Sampling and analysis in environmental chemistry

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RECETOX

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Content

- A bit of theory
  - Why do we need to sample?
  - How to sample?
  - Active vs. passive
  - Sampling artefacts
  - Sample preparation and analysis
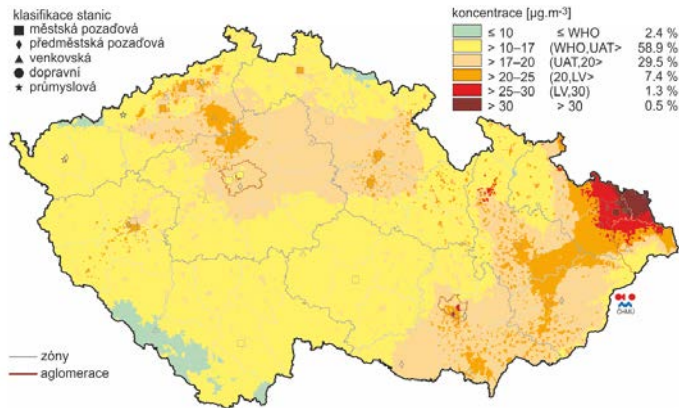 - Case studies
- A bit of observation

What is sampling about?

- Definitions (Oxford dictionary):
  - To sample: Take a sample or samples of (something) for analysis
    - Example: one hair on a jacket, orange in a supermarket

  - A sample: A small part or quantity intended to show what the whole is like

Why do we need to sample?

- ▶ To know levels of pollution prior to take specific measures
- ▶ To understand emissions of specific pollutants or from specific sectors
- ▶ To understand time trends (diurnal, weekly, seasonal variations?)
- ▶ To understand specific processes (e.g. air-surface exchange)
- ▶ To support legislation

Why do we need to sample?
To know levels of pollution

At a national level

At a European level

Prior to take actions (e.g. drinking water)

Source: chmi.cz, Jaward et al; 2004, Martinez-Trinidad et al; 2013

Why do we need to sample?
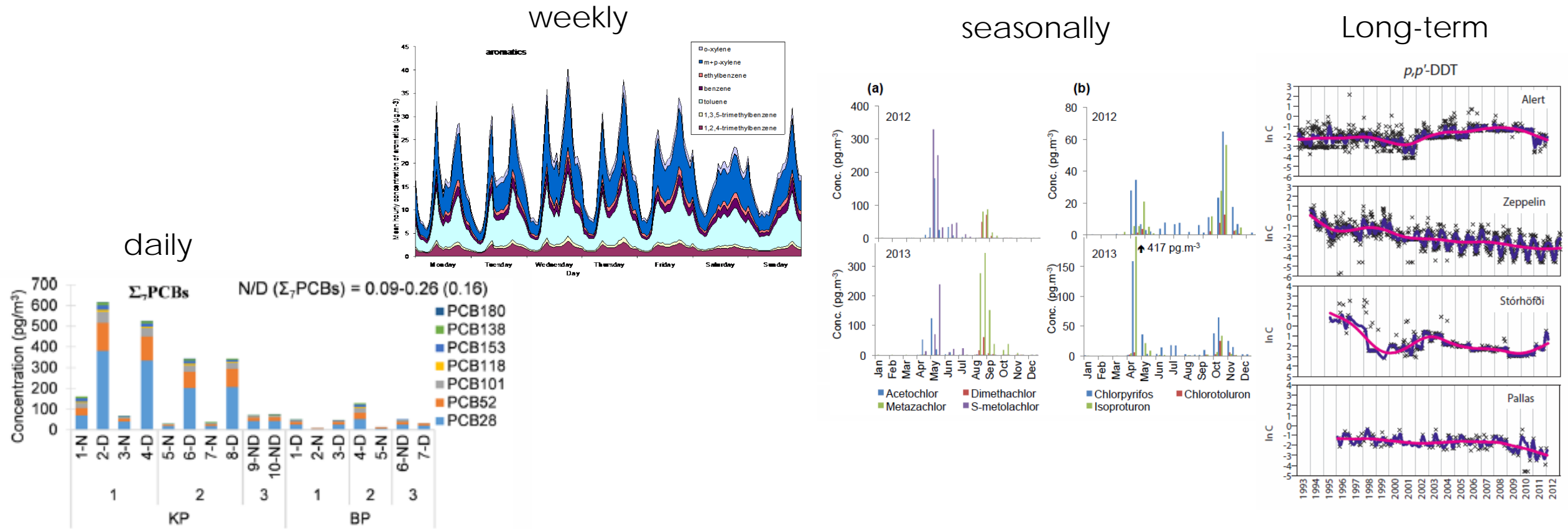# To understand emissions

Emissions from specific sector e.g. traffic

Emissions of specific pollutants from consumer products e.g. flame retardants in computers
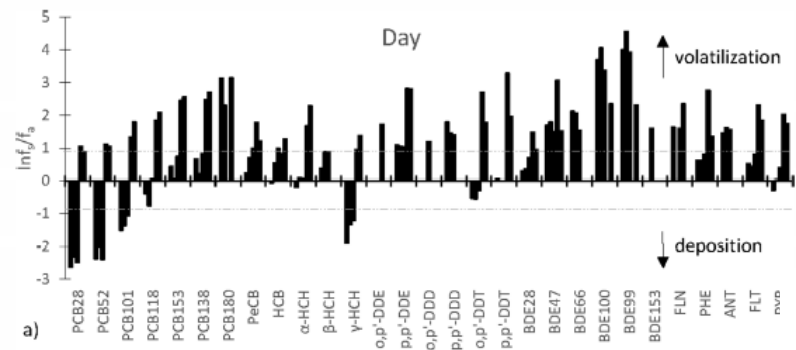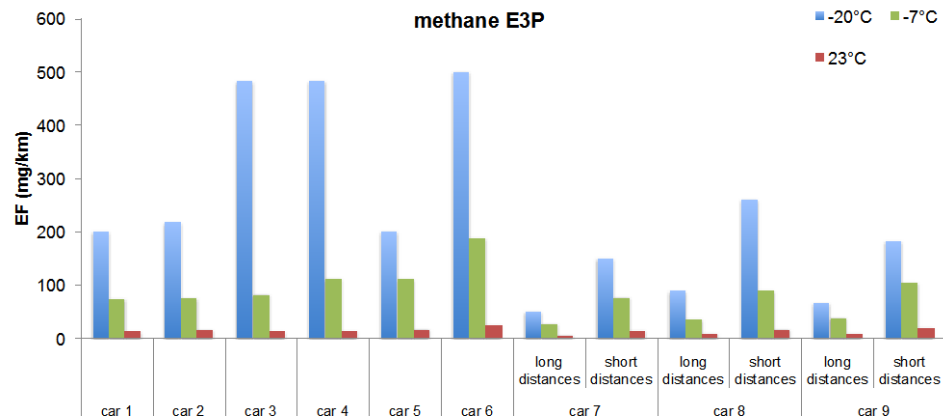
Why do we need to sample?
To understand time trends

weekly

seasonally

Long-term

daily

Why do we need to sample?
To understand specific processes

Air-soil exchange

Gas-particle partitioning

Influence of temperature on cold start emissions from passenger vehicles
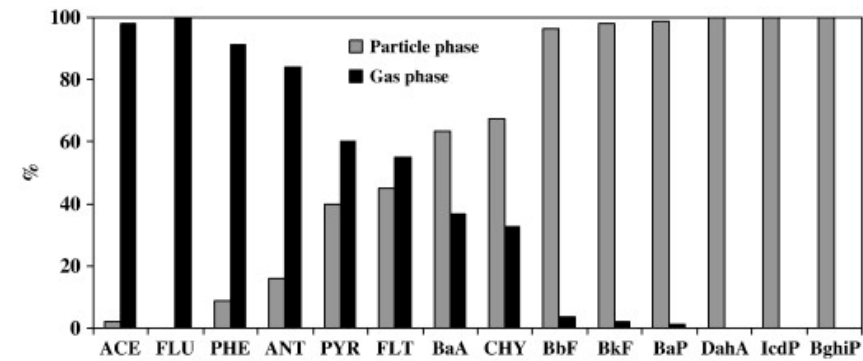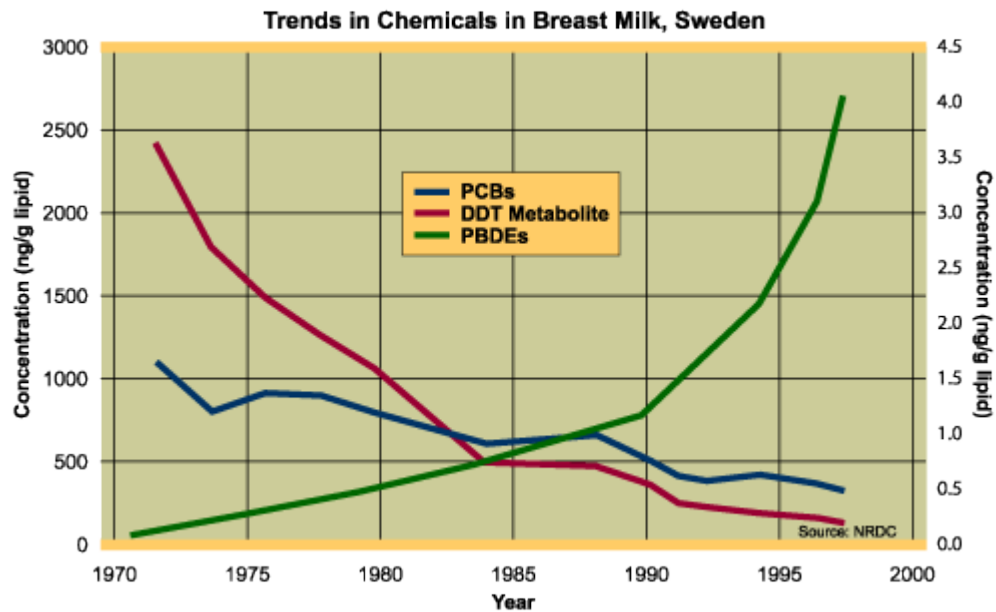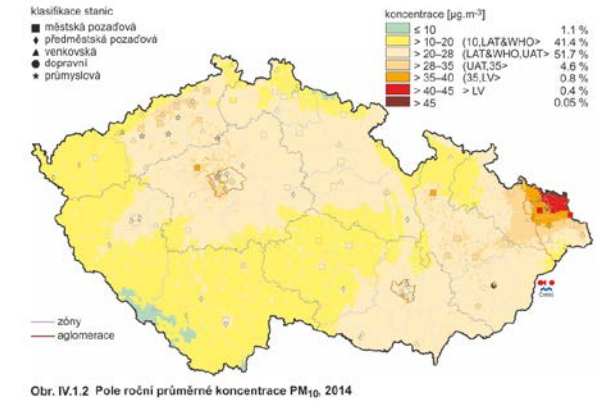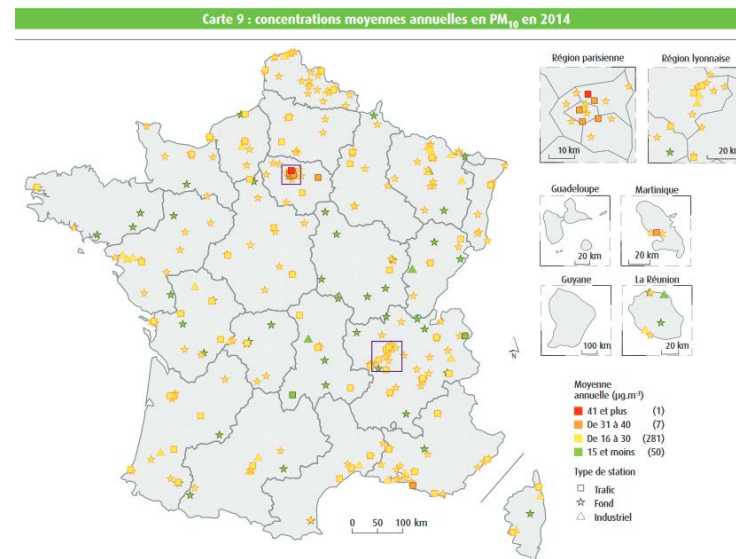
▶ Source: Degrendele et al; 2016 (ES&T), Degrendele et al; in prep., Akyüz and Çabuk (2010)

Why do we need to sample?
To support legislation

- E.g. Stockholm Convention on Persistent Organic Pollutants

- E.g. European regulation about air quality

Trends in Chemicals in Breast Milk, Sweden
- PCBs
- DDT Metabolite
- PBDEs
Source: NRDC

Carte 9 : concentrations moyennes annuelles en PM₁₀ en 2014

Obr. IV.1.2 Pole roční průměrné koncentrace PM₁₀, 2014

- Source: Meironyte et al; 1998; CGDD (2015); www.chmi.cz

How to sample?

Air

Soil

Water

Syringes for gas sampling, 1-100 mL

- Ideal for corrosive, radioactive, or sterile materials
- Removable handle minimizes heat transfer from hand to sample, making the syringe easy to hold
- Accurate and reproducible to +/- 1%
- Field repairable

Soil Sample Cores

How to sample?

- This should be connected to the answer of why do we need to sample?

- E.g. No need for the same type of air sampler if one wants to understand long term trends vs. specific processes

Air sampling: Active vs. passive sampling

- Active air sampling requires the use of a mechanical pump (i.e. the use of electricity)

- Passive sampling functions on the diffusion (accumulation) of a pollutant onto the sampling media over a certain period of time

Active air sampling (related to POPs)

▶ Bags or syringes: First methods developed but generally not suitable for POPs analysis due to the large amount of air needed in order to quantify these trace contaminants.

▶ For POPs, active air sampling usually consists of pumping air through a filter and a solid adsorbent collecting particles and gases

▶ High volume air sampler (13-70 $m^3.hour^{-1}$) vs. Low volume air sampler (0.5-5 $m^3.hour^{-1}$)

▶ Glass fiber filters vs. quartz fiber filters to trap particles

▶ XAD resin vs. polyurethane foam to trap gases -> Type of sorbent can largely affect the overall efficiency of the AAS to trap gaseous POPs
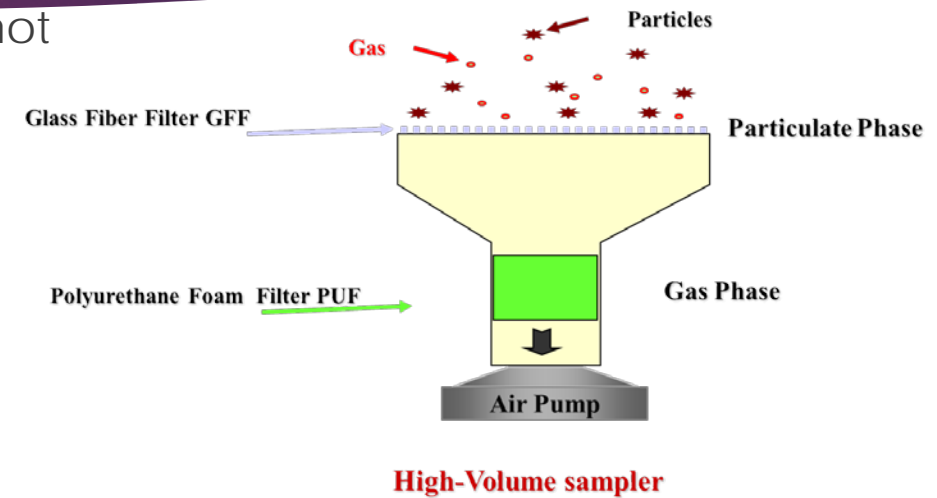

High-Volume sampler

▶ Source: Dobson et al; 2006

Table 2 Sum of pesticide concentrations (in pg m^{-3}) in filters and in resins for each of the campaigns performed (the sum includes trifluraline, alachlor, metolachlor, captan, alpha endosulfan, beta endosulfan and diflufenican)

	SERIE 1		SERIE 2		SERIE 3		SERIE 4	
	Sampler 1 PUF	Sampler 2 XAD-2	Sampler 1 PUF	Sampler 2 XAD-4	Sampler 1 XAD-2+PUF	Sampler 2 XAD-2	Sampler 1 PUF+XAD-4	Sampler 2 PUF
∑ Filter	3063±450	2991±450	4480±650	2850±400	1501±200	1018±150	437±65	635±100
∑ resin	806±100	8012±1000	2242±330	9178±1300	3052±450	2657±400	1703±250	681±100

Samplers for assessing particle size distribution of POPs

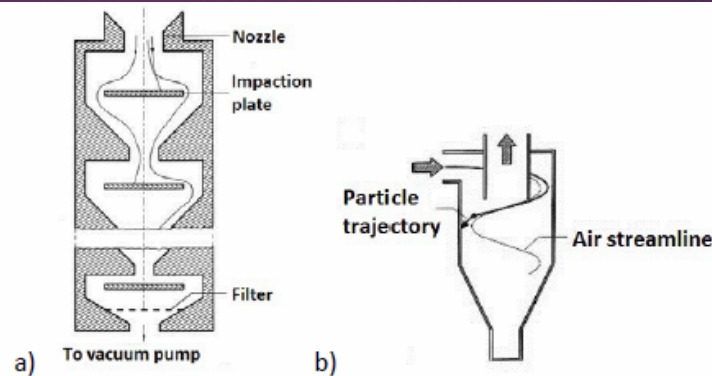Figure 15: Schematic design of a cascade impactor (a) and a cyclone (b)

▶ Principle: To separate the particles based on inertia or gravity and to collect particles of a given size range according to the sampler flow.

▶ Cut-off diameter = the size at which particles are collected with 50% efficiency.

▶ For cascade impactor: air containing particles is accelerated through an orifice or nozzle towards a plate located below the orifice, causing a sudden change of direction of the airstream. Particles that are too large hit or impact the plate while those small enough to follow the stream lines remain suspended and follow the air until the next plate.

▶ For cyclone, same principle as cascade impactor but the impaction takes place on the sampler walls.

Sampling artefacts with active air samplers

- Blow-on = gaseous compounds being adsorbed to particles on the filter or to the filter material itself resulting in an overestimation of the particle phase

- Blow-off = volatilization of particle-bound compounds from the filter, resulting in an underestimation of the particle phase

High-Volume sampler
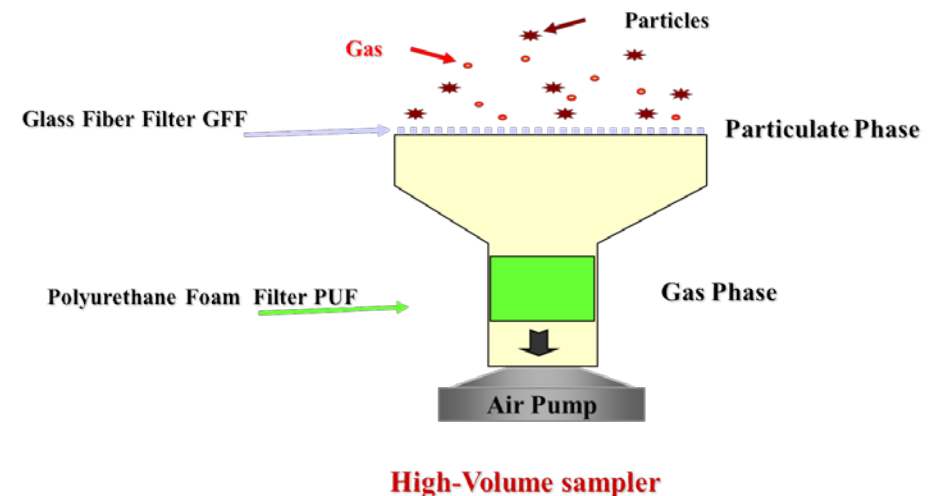
Sampling artefacts with active air samplers

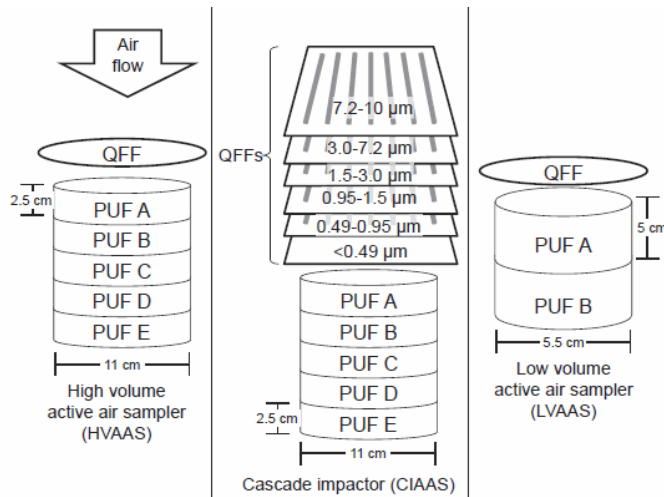▶ Breakthrough = loss of compounds downstream of the gas-phase sampling medium

Fig. 1. Schematic representation of sampling trains.
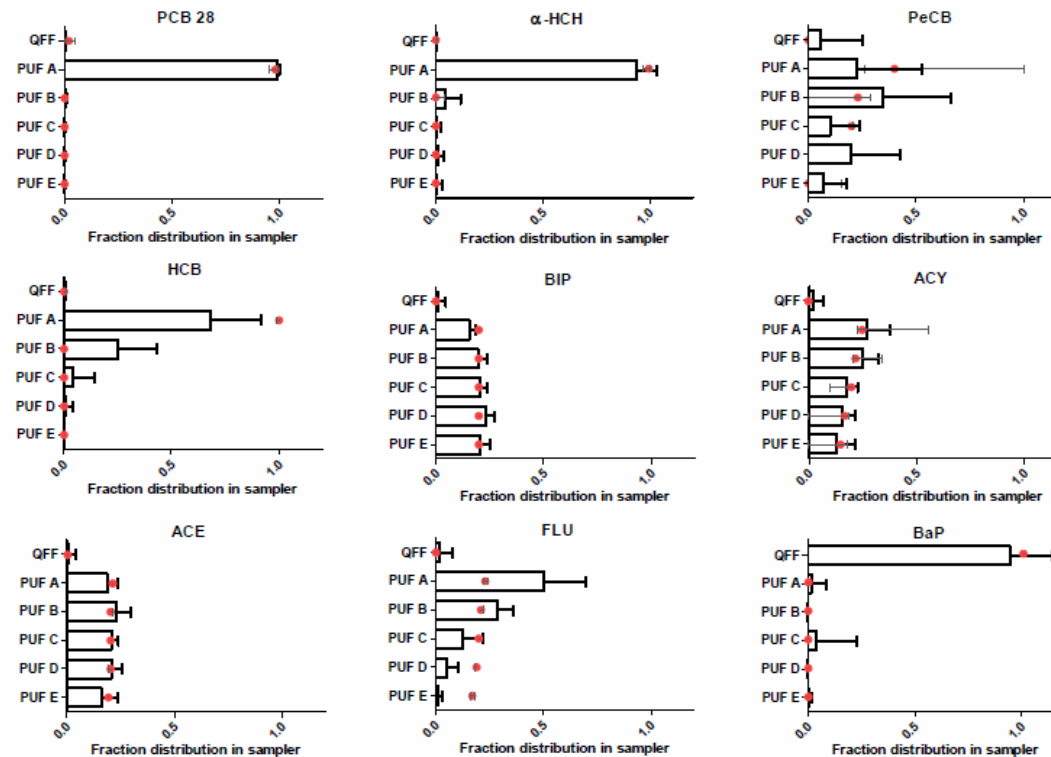
Fig. 3. Average measured and estimated distributions of selected SVOCs within the baseline HVAAS (24 h, ~700 m³ sample volume) relative to the total mass captured by the sampler. Horizontal bars show the average distribution of 28 daily samples, and the black error bars show the standard deviation. Red points represent the theoretically-estimated distribution (described in SI) and grey error bars represent the uncertainty in the estimates due to the range of temperatures during sampling. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

▶ Source: Melymuk et al; 2016

Sampling artefacts with active air samplers

▶ Degradation = reaction with trace gas oxidants that are also drawn through the sampler

Fig. 2. Average ratios of concentrations measured by the two sampling systems for particulate (PD/P) and gaseous (GD/G) PAHs. Fluorene (Fl); Phenanthrene (Ph); Anthracene (An); Methyl-phenanthrene (C1-Ph); Fluoranthene (Flu); Dimethyl-phenanthrene (C2-Ph); Pyrene (Py); Methyl-pyrenes (C1-Py); Cyclopentane[cd]pyrene (Cy[cd]Py); Benzo[a]antrhacene (B[a]A); Chrysene/triphenylene (Chr/T); Methylchrysene (C1-Chr); Benzo[b]fluoranthene (B[b]F); Benzo[k]fluoranthene (B[k]F); Benzo[e]pyrene (B[e]P); Benzo[a]pyrene (B[a]P); Anthanthrene (Ant); Indeno[1,2,3-cd]pyrene (In[cd]Py); Benzo[ghi]perylene (B[ghi]P); and Coronene (Co).

High ozone conc. and sampling duration

High ozone and short sampling time

Low ozone conc. and long sampling time

M. Tsapakis, E.G. Stephanou / Atmospheric Environment 37 (2003) 4935–4944

▶ Source: Tsapakis and Stephanou (2003)

Passive air sampling
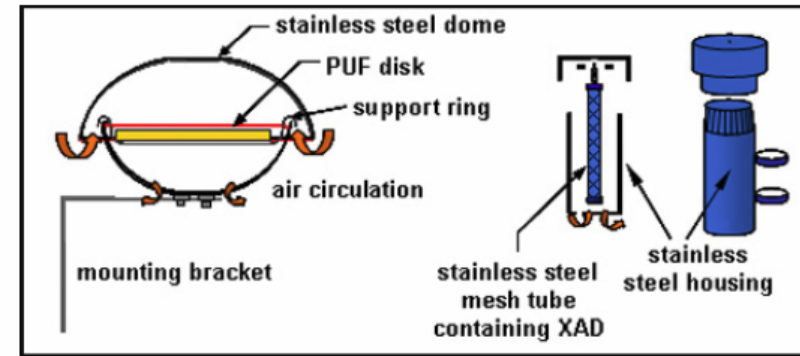
Figure 16: Schematic of passive air sampler using PUF disks and XAD resins adapted from Environment Canada (2014).

- A passive air sampler consists of an accumulating medium that collects chemicals from the atmosphere without the aid of a pump

- Different devices have been developed: semi-permeable membrane devices, versatile easy rapid atmospheric monitors and polymer coated glass samplers

- But for POPs analysis, mainly PUF-PAS and XAD-PAS

Passive air sampling: PUF-PAS
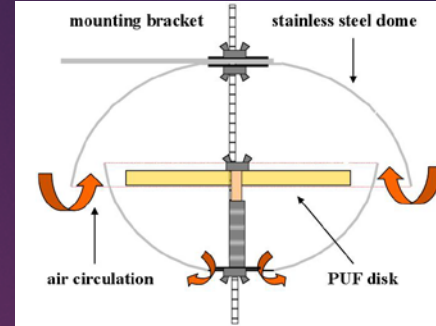
- PUF-PAS consists of a PUF disk housed in stainless steel chamber which reduced the influence of wind speed on the uptake rate and protects the PUF discs from precipitation, particle deposition and photodegradation

- Sampling rates ranged from 0.2 to 9.3 m³/day

- So long sampler deployment is needed: several weeks up to 4 months

Passive air sampling: XAD-PAS

- Resin filled container placed in a protective sampling shelter with an opening at the bottom.

- Sampling duration is from few weeks up to one year.
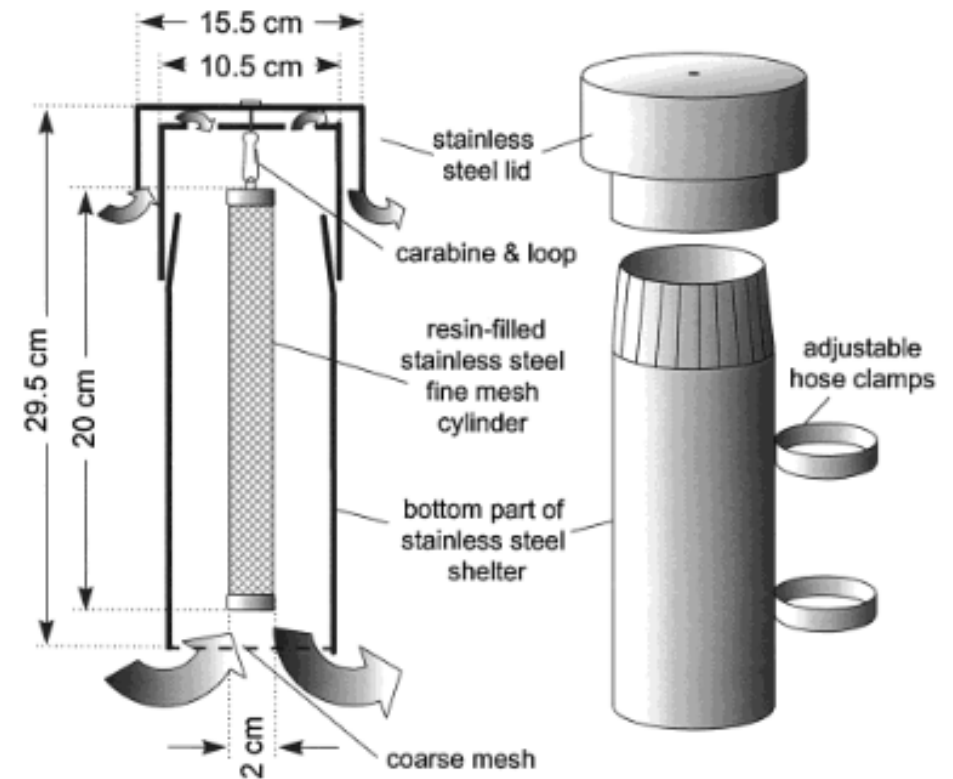
FIGURE 2. Design and dimensions of the XAD-2-based passive air sampling system for persistent organic pollutants.

- Source: Wania et al; 2003

Limits of passive air sampling

- Complicated estimation of the sampling rates used to derive the atmospheric concentrations from the sampler concentrations, particularly at variable meteorological conditions

- Sampling rates are calculated from

  - Field calibration experiments

  - Depuration compounds (rate of uptake = rate of loss)

- Some researchers use a single value for sampling rate
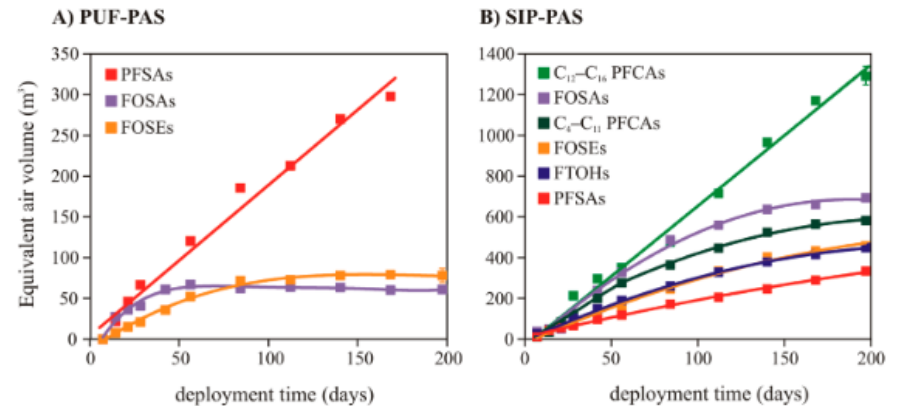
Figure 1. Uptake profiles of PFASs for (A) PUF-PAS and (B) SIP-PAS.

Air sampling: Active vs. passive sampling

Active sampling

- ☺ Accurate (?)
- ☺ Ideal for understanding processes
- ☺ High temporal resolution (e.g. pesticides application)

- ☹ Expensive, "hard" to use, large size
- ☹ Source of electricity needed
- ☹ High request on personal involvement, maintenance and support
- ☹ Subject to sampling artefacts
- ☹ Noise

Passive sampling
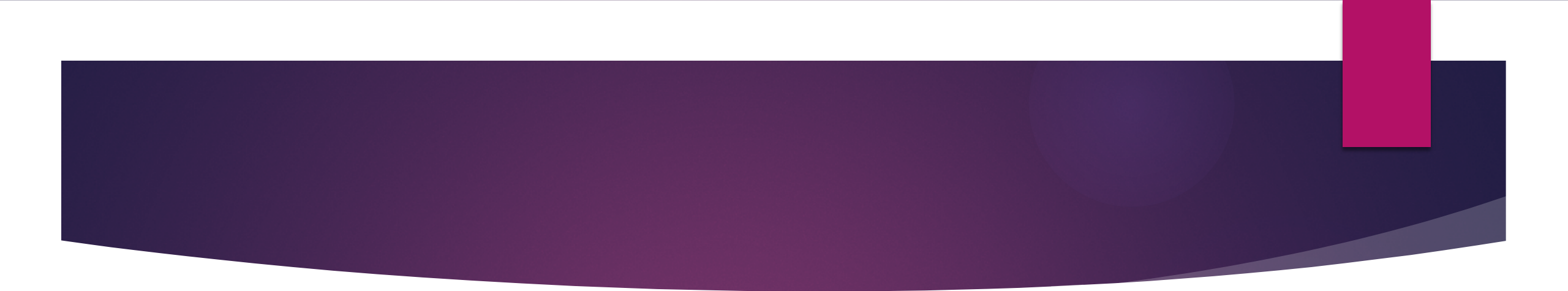
- ☺ Cheap, easy to use, small size
- ☺ No electricity needed (remote areas)
- ☺ Low need on personal involvement
- ☺ No noise (working environment, bedrooms)

- ☹/ ☺ Long term studies
- ☹ Uncertainty with assessment of concentration (a factor of 2-3 of the "true" air concentrations)
- ☹ Strong influence of meteorological parameters
- ☹ Subject to sampling artefacts
- ☺ Collect mainly the gas phase (less efficient for particle-bound compounds)
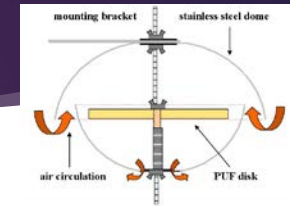
Other considerations to take into account prior sampling

- Esthetic (e.g. hair samples)
- Intrusion to personal domain (i.e. noise, dust behind huge wardrobe)
- Budget
- Representativeness of the samples (i.e. one sample per house)
- Spatial variation

Concentration [µg/m²]

Novel flame retardants

	0.05-0.1
	0.1-0.5
	0.5-1
	1-5
	5-10
	10-50

samples

Source: Lisa Melymuk, Personal communication
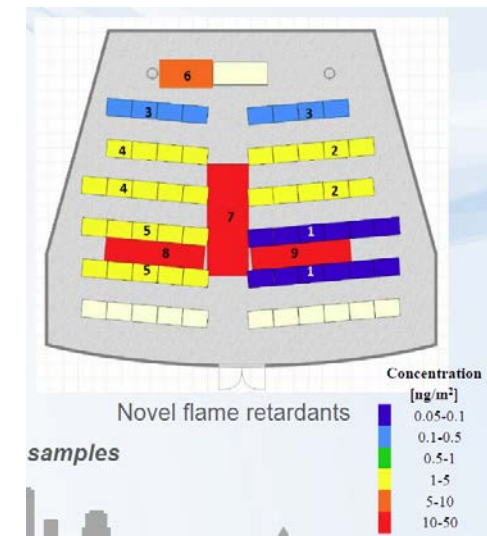
▶ Well, we now have our samples but what to do with it???

Sample preparation and analysis: Extraction

- Many different types of extraction techniques Soxhlet, pressurized liquid extraction (PLE), supercritical fluid extraction (SFE), microwave assisted extraction (MAE), ultrasound assisted extraction (UAS) and solid phase extraction/micro-extraction (SPE/SPME)

- But Soxhlet extraction is common because it is simple and low cost.

- But it is time and solvent consuming + potential degradation and lost (e.g. naphthalene)

Sample preparation and analysis: Clean-up

▶ During extraction, not only the target compounds are accumulating but also many interfering compounds (e.g. fats, carbohydrates, water, chlorophyll, …)

▶ Extract purification is usually needed in order to reduce matrix effects and to allow identification and quantification of target compounds

▶ E.g. silica gel or fluorisil columns have been commonly applied for the separation of non-polar compounds to more polar compounds.

Sample preparation and analysis: Separation and quantification

- Separation:
  - Usually done by gas chromatography or liquid chromatography depending on the physico chemical properties of the compounds investigated (i.e. polar and non volatile compounds with LC)

- Detection and quantification:
  - Production of ions
  - Separation of ions
  - Detection of ions

- https://www.youtube.com/watch?v=6HJWUf7dlLc

Sample preparation and analysis: Examples of chromatograms
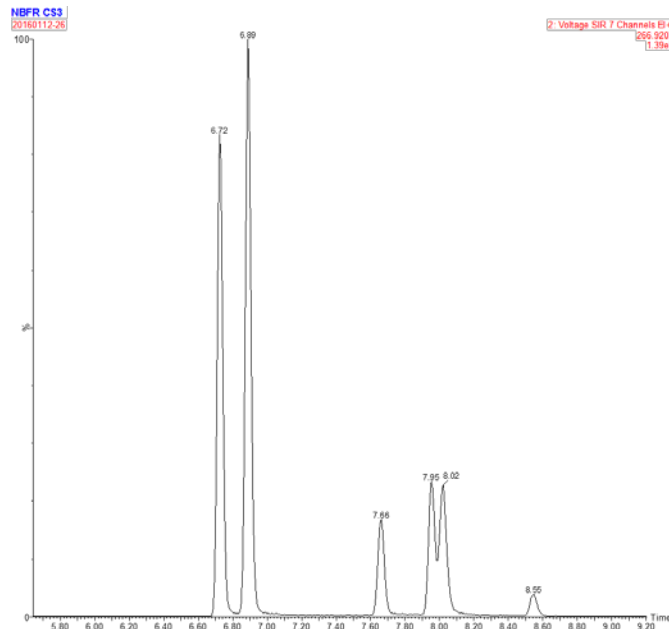
Standard
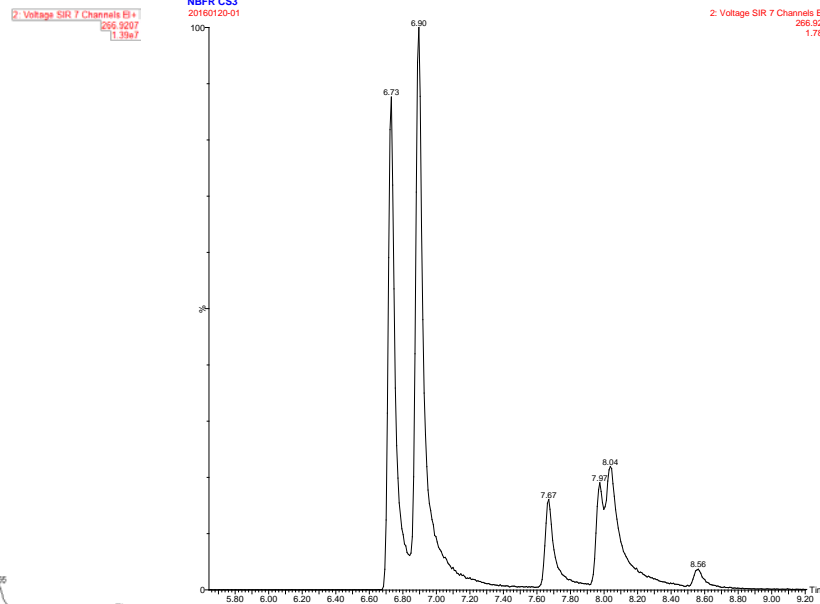
Standard, but likely dirty column
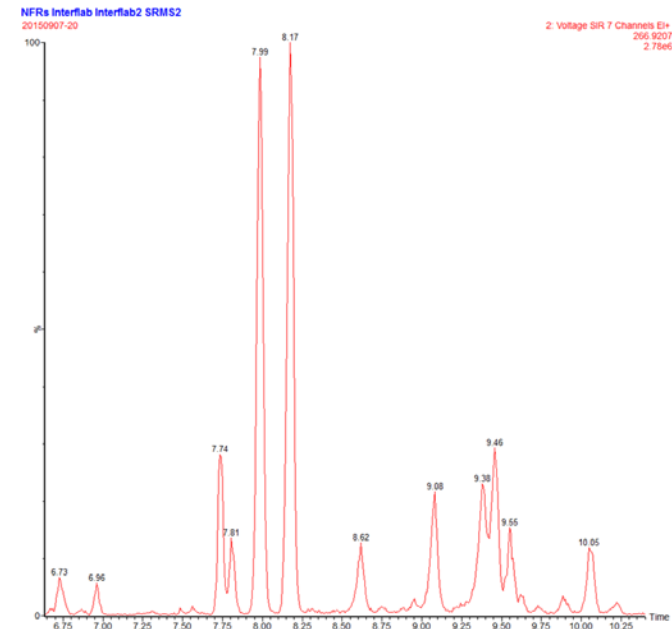
Dust sample

Case study 1: Air-soil exchange of POPs

- Sampling were performed at two background sites in Hungary

- At each site, 3 soil samples, each consisting of 9 individual plots (uppermost 5 cm) have been collected

- At both sites:
  - Low volume active air sampler at 94-114 cm agl
  - 2 soil fugacity samplers at 3 cm agl (Cabrerizo et al., 2009) collecting **air that has been equilibrated with the soil** (primordial for the assessment of soil fugacity)
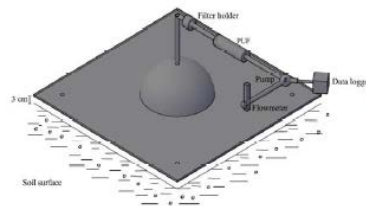
Cabrerizo et al., 2009

  - Soils were artificially watered and air was sampled for the following ~12 hours

- Sample preparation and analysis:
  - Extraction and fractionation
  - Quantification of PAHs, PCBs, OCPs and PBDEs using gas chromatography and mass spectrometry

Case study 1: Concentrations in the soils
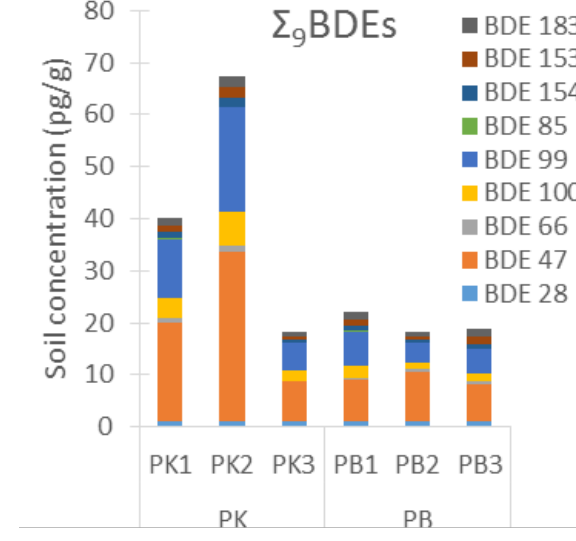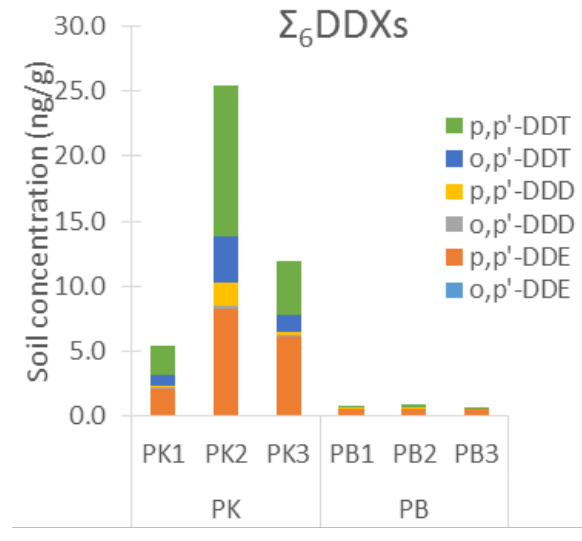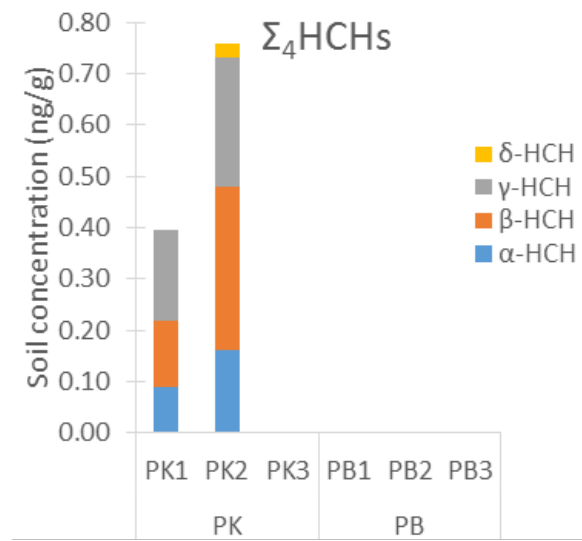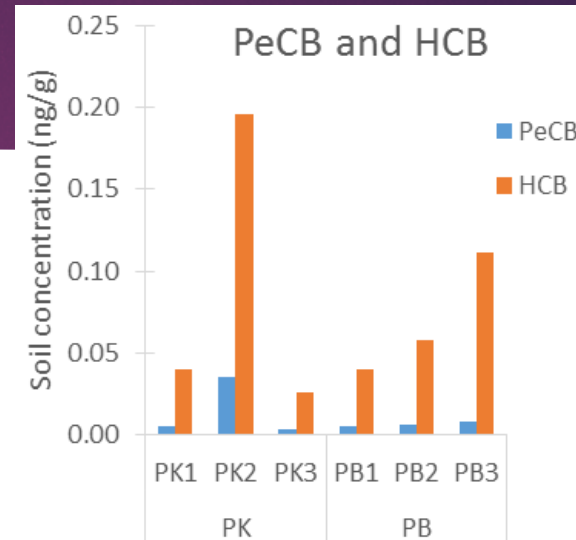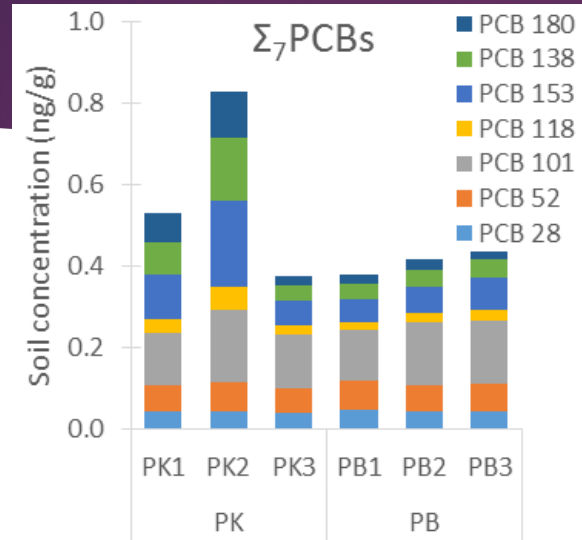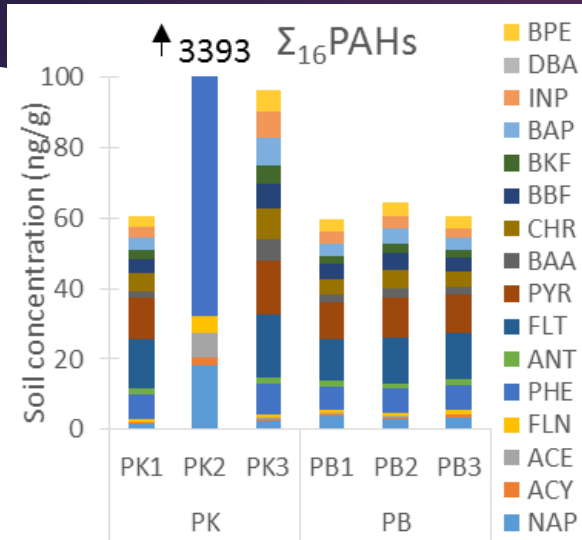
Huge spatial variation of POPs concentrations in soils (Less important for air).

Case study 1: Air-soil exchange
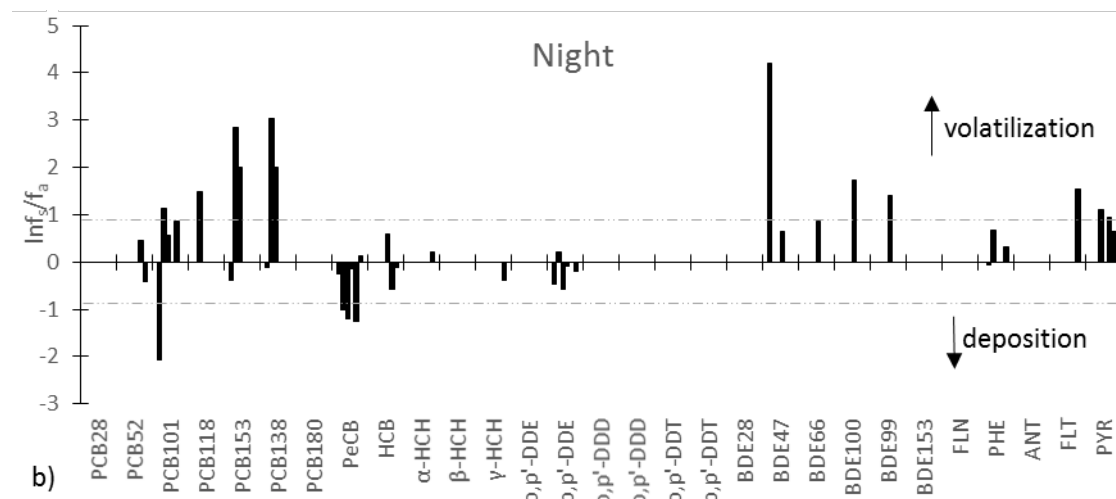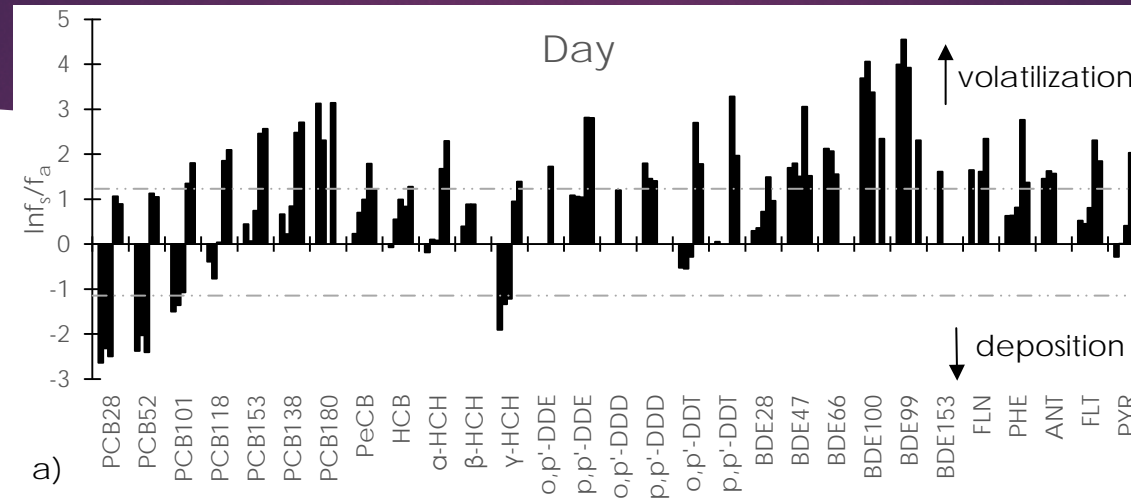
Case study 2: Pesticides in the air

▶ Weekly air samples were taken from January 2012 to December 2013 (N=104) at a background site using a HVAS, collecting gas and particles

▶ Air was sampled at a rural and urban site using a HVAS equipped with a cascade impactor. Six particle size fractions were sampled (< 0.49 μm, 0.49-0.95 μm, 0.95-1.5 μm, 1.5-3.0 μm, 3.0-7.2 μm and 7.2-10.0 μm). Weekly air samples were collected from October 2009 to October 2010 and were grouped on a seasonal basis.
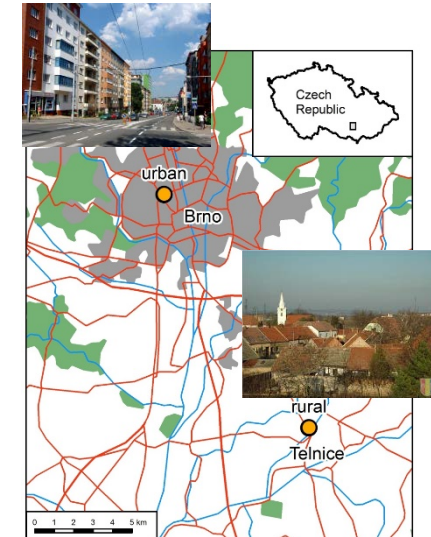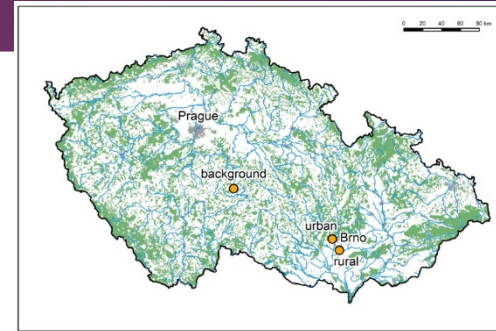
Case study 2: Seasonal variations
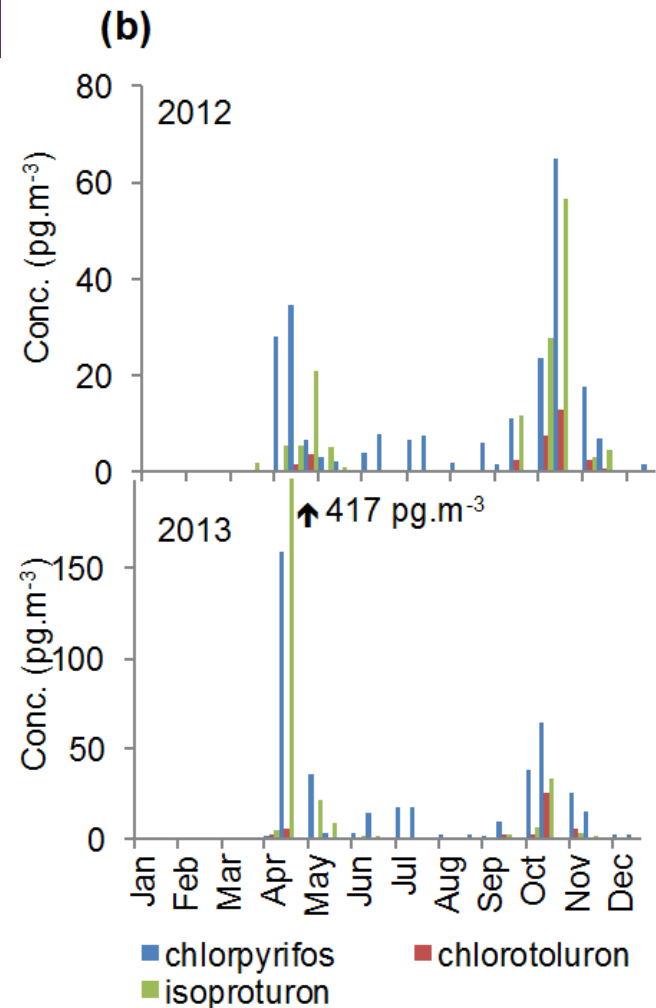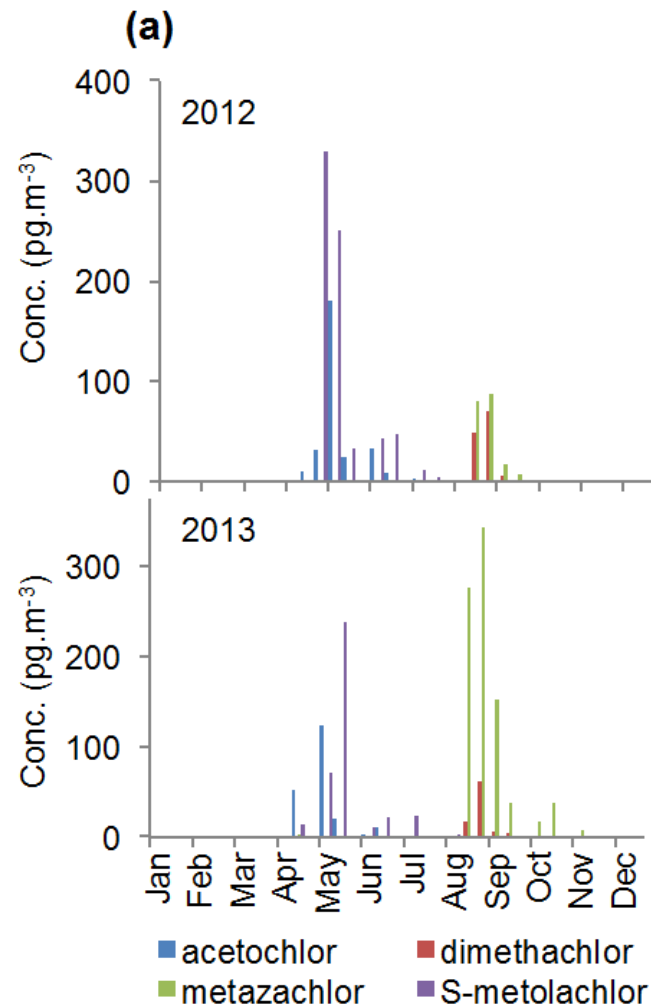
Case study 2: Particle size distribution

(a) Fenpropimorph

(b) Isoproturon

Size fraction (in μm)
- <0.49
- 0.49-0.95
- 0.95-1.5
- 1.5-3.0
- 3.0-7.2
- 7.2-10
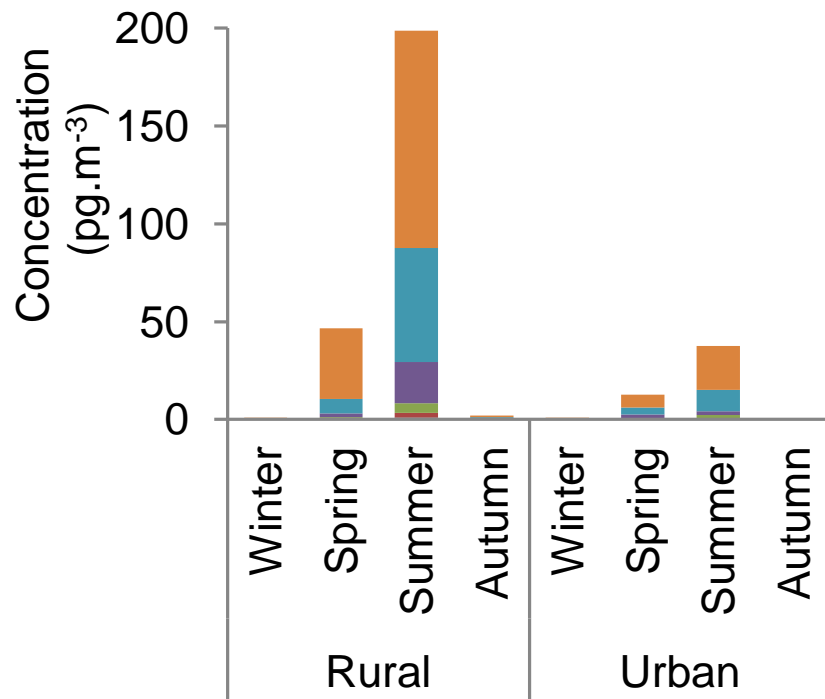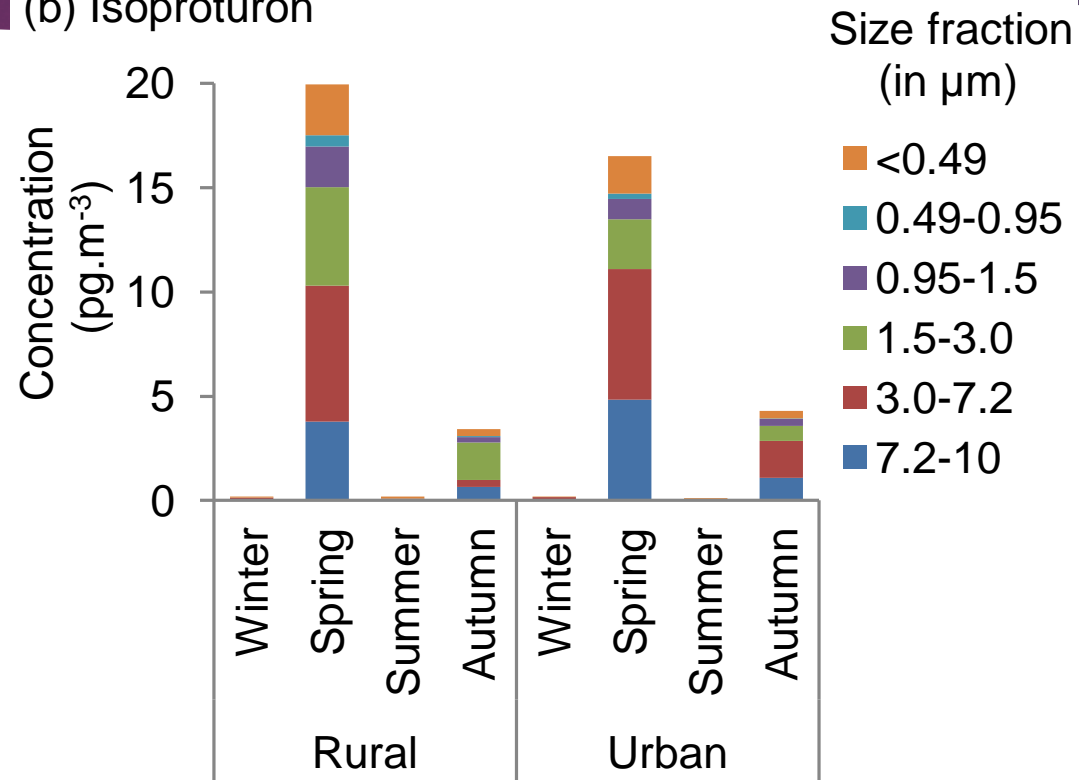
9 CUPs and 2 OCPs were 35-91% associated with fine particles

4 CUPs were 45-70% associated with large particles (>3.0 μm)

Case study 3: Emissions of VOCs from passenger cars
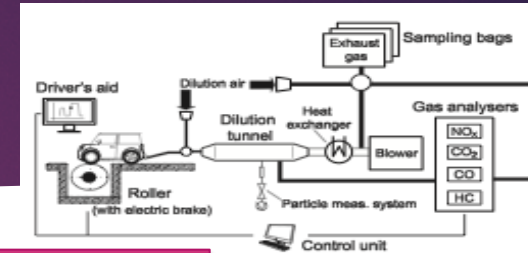
93 light-duty vehicles:
12 pre-Euro 1 petrol (PEP), 4 pre-Euro 1 diesel (PED), 9 Euro 1 petrol (E1P), 7 Euro 1 diesel (E1D), 15 Euro 2 petrol (E2P), 22 Euro 2 diesel (E2D), 18 Euro 3 petrol (E3P), 4 Euro 3 diesel (E3D) and 2 Euro 4 petrol (E4P)

5 laboratories

1200 individual tests

Ambient temperatures ranging from -20 to 23°C

Hot/cold start

20 different driving cycles: 14 real-world cycles and 6 legislative cycles

Urban, rural and motorway driving conditions

Franco et al; 2013

Case study 3: Validation of the database

- **$\Sigma_i EF(VOC_i) < EF(HC)$**

- Data missing for 28 tests

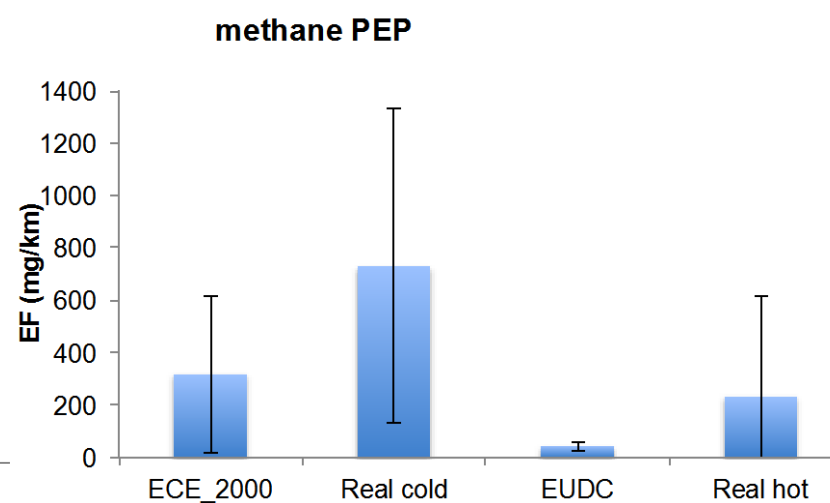- $\Sigma_i EF(VOC_i) > EF(HC)$ for 199 tests

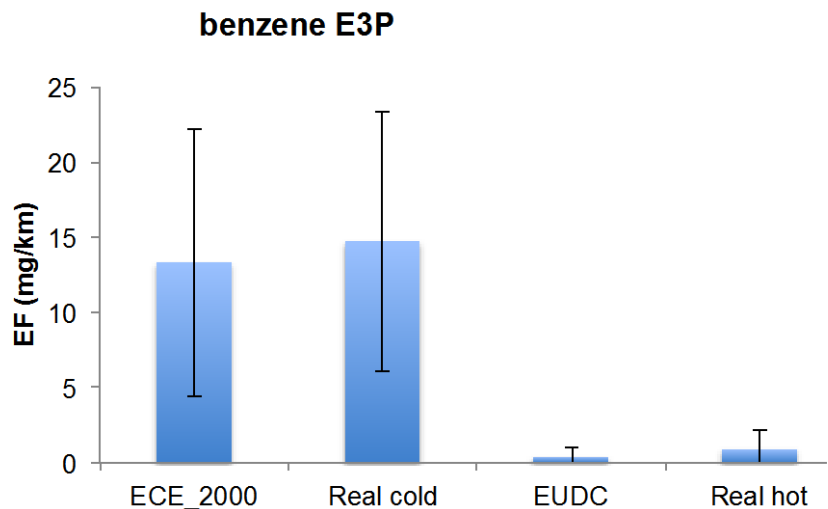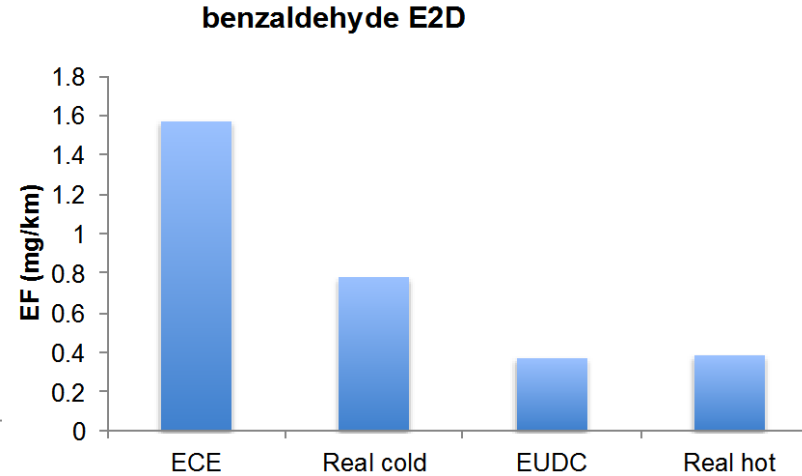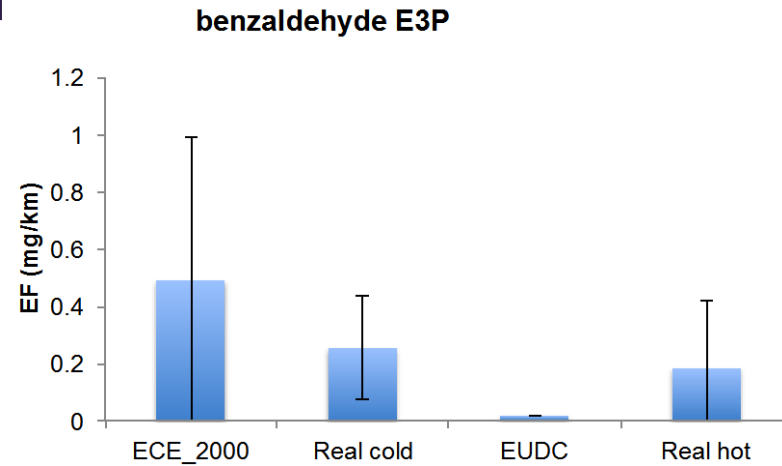- **Total database: 983 tests**
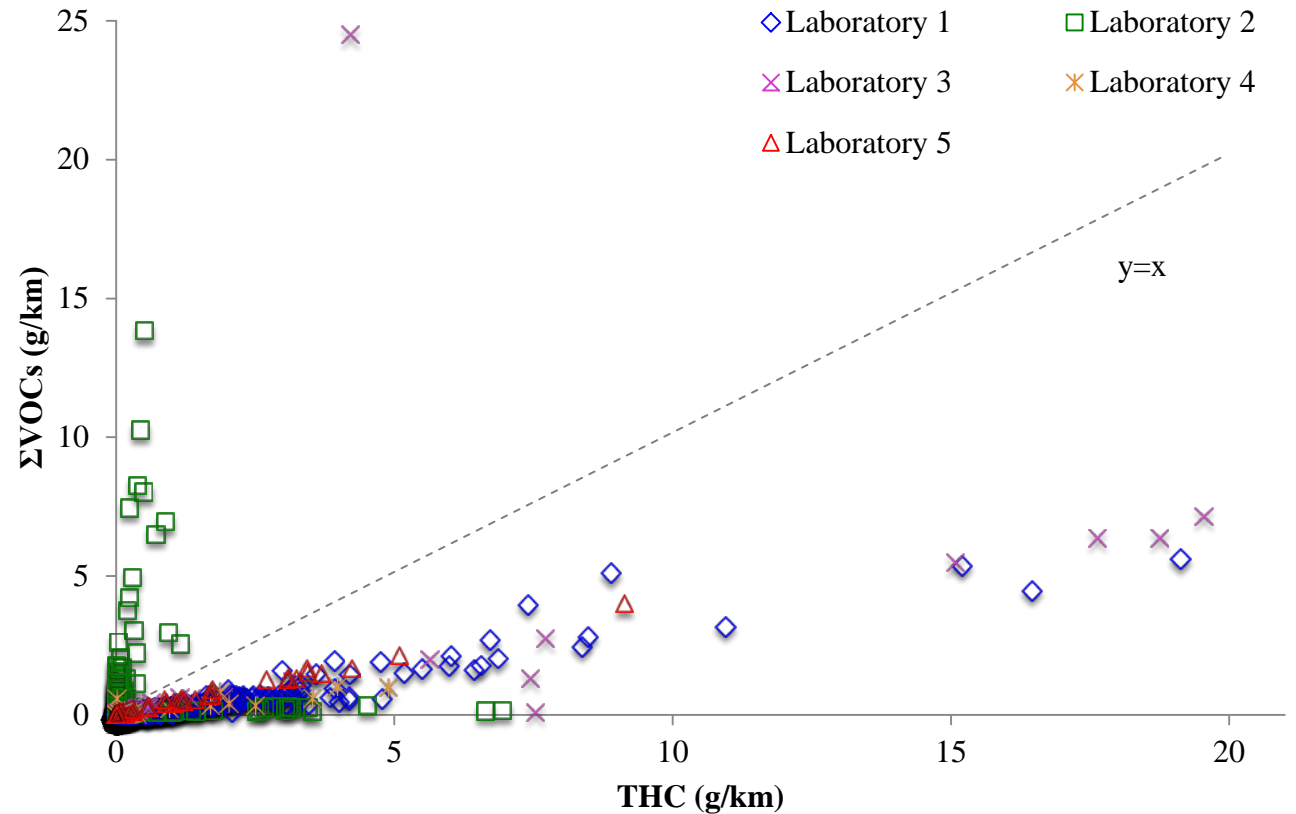
Case study 3: Influence of cold start
Urban roads
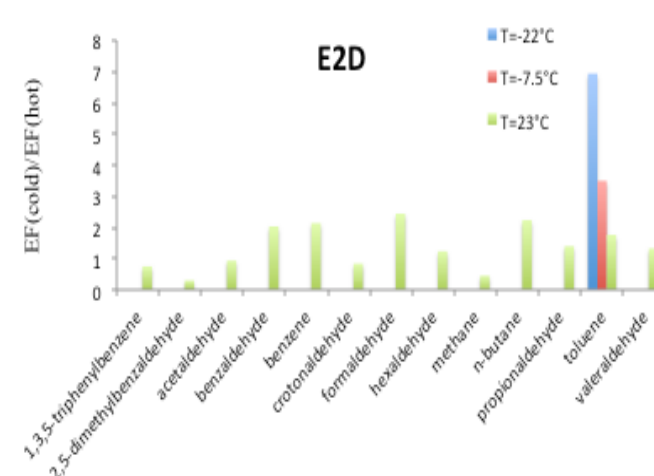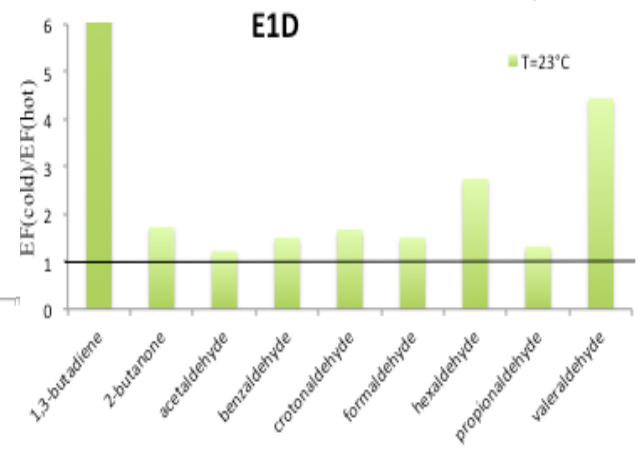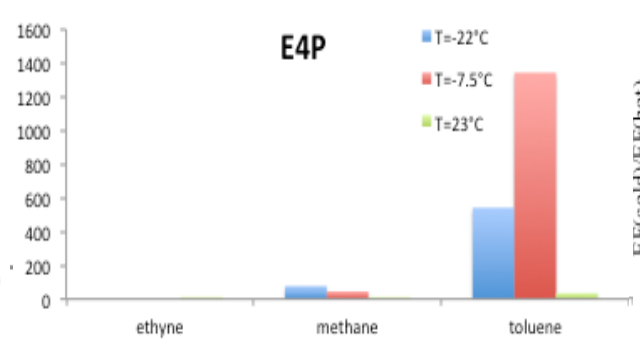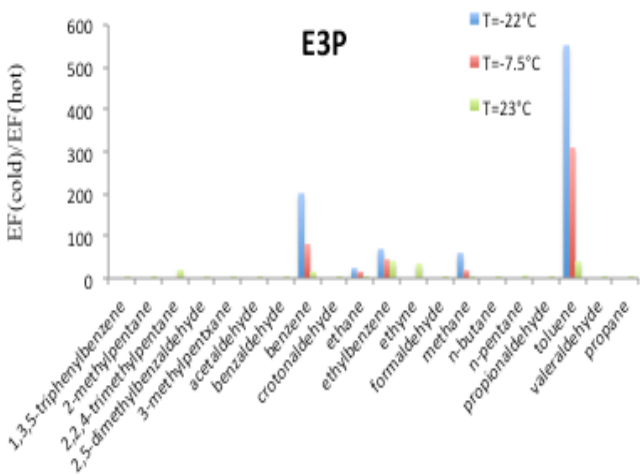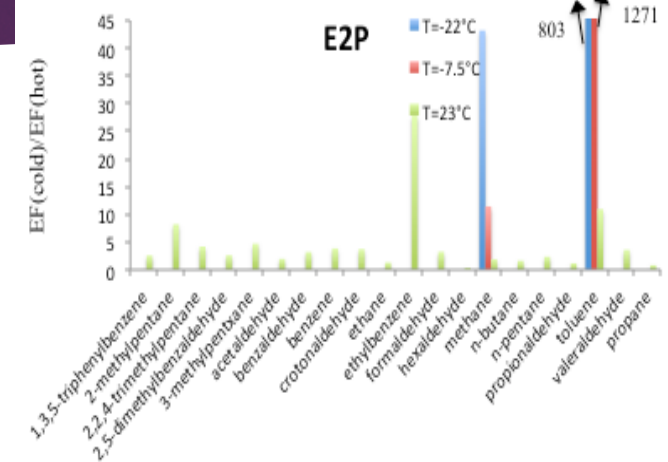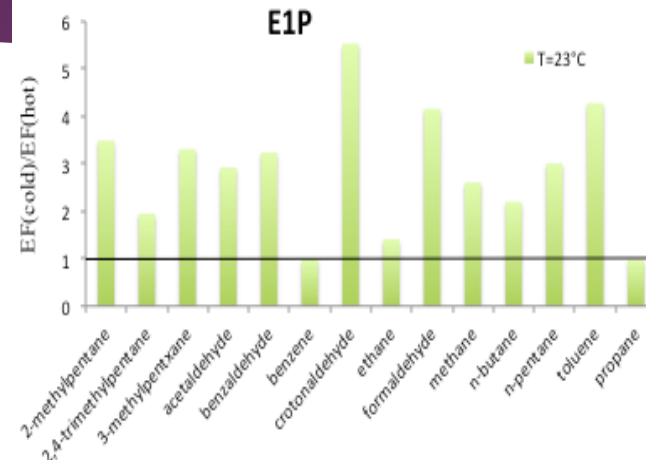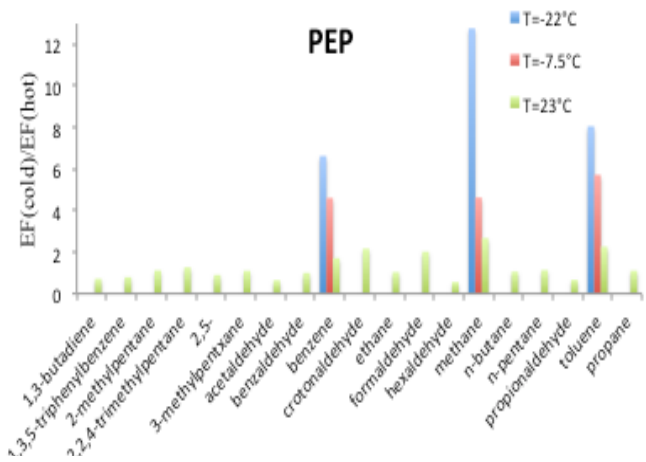
For toluene, E3P and at -7.5°C, **EF(cold) ≈ 300 EF(hot)**

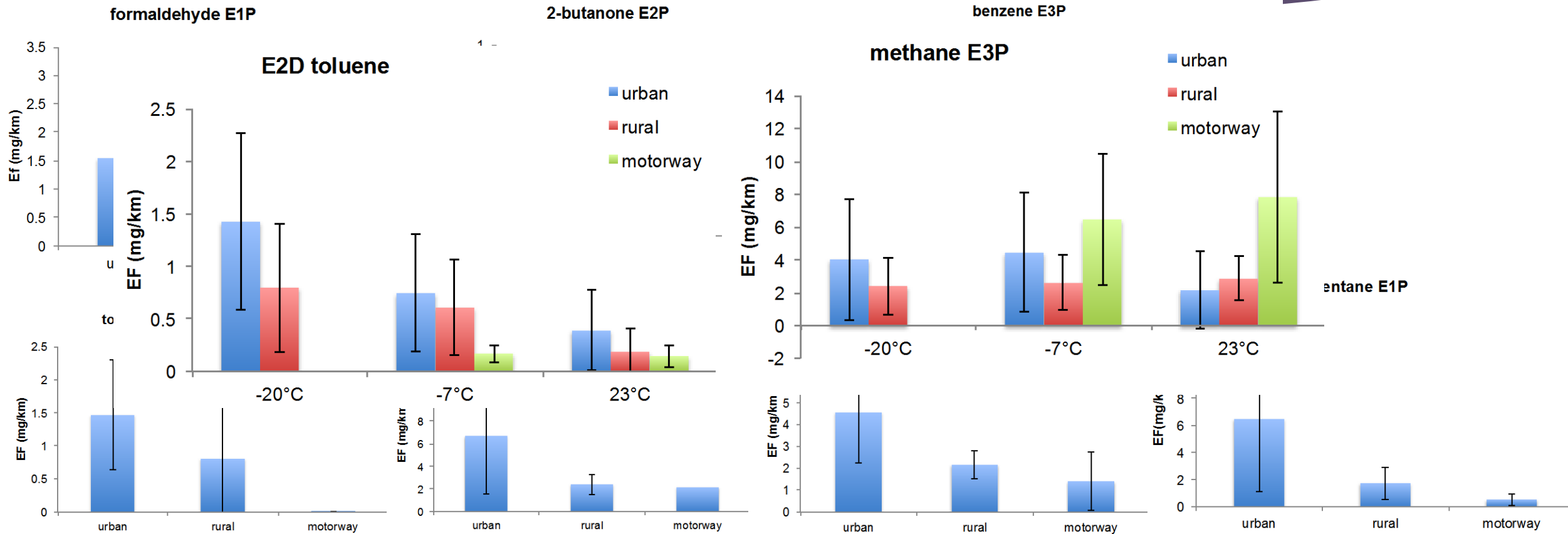# Case study 3: Influence of cycle class Urban – Real world driving vs. legislative cycles

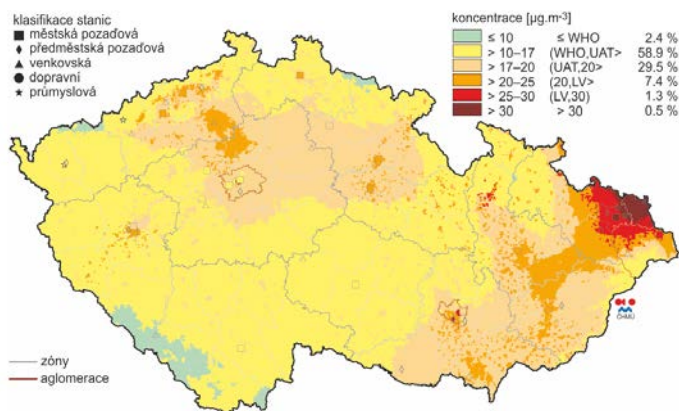Overall good agreement for cold start conditions

In hot conditions, legislative emissions are generally lower than "real" emissions

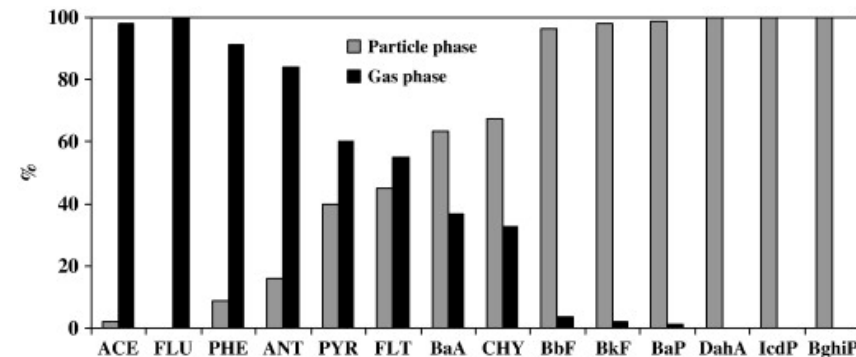# Case study 3: Influence of driving conditions

EF(urban) ≈ 2.5 EF(rural) ≈ 5 EF(motorway)

Any questions????

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