"Chemodynamika znečištění životního prostředí / Chemodynamics of environmental pollution" research group

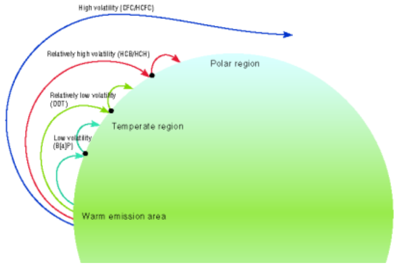
Motivation:

- Understand the fate of persistent semivolatile substances

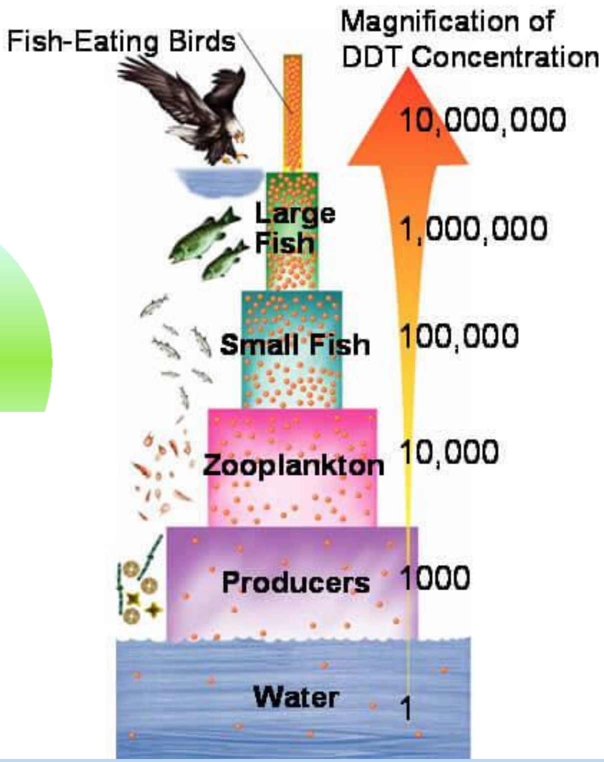
Large-scale cycling of bioaccumulative and/or health hazardous substances → Exposure of the environment and humans

Motivation

- ➢ Pollutants distributed across and within the multiphase systems air, seawater, soil, biota
- ➢ Bioaccumulative substances do cycle in ecosystems even decades after emission bans
- ➢ Tendency to accumulate in polar regions; cycling is enhanced by the grasshopper effect
- ➢ Many combustion byproducts are carcinogens (or precursors thereof), many environmental chemicals are endocrine disruptors.



(UNEP, 2003)

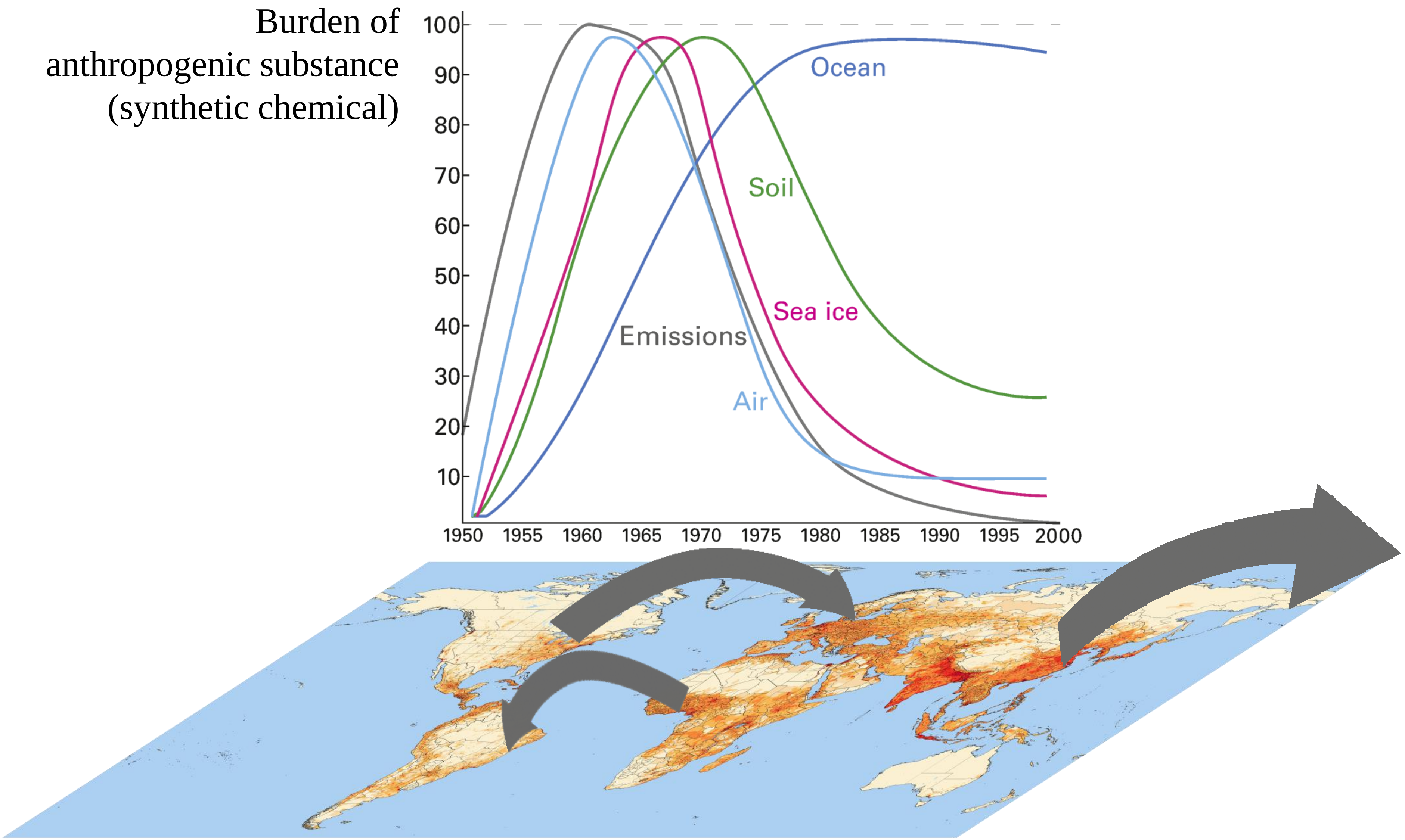


Stockholm Convention on persistent organic pollutants (POPs)

Towards

- understanding pollutant distributions in abiotic environment on large spatiotemporal scales
- characterisation of exposure of ecosystems and humans

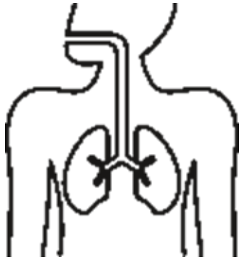
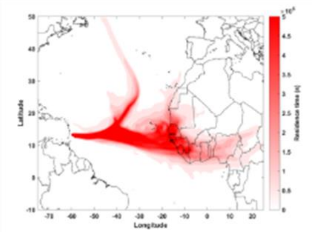
Large-scale cycling, bioaccumulative, health hazardous substances
→ Exposure of the environment and humans



"Chemodynamika znečištění životního prostředí / Chemodynamics of environmental pollution - **Air**" research group

prof. Gerhard Lammel, Ludovic Mayer MSc, Dr. John K. Mwangi, Dr. Karla Pozo G. (office = D29-423)





Elements of research work

- Translate question or hypothesis into experimental design
- Sample air gas-phase, particulate phase on adsorbents and filter membranes; soil, water using polymeric sorption materials; generate field blanks
- Extract the sampling medium, clean-up of the extract, chromatographic analysis
- Derive concentrations in air, soil, water, concentration gradients, ratios, time series, mass fluxes; discuss uncertainties
- Get supporting data from meteorological/oceanographic services and cooperating groups on site
- Predict concentrations gradients, ratios, time series, mass fluxes based on theory or hypothesis ('modelling'), and compare with measured (statistical tools), eventually limit values; draw conclusions

Studies

- Field campaigns in Czech Rep. 2016, '17, '18, '19, '21, '22, Greece and Turkey 2012, Hungary 2013, India 2014, Chile 2014, '21, '22, Svalbard 2022, open ocean 2010, '16, '17, '19, '22, '23
- 20 studies published as articles in scientific journals 2011-20 with journal impact factor 3-6, cited by average 30 times/paper
- Contributed to 12 studies lead by others and published 2011-20, cited by average 20 times/paper

Cooperations - internal:

- doc. Branislav Vrana: water sampling techniques for ocean surface waters
- doc. Klára Hilscherová: bioassays to determine toxicity of atmospheric aerosols and gaseous samples
- prof. Jakub Hofman: sampling and characterization of soil samples

- external:

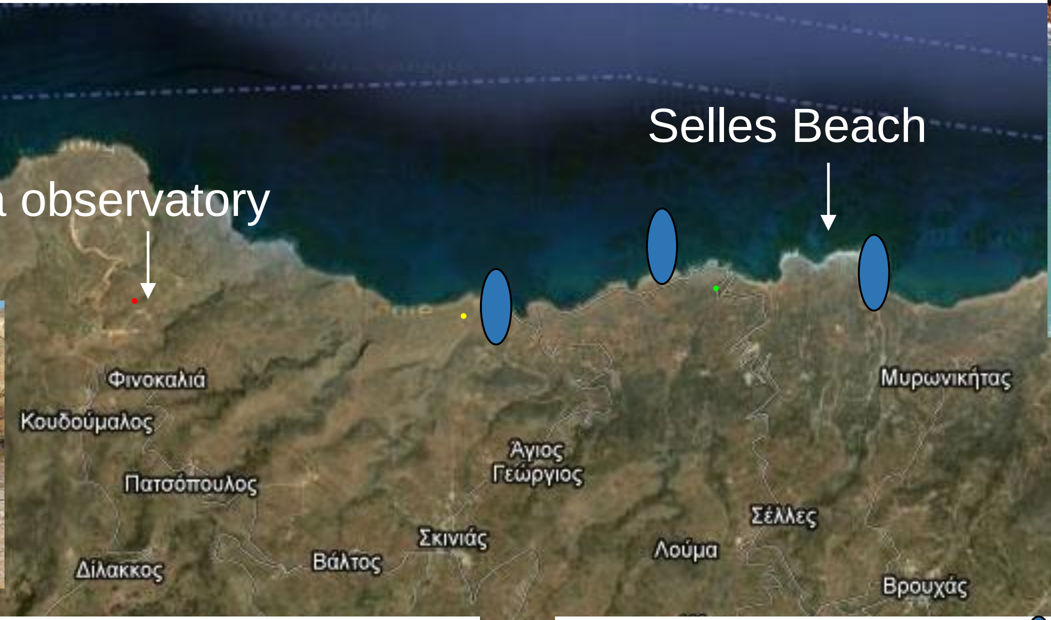
- Max Planck Institute for Chemistry (Mainz/DE): bioaccessibility, analysis
- Czech Acad. Sci.- Inst. Chemical Process Fundamentals, Praha, Natl. Observatory Košetice: sampling, supporting data
- Hellenic Centre for Marine Research; University Centre of Svalbard; USS Concepción/Chile; …

Motivation:

- Understand chemodynamics of persistent semivolatile substances (which are bio-accumulative and toxic)
- which are re-volatilising from ground compartments (multi-hopping)
- → study the processes and understand large scale spatiotemporal trend

Air-sea	N Sea 2009	episode	Mai et al. ESPR 2016
	E Mediterranean 2010	seasonal	Mulder et al ACP 2014
	E Mediterranean 2012	episode	Lammel et al ESPR 2015, ACP 2016
	ConcepciónBay Chile 2014	seasonal	Pozo et al MPB 2022
	S Atlantic 2016	episode	Sobotka et al MPB 2021
	Mediterranean, Red Sea, Arabian Sea, Persian Gulf 2017	episode	Wietzoreck et al ACP 2022
	Eq Atlantic 2019, 2023	episodes	unpublished
Air-soil	W Balkans 2008	episode	Lammel et al. J Env Mon 2011
	Pannonian Plain 2013	episode	Degrendele et al. EST 2016
	India 2014	seasonal	Lammel et al. ACP 2018





Active air sampling (2-13 July 2012)
Selles (0.5 m a.s.l.)

- 12hly vertical gradient low-vol sampling gaseous fraction (PUF) +PM_{10} particulate fraction (QFF)
- Passive (PUF disk)
- Supporting data: meteorology, micrometeorology

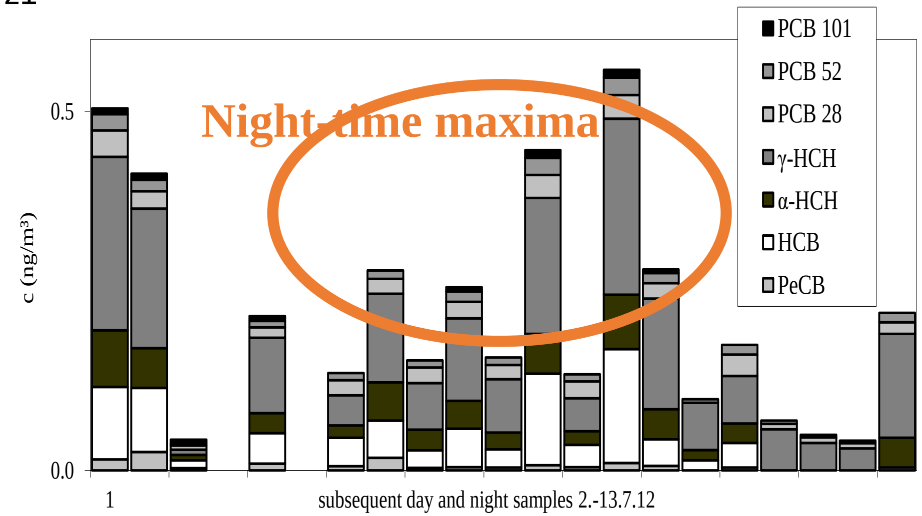
Water sampling, 3 sites (3-31 July 2012)

1 = ca. 8 m each from 2 cliffs (no anker), d = 2.5 m
2 = ca. 30 m from cliffs, 50 m from pebble beach, d = 4 m
3 = ca. 50 m from cliffs, d = 4 m

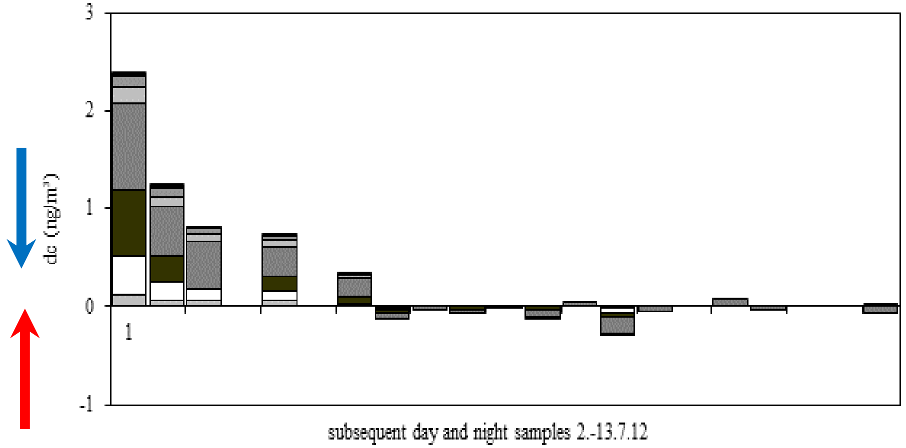
- Passive (silicon rubber strips) + TOC (grab water sample); PSM-associated = total – dissolved

Crete coast (night and day sampling):
Gaseous halogenated semivolatile compounds‘ vertical gradients

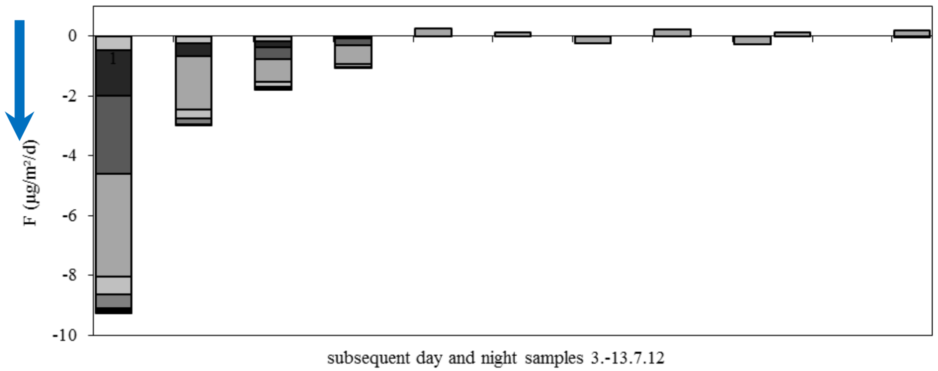
c_{z1} =1.05m



$\Delta c_z = c_{z1} - c_{z2}$



- downward in 18 cases ranging F_c = -0.56±0.80 µg m^{-2} d^{-1})
- upward in 7 cases, ranging F_c = 0.26±0.30 µg m^{-2} d^{-1}; these were 0.11-0.26 for γ-HCH, 0.04 for both PCB28 and DDE and 0.91 µg m^{-2} d^{-1} for BDE47
- insignificant in 29 cases ($|F_c| \lesssim$ 0.15±0.39 µg m^{-2} d^{-1}) (

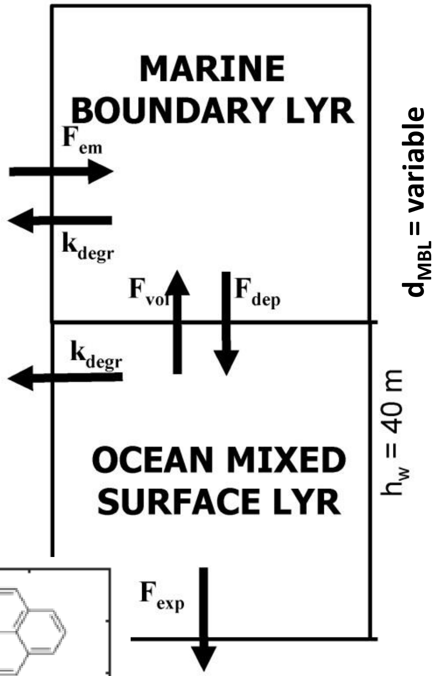


Aegean, 5 days of homogeneous advection

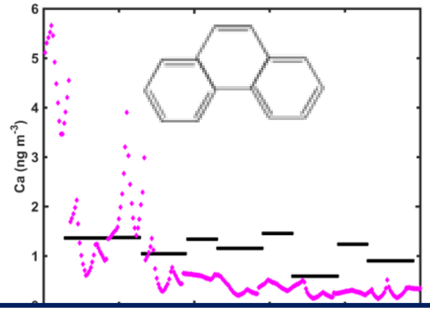
2-box model for SOC cycling b [µg m^{-2}], part. mass fractions θ

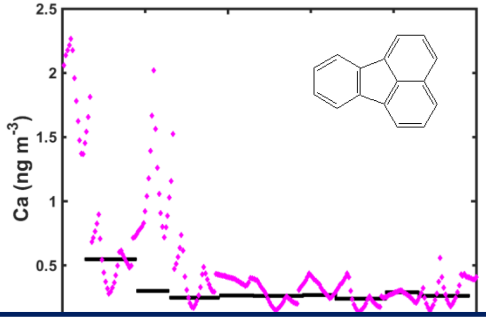
$$db_a/dt = F_{em}/h_a + F_{vol}b_w/h_a - \theta_a\, b_a v_{dep}/h_a + k_{vol}c_w - (1-\theta_a)\, k_{OH}c_{OH}c$$

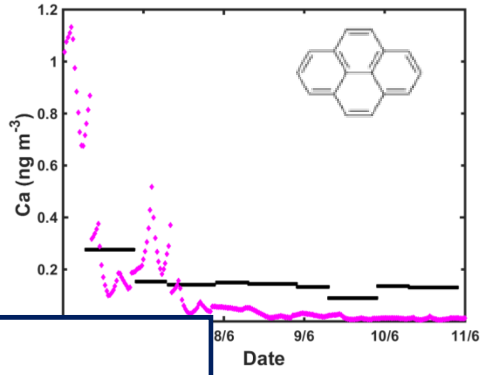
$$db_w/dt = \theta_w\, v_{exp}b_w/h_w - (1-\theta_w)\, F_{vol}b_w/h_w + \theta_a\, b_a v_{dep}/h_w - k_{oc}b_w$$

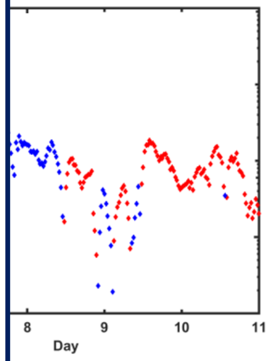


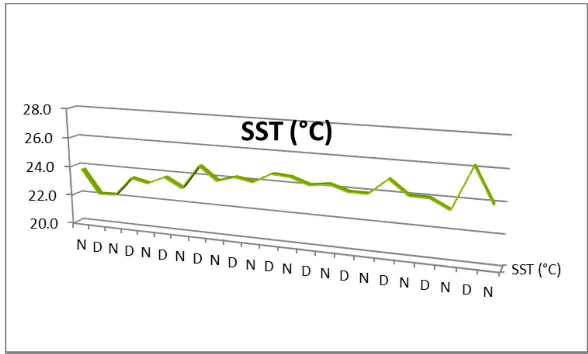
Observed and model predicted concentrations in air and diffusive air-sea exchange mass flux of **PAHs** (pg m^{-2} d^{-1}; **downward** **upward**)

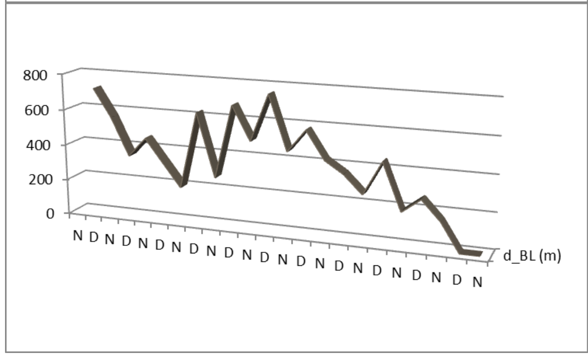












→ Volatilisation from the sea surface has significantly contributed to the night-time maxima of (at least) HCB, HCH, PCB28, PCB52 and PYR. in combination with variation of d_{MBL}

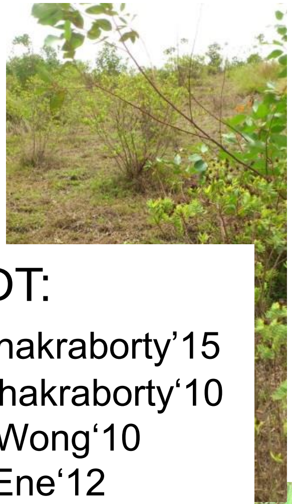
↓ : FLT, PYR, PCB52, PBDEs

↕: PYR, PCB52

↑: HCB, PCB28

Canopy and soil at 3 soil sampling plots. Soil type: nitisol (GOI, 1985; FAO, 2014)

Tea garden	Shrub	Forest
TOC = 4.4%	10.7%	4.0 %

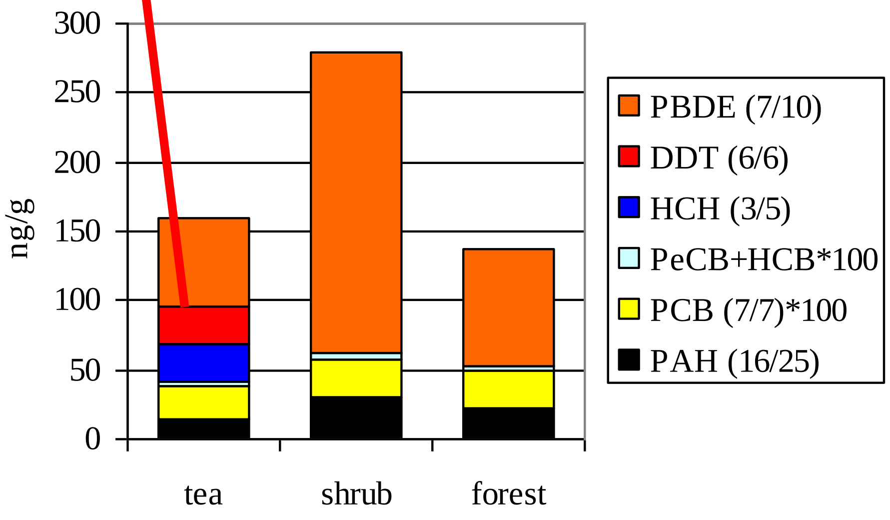


o,p'-DDE	1.84
p,p'-DDE	12.13
o,p'-DDD	0.49
p,p'-DDD	0.17
o,p'-DDT	11.34
p,p'DDT	1.90

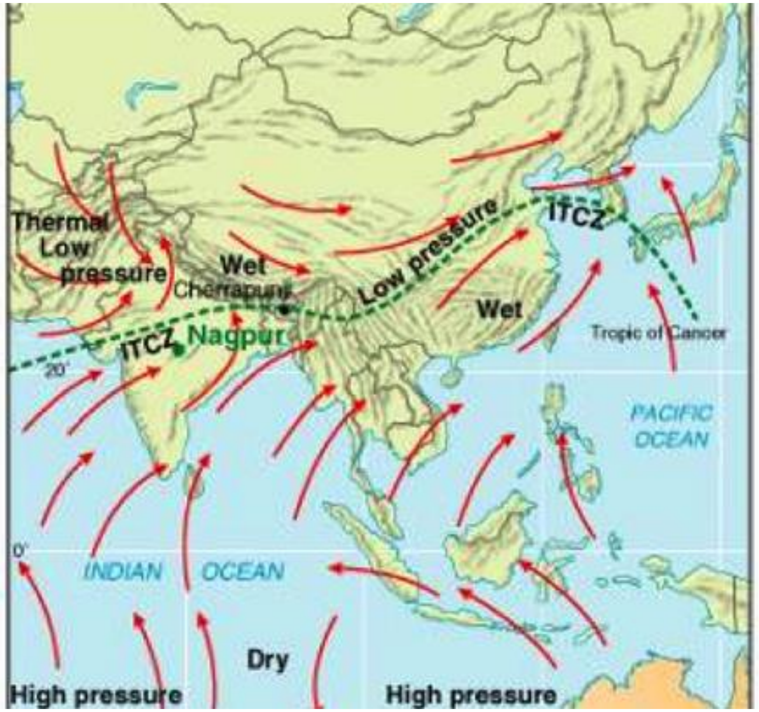
opDDT/ppDDT:

≈ 1 most IND Chakraborty'15
Chakraborty'10

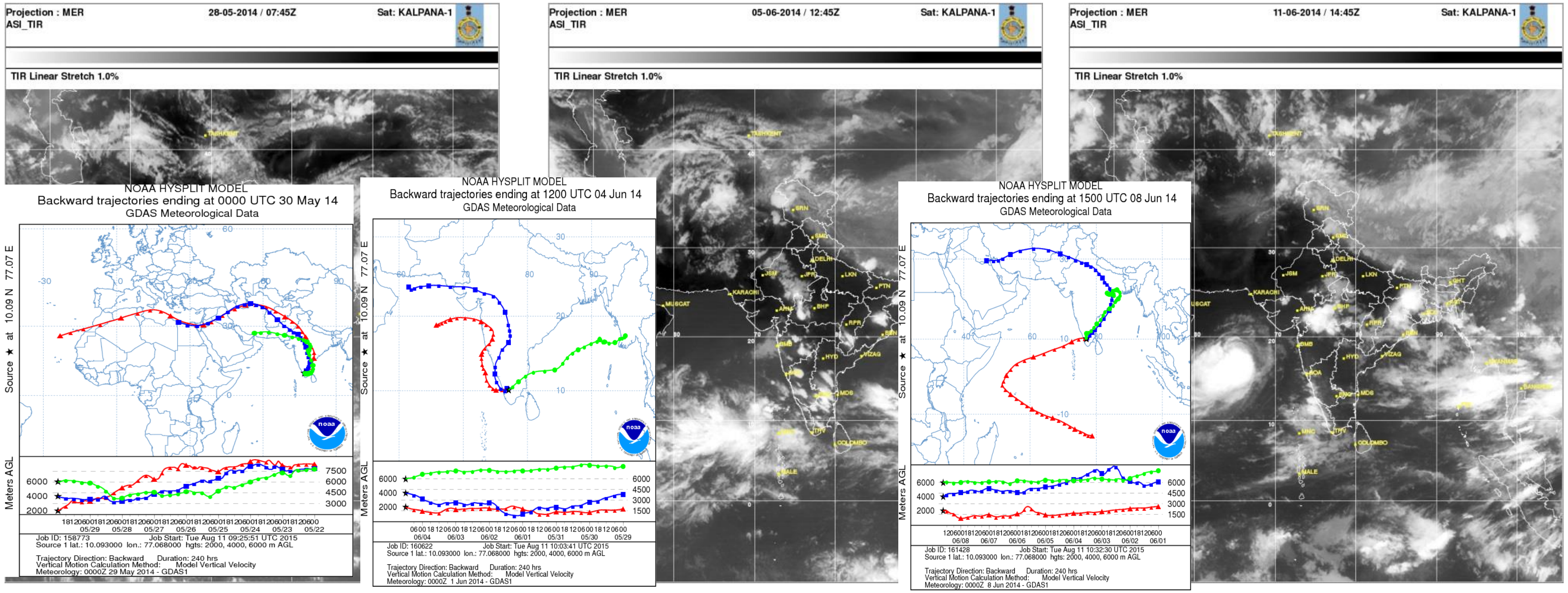
>>1 some MEX Wong'10
3/5 RO Ene'12



Arrival of extremely clean air with the southwest monsoon in southern India early June



2014:



Air-soil exchange in India before and during the onset of the southwest monsoon 2014

Change of **air-soil fugacity ratio** (2-film model; *Harner et al., 2001)*,

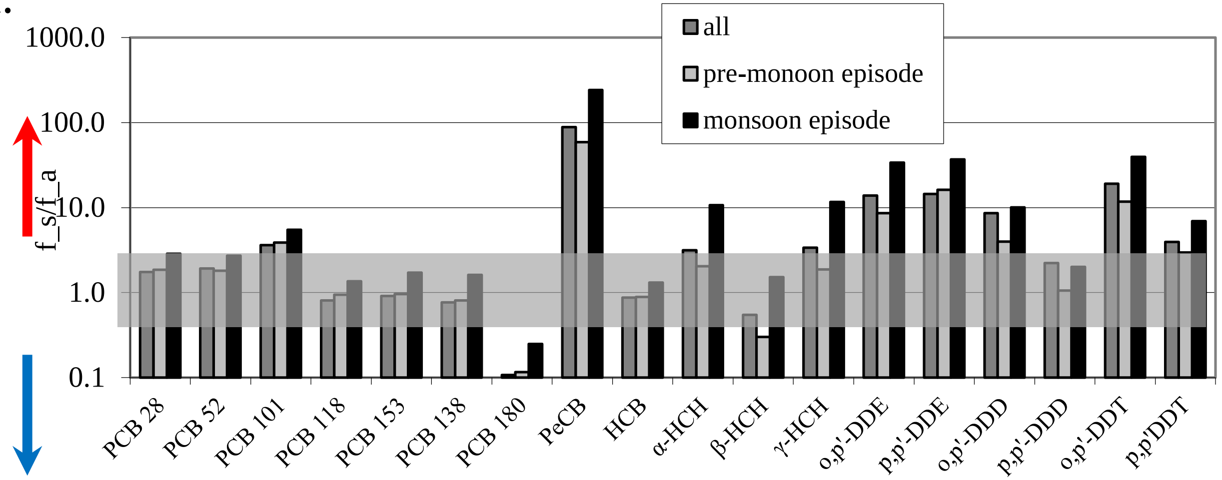
$f_s/f_a = c_s\, H(T) / (0.411\, \phi_{OM}\, K_{OW}) / [c_a\, R_g\, T]$, with the onset of monsoon

in tea plantation:

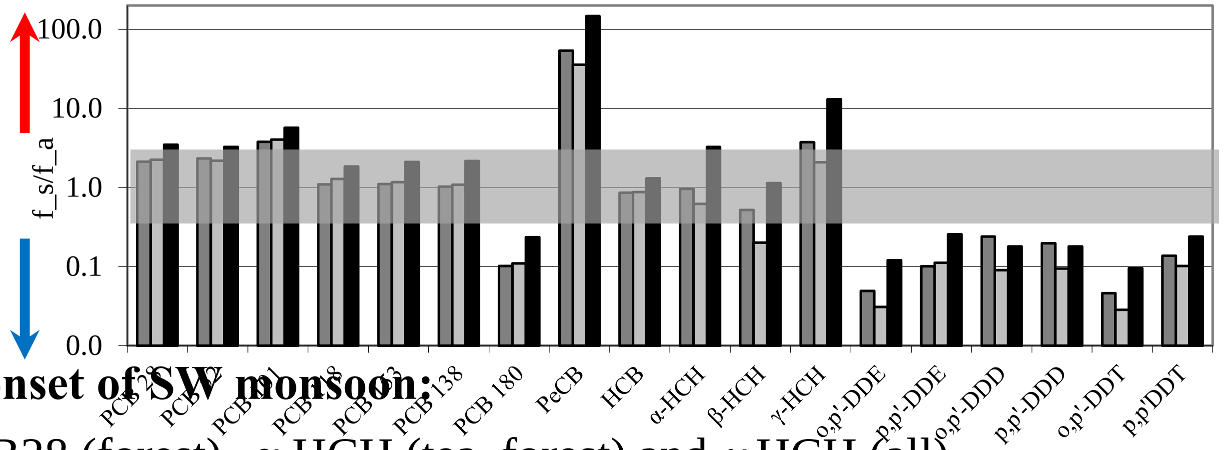
Mass flux

from soil to air

from air to soil



in forest:



…and upon onset of SW monsoon:

↑ upward: PCB28 (forest), α-HCH (tea, forest) and γ-HCH (all)

↓ predominantly downward: (g) PHE, FLT, PYR, α- and γ-HCH, BDE47 and -99

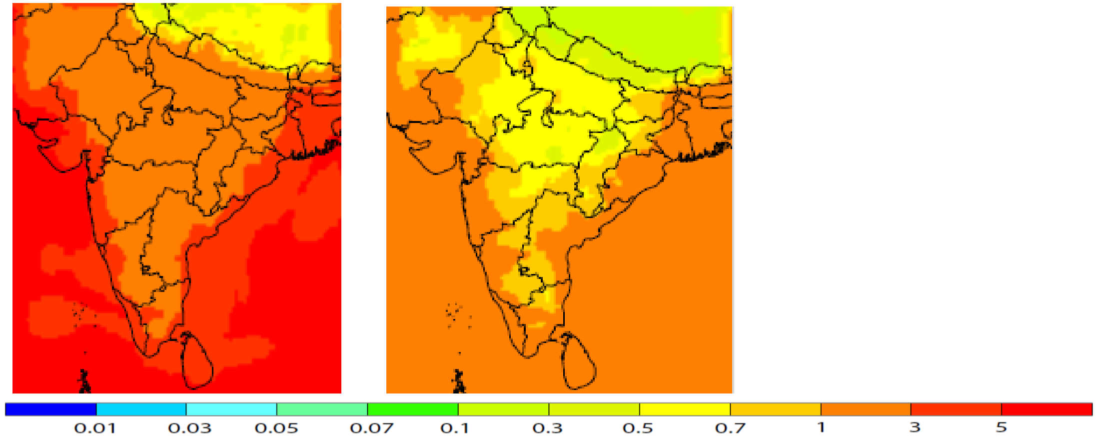
Air-soil exchange India before and during onset of SW monsoon 2014

volatilisation triggered by the drop of air pollution levels ? → Modelling the chemodynamics

Response of the air-soil chemical sub-system to meteorological and chemical changes in advection: regional simulation of the episode (WRF/Chem with soil compartment)

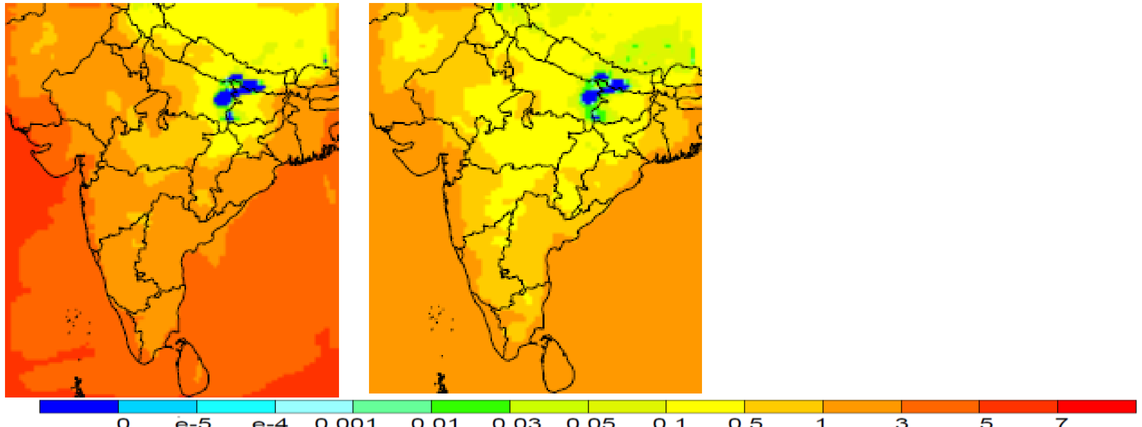
γ-HCH (pg m^{-3}) p,p'-DDE (pg m^{-3})

$c_{pre\ monsoon}$ in air (ground level, mean of 1-3 June)



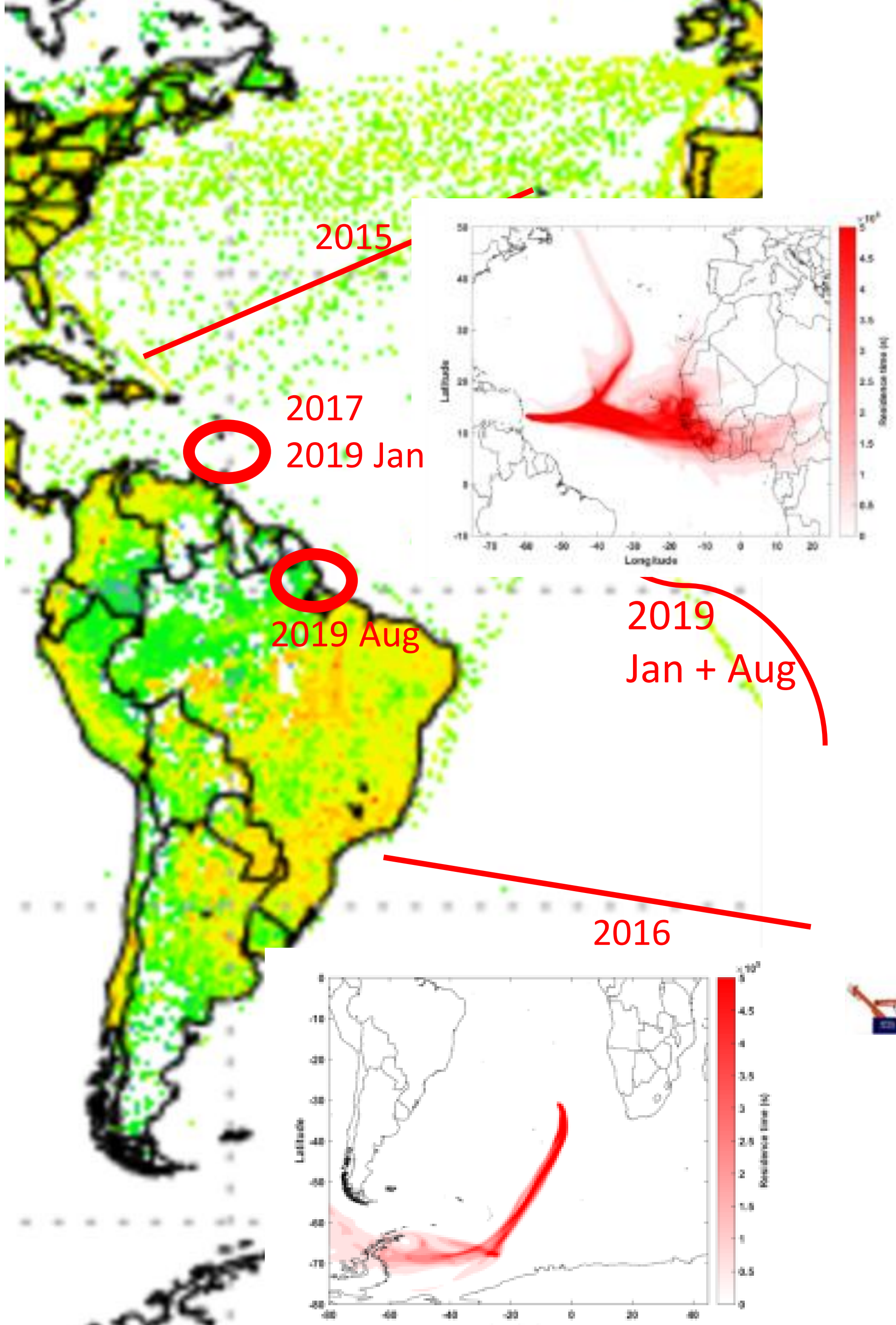
	$\Delta c_{obs}/c_{obs}$ S India (%)
PHE	-91
CHR	-83
***α*-HCH**	-85
***γ*-HCH**	-89
***p,p'*-DDE**	-91
h_{BL}	n.d.

Pollution drop: $c_{pre\ monsoon}$ - $c_{monsoon}$ (means of 1-3 and 8-10 June, respectively)

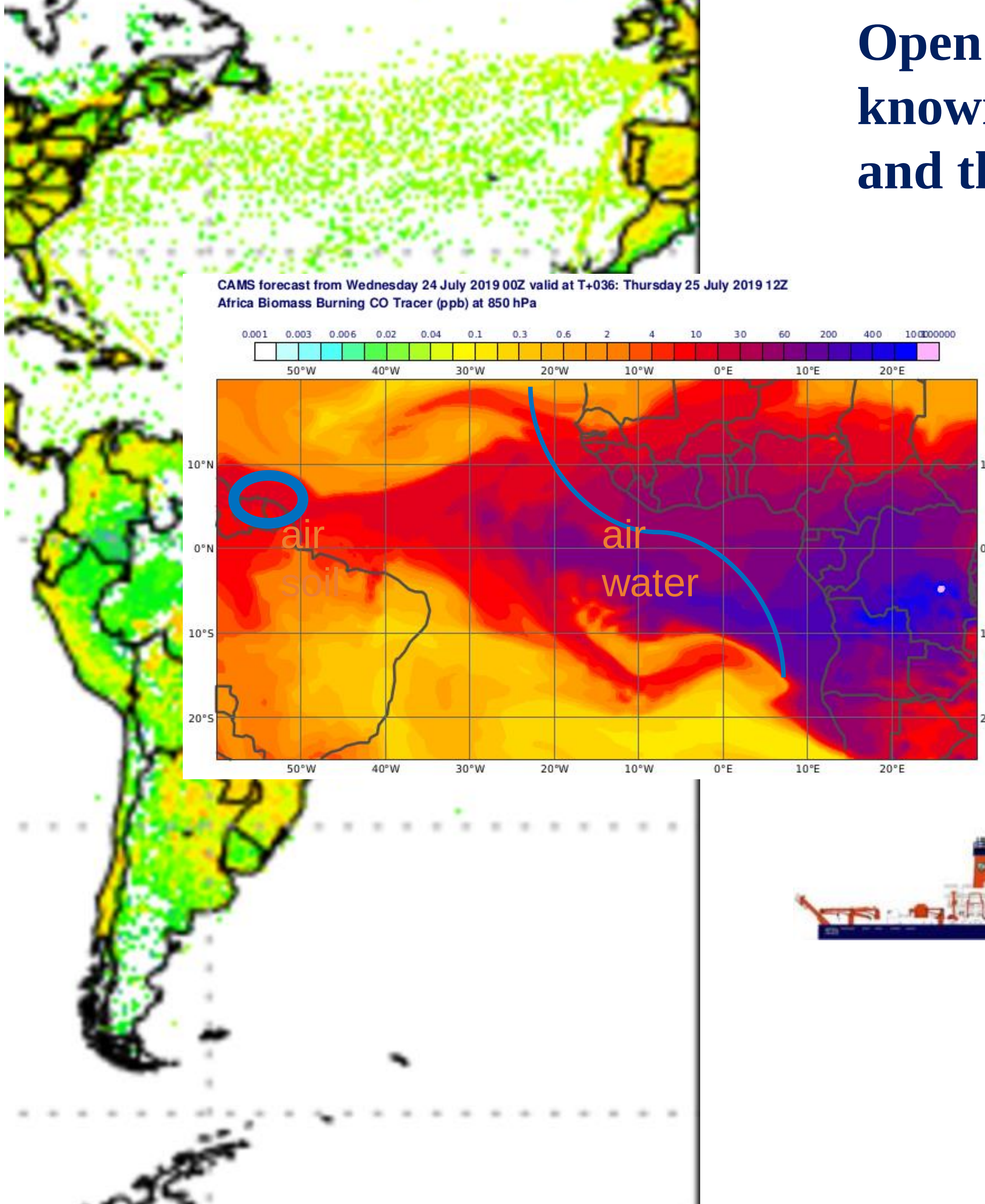


→ In S India the change of pollutant level reflects the drop in the advected, clean air, while with propagation northward the signal decreases for the pesticides

Open ocean measurements known history of air masses

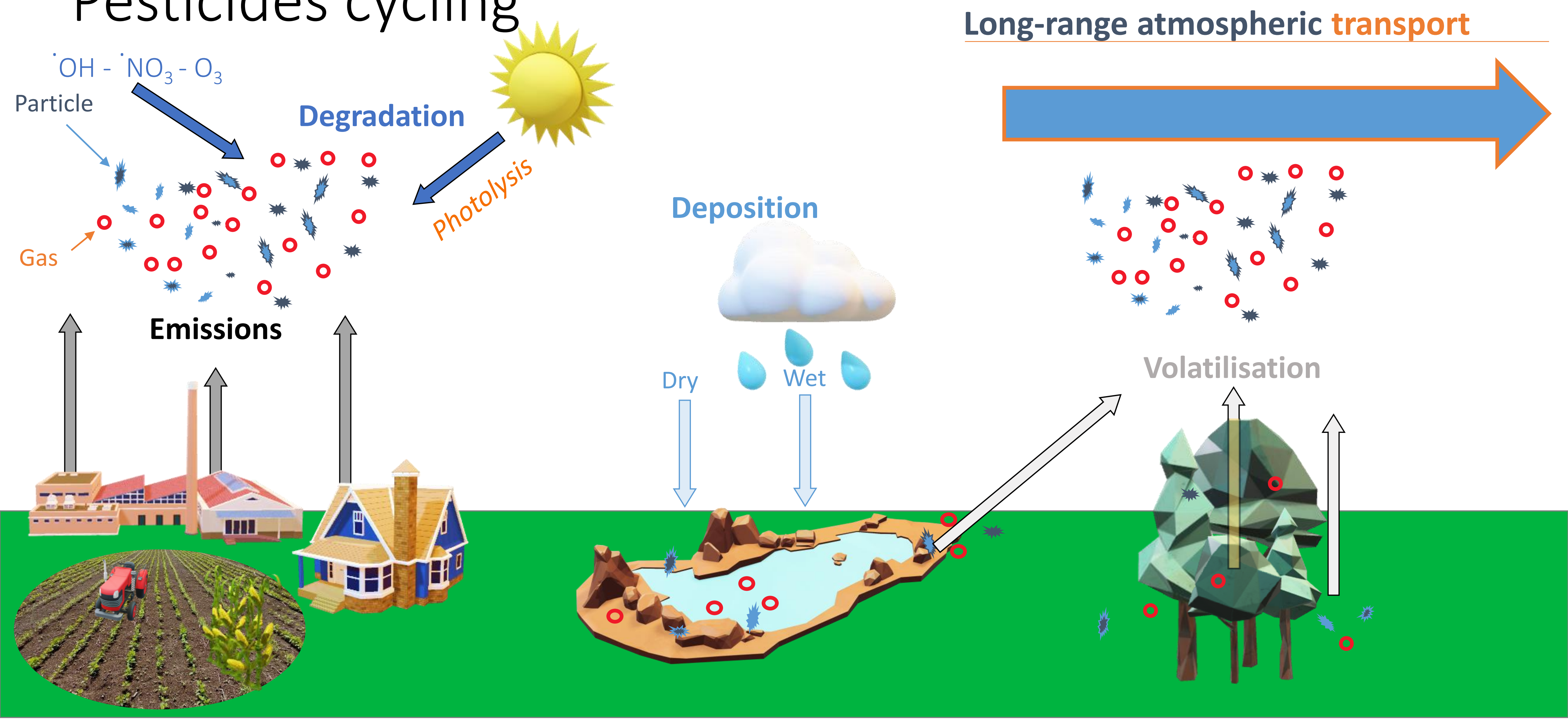


Open ocean measurements
known history of air masses
and the trace substances transported

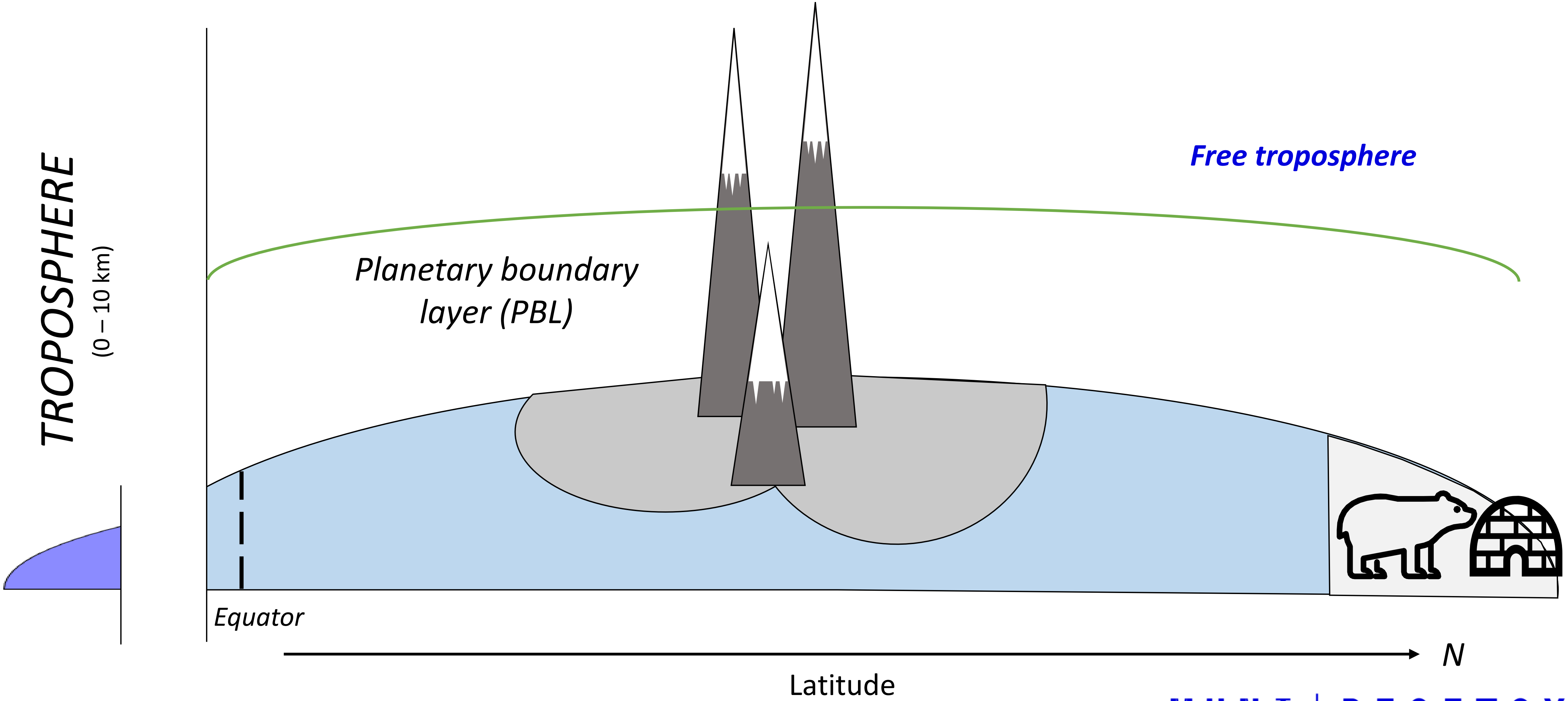


Emission and transport
Predictions
ECMWF-CAMS 2019

Pesticides cycling



Results - Long-Range Atmospheric Transport

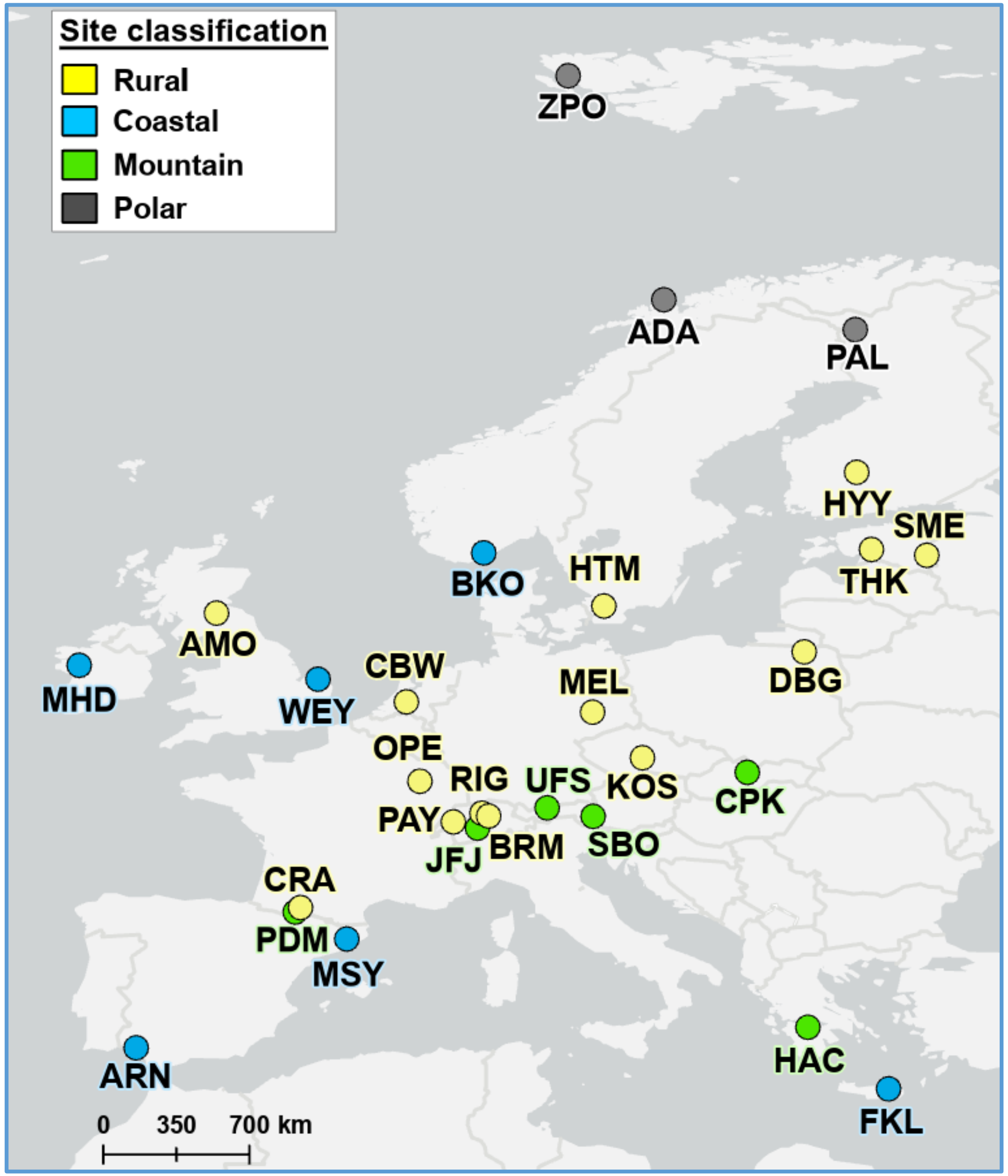


Pesticide long-range transport over Europe project (Ludovic Mayer)

– Air sampling campaign
  – **Active air samplers**

– Spring 2020
  – **Simultaneously**

– 29 sampling sites in 17 countries
  – **25 partner institutions**



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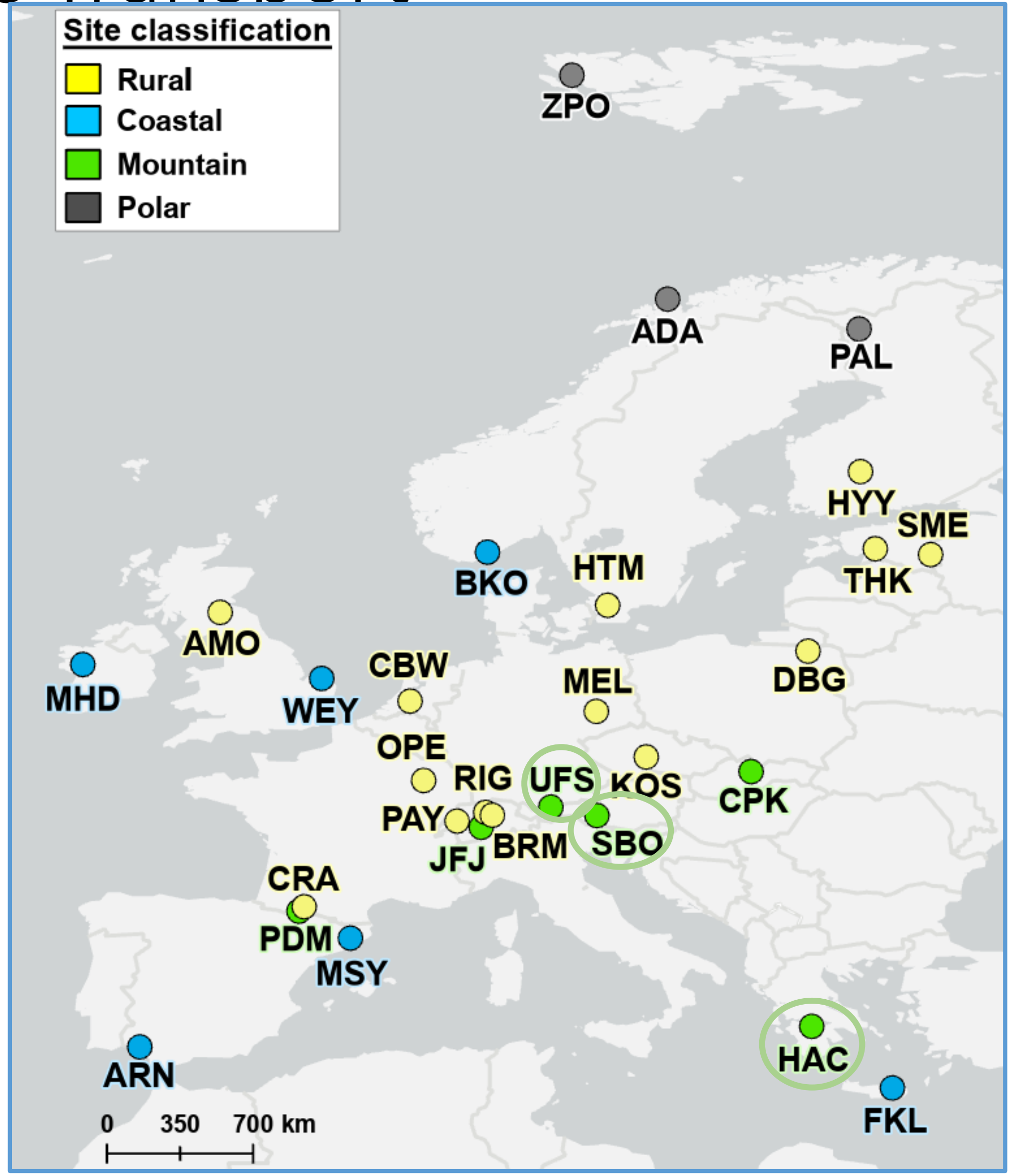
Results – Long–Range Atmospheric Transport

Mountain sites

- 5 out of 10 samples in **Free Troposphere**
- From 3 sites (HAC, SBO & UFS)

CUPs found in Mountain *free tropospheric* sites	
Atrazine	Metazachlor
Boscalid	Prochloraz
Chlorpyrifos	S-metolachlor
Cyprodinil	Spiroxamine
Fenpropidin	Tebuconazole
Fenpropimorph	Terbuthylazine
Iprovalicarb	Thiacloprid



"Chemodynamika znečištění životního prostředí / Chemodynamics of environmental pollution - **Air**" research group

Scientists (since 2012):

- John K. Mwangi (since 2020)
- Karla Pozo G. (since 2012)
- Céline Degrendele (2016-21; now U Aix-Marseille)
- Marie D. Mulder (2012-18, now Austrian Hydromet., Wien)
- Jana Matejovičová (part time, 2012-16, Slovak Hydromet., Bratislava)
- Christos Efstathiou (2011-15, now U North Carolina, Chapel Hill/US)

Doctoral students (since 2010):

- Ludovic Mayer: Fate of currently-used pesticides in the atmospheric environment (PhD ongoing)
- Barbora Nežiková: Investigation of semivolatile pollutants' partitioning in and wet scavenging from aerosols (PhD 2022)
- Marie D. Mulder: Semi-volatile organic pollutants in the Mediterranean: Long-range atmospheric transport, (photo)chemistry and air-sea exchange (PhD 2019)
- Lenka Škrdliková: Scavenging by rain and aerosol size distributions of persistent organic pollutants in near-ground air (PhD 2014)

MSc, BSc, internships (since 2010):
- Baptiste Delaunay: Uptake of PAHs into plants (Erasmus internship, 2022)
- Hippolyte Leuridan: Spatial and temporal variation in air quality at Brno (Erasmus internship, 2020)
- Nils Paragot: Multi-year atmospheric concentrations of per- and polyfluoroalkyl substances (PFASs) at a background site (Erasmus internship, 2019)
- Dušan Lago: model (data processing, scripting) (student assistant 2013-15)

Open

BSc (defense June 2023):
- Pesticides in air – sampling of particles and gas-phase (supervisor Gerhard Lammel/Ludovic Mayer)
- Evaluation of a novel passive air sampler and determination of organic pollutants

gerhard.lammel@recetox.muni.cz