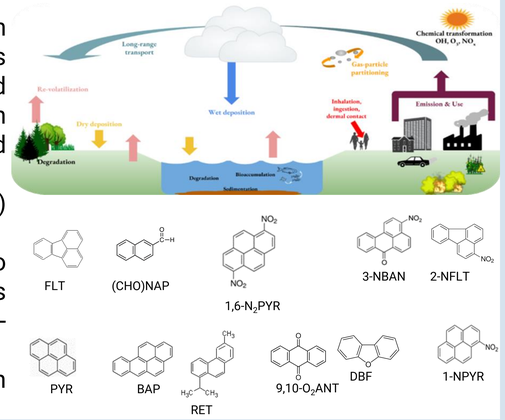
Re-emissions of polycyclic aromatic compounds from land and sea surfaces in source and receptor areas

G. Lammel[1,2], D.Bezdeková[1], P.Bohlin-Nizzetto[3], A.K. Halse[3], M. Iakovides[4], P. Kukučka[1], O. Letocha[1], J. Martiník [1], L. Mayer[1], J.K. Mwangi[1], B. Palátová Nežiková[1], P. Přibylová[1], R. Prokeš[1,5], E.G. Stephanou[4,6], M. Tsapakis[7], M. Wietzoreck[2], B. Vrana[1]

[1] RECETOX, Faculty of Science, Masaryk University, Brno, Czech Republic, gerhard.lammel@recetox.muni.cz; [2] Multiphase Chemistry Department, Max Planck Institute for Chemistry, Mainz, Germany; [3] Norwegian Institute for Air Research (NILU), Kjeller, Norway ; [4] Cyprus Institute, Climate and Atmosphere Research Centre, Nicosia, Cyprus; [5] Czech Academy of Sciences, Global Change Research Institute, Brno, Czech Republic; [6]University of Crete, Department of Chemistry, Heraklion, Greece; [7]Hellenic Centre for Marine Research, Institute of Oceanography, Gournes-Pediados, Greece

Introduction, motivation

- Polycyclic aromatic hydrocarbons (PAHs) are released to air in combustion processes. Oxygenated (OPAHs) and nitrated PAHs (NPAHs) are co-emitted with parent PAHs from fossil fuel and biomass combustion processes, and many are formed in photochemical and microbiological reactions of PAHs in air and soil.
- Polycyclic aromatic compounds (PACs = PAHs + OPAHs + NPAHs) are semivolatile organics (SVOCs)
- SVOCs resisting biodegradation in soils and surface waters to some extent, are subject to re-volatilisation, which may turn soils and surface waters into secondary sources and enhances the long-range transport potential (multihopping, grasshopper effect).
- Such emissions were never characterised nor considered in emission inventories.



Methods

- **Sampling** phase-selective air (gas in PUF plugs, particles on quartz filters), water (dissolved phase only, in passive samplers i.e., silicon rubber sheets [1]) and soil (A horizon, in forest also organic horizon Ofh [2-3])
- Sample preparation and analysis 16-28 PAHs, 10-12 OPAHs, 17-19 NPAHs: Soxhlet DCM, silica column, GC-atmospheric pressure chemical ionization (APCI) - MS/MS [2-7]
- **Direction of air-soil exchange** indicated by the fugacity ratio, f_s/f_a, or f_s'/f_a from

air fugacity $f_a = c_a R T_a$

effective soil fugacity $f_s = c_{as} R T_s$ [8], or

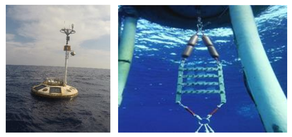
potential soil fugacity $f_s' = c_s H(T_s)/(0.411 K_{OW} \phi_{OM})$

with c_a, c_s = concentrations in air and soil, c_{as} = gas-phase concentration equilibrated with soil ('soil fugacity sampling'), soil organic matter fraction ϕ_{OM}, soil and air temperatures T_s, T_a [9]

- **Direction of air-sea exchange** indicated by the fugacity ratio, f_w/f_a, from

$f_w = c_w H(T_w,S) = c_s H(T_w)\ 10^{S*(0.04\ K_{OW}+0.114)}$

with $H(T_w)$ (Pa m^3 mol^{-1}), salinity S (mol L^{-1}), K_{OW}, R, water temperature T_w [10]



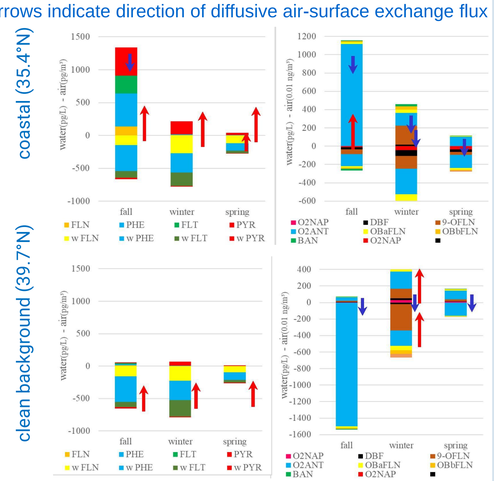
Aims

- Characterise levels and long-range transport potential of NPAHs, OPAHs and NMAHs in ambient air, topsoils and surface waters far from the primary emissions
- Identify emitted PACs and quantify the fluxes

Results Air-Water

- Aegean Sea various seasons 2021-22, clean background (39.7°N) and coastal (35.4°N, near Iraklion) moored buoys
- Mediterranean transects 2017 indicate very similar results

Arrows indicate direction of diffusive air-surface exchange flux



→ 3-4 ring PAHs: all net volatilizing; less in coastal waters

→ 3-4 ring OPAHs: DBF net volatilizing, OBaFLN in equilibrium, 9-OFLN, O_2ANT, OBbFLN depositional

→ The main source of PAC in seawater is atmospheric deposition

Results Air-Soil

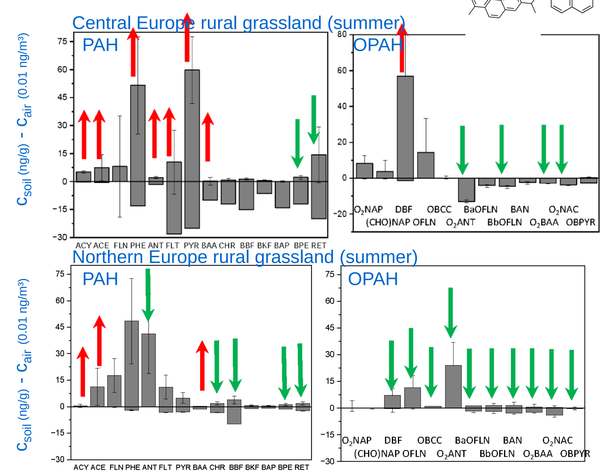
Grassland and forest soils in a PACs source area (i.e., central Europe, Košetice /CZ 50°N) and PACs receptor areas in northern Europe (Birkenes /NO 58°N, Hyytiälä /FI 60°N) [2, 4]

		Northern Europe		Central Europe				
		Grassland	Forest	Grassland			Forest	
		Summer[a]	Spring[b]	Summer[a]	Fall[b]	Winter[a]	Summer[a]	Winter[a]
Number of PAH/ NPAH/OPAH species detected	in soil	23/6/2	25/2/8	22/8/1	25/6/10	25/9/2	24/7/6	24/10/3
	in air	25/11/8	26/8/12	17/11/13	25/13/12	25/11/12	15/11/3	25/11/12
Species with upward flux	Effective $\log(f_s/f_a)$> 0.5	n.d.	ACY, ACE, RET/ / (CHO)NAP	BAA/ 1-NNAP, 2-NNAP, NPHE, NBAA/ OBPYR	TPH/ /	BAA/ / O_2BAA	FLT, PYR, CHR, BBF, BGF/ 1-NNAP, 2-NNAP/ BbOFLN, BAN, O_2BAA, OBPYR	

	Rural grassland		Boreal forest			Rural grassland		Boreal forest	
Substance	f_s'/f_a	f_s/f_a	f_s'/f_a	f_s/f_a	Substance	f_s'/f_a	f_s/f_a	f_s'/f_a	f_s/f_a
NAP	↑				1-NNAP	↓			
ACY	↑	↓↕	↑	↑	2-NNAP	↑	↓↕	↓	
ACE	↑	↓↕	↑	↕↑	3-NACE	↑			
FLN	↑			↕	5-NACE				
PHE	↓↕	↓↕	↕	↕	2-NFLN			↓	
ANT	↑				9-NANT				
FLT	↕	↓↕	↕		9-NPHE				
PYR	↕↑	↓↕	↕		3-NPHE				
BAA	↑	↕	↑		2-NFLT	↓			
CHR	↓↕	↓↕	↓↕		3-NFLT				
BBF			↓↕		1-NPYR			↓	
BKF	↓↕		↕		2-NPYR	↓		↓	
BAP			↑		7-NBAA	↓		↓	
INP	↓		↓		6-NCHR				
DBA	↓				1,3-N_2PYR				
BPE	↓		↓		1,6-N_2PYR				
BJF	↓		↓↕		1,8-N_2PYR				
BBN	↓	↓↕	↓		3-NBAN				
BGF	↓	↓↕	↓		6-NBAP				
TPH	↓	↕↑	↓		1,4-O_2NAP				
CPP	↓		↑		(CHO)NAP		↓↕	↓	↕↑
BEP	↓		↓↕		DBF	↓		↓↕	
PER	↓		↓		9-OFLN	↓	↓	↓	
DCA	↓				6-OBCC	↓		↓	
ATT	↓				9,10-O_2ANT	↓		↓↕	
COR	↓				OBaFLN	↓		↓	
RET	↓		↓↕	↑	OBbFLN	↓		↓	
BNT	↕↑	↕	↕		BAN	↓		↓	
BIP	↑		↑		O_2BAA	↓		↓	
					O_2NAC	↓		↓	
					6-OBPYR	↓		↓	

Central Europe: a number of 2-4 ring PACs found to volatilise from grassland and more from forest soils in summer, much less in winter.

Receptor areas: net deposition of PACs prevails but re-volatilisation is occurring, too: ACY, ACE, RET, (CHO)NAP



Arrows indicate direction of diffusive air-surface exchange flux

Discussion

- Spatial representativity of c_s limited by high spatial variability of c_s, even within field.

  Spatial variability of c_s + soil hydrology → Δf_s? vertical gradient ΔT_s → $\Delta f_s'$?
- Temporal representativity of campaign-means c_a, f_s [2] or season-means c_a, f_s' ? [5-6]

Conclusions

→ PACs emitted from surface waters and soils in source areas, but more relevant also far from sources, in receptor areas. Strong mutagens, 1-NPYR, 2-NFLT, BAP, CPP not observed emitted yet, but have approached chemical equilibrium

→ Secondary emissions of PAHs in boreal climate are in the same order of magnitude than primary emissions

REFERENCES

[1] Sobotka et al. 2022. Performance comparison of silicone and low-density PE as passive samplers in a global network for aqu. organic contaminants *Environ Pollut* 302, 119050

[2] Mwangi et al. 2024. Air-soil cycling of oxygenated, nitrated and parent PAHs in source and receptor areas. *Sci Total Environ* 921, 170495

[3] Wietzoreck et al. 2022. Nitro- and oxy-PAHs in grassland soils from decade-long sampling in central Europe. *Environ Geochem Health* 44, 2743–65

[4] Bezdeková et al. 2026. Air-soil cycling of polycyclic aromatic compounds – on the significance of re-volatilisation. *submitted*

[5] Lammel et al. 2020. Oxygenated and nitrated PAHs in ambient air - levels, phase partitioning, mass size distributions and bioaccessibility. *Environ Sci Technol* 54, 2615-25

[6] Nežiková et al. 2021. Three years of atmospheric concentrations of NPAHs and OPAHs at a central European background site. *Chemosphere* 269, 128738

[7] Wietzoreck et al. 2022. PAHs and their (…) derivatives in the atmosphere over the Mediterranean and Middle East seas. *Atmos Chem Phys* 22, 8739–66

[8] Cabrerizo et al. 2009. Dvlpmt. of a soil fugacity sampler for determination of air–soil partitioning of POPs under field controlled conditions. *Environ Sci Technol* 43, 8257-63

[9] Harner et al. 2001. Soil-air exchange model of persistent pesticides in the U.S. Cotton Belt. *Environ Toxicol Chem* 20, 1612–21

[10] Bidleman & McConnell 1995. A review of field experiments to determine air–water gas-exchange of persistent organic pollutants. *Sci Total Environ* 159, 101–7

ACKNOWLEDGEMENTS

Czech Science Foundation (No. 25/17534S); Max Planck Society; Czech Ministry of Education, Youth and Sports (RIs ACTRIS-CZ No. LM2023030, RECETOX No. LM2023069, OP RDE CETOCOEN EXCELLENCE No. CZ.02.1.01/0.0/0.0/17_043/0009632)

Sharing is encouraged