma et al. 2006	Meyer et al. 2004

Influence of STP in the aquatic environment

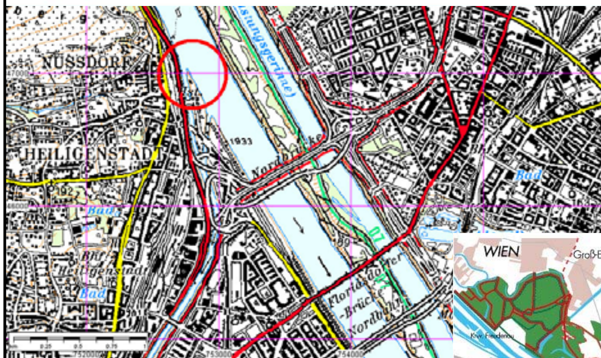
Results Effluent – Sediments Danube

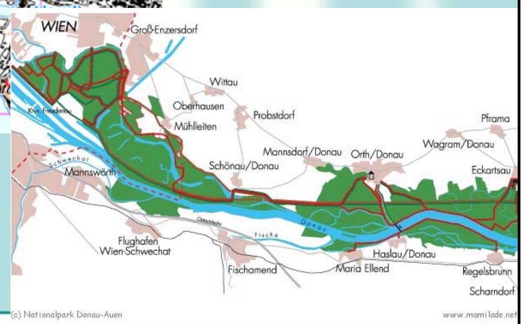
	Effluent Linz ng/l	Asten right [µg/kg TM]	Asten left [µg/kg TM]
TEP	120	5,7	<3,3
TCEP	140	13	n.n.
TCPP	1400	110	7
TPhP	27	29	<1.3
TDCPP	1400	n.n.	n.n.
TBP	420	<11	<11
TBEP	57	3,4	2,9
TCP	n.n.	8,1	<1.5
TEHP	n.n.	1,7	3,3

River and sediment monitoring

- Danube
  - Two sample points
  - 2nd largest river in Europe
  - 1900 m^3/s (Vienna)
- Schwechat
  - Influenced by industry and high density population
  - nearby Vienna
  - 7.9 m^3/s
- Liesing
  - Influenced by industry and high density population
  - nearby Vienna
  - 0.38 m^3/s

Danube, Schwechat and Liesing





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Liesing

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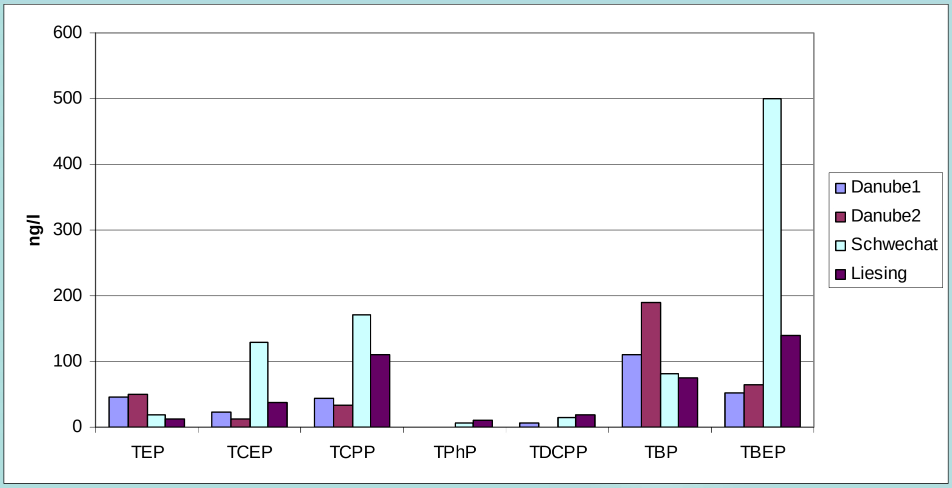
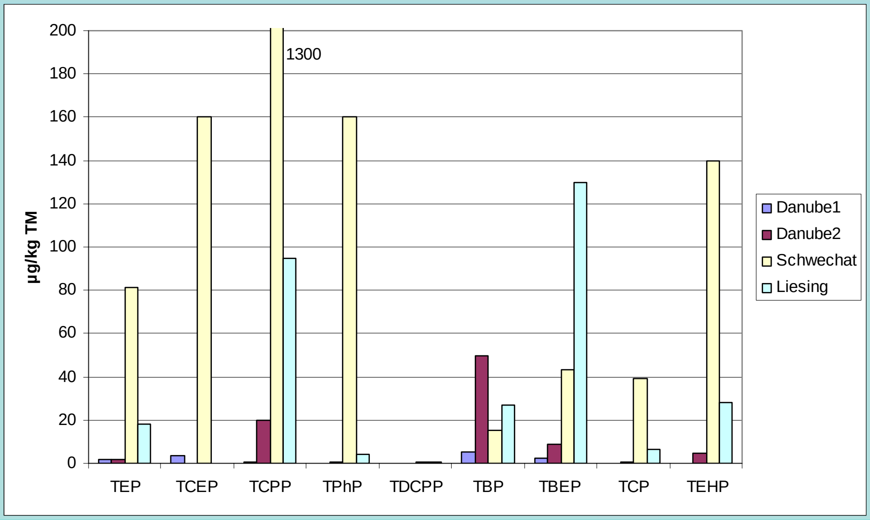
Results – Danube, Schwechat, Liesing



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



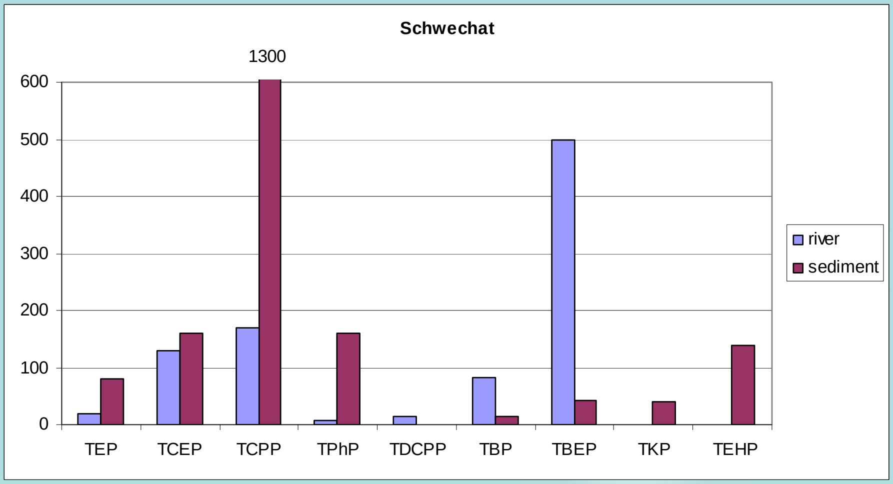
Conclusions

- 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

Schwechat – comparison sediment to the water phase



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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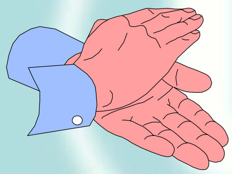

- for your attention

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