GOETHE UNIVERSITÄT FRANKFURT AM MAIN

www.goethe-universitaet.de

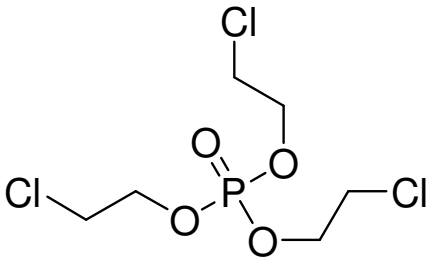
Trinkwasserrelevanz von chlorierten Organophosphaten (Flammschutzmittel)

Wilhelm Püttmann

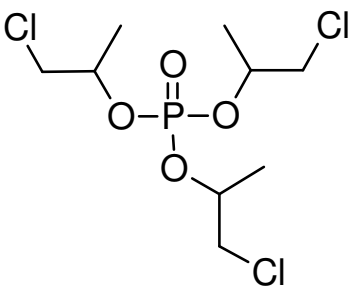
Goethe-Universität Frankfurt am Main
Institute für Atmosphäre und Umwet
AG Umweltanalytik

UBA-Fachgespräch
Dessau, 19. 01. 2011

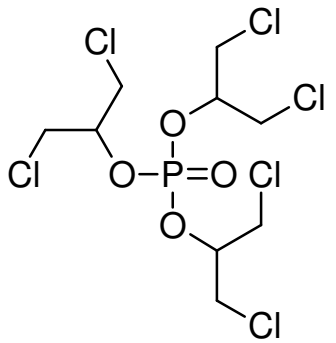
Target compounds



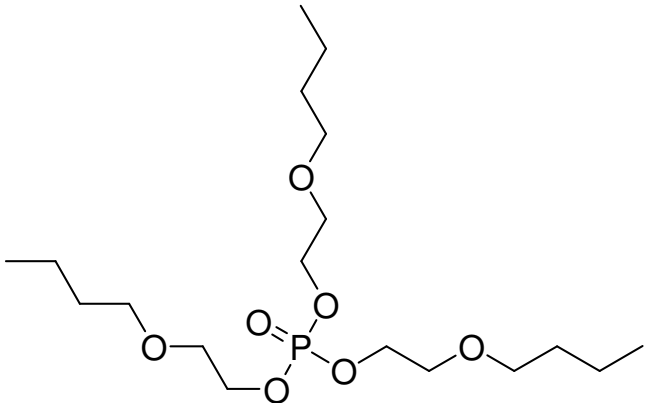
TCEP
Tris(2-chloroethyl) phosphate



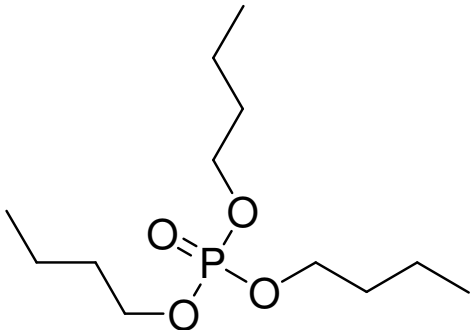
TCPP – Isomer 1
Tris(2-chloro-1-methylethyl) phosphate



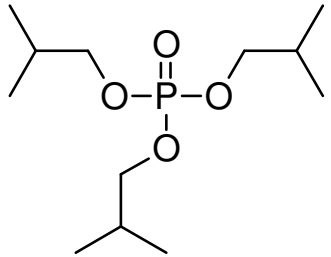
TDCP
Tris(1,3-dichloro-2-propyl) phosphate



TBEP
Tris(2-butoxyethyl) phosphate



TnBP
Tri-n-butyl phosphate



TiBP
Tri-iso-butyl phosphate

Use and toxicology

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

Bester (2007): Personal Care Compounds in the Environment. Wiley-VCH.

http://www.hanno.at
http://www.recticelinsulation.fr
http://www.allproducts.com

Risk Assessment TCEP (EU 2009), TCPP, TDCP (EU 2008)

	TCEP	TCPP	TDCP
Henry`s law constant (at 25 °C)	$4.155 * 10^{-5}$ Pa * m^3 * mol^{-1}	$3.96 * 10^{-4}$ Pa * m^3 * mol^{-1}	$1.24 * 10^{-4}$ Pa * m^3 * mol^{-1}
Vapor pressure (at 25 °C)	$1.14 * 10^{-3}$ Pa	$1.4 * 10^{-3}$ Pa	$5.6 * 10^{-6}$ Pa
Log K_{ow}	1.78	2.68 ± 0.36	3.69 ± 0.36
Water solubility (at 20 °C)	7820 mg L^{-1}	1080 mg L^{-1}	18.1 mg L^{-1}
Hydrolysis (pH = 7)	t ½ = >1 a	t ½ = >1 a	t ½ = >1 a
Photodegradation in the atmosphere ($5 * 10^5$ OH mL^{-1})	t ½ = 17.5 h	t ½ = 8.6 h	t ½ = 21.3 h

Risk Assessment TCPP (EU 2008)

„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

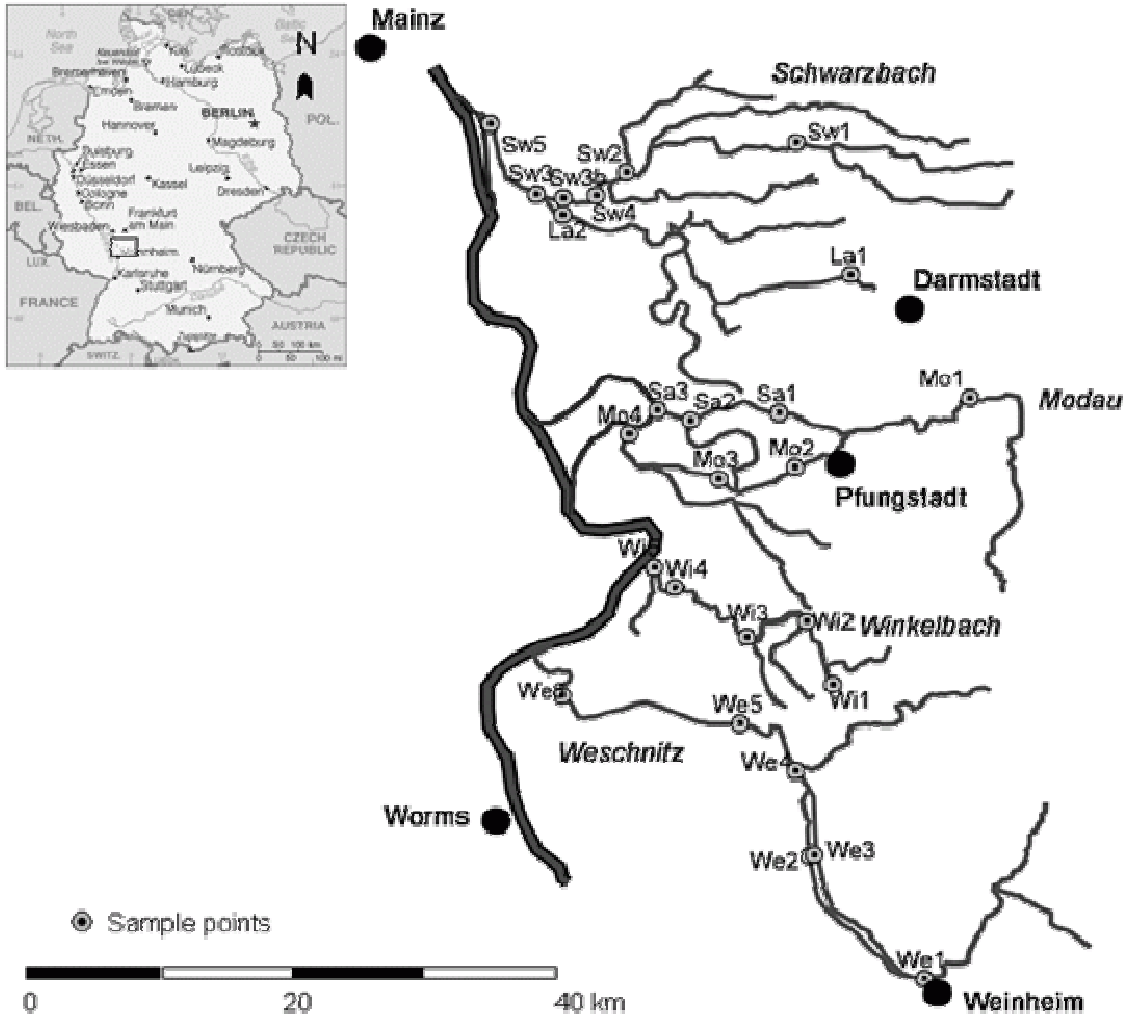
Motivation and aims

- 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**

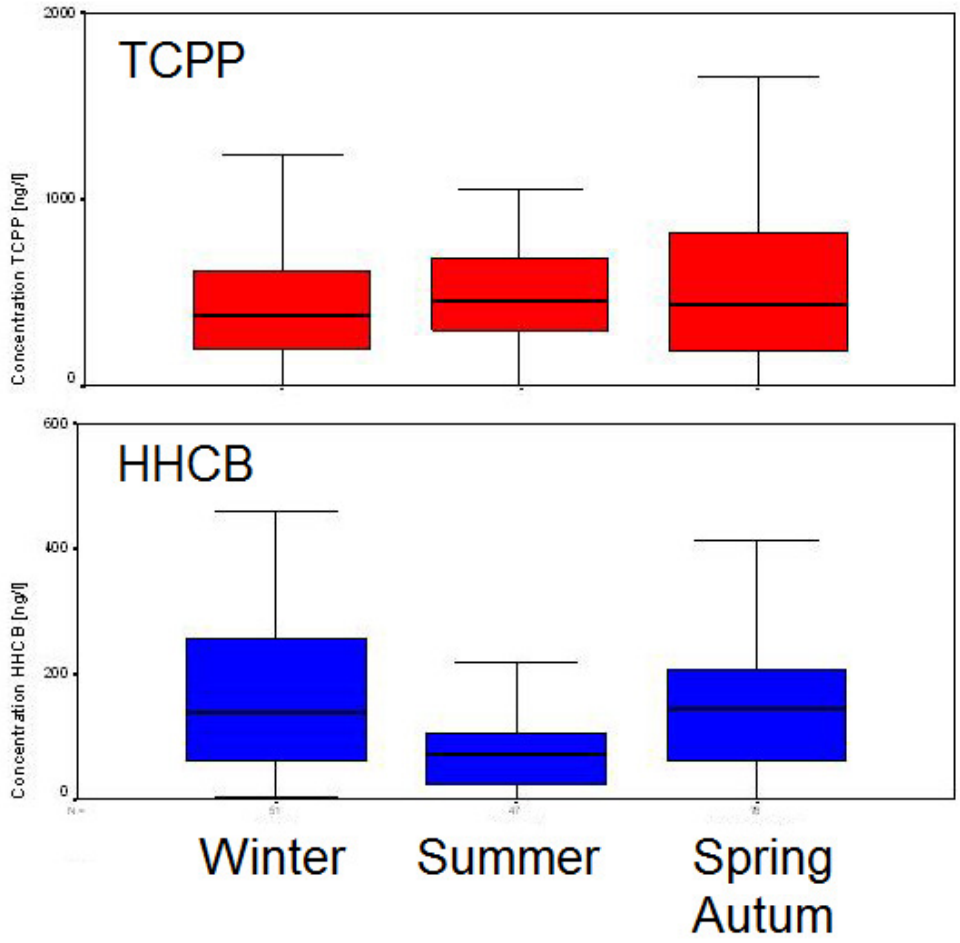
TCCP in rivers and creeks of Hessisches Ried
Sampling area and location of the sampling points

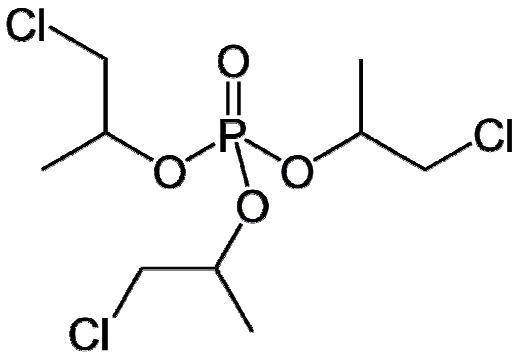


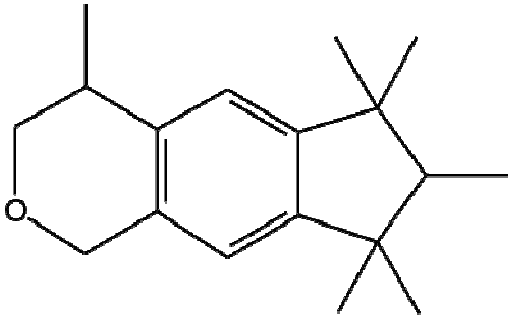
(Quednow, 2008)

Seasonal Variation of TCPP and HHCB concentrations in Rivers of Hessisches Ried

Sampling time: 2003-2006 (n= 175)

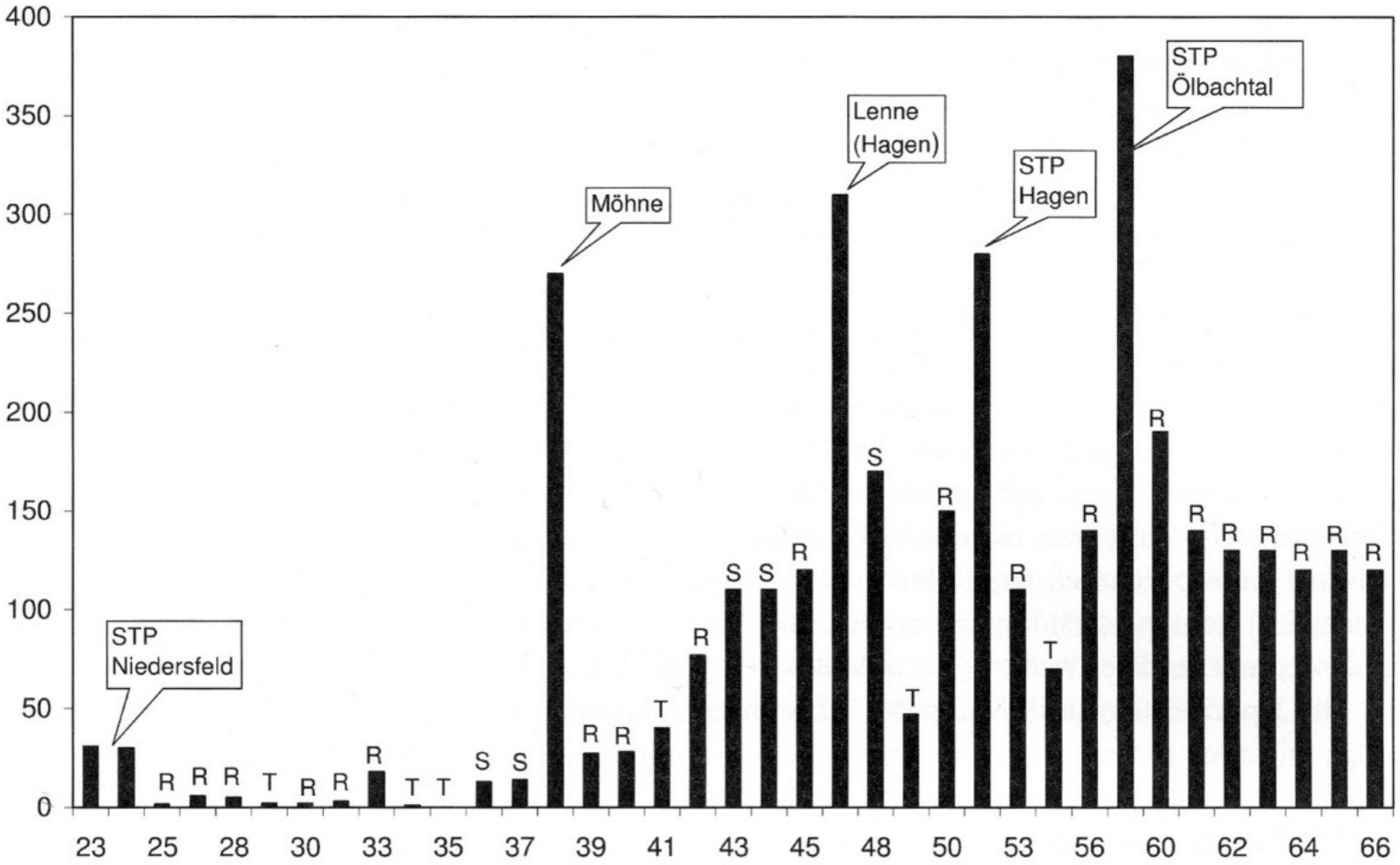






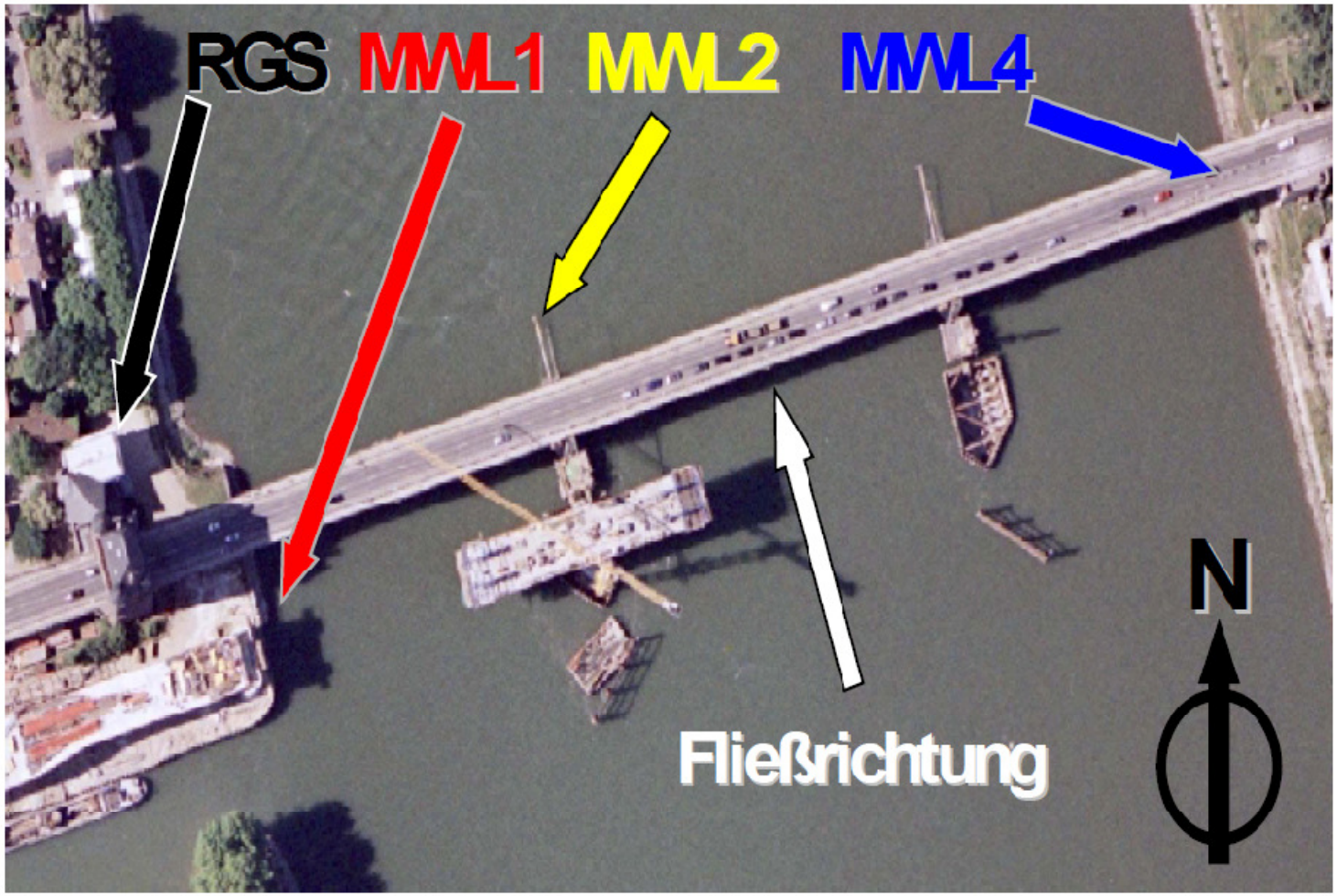
(Quednow, 2008)

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

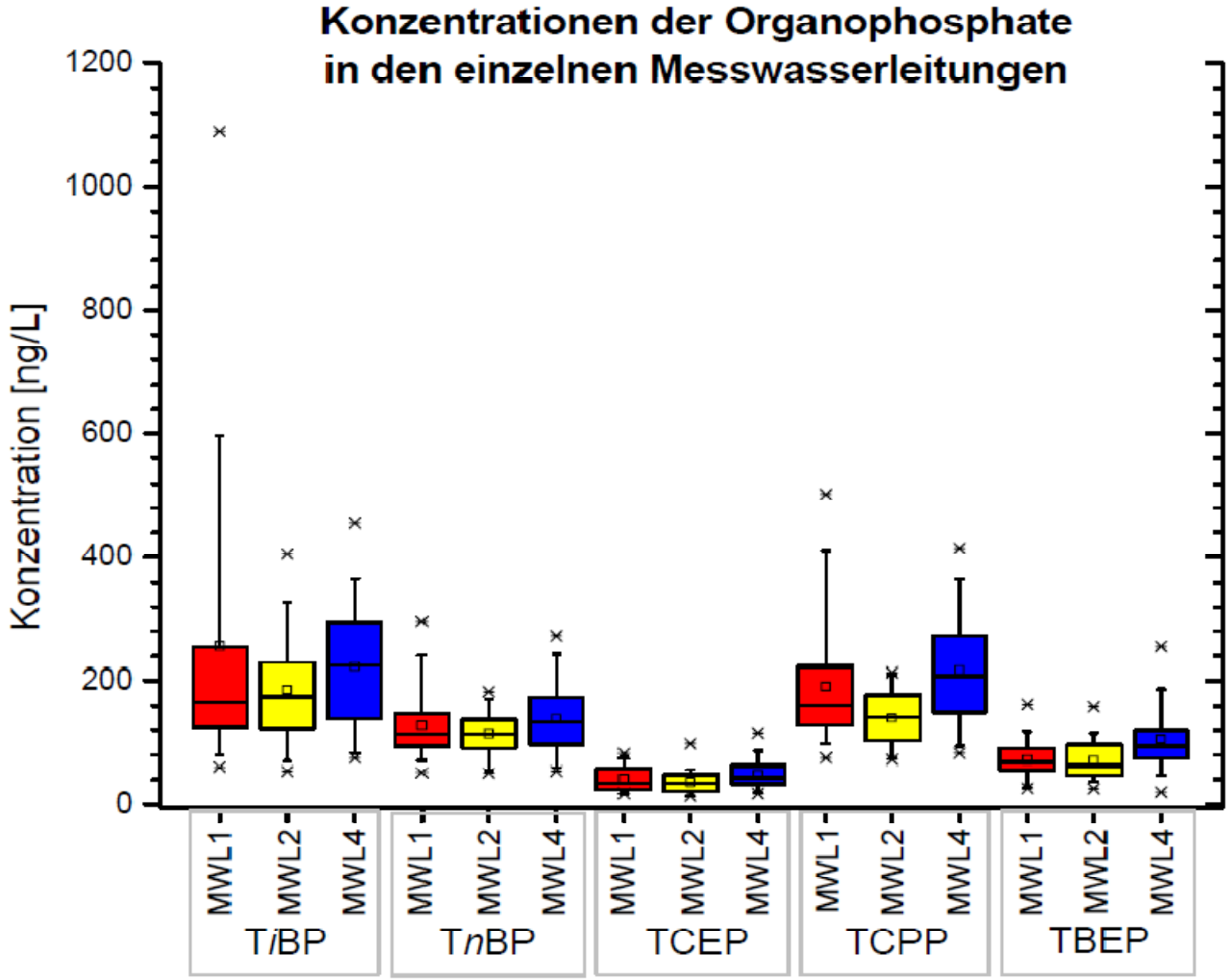


Andresen et al, Sci Total Environ, 2004

Rheingütestation Worms (Rheinkilometer 443,1)



Konzentrationen (ng/L) verschiedener Organophosphate im Rhein an der Rheingütestation in Worms, Messzeitraum Nov. 2007- Jan. 2008, n = 147



Diplomarbeit Frömmel (2008)

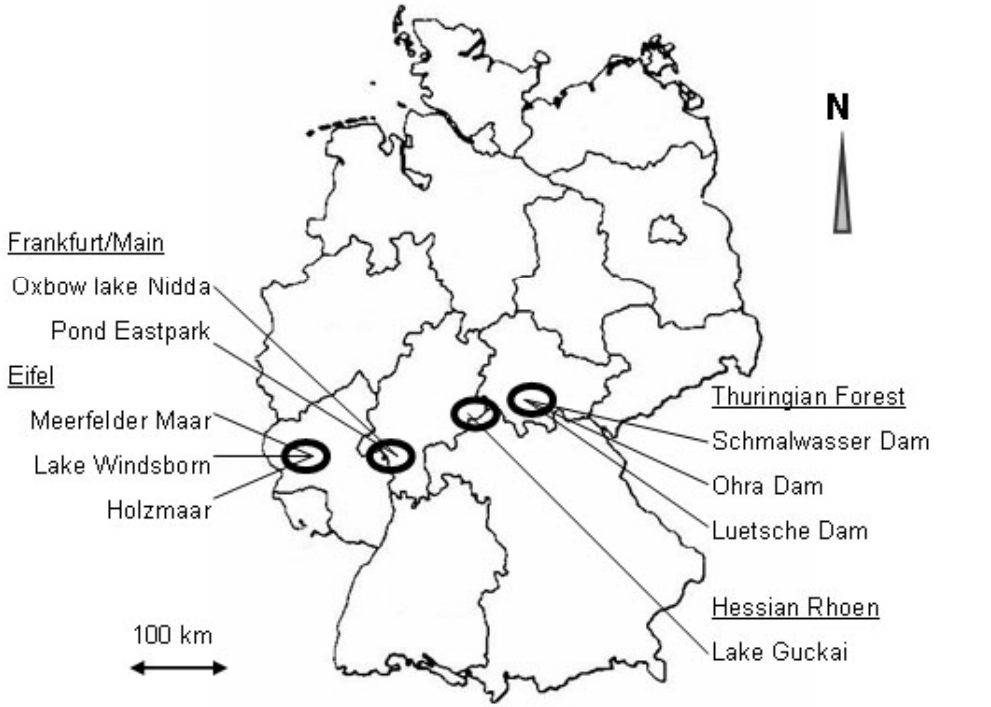
Sampling sites

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**

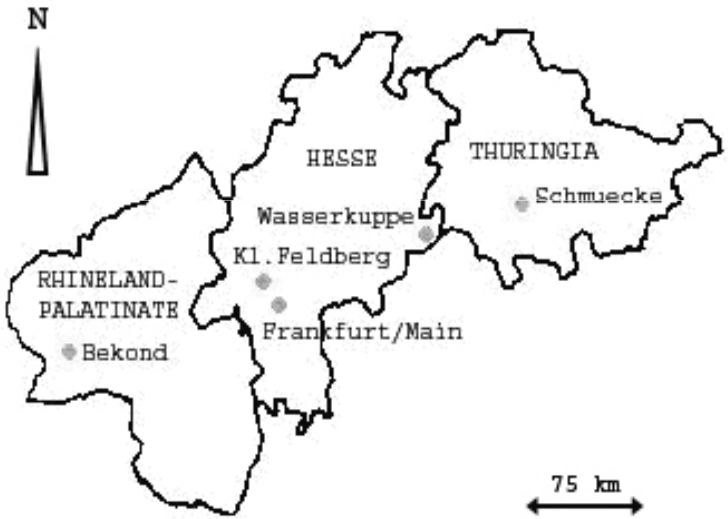


Regnery et al Water Res. (2010), 44, 4097-4104

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**



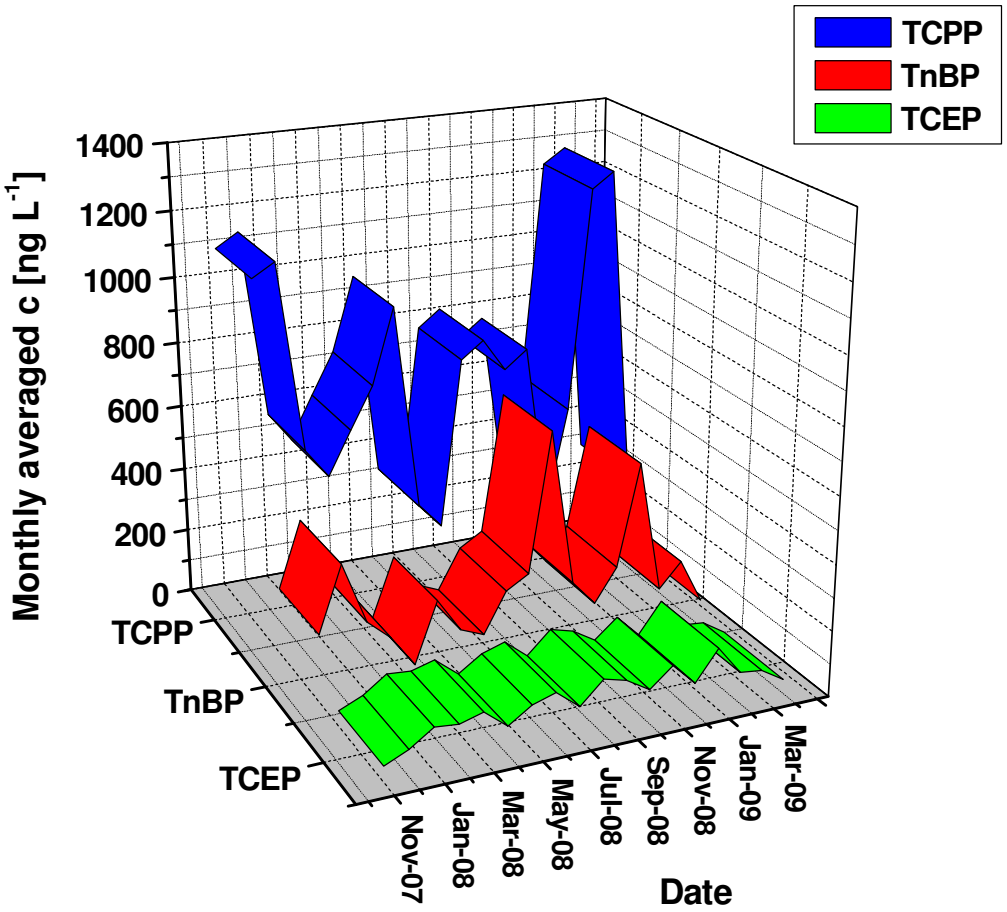
Storm water holding tank (SWHT):

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

Clean-Soil Air Water (2009), 37, 334-342

Precipitation Frankfurt am Main

- 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

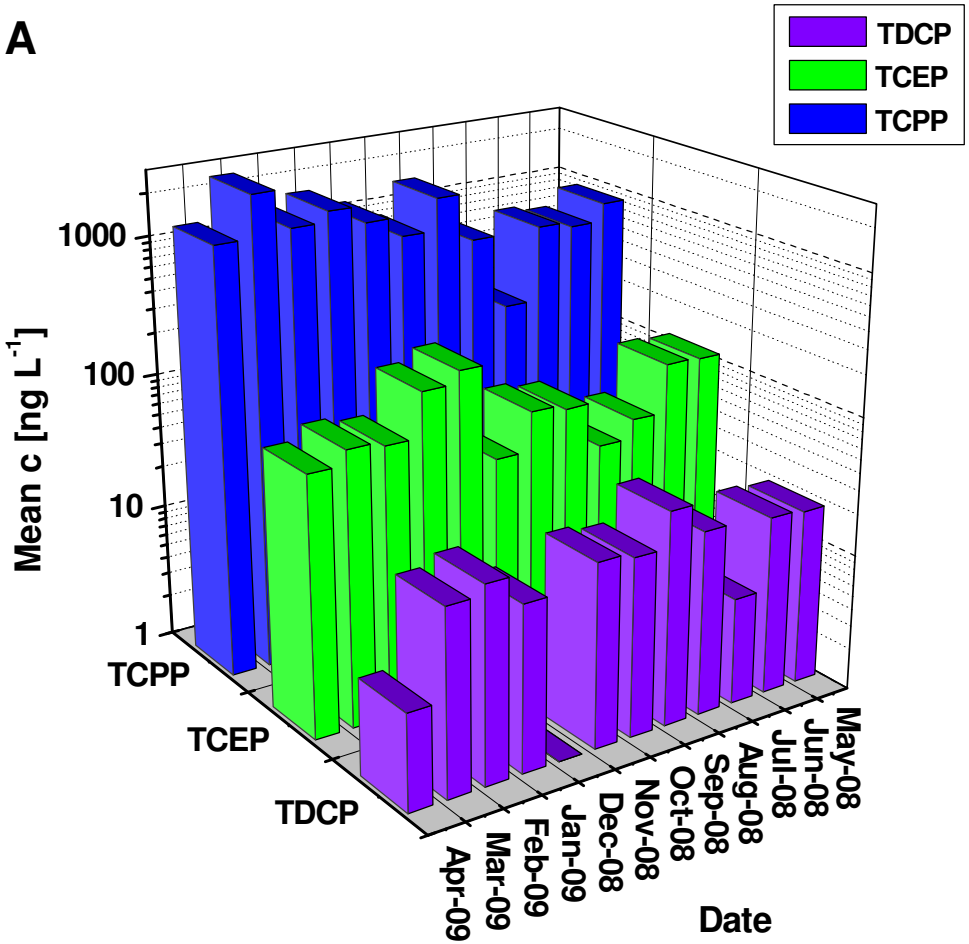


Regnery et al.,Chemosphere (2010), 78, 958-964

Storm water holding tank Frankfurt am Main

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)

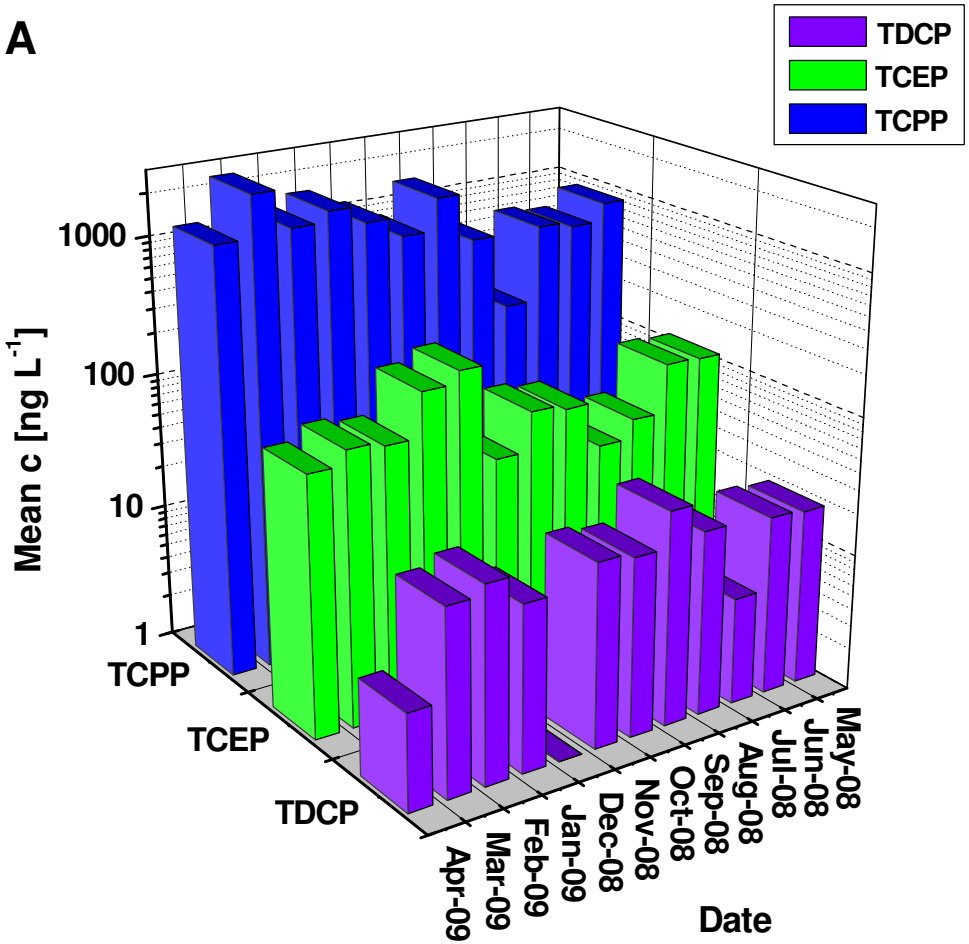


Chemosphere (2010), 78, 958-964

Storm water holding tank Frankfurt am Main

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)



Chemosphere (2010), 78, 958-964

Results (precipitation and SWHTs)

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

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

[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

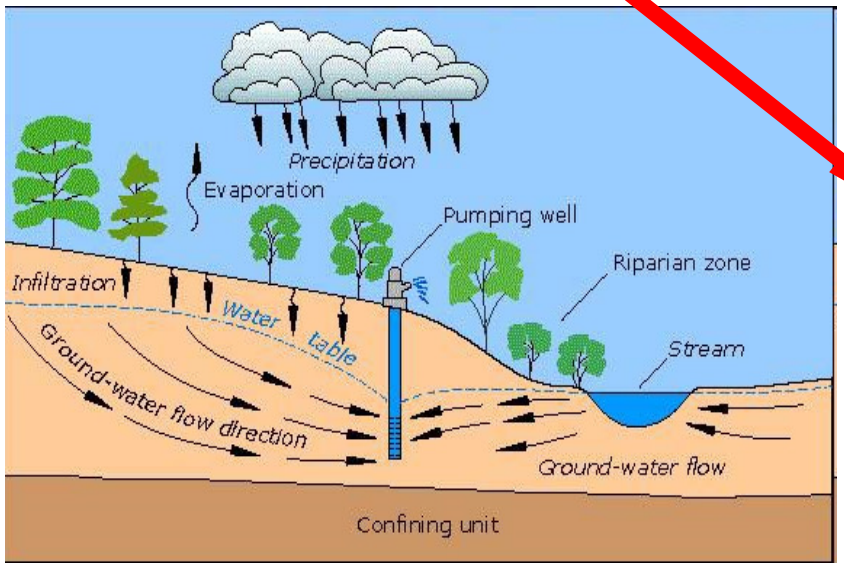
Regnery et al.,Chemosphere (2010), 78, 958-964

Results (groundwater)

A Infiltration via precipitation
→ Hessian Ried

B Riverbank filtration
→ Hessian Ried

C Polluted landfill site
→ Monte Scherbelino



http://groundwater.sdsu.edu

Site	Compound	Frequency of detection [%]	Median c [ng L^{-1}]	Max. c [ng L^{-1}]
A	TCEP	40	< LOQ	24
(n = 10)	TCPP	30	< LOQ	6
	TBEP	20	< LOQ	< LOQ
	TiBP	20	< LOQ	7
B	TCEP	67	7	148
(n = 15)	TCPP	74	38	1795
	TDCP	20	< LOQ	< LOQ
	TBEP	40	< LOQ	1813
	TiBP	67	5	105
	TnBP	67	5	51
C	TCEP	91	141	318
(n = 11)	TCPP	91	191	343
	TDCP	55	< LOQ	45
	TBEP	9	< LOQ	199
	TiBP	100	92	697
	TnBP	100	90	213

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

Conclusions

- „Short- and mid-range“ transport of organophosphates in atmosphere
- High organophosphate concentrations in precipition 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

Acknowledgements

PhD-Students Julia Regnery (2010) und Kristin Quednow (2008)

Providing of samples and data

- R. Junek, T. Neumann (Federal Environmental Agency, UBA)
- S. Kothe and co-workers (German Weather Service, DWD)
- Dr. H. Bingemer, D. Vogler (Goethe University Frankfurt am Main)
- H. Schenk, M. Kapp (BGS Umwelt)
- Dr. G. Berthold, C. Krieger (Hessian Agency for the Environment and Geology, HLUG)
- Dr. C. Merz and co-workers (Leibniz-Centre for Agricultural Landscape Research, ZALF)
- JProf. Dr. E. Fries (University of Osnabrueck)
- R. Regnery, K. Schollenbruch, S. Koch

Financial support (*e.g.,* travel grants)

- German Research Foundation (DFG, SFB 641, Project B8)
- German Academic Exchange Service (DAAD)
- German Chemical Society (GDCh)
- Vereinigung von Freunden und Förderern der J.W.Goethe Universität Frankfurt am Main