Bulk atmosperic deposition of persistent organic pollutants and polycyclic aromatic hydrocarbons in central Europe

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Introduction

Polycyclic aromatic hydrocarbons (PAHs) and persistent organic pollutants such as polychlorinated biphenyls (PCBs) and organochlorine pesticides (OCPs) are widespread and toxic contaminants. These semi-volatile organic compounds (SOCs) may be removed from the air via deposition (dry and wet). Efforts have been made over the last decades to quantify deposition fluxes for various SOCs. Fluxes for large areas or entire regions have been estimated based on multicompartmental modelling. It is important to verify the modelling results by direct measurements of atmospheric deposition.

Aims of this study:

- novel deposition data of these chemicals for central Europe
- the seasonal and spatial variations of total deposition fluxes

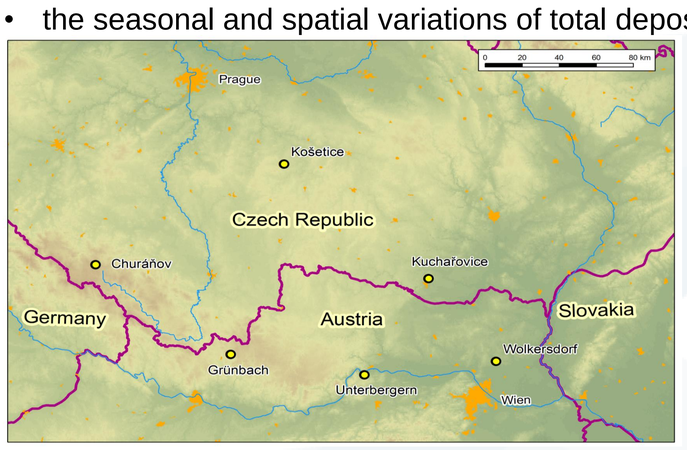

Figure 1 Map of the sampling sites:
Kuchařovice (KUC)
Košetice (KOS)
Churáňov (CHU)
Wolkersdorf (WOL)
Unterbergern (UNT)
Grünbach (GRU)

Methodology

Sampling:

- Total deposition sampler
- Sampling period: 3 months
- Site type: all background with exception of KUC (rural site)
- Sampling time: September 2011 – August 2015

The deposition samplers used[1] consist of:

- Collecting vessels (250 mm diameter) made of borosilicate glass
- A filter located at the bottom of the collection vessel
- A glass column containing XAD-2 sorbent

Particulate deposition is collected separately.

Sample processing:

- Soxhlet extraction in dichloromethane
- Pre-cleaning on silica column
- Gas chromatography and mass spectrometry.

The targeted compounds were 15 PAHs, 6 PCBs and 12 OCPs.

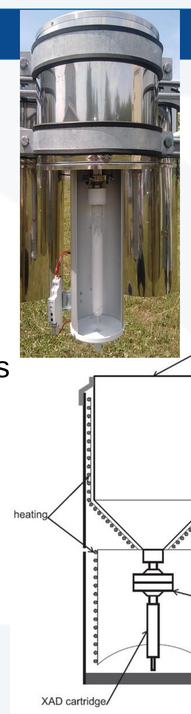

Figure 2 Photo and sheme of atmospheric deposition sampler

List of compounds

15 PAHs: acenaphthylene (ACY), acenaphthene (ACE), fluorene (FLN), phenanthrene (PHE), anthracene (ANT), fluoranthene (FLT), pyrene (PYR), benzo(a)anthracene (BAA), chrysene (CHR), benzo(b)fluoranthene (BBF), benzo(k)fluoranthene (BKF), benzo(a)pyrene (BAP), indeno(1,2,3-cd)pyrene (IPY), dibenz(a,h)anthracene (DHA) and benzo(ghi)perylene (BPE);
6 PCBs: PCB28, PCB52, PCB101, PCB138, PCB153 and PCB180;
12 OCPs: 4 HCH isomers (α, β, γ, δ), 6 DDX compounds - o,p'- and p,p' – dichlorodiphenyltrichloroethane (DDT), dichlorodiphenyldichloroethene (DDE) and dichlorodiphenyldichloroethane (DDD), penta- and hexachlorobenzene (PeCB and HCB).

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General results

- Σ_{15}PAHs total deposition fluxes ranged from 23 to 1100 ng m^{-2} d^{-1} (AVG 190 ng m^{-2} d^{-1})
- Main contributors: FLT and PYR (on average 19% each)
- Σ_6PCBs total deposition fluxes ranged 64 – 4400 pg m^{-2} d^{-1} (AVG 400 pg m^{-2} d^{-1})
- Main contributors: PCB153 (on average 26%), PCB28, PCB138, PCB180
- Σ_{12}OCPs total deposition fluxes ranged 410 – 7800 pg m^{-2} d^{-1} (AVG 1900 pg m^{-2} d^{-1})
- Main contributors: γ-HCH (on average 30 %) with the exception KUC

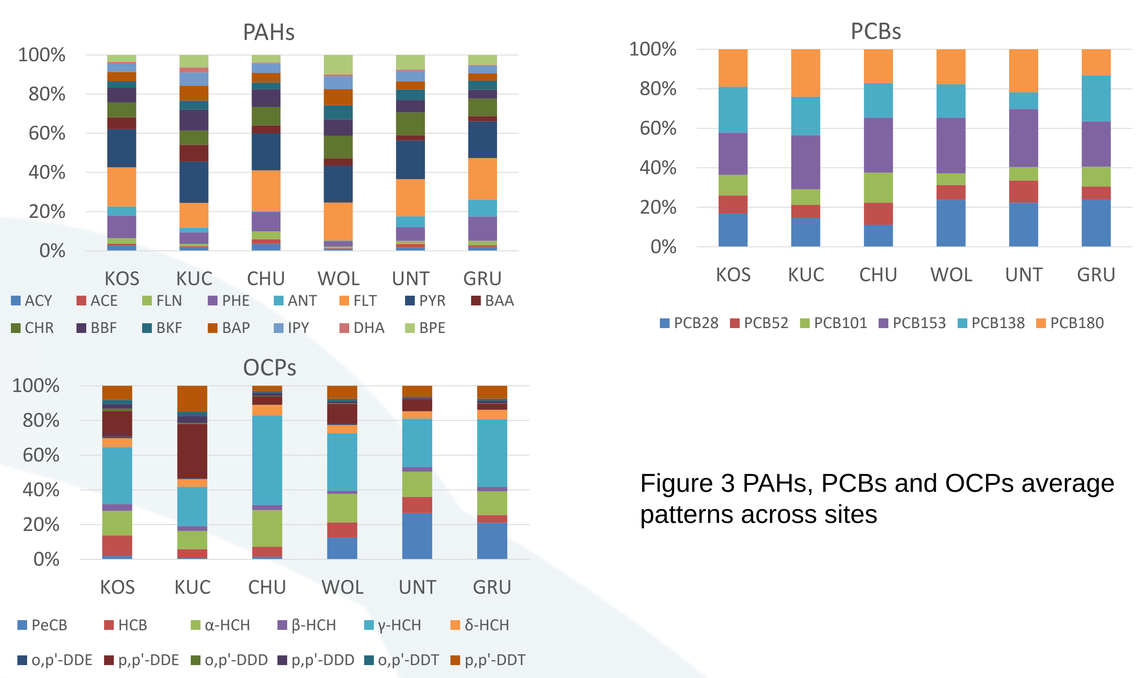

Figure 3 PAHs, PCBs and OCPs average patterns across sites

Seasonal and spatial variations

- Highest Σ_{15}PAHs deposition fluxes were observed at KUC and in spring
- Highest deposition fluxes of Σ_6PCB were measured at KUC and did not show any clear seasonal trend
- The Σ_{12}OCPs deposition fluxes observed for the different sites were not statistically different from each other and were highest in summer

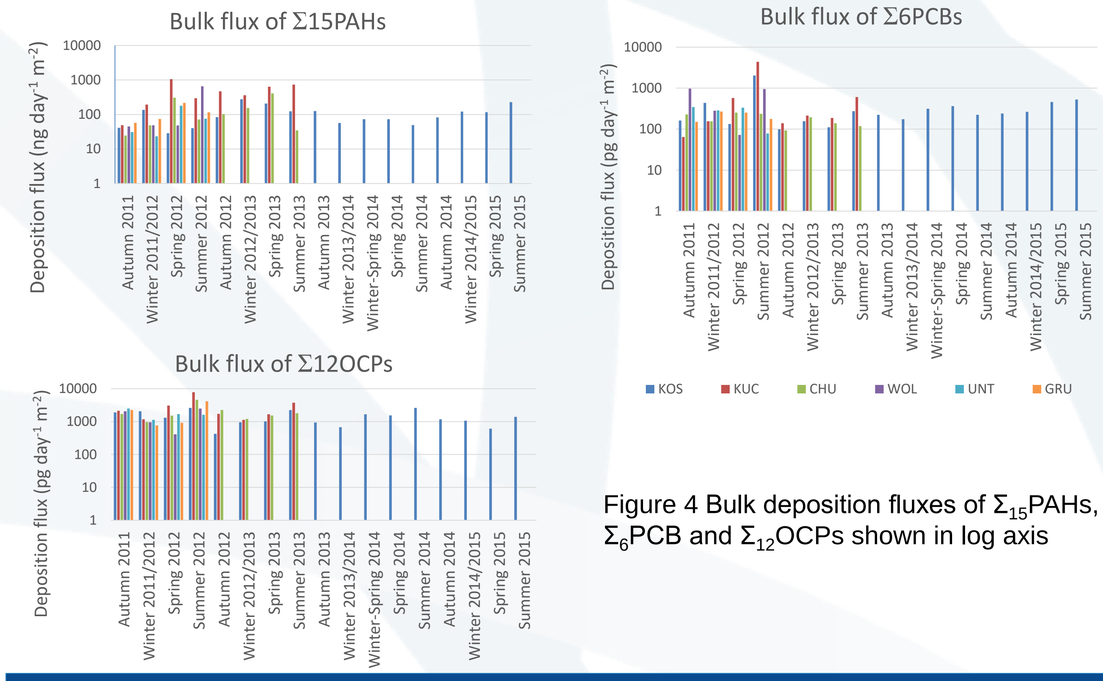

Figure 4 Bulk deposition fluxes of Σ_{15}PAHs, Σ_6PCB and Σ_{12}OCPs shown in log axis

Distribution between GFF and XAD (θ_{dep})

- For PAHs and PCBs, θ_{dep} generally increased with decreasing volatility of the compounds
- θ_{dep} was generally higher in summer than in winter for all groups of compounds
- θ_{dep} was influenced by meteorological conditions and sampling artefacts

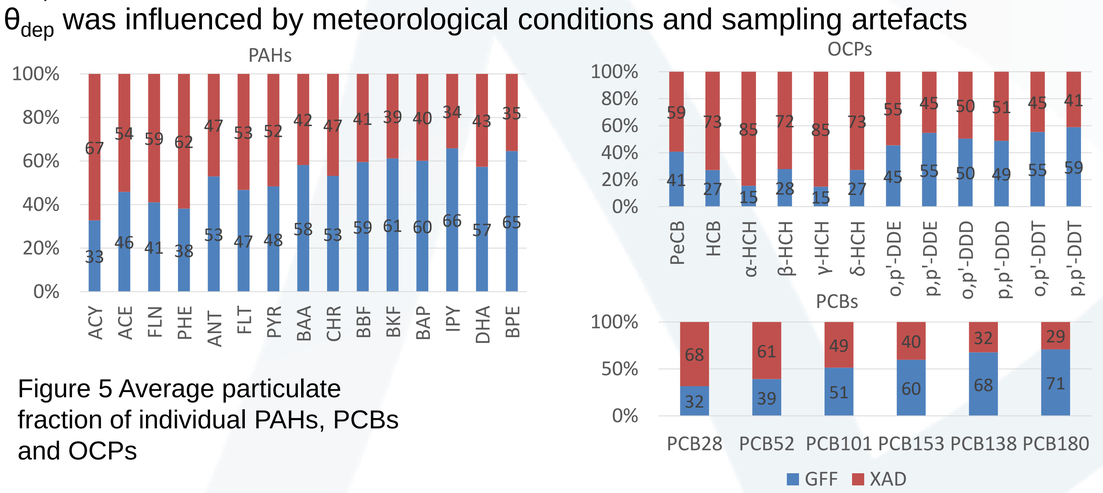

Figure 5 Average particulate fraction of individual PAHs, PCBs and OCPs

Conclusions

- Maximum deposition fluxes of Σ_{15}PAHs were not observed in winter. This is not in agreement with literature[2, 3, 4]. Obviously, wet deposition efficiency is higher in winter.
- No seasonal trend was found for the deposition flux of Σ_6PCBs, in agreement with literature[4, 5]
- The highest flux of Σ_{12}OCPs was generally measured in summer, however not significantly ($p>0.05$), which is in agreement with other studies[6, 7].
- Significantly different ($p<0.05$) results (for PAHs and PCBs) were found at the rural site KUC which indicates local influences.
- θ_{dep} was generally higher in summer than in winter and increasing with decreasing volatility of compounds