Environmental sampling and analysis of organic contaminants in the environmental samples

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1. **Environmental analytical chemistry**
Specific features, general scheme

2. **Sampling**
Sampling plan, strategy, sampling protocol, sample size and quality, transport, storage

3. **Sample preparation**
Extraction of solid (Soxhlet, automatic extraction, MAE, ASE, SFE) and liquid (L-L, SPE, SPME, head-space) samples, fractionation and clean-up (column chromatography, gel permeation)

4. **Analytical techniques**
Chromatographic techniques, principals, instrumentation, HPLC, GC, GC-MS

5. **Target pollutants**
Priority pollutants (PCBs, PCDDs/Fs, PAHs, pesticides), emerging pollutants (SCCPs/MCCPs, antibiotics, degradation products)

6. **QA/QC**
Calibration, limit of detection and quantification, internal and recovery standards, blanks, certified reference materials, interlaboratory calibration tests, method validation and verification, GLP

7. **Environmental monitoring**
Monitoring programs, Global monitoring plan under Stockholm Convention

Environmental science brings together scientists from many fields to perform complex studies of environmental processes and interactions.

They may include:

- water and food quality monitoring
- level of contamination of environmental compartments
- ozone depletition as a result of the presence of certain chemicals in the atmosphere
- regional contamination studies
- evaluation of the impact of local sources of pollution
- toxicity of chemical compounds as a function of their chemical structure
- impact of chemical substances on living organisms
- bioavailability
- bioaccumulation
- biotic and abiotic transformations
- transport of pollutants in the environment
- global fate of pollutants
- international directives and their impact on the global contamination
- remediation actions and their quality control
- sustainable development

Most of them involve the chemical analysis as one of necessary steps.

Environmental analytical chemistry chalenges:

- international conventions focus attention on the **new groups of pollutants**
- old contamination brings the problem of **residue analyses**
- lowering limits as well as environmental levels require **low detection limits**
- **large-scale monitoring** is crutial for the studies of the long-range transport
- development of **new sampling techniques** is encouraged
- increasing number of samples stresses the **need for automatization**
- fate studies require **understanding of distribution processes** and equilibria
- **photochemical reactions** complicate the sampling and data interpretation
- consideration of both, **analytical and toxicological data** is important for successful **risk assessment**
- methods of **biochemistry and molecular-biology** are often implemented in toxicological studies
- international studies require **standardization of all procedures**

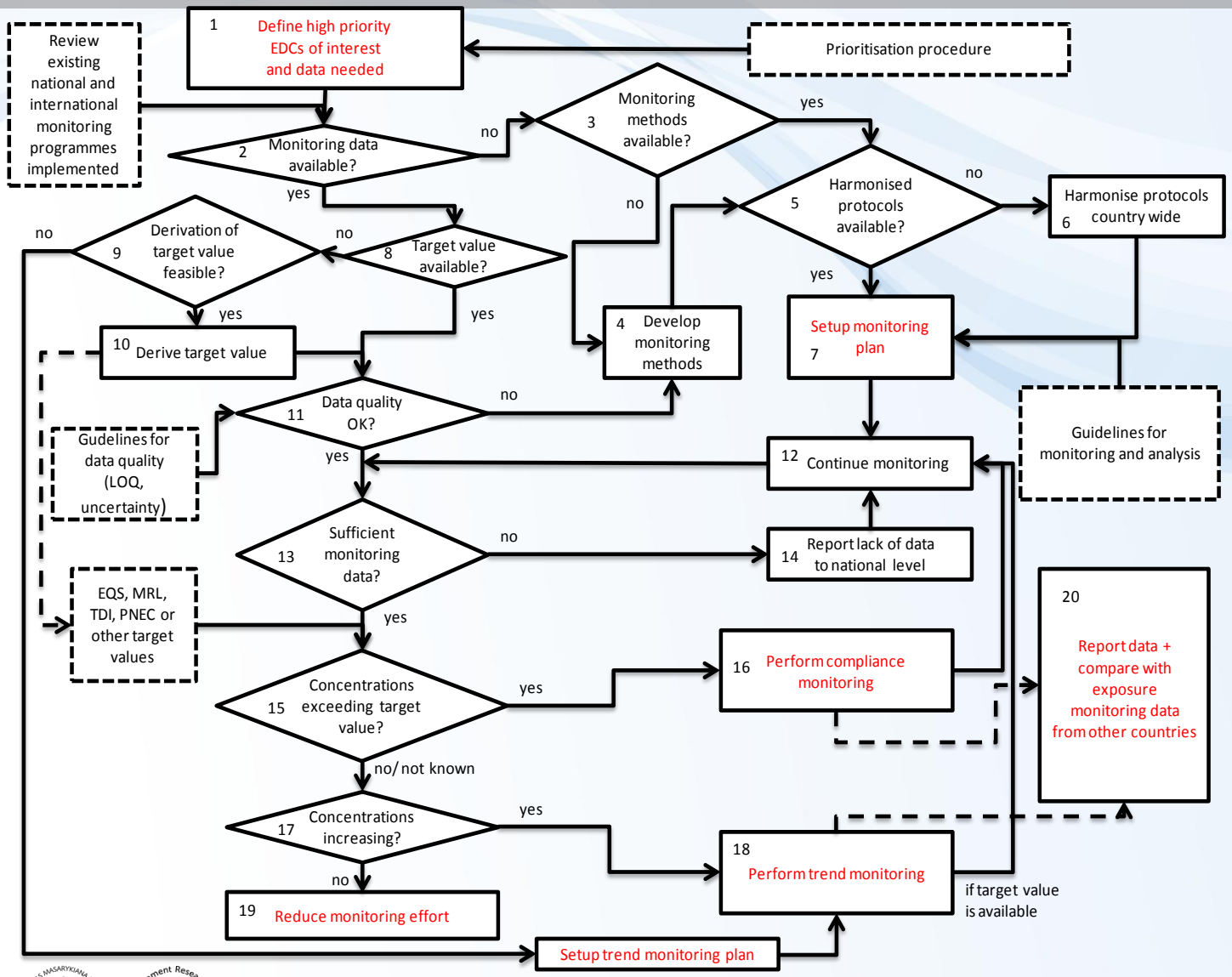
Specific problems of environmental analysis

- low **homogenity** of samples (soil)
- low **stability** of samples (biota)
- various matrices (**methods for extraction** of analytes from matrices)
- wide **range of analytes** (method development)
- wide **range of concentration** (robust methods)
- monitoring on the levels close to the **detection limits** (high deviations)
- risk of **secondary contamination**
- price of **ultra-trace analysis** (instrumentation, chemicals, standards)

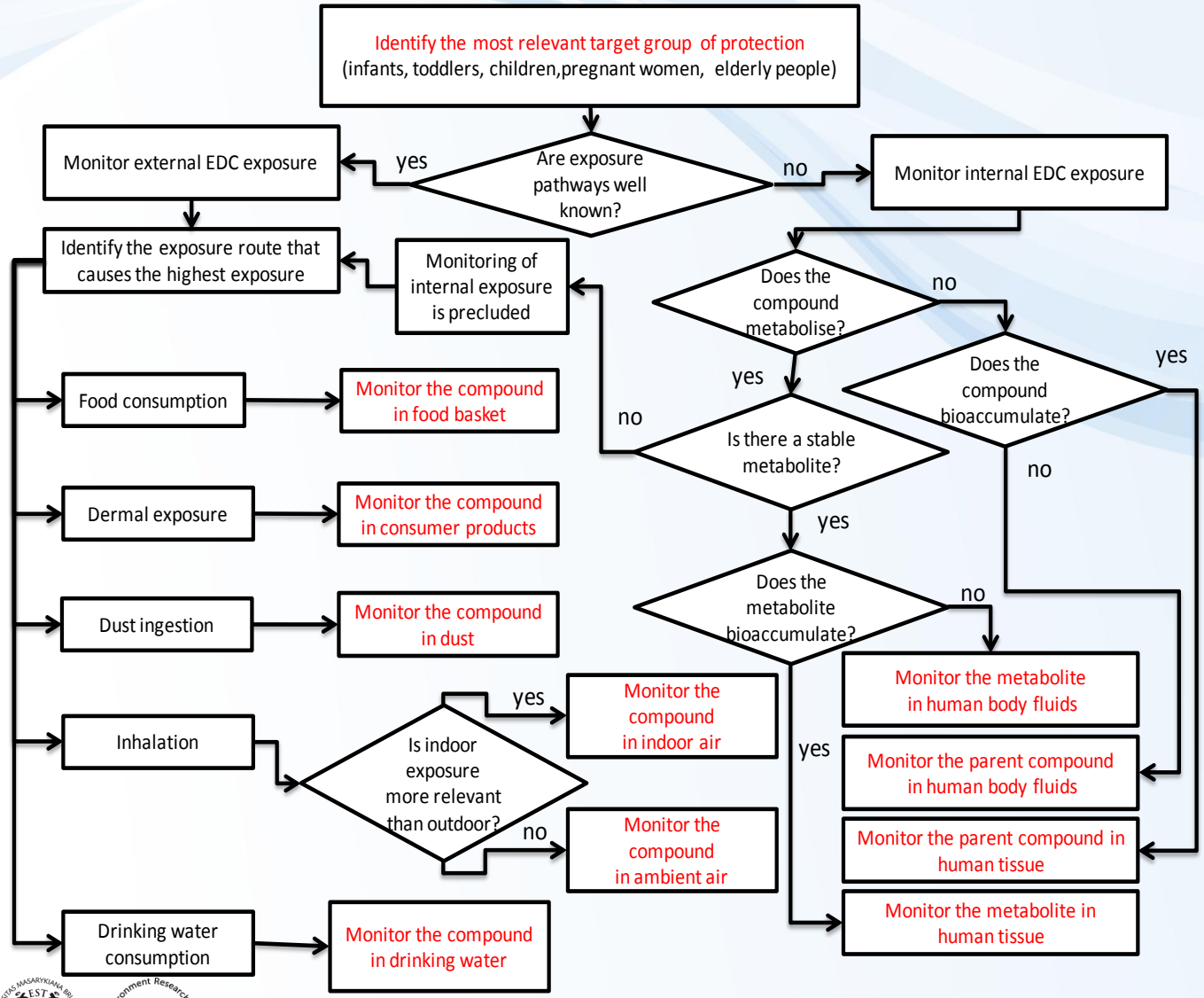
Priority pollutants ?

- polychlorinated biphenyls
- polychlorinated naphthalenes
- organochlorinated pesticides and their metabolites
- polychlorinated dibenzo-*p*-dioxins and furans
- polyaromatic hydrocarbons
- chlorinated benzenes
- fenol and chlorinated fenols
- short and medium chain chlorinated paraffins
- brominated flame retardants
- organophosphorus flame retardants
- perfluorinated compounds
- alkylphenols
- musks
- estrogens
- sunscreens
- siloxanes, parabens and other additives to cosmetic products

Decision tree - compounds



Decision tree - matrices



Sampling

- initial stage
  - selection of analytes
  - selection of sampling sites
  - number of samples, sampling frequency
  - sampling methods and strategy
- quality assurance
  - representative samples
  - sufficient size
  - stability
- optimal data value : cost ratio

Sampling – documentation required

- **sampling plan** (a goal, selection of sampling sites, analytes, sampling method, number of samples, sampling period and frequency, safety procedures), seeks the balance between the value of data and its price

- **standard operational procedure** for sampling various matrices (sampling devices, steps involved in collecting of representative sample – homogenous, of reasonable size and stability, quality of transport and storage)

- **sampling protocols** (name and number of the sample, sampling site, matrix, date of sampling, local conditions and measurements, methods, sample size, responsible person)

Air sampling

Air is a key medium - **responds quickly** to sources

Air concentrations **fluctuate widely** in the space and time

Various concentrations in the **gas/particulate phases** - compromise over the sample time/volume/technique

Short-term sampling/bulking

Air sampling

- ambient air
  - permanent gases
  - volatile/semivolatile compounds
  - particules
- indoor air
- working environment
- emissions
- imissions

Fixed volume containers

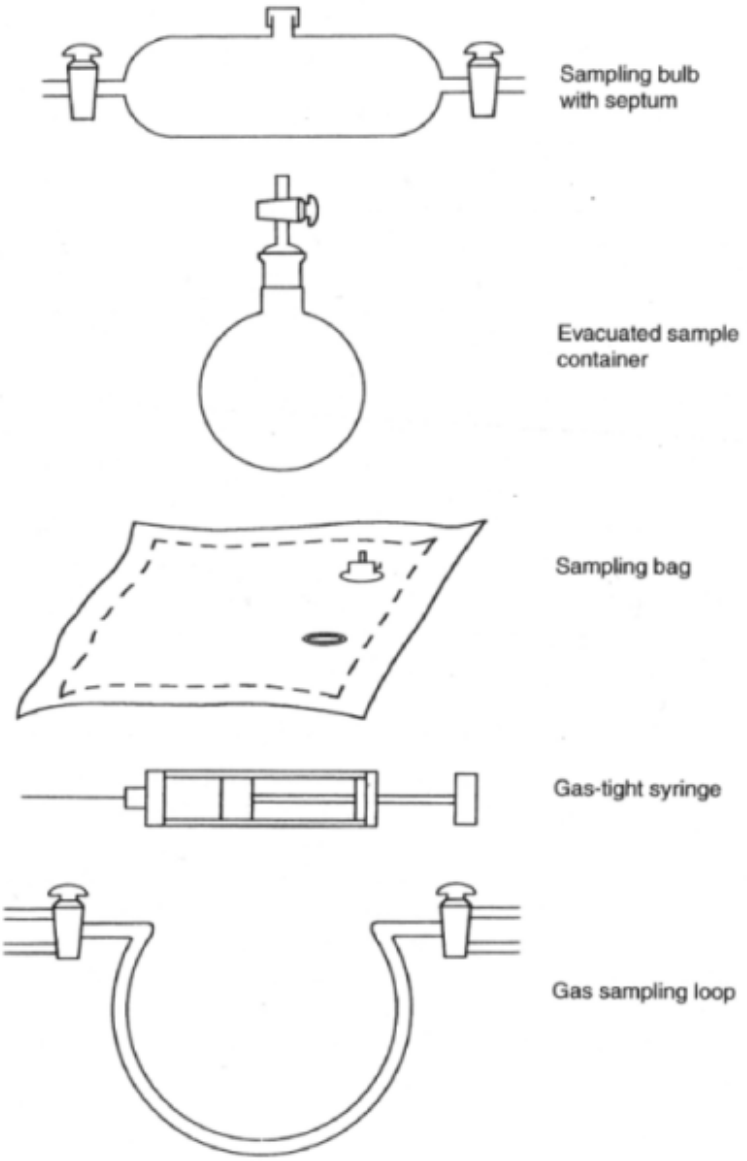
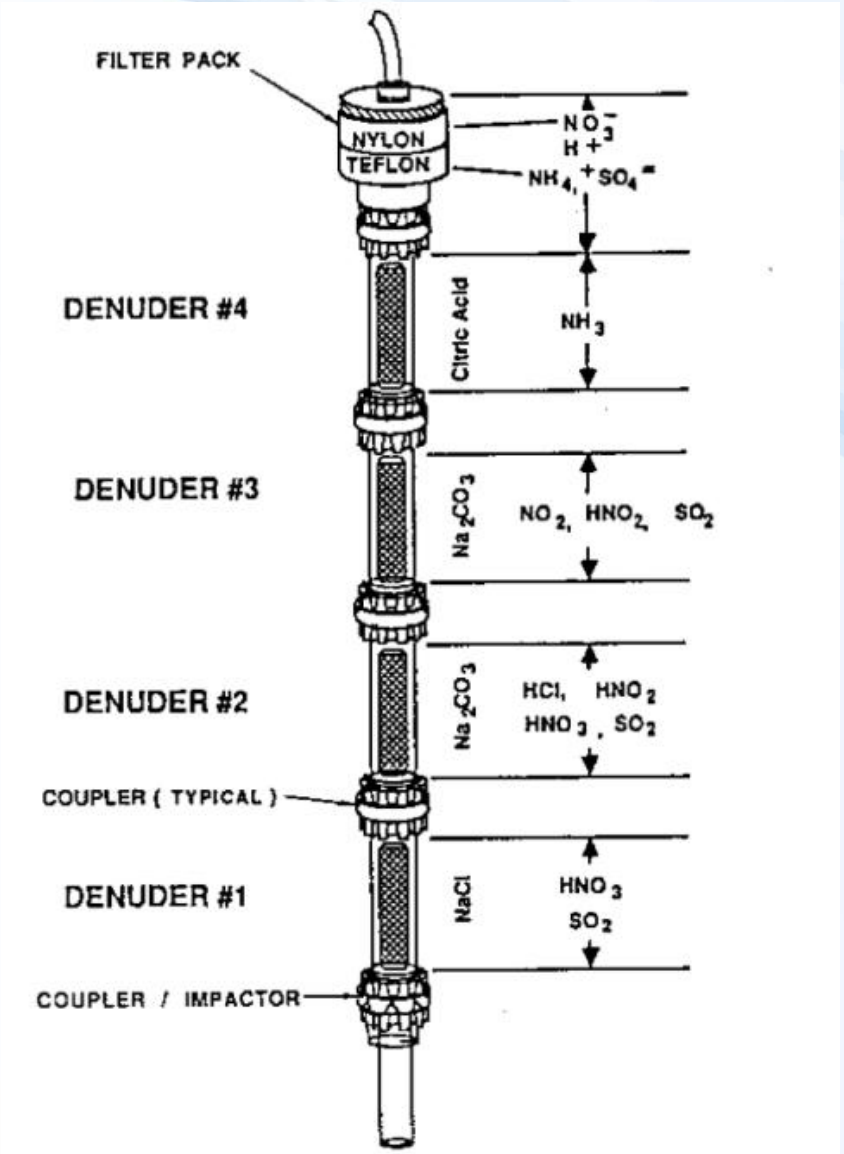


Figure 6.16 Some examples of the equipment used for gas sampling.

Denuders



gure 1. Schematic View of Annular Denuder Showing Species Collected

High volume active samplers

Samplers of the particulate matter

Samplers of the particulate matter

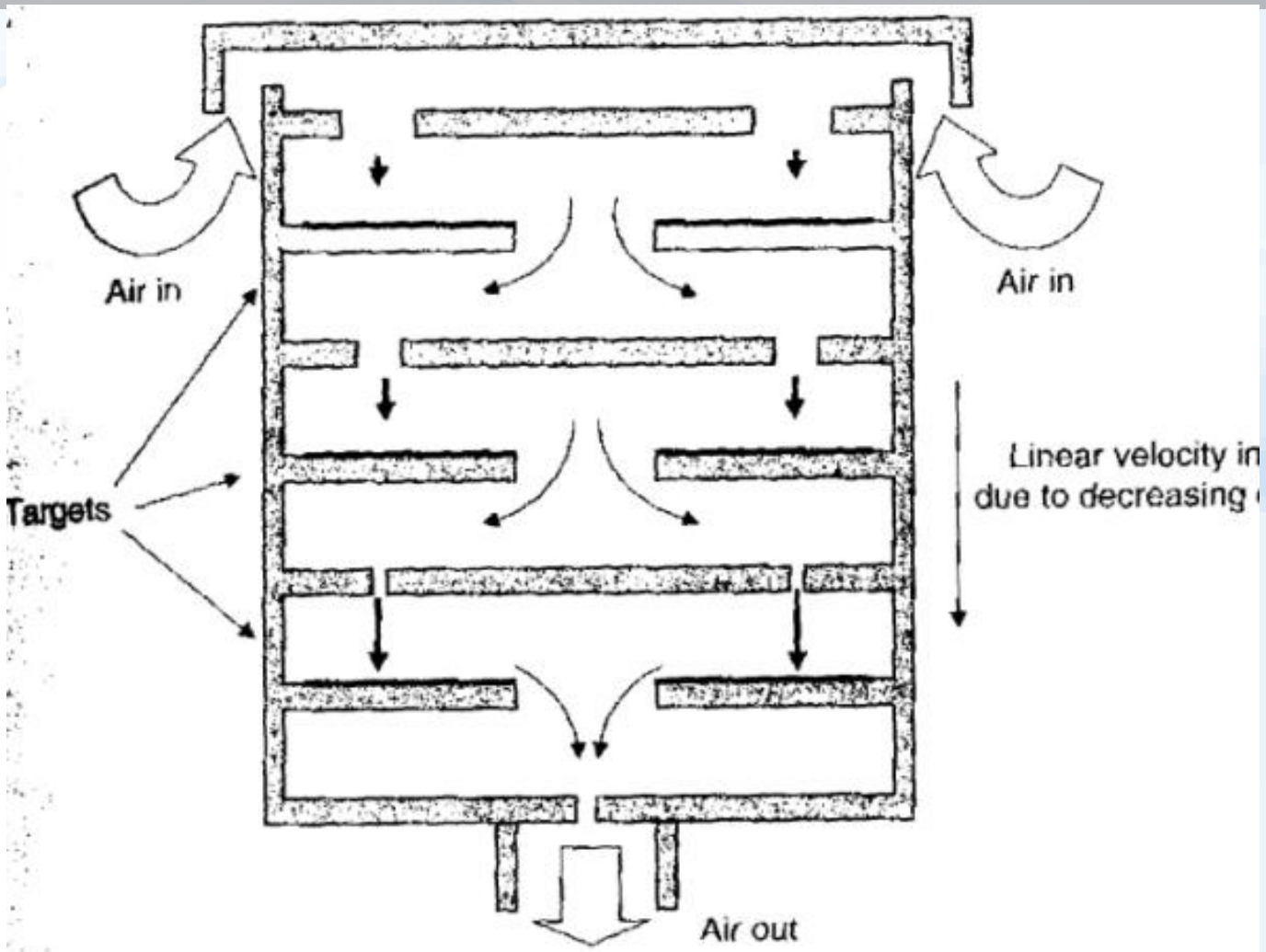
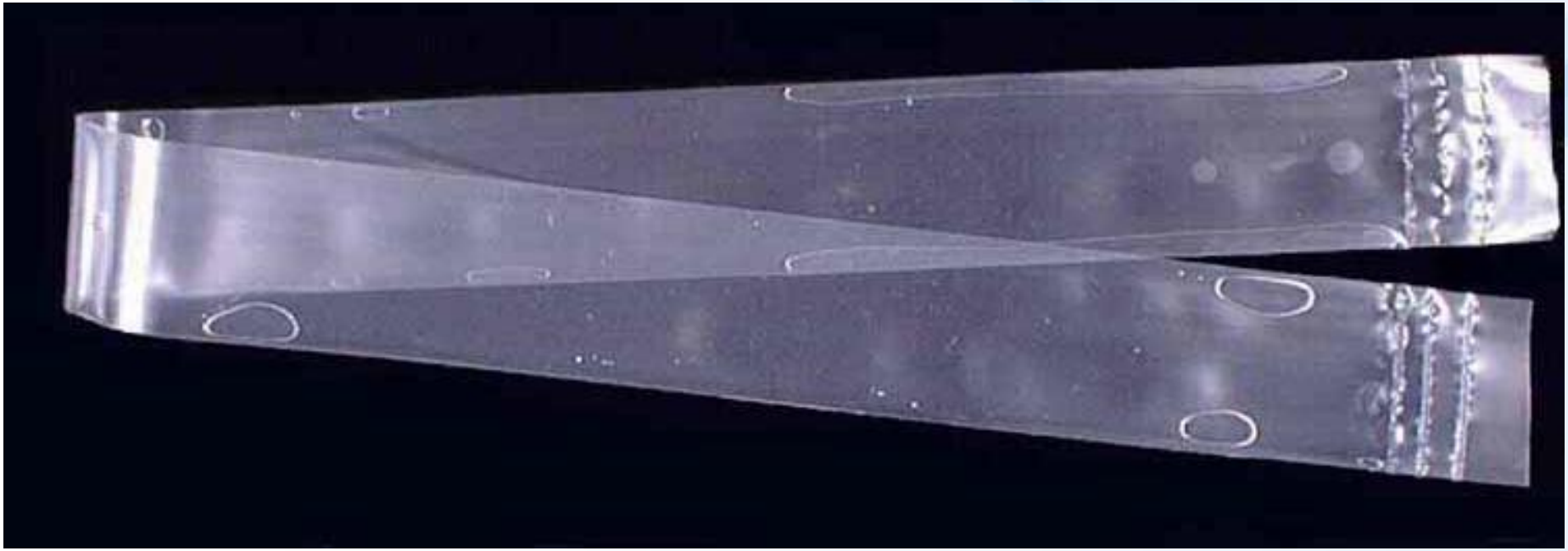


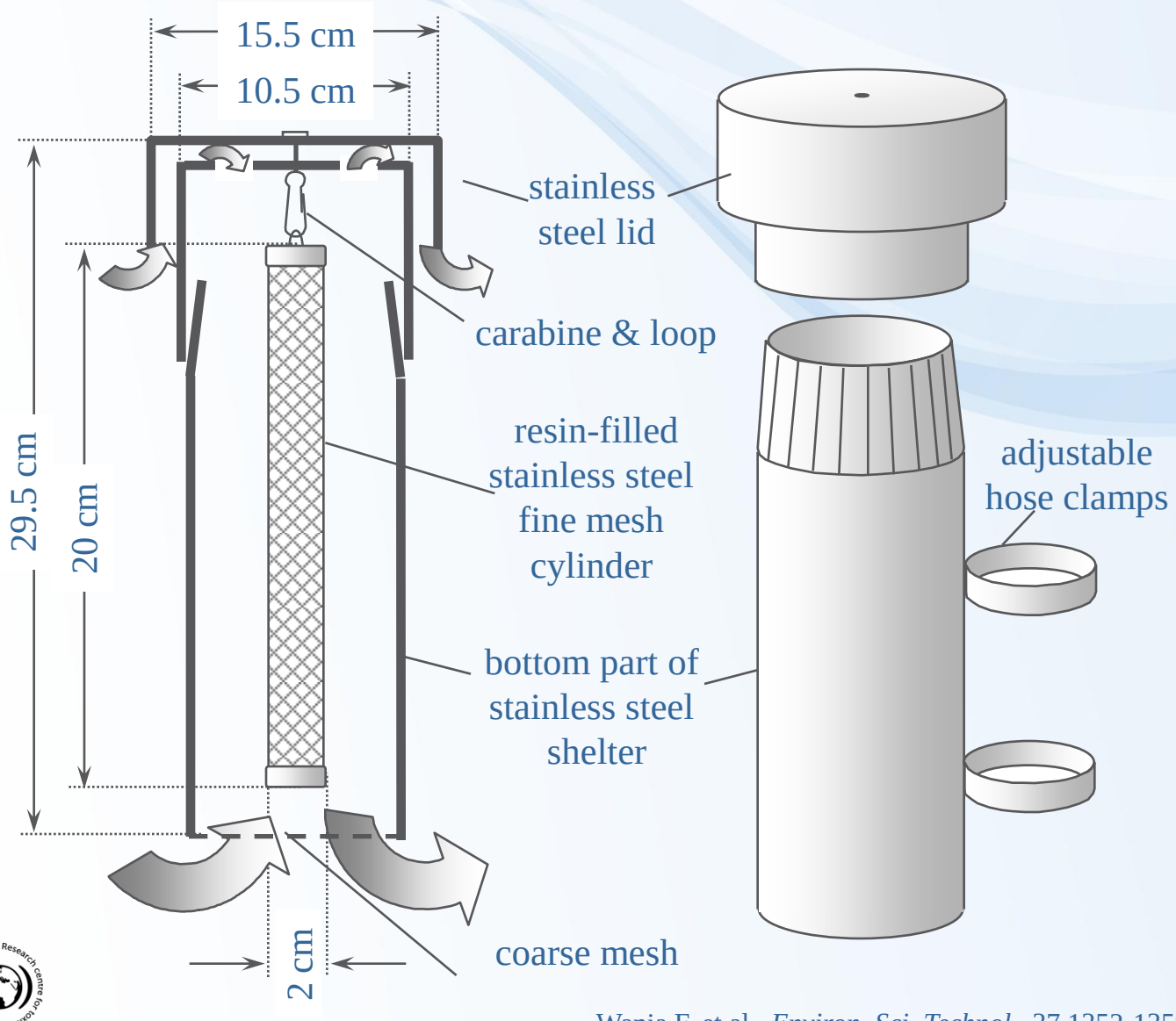
Figure 7.3 Schematic showing the operation of a cascade impactor.

Semipermeable membrane device

Polyethylene, low density, thickness 75 – 90 mm, sleeve of 91 cm * 2,5 cm with 1 ml of trioleine



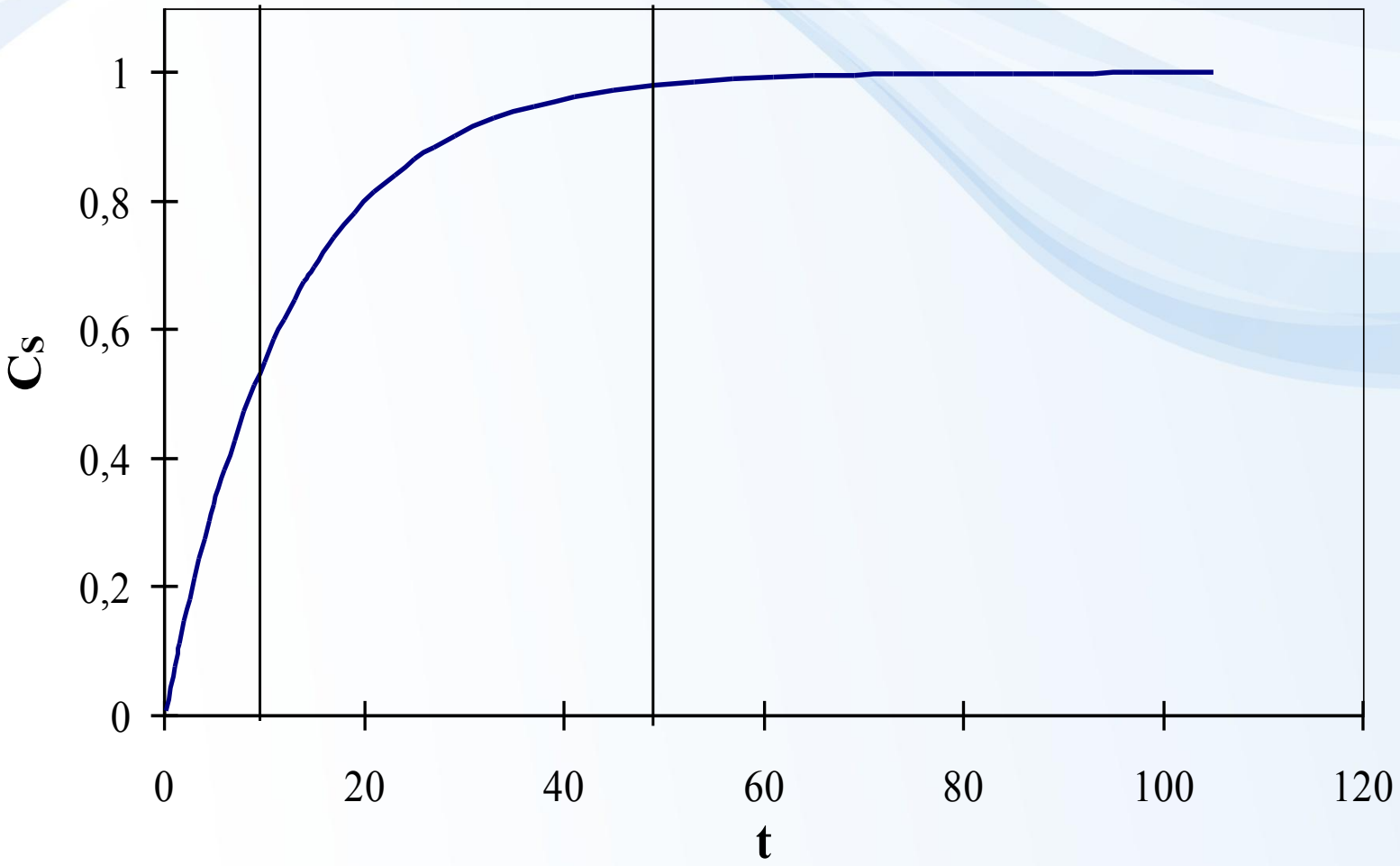
XAD-Resin Based Passive Air Sampling System for POPs



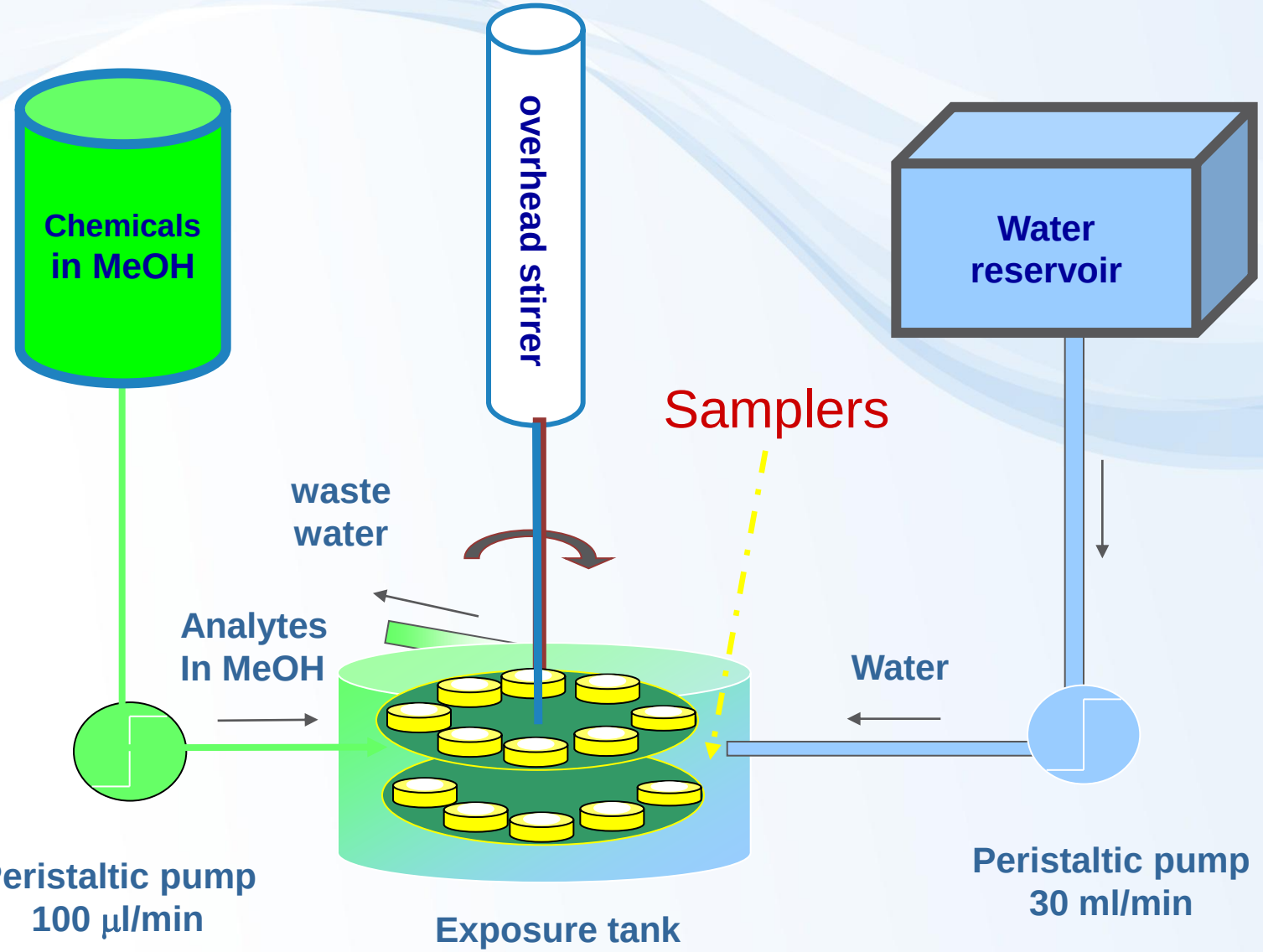
Wania F. et al., *Environ. Sci. Technol.*, 37,1352-1359 (2003)

PUF based passive samplers

Time dependence of the analyte concentration in media



Calibration of a passive sampler in a flow-through system



B. Vrana, R. Greenwood, G. Mills

Atmospheric deposition

- wet (delivered by rain and snow, major in the clean and background sites)

- dry (sedimentation of atmospheric dust particles, prevailing in urban sites)

Atmospheric deposition sampling

- wet (sampling of rain only, automatic devices)

- dry (deposition in the sampling containers is a function of the air concentration of particles and the sedimentation rate)

- sum of the wet and dry deposition (open containers)

Sampling of wet atmospheric deposition

- **Vertical deposition** – rain, snow, particles

- **Horizontal deposition** - aerosol, fog

Horizontal sampling of aerosols is the analogy to the gas phase sampling

- membrane filters (Sympor)
- flow measurement (rotameter)
- volume measurement (gas meter)
- air pump

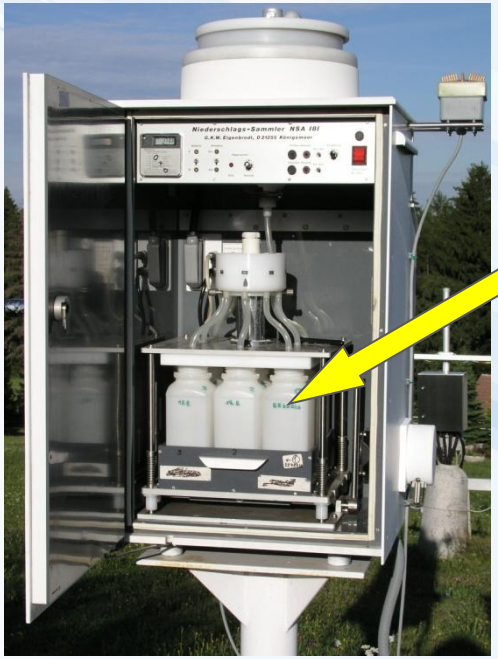
Samplers for vertical deposition

manual samplers

Samplers for vertical deposition

Colective area

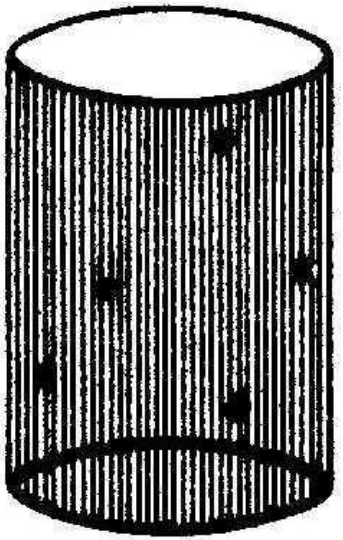
Lid



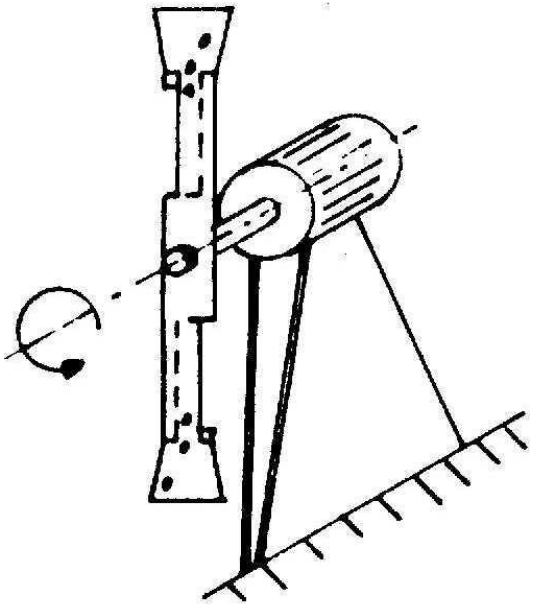
Reservoir

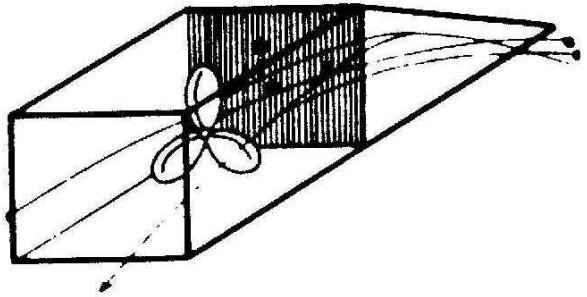
automatic samplers

Horizontal sampling of fog and icing



passive





active

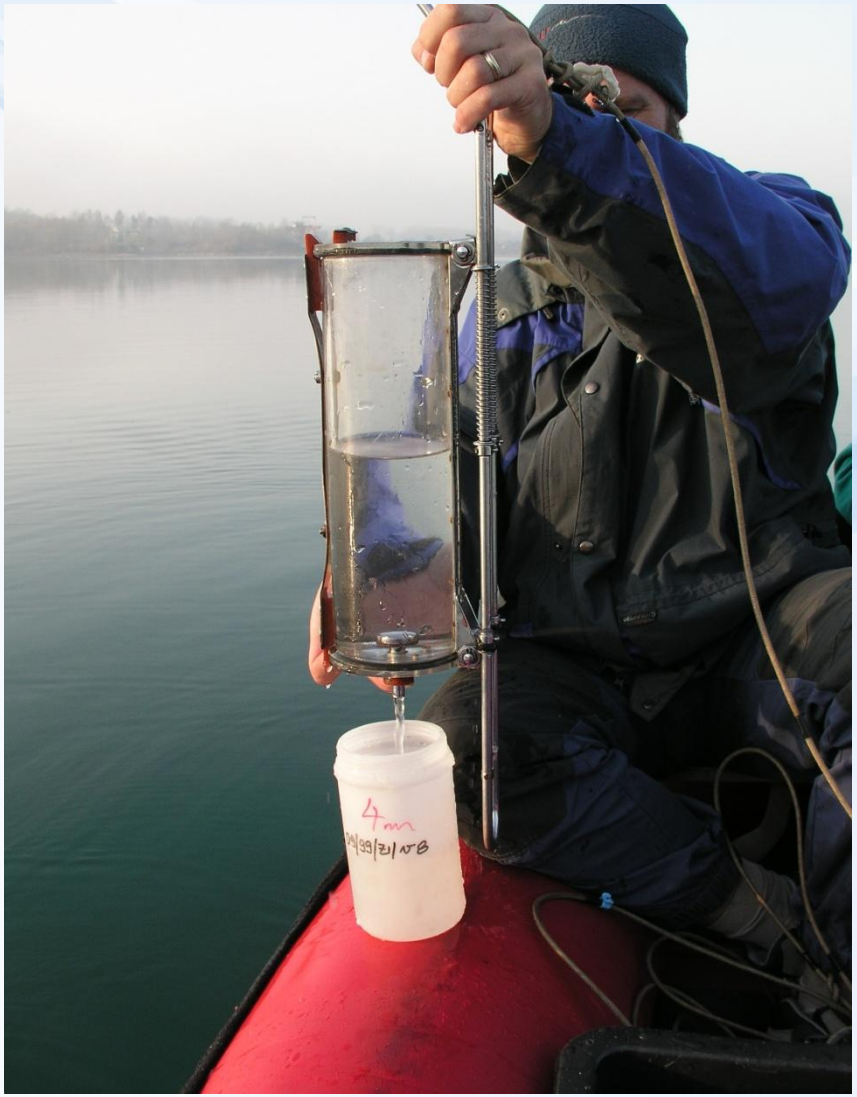
Surface water pollution

Primary – waste water, deposition, leaching

Natural - humic substances, phenols

Anthropogenic - oil pollution, pesticides, detergents, PCBs

Equipments and apparatus for depth sampling



Water monitoring using SPMDs

Mussel cage

Sampling of sediments and soils

- most difficult matrix for sampling
- **heterogenous** materials, limited migration
- influenced by **biological activity**, fertilization, rain
- pilot sampling to gain the first information about the variability
- several samples are mixed to produce the **composite sample**
- common sampling depth 15-20 cm

  (unless interested in the soil or sediment profile)

Soils and sediments

High environmental **burdens** – important for global balances

Slow response times

Background soils and sediments reflect spatial differences in cumulative atmospheric deposition/net air-surface exchange

Very heterogeneous - important questions of depth, ecosystem type etc.

Can show **spatial trends**, but **poor for time trends**

Sediment sampling

Historical data

collection of samples from the bottom depth horizons with the limited sediment mobility

Actual state

sampling of the upper horizon (max. 15 cm) of the bottom sediment

sampling using the sedimentation traps in the profile of the river

The choice of the sampling method is derived from the granularity of sediments.

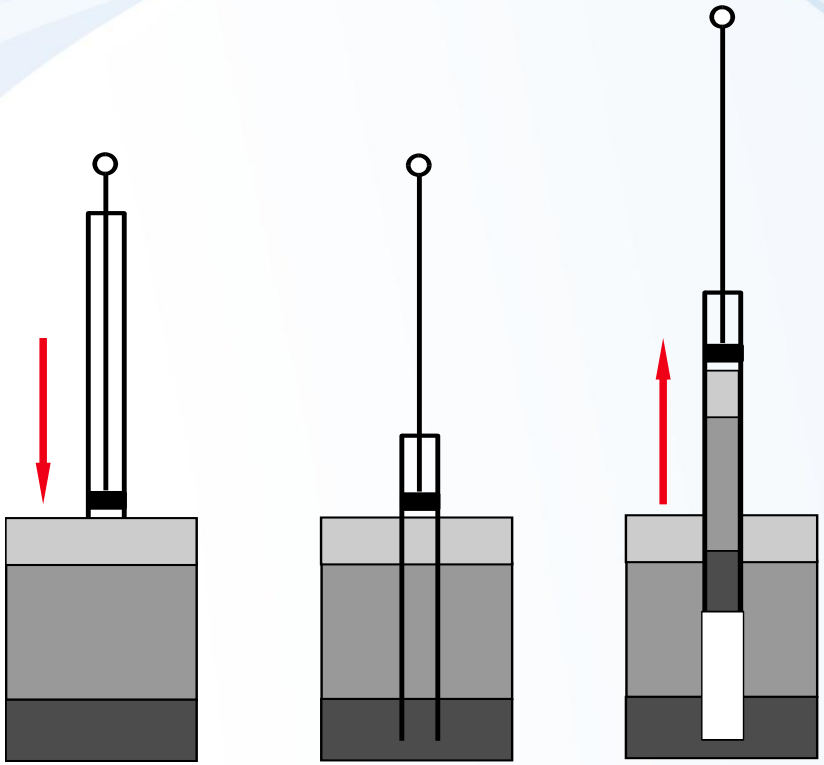
Most important

Sediment fraction with granularity **finer than 1 mm** is responsible for majority of sorption processes

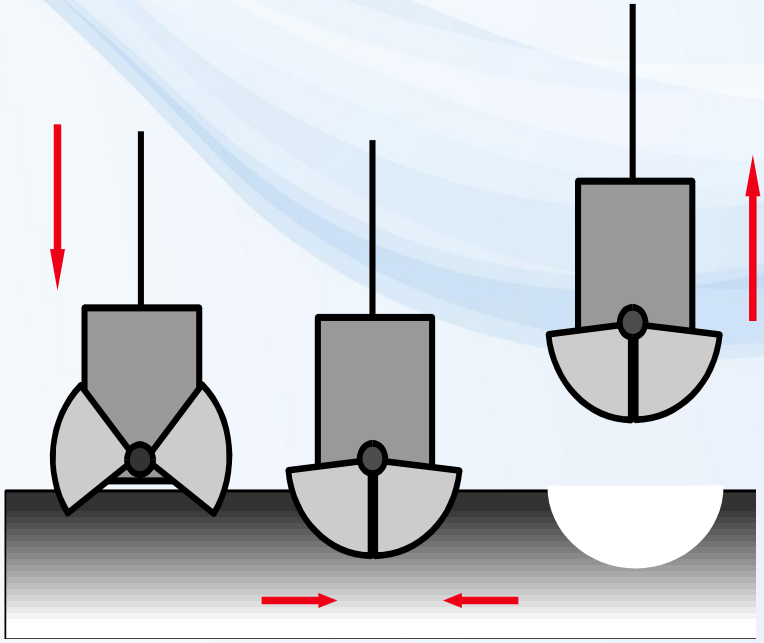
Coloid and rough dispersions of endogennous and autigennous components.

Probe for sampling of fine compact sediment

Sediment sampling

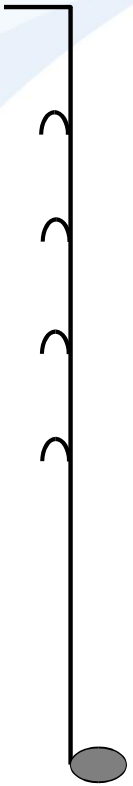


Piston probe

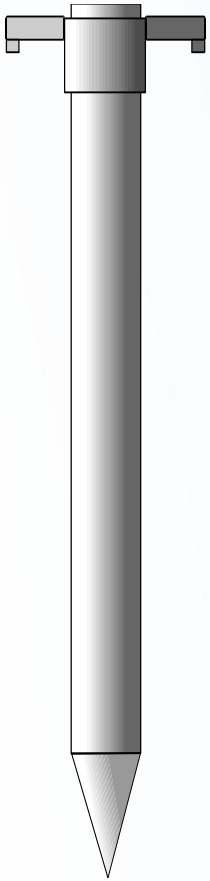


Grab probe

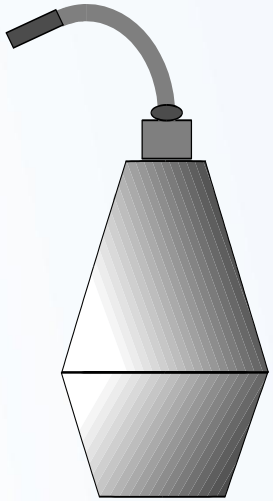
Freezing sampling



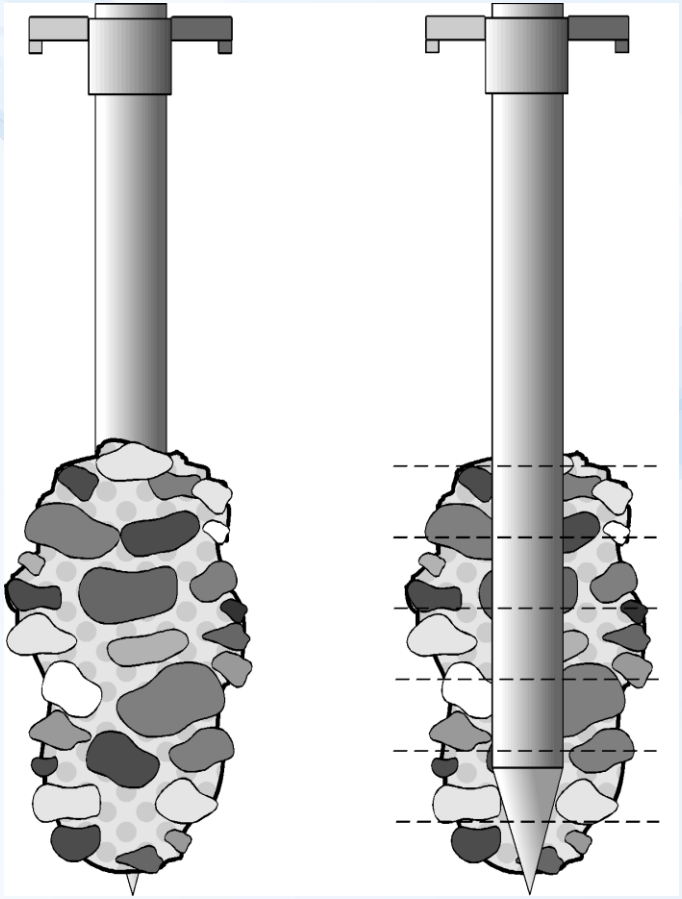
Disperser of media flow



Tube probe



Freezing medium



Frostbitten sediment

Wildlife

- POPs bioaccumulate in animals because of their high lipid content and their long lifetimes
- Some POPs bioconcentrate up food chains
- Choice of species/matrix?
- Species range and ecosystem differences
- High variability in biological systems
- Birds eggs; marine mammals

Human foodstuff

Link between 'environment' and 'exposure'

Many countries already have food sampling programmes

Agricultural animals – wide distribution & 'control' - milk, eggs

- high concentrations
- clear AIR – GRASS – COW – FOOD link
- easily homogenised, pooled to represent a large area

BUT, also affected by husbandry practices

EU milk monitoring, for source and exposure reduction

Human tissues

Humans - truly global distribution, which allows complete spatial mapping of POPs in the global environment.

Direct, integrated measurements of exposure – is the source and exposure reduction working ?

Blood – variable but easy to sample; existing programmes ?

Milk – babies are a key sub-group; better integrator?

Preparation of the sample before extraction

Soil samples
- lyofilization or air-drying
- sieving (< 2mm) and homogenization
- appropriate storage (protected from light, heat, humidity)

Sediment samples
- stone and water removal, lyofilization or air-drying
- grating and sieving (<63um), homogenization
- powder copper treatment for sulphur removal

Plant samples
- lyofilization or air-drying
- grating, homogenization

Animal samples
- lyofilization or
- homogenization of a wet sample with sodium sulphate

Extraction and clean-up

The goal: transfer of analytes to the chemical phase suitable for analysis, removal of interferences and pre-concentration of the sample.

Extraction techniques:
- solvent extraction (Soxhlet, automatic Soxtec, MAE, ASE, SFE)
- liquid-liquid extraction
- solid phase extraction and microextraction (SPE, SPME)
- semipermeable membrane separation
- head space analysis

Clean-up techniques
- sulphuric acid treatment
- column liquid chromatography (silica gel, alumina, florisil)
- gel permeation chromatography

Solid sample extraction

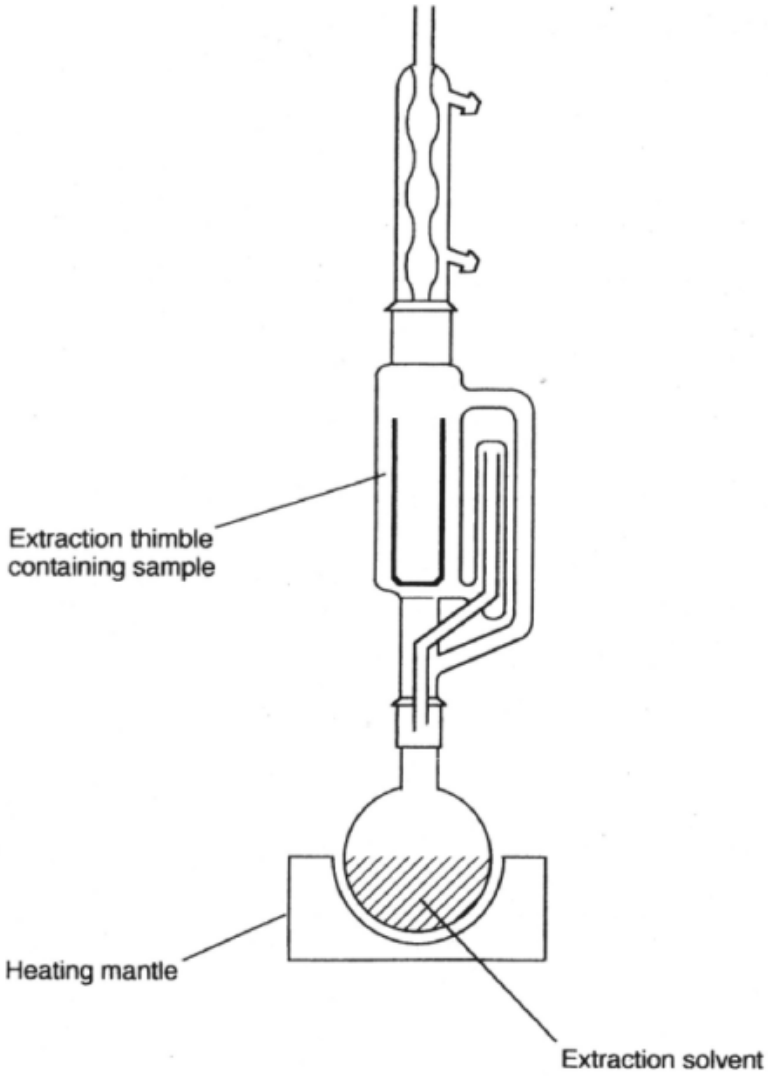


Figure 5.1 Schematic of a Soxhlet extraction system.

Liquid sample extraction

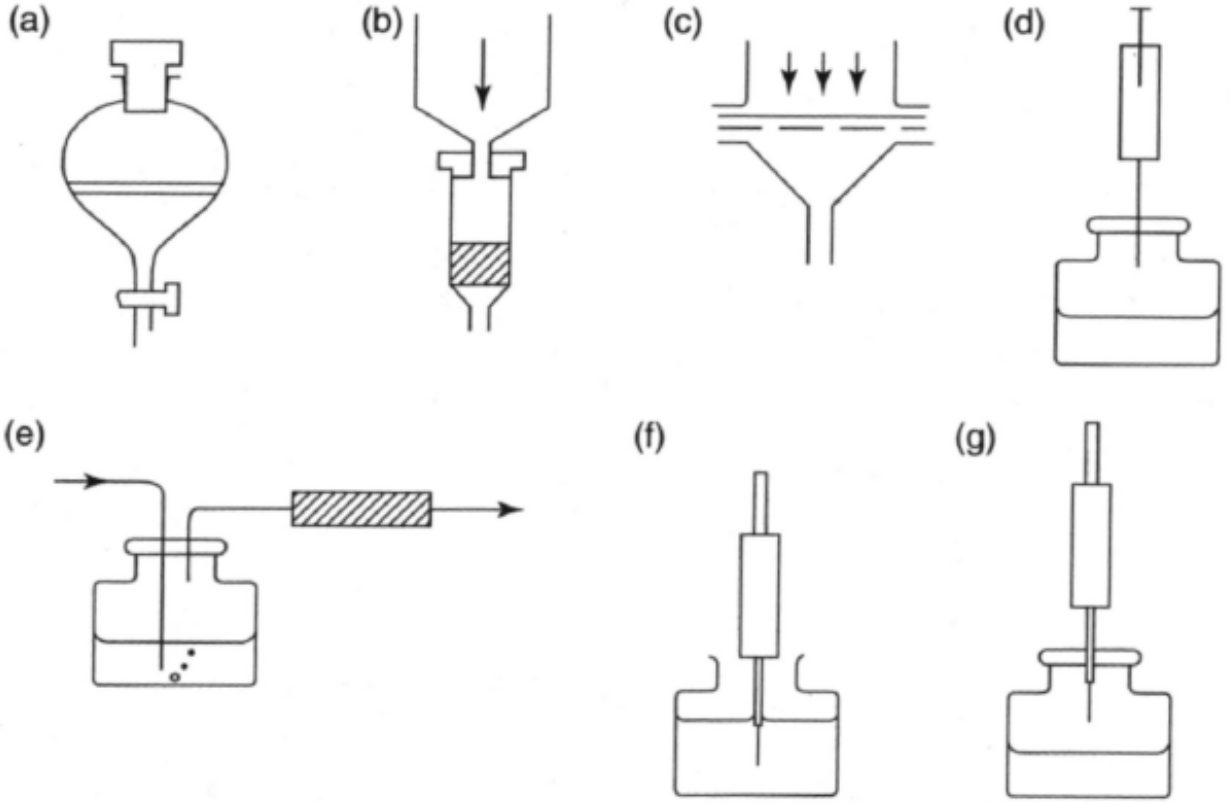


Figure 4.1 Summary of extraction methods: (a) solvent extraction; (b) solid-phase extraction – cartridge; (c) solid-phase extraction – disc; (d) head-space analysis; (e) purge and trap; (f) solid-phase microextraction – direct; (g) solid-phase microextraction – head-space.

What are we interested in?

Presence	Availability	Activity
Total mass	Fraction of total mass	Measure that drives Diffusion and partitioning
How much is there?	How much is available for?	How high is the diffusive pressure into other media?
Exhaustive Extraction	Depletive Extraction/ Sampling	Equilibrium Sampling Devices

P. Mayer, F. Reichenberg

Supercritical fluid extraction

High pressure CO_2 (100 to 400 bar, 40 to 150 °C) is pumped through a sample, and extracted analytes are collected in a suitable solvent for GC analysis.

Why to use supercritical carbon dioxide?

- CO_2 is a lipophilic solvent much like biological lipids in polarity
- PAH solubilities in CO_2 are proportional to those in water, but ca. 10^4 higher
- pressure and temperature gradients enable the extraction of both, non-polar and

  polar compounds
- mild SFE can be used to predict bioavailability of compounds

Earthworm Mortality Depends on Available PAHs (measured by SFE), not on Total PAH Concentrations

Soil	Total PAH (ug/g soil)	Available Fraction (SFE)	Available Total PAH (ug/g C)	Mortality %
1	1020	0.25	1040	0
2	168	0.46	2720	0
3	15600	0.06	3280	0
4	3790	0.16	7880	0
5	17200	0.27	9720	0
6	1870	0.41	11100	0
7	42100	0.33	16300	0
8	4100	0.83	45700	100
9	17300	0.74	50100	100

S. B. Hawthorne, C. B. Grabanski, D. J. Miller

Sample analysis

Chromatographic separation (GC, HPLC) is the most common technique for the analysis of environmental samples.

It is a physical method based on the **distribution of compounds between two phases** (stationary and mobile). Process of continuous sorption and desorption of compounds in contact with the stationary phase is responsible for different migration times and for separation of analytes.

Two dimensional (GC-GC) and **two modal** (HPLC-GC) chromatography provide even more sofisticated tools for environmental analysis

GC-MS, HPLC-MS and HRMS enable the trace and ultra-trace analysis

Gas chromatography

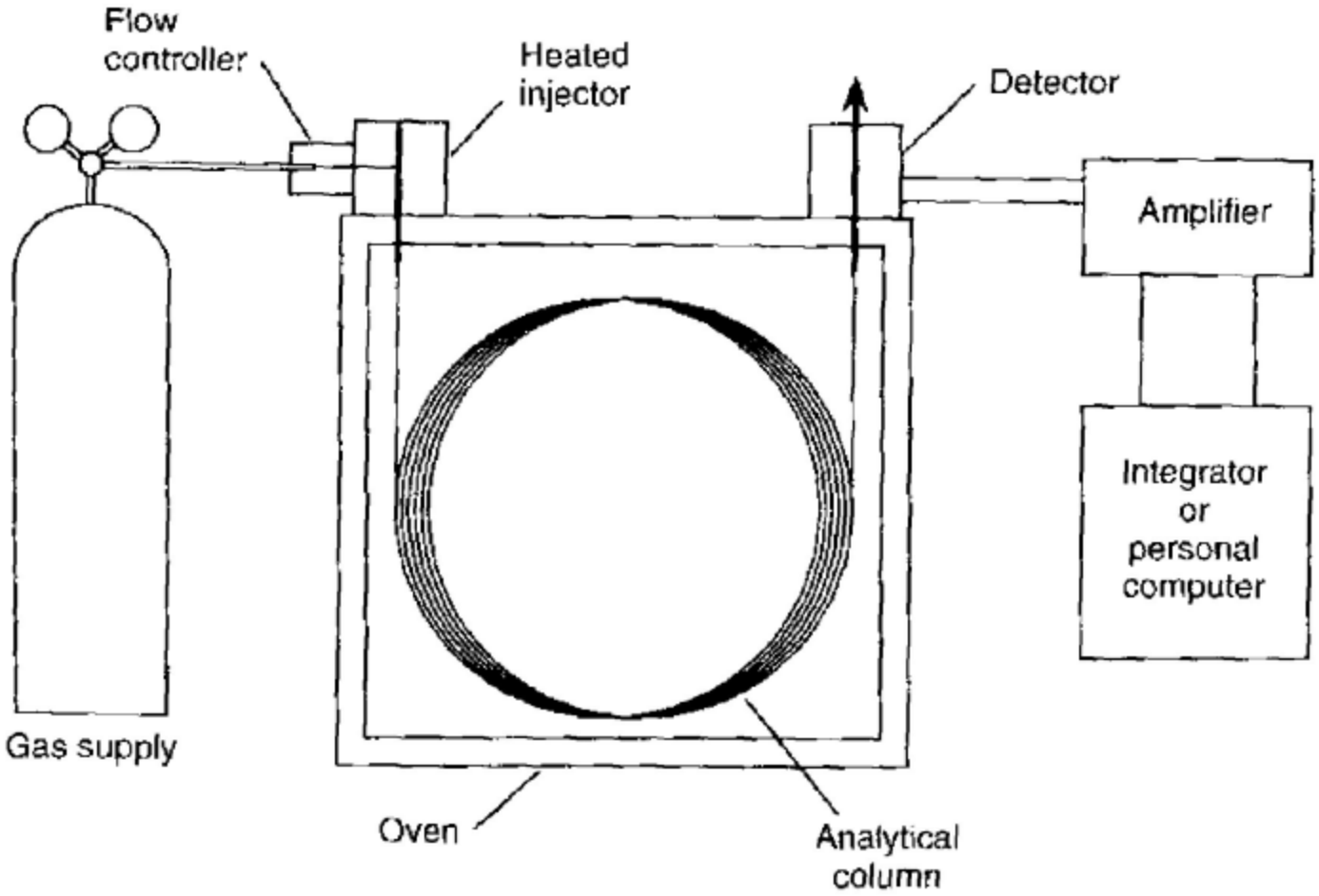
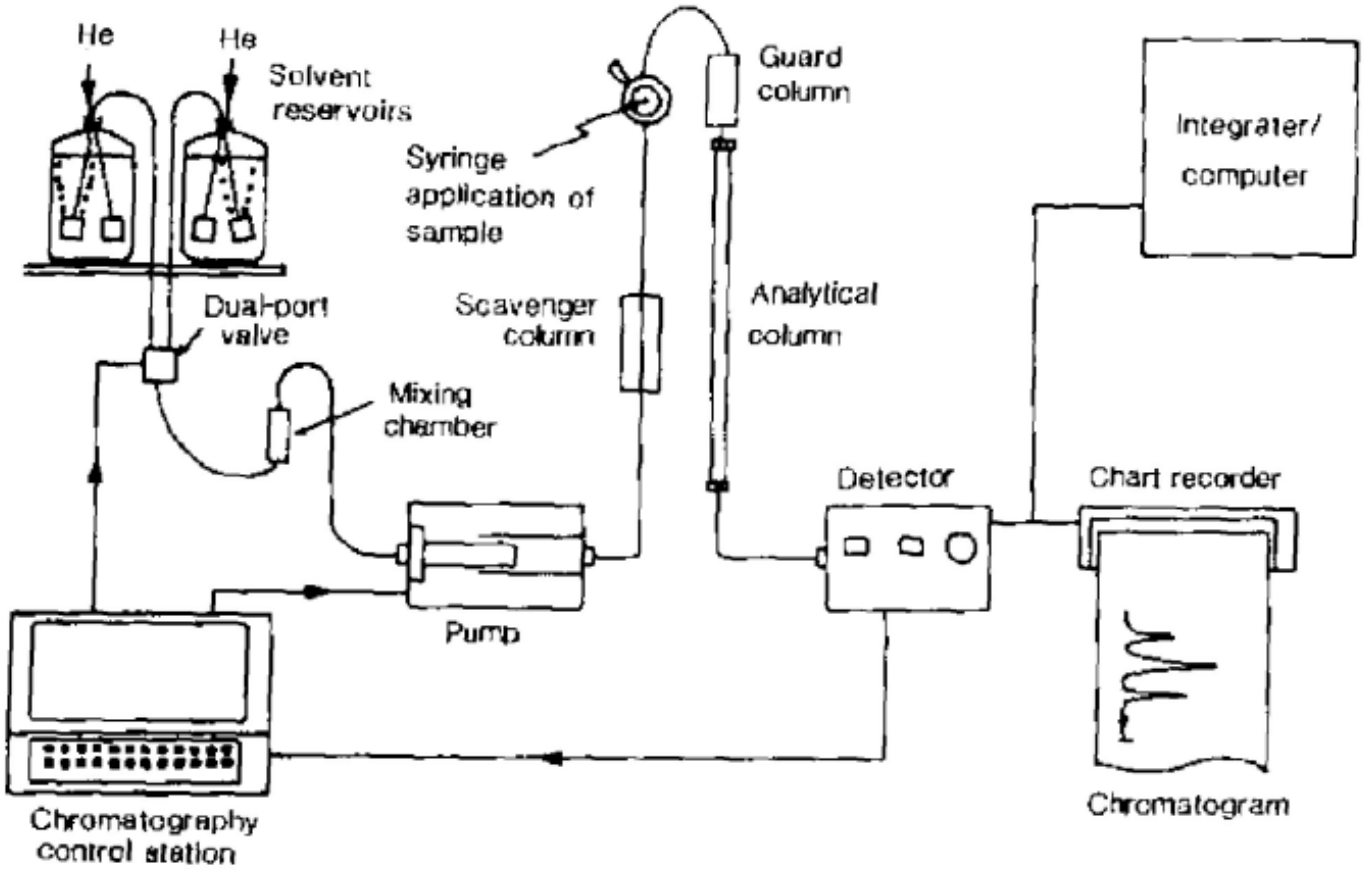


Figure 4.4 Major components of a gas chromatograph.

Liquid chromatography



: 5.7 Schematic diagram of a binary (two-solvent) HPLC system. Source: Fifield, F.W. Kealey, D. (1995) *Principles and Practice of Analytical Chemistry*, 4th edition, Blackie Academic & Professional, Glasgow.

Chromatogram

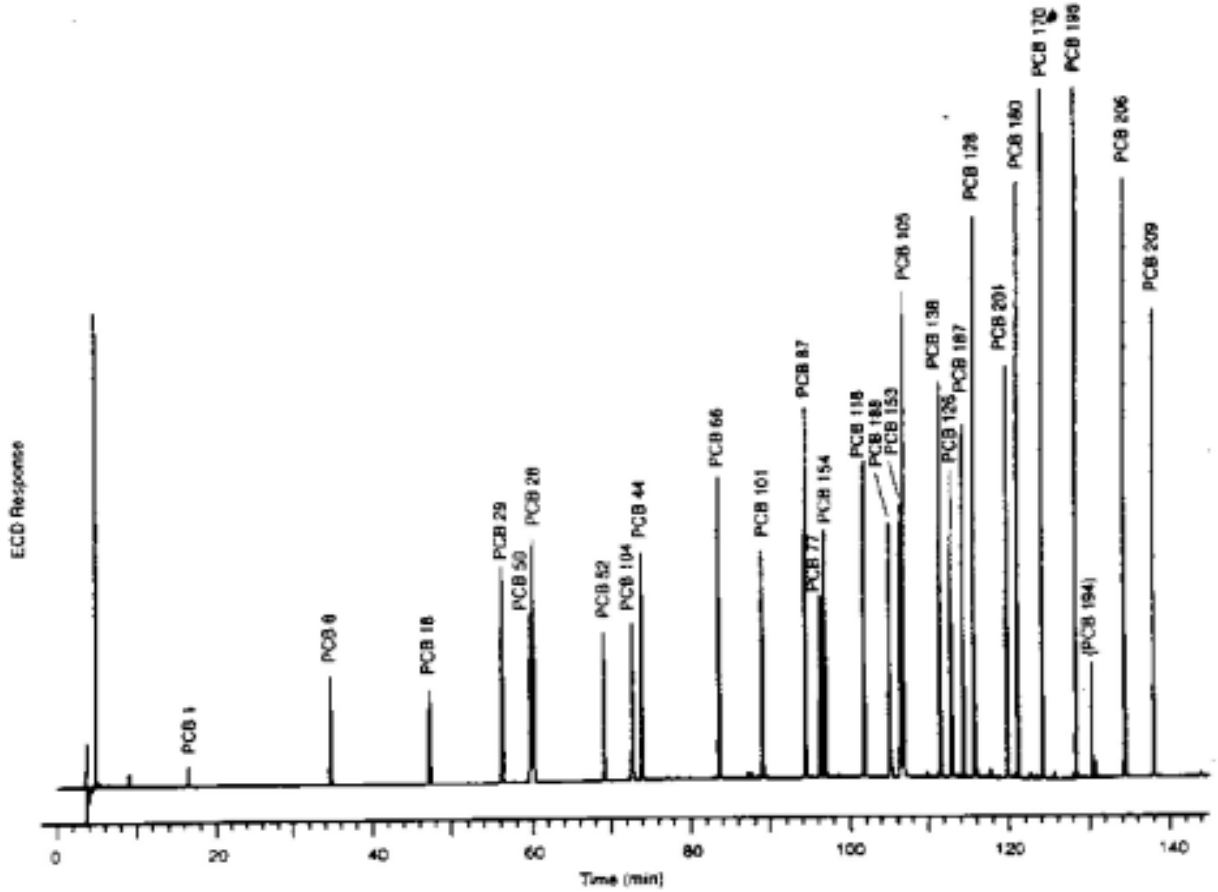
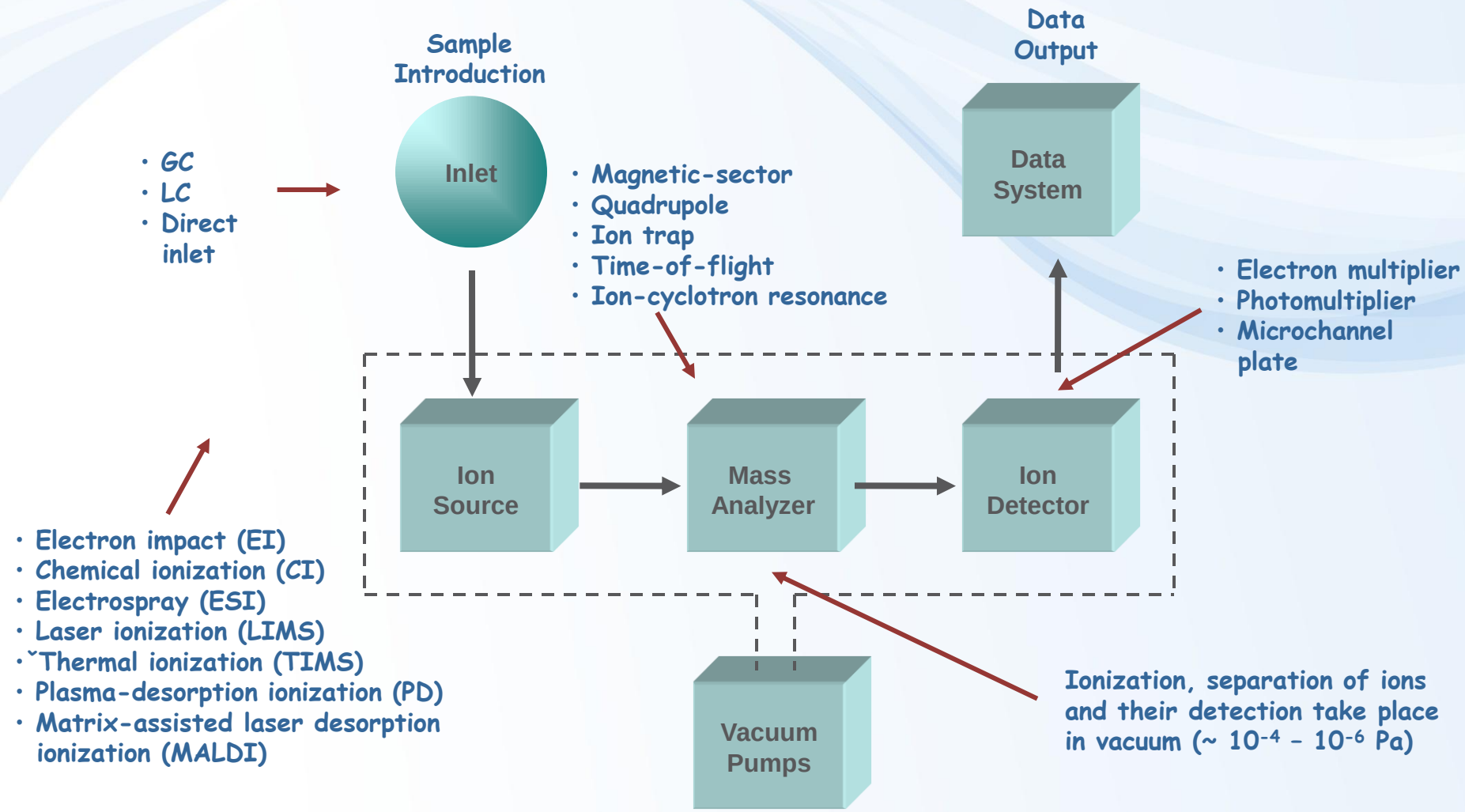


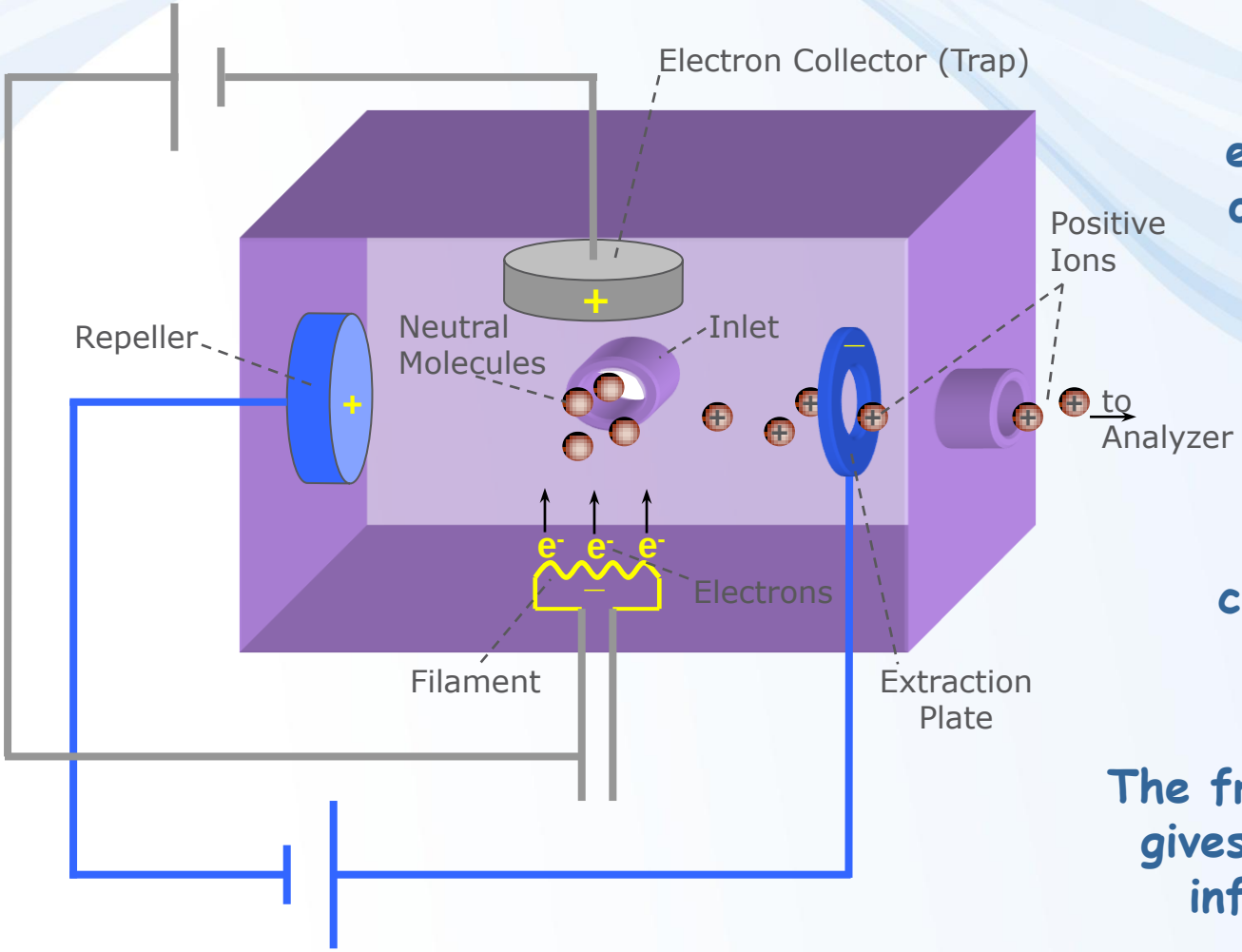
Figure A-1. Chromatogram of NIST SRM 2262 by GC-ECD using a 0.25-mm i.d. x 60-m fused silica capillary column with a 5% phenyl-substituted methylpolysiloxane phase (0.25 µm film thickness) (DB-5, J&W Scientific, Folsom, CA) Temperature Program: 150 °C (40 min) to 220 °C (0 min) at 1 °C/min to 280 °C (25 min) at 3 °C/min.

Mass spectrometer



Electron impact ionization source

~70 Volts **10 to 20 eV out of those 70 eV are transferred to the molecules**



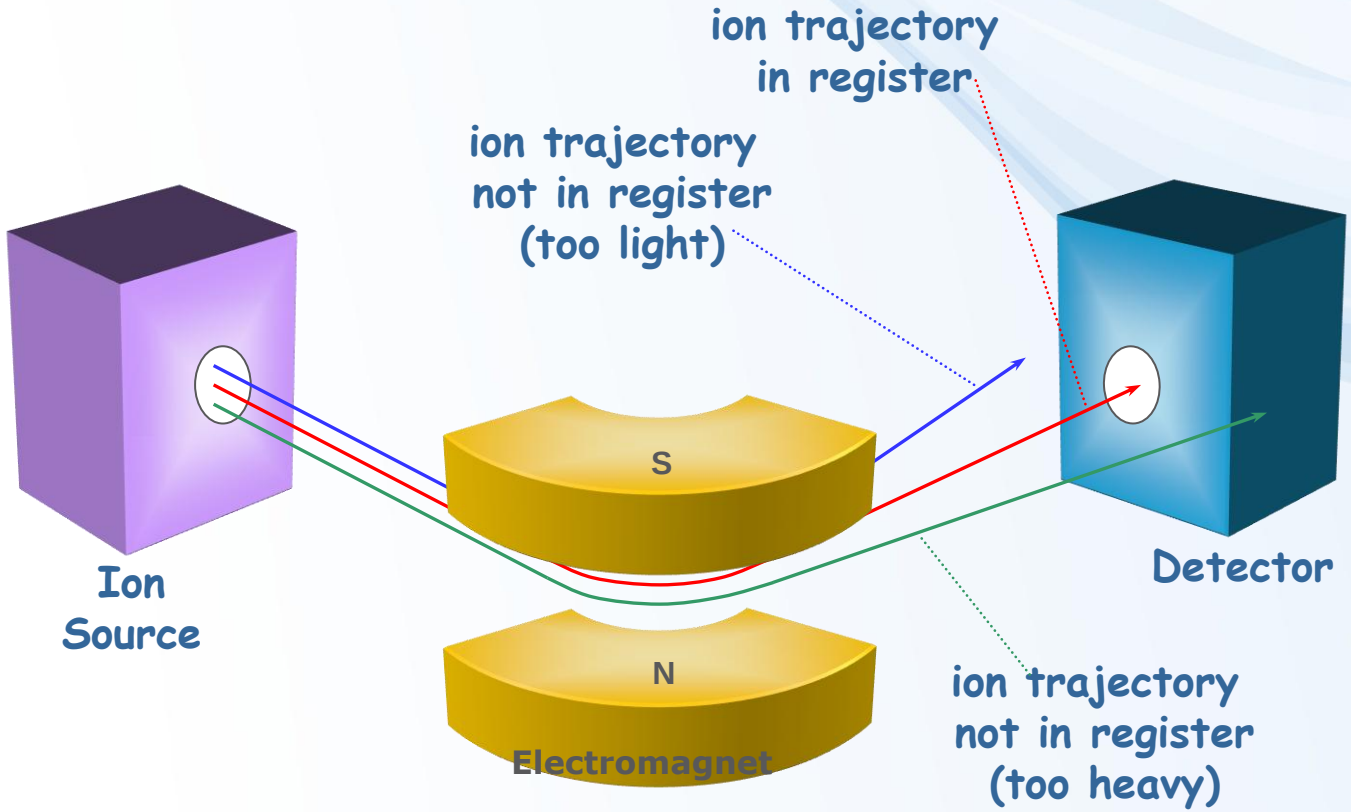
Since ~ 10 eV are enough to ionize most organic molecules the excess energy leads to extensive fragmentation;

Hence EI is classified as a „hard" ionization technique

The fragmentation gives structural information

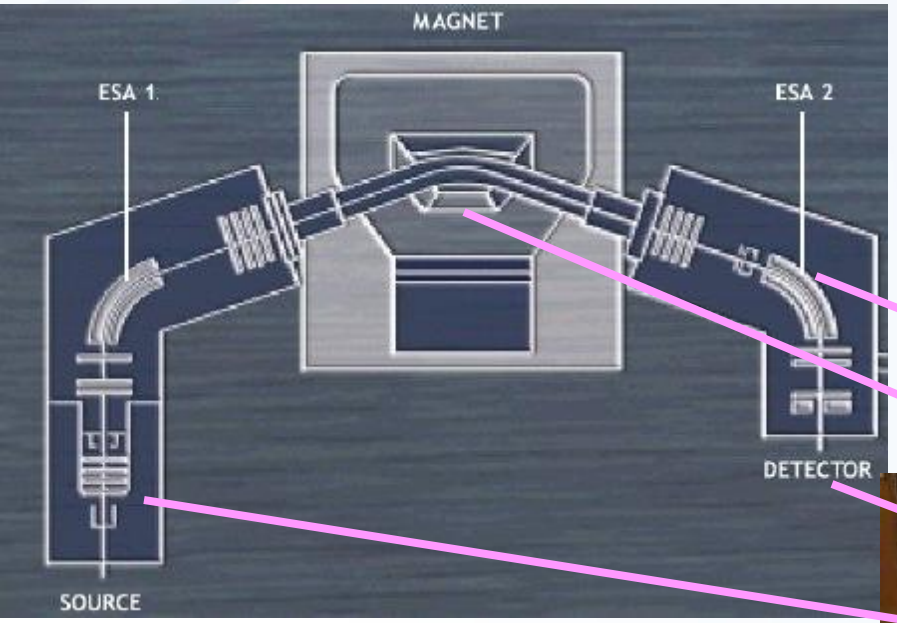
A. Kočan, Slovak Medical University

Magnetic sector mass analyzer

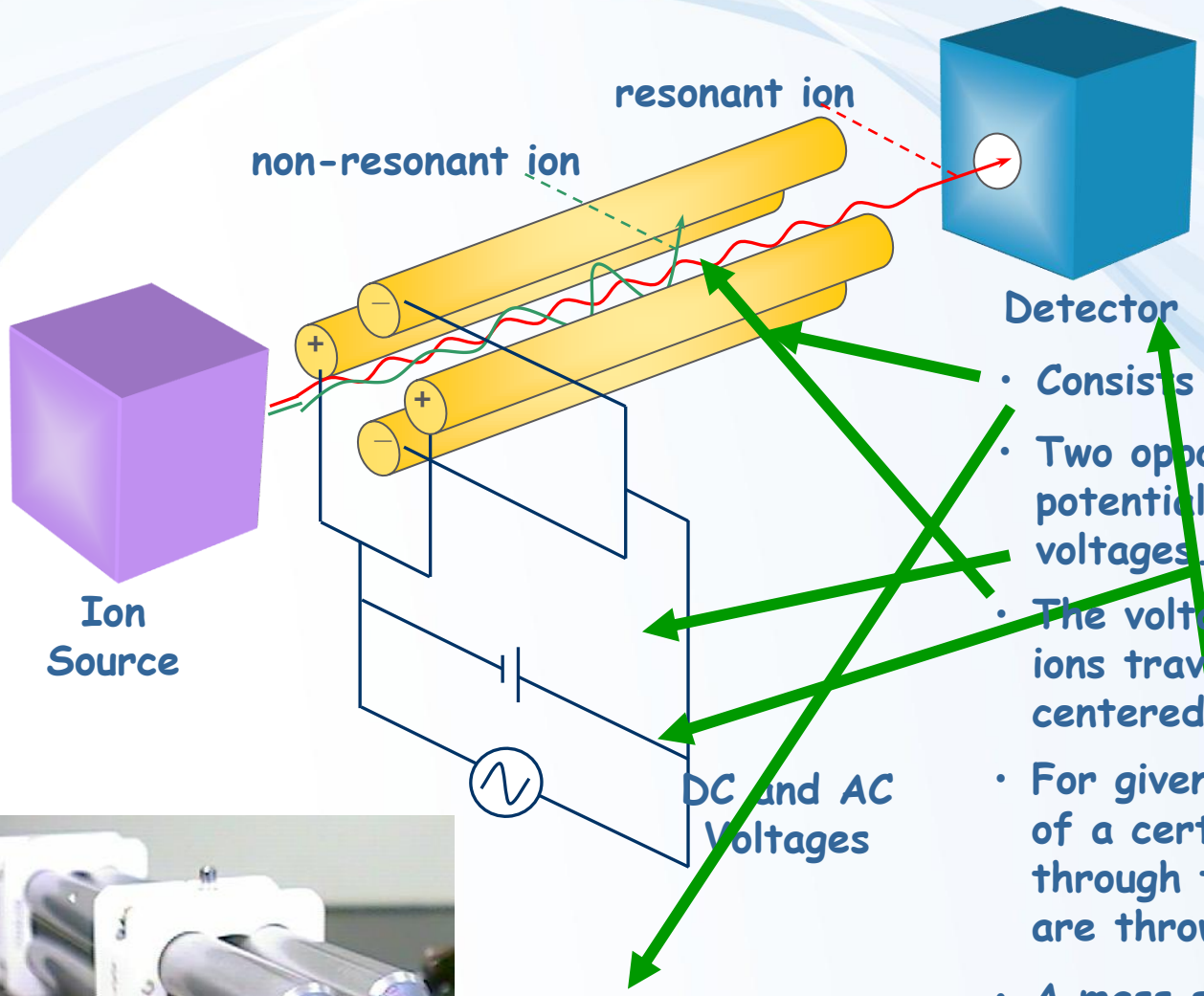


High resolution mass spectrometer

- 3-sector instrument (2 electrostatic sectors, 1 magnetic sector)



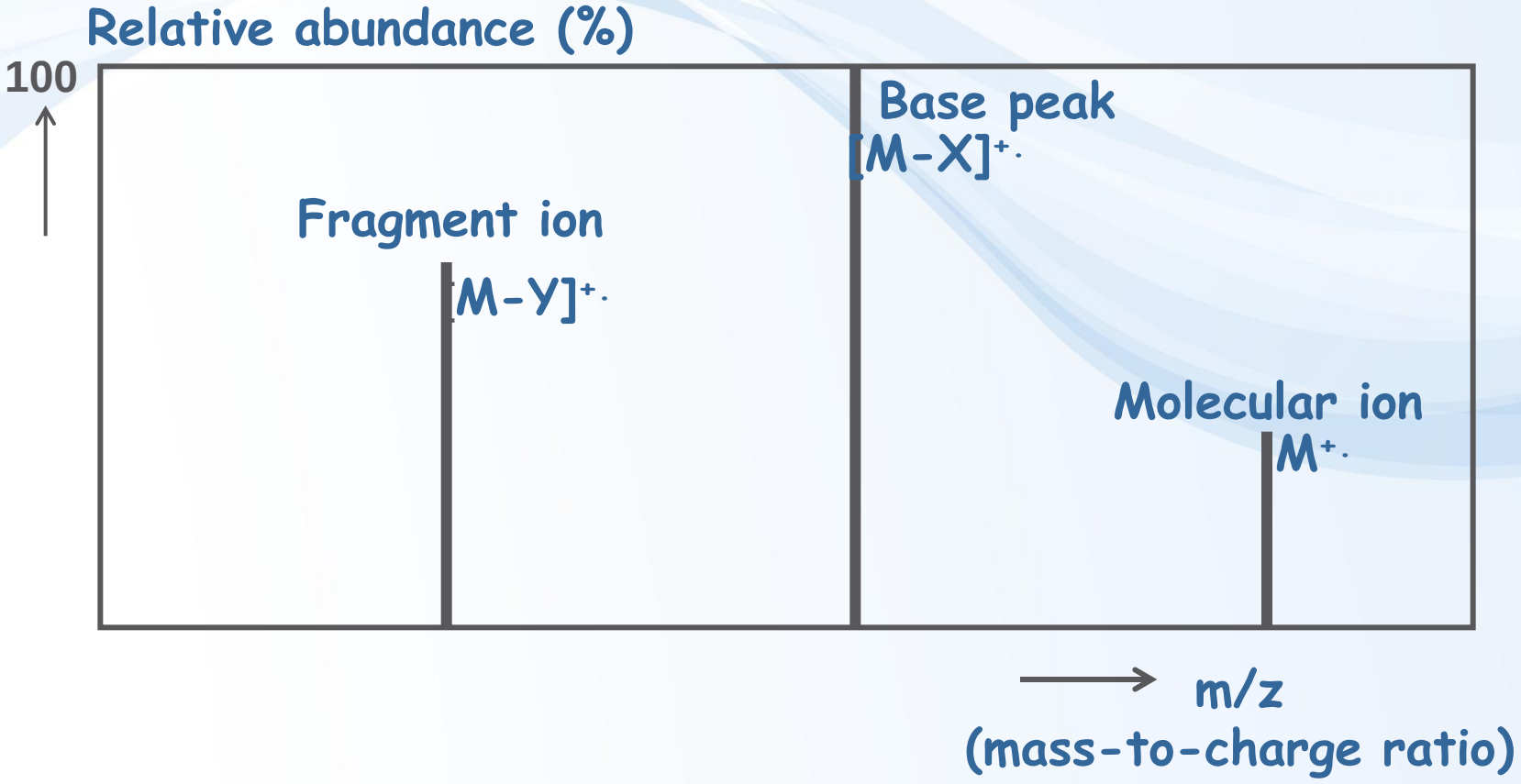
Quadrupole mass filter



- Consists of 4 parallel metal rods.
- Two opposite rods have an applied potential combined from DC and AC voltages.
- The voltages affect the trajectory of ions traveling down the flight path centered between the rods.
- For given dc and ac voltages, only ions of a certain mass-to-charge ratio pass through the filter and all other ions are thrown out of their original path.
- A mass spectrum is obtained by monitoring the ions passing through the quadrupole filter as the voltages or frequency on the rods are varied.

A. Kočan

Mass spectrum

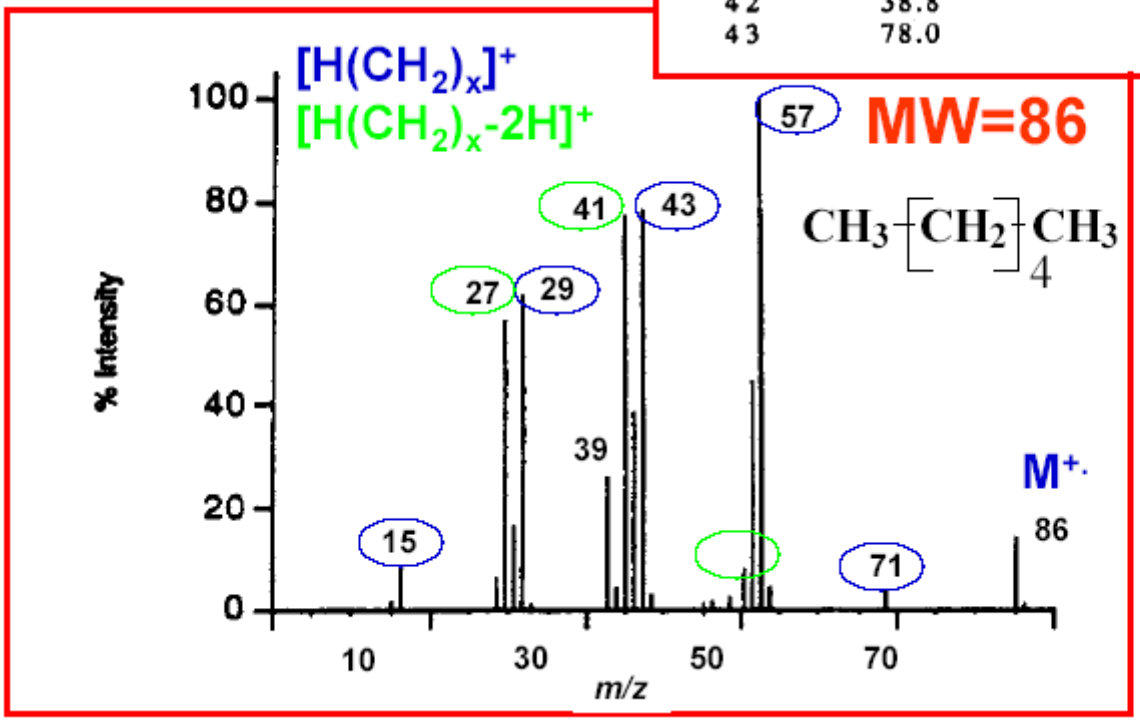


There are Internet-accessible databases containing mass spectra of thousands of compounds (*http://www.aist.go.jp/RIODB/SDBS/menu-e.html*, *http://webbook.nist.gov*)

Mass spectra interpretation

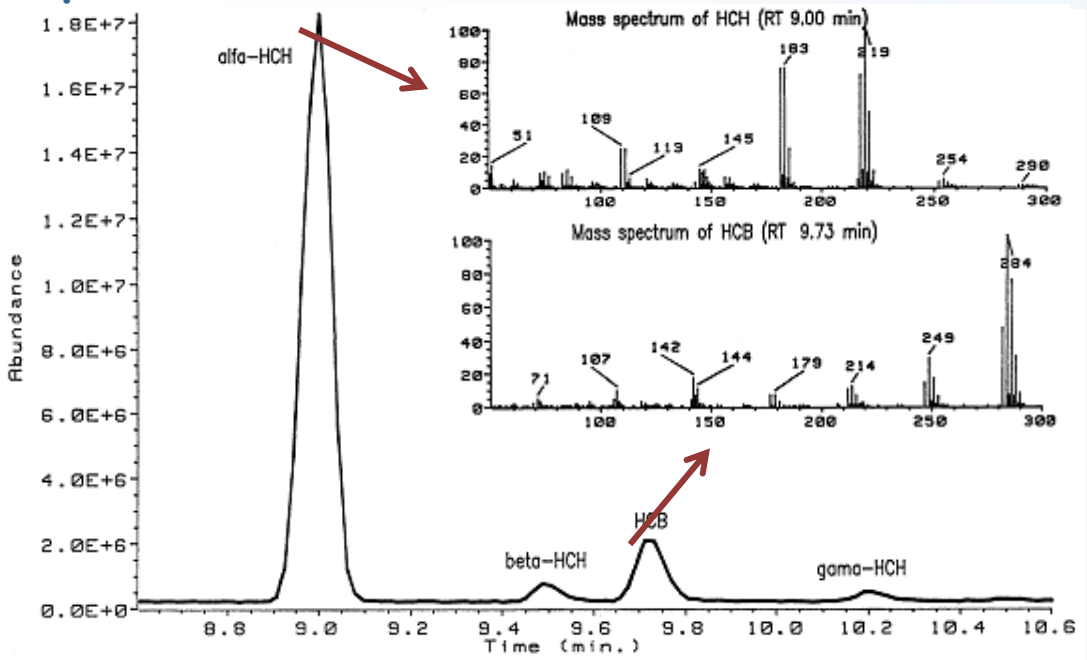
No. 3

m/z	%	m/z	%
14	1.4	44	2.6
15	10.2	50	1.3
26	6.4	51	1.8
27	56.9	53	2.5
28	16.1	55	8.0
29	61.2	56	44.8
30	1.3	57	100.0
39	27.3	58	4.5
40	4.2	71	5.2
42	38.8	86	14.0
43	78.0	87	0.9



What is the SCAN Mode in Mass Spectrometry ?

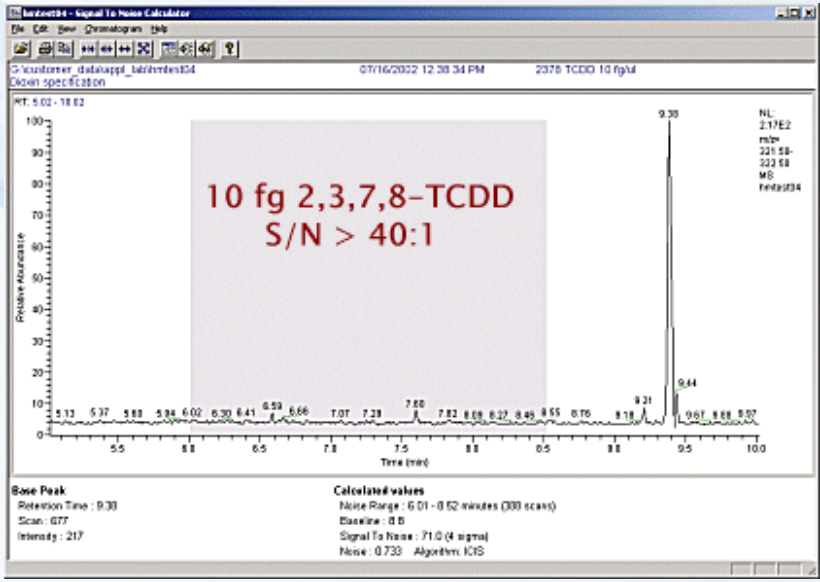
- The scanning mode provides mass spectra. They are recorded (scanned) at regular intervals (typically 0.5 – 1 /s; much faster if TOFMS is used) during the GC separation and stored in the instrument data system for subsequent qualitative or quantitative evaluation.
- From mass spectra, it is often possible to deduce structural features (mass spectral interpretation) but this requires experience and can be very time-consuming, particularly as a complex mixture might contain hundreds of components.

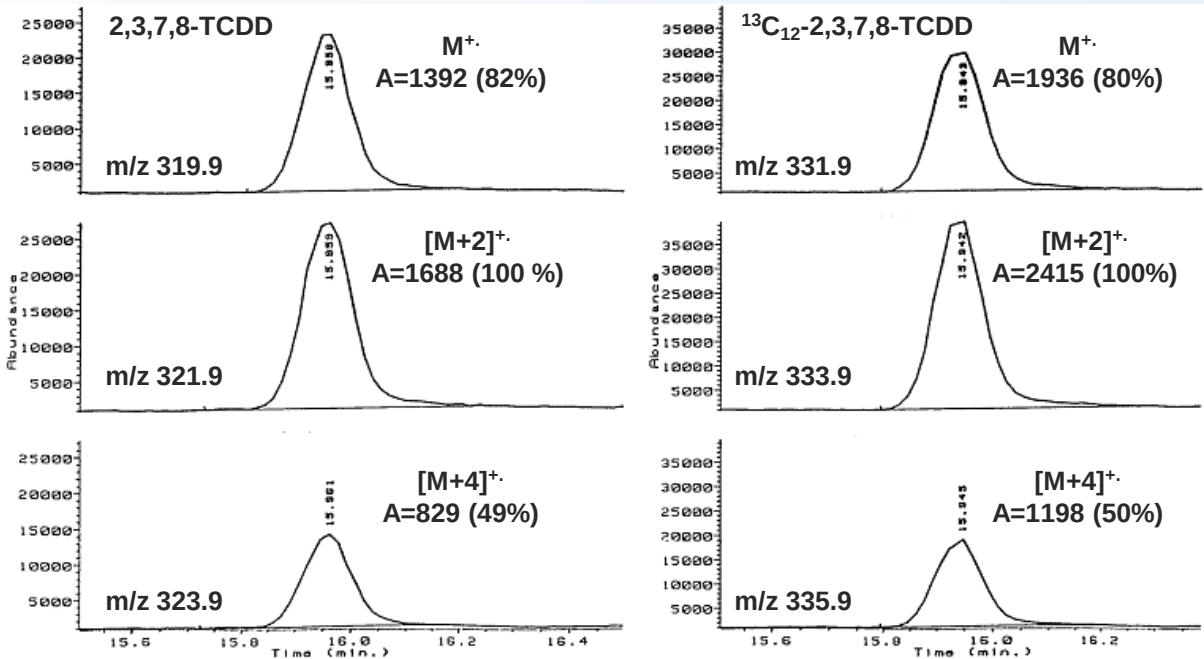


- The spectra can also be compared with those stored in mass spectral libraries. Although library searching is a very useful and timesaving technique, it is important to remember that such searches do not identify compounds – analysts do!

What is the SIM (or MID) Mode in Mass Spectrometry ?

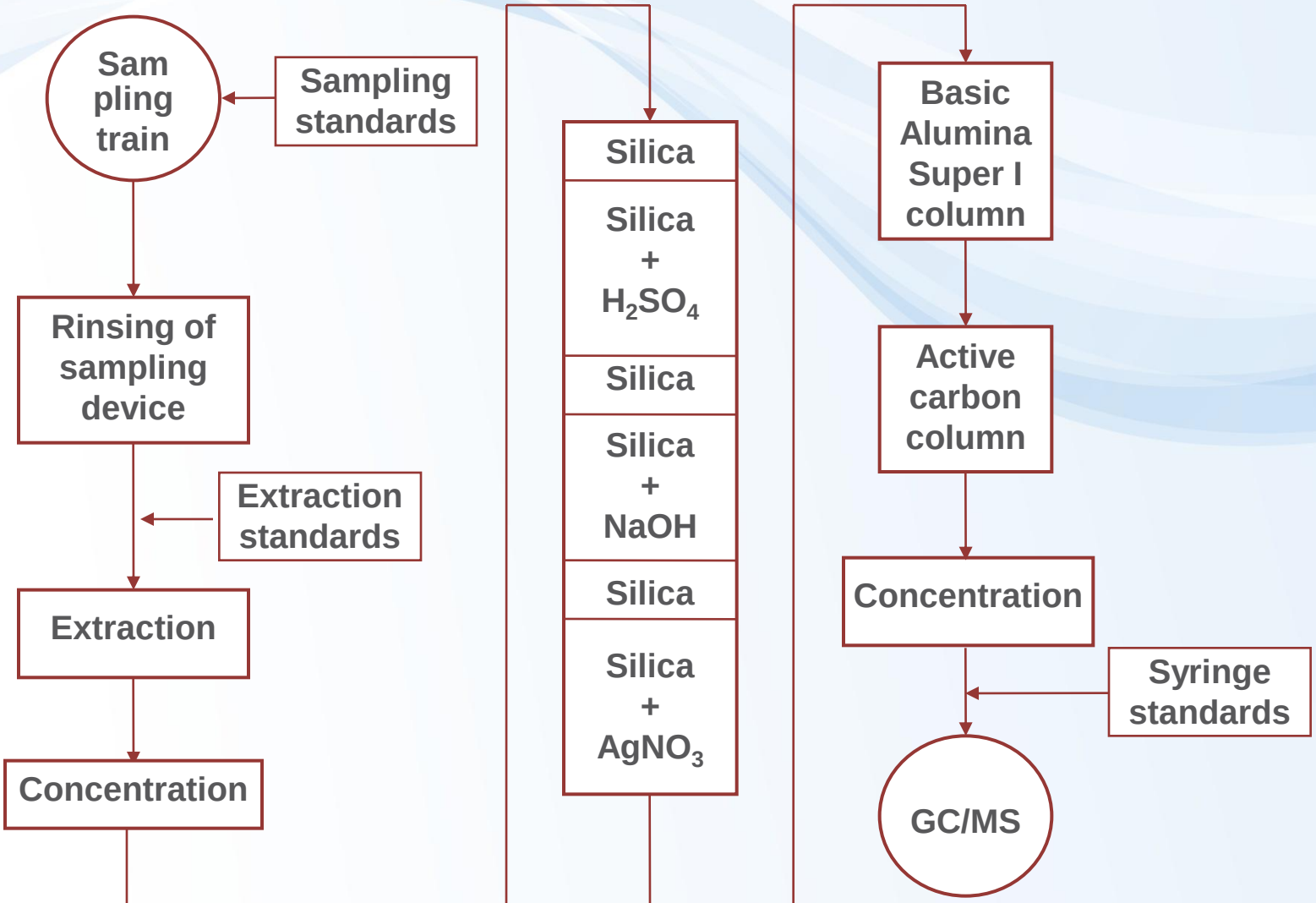
- SIM (Selected Ion Monitoring) is much more sensitive technique suitable for trace analysis. Here, instead of scanning a whole spectrum, only a few ions (the most abundant but characteristic) selected from the mass spectrum are detected.
- This can result in as much as a 500-fold increase in sensitivity, at the expense of selectivity. Depending on the analyte, low picogram to even low
- femtogram amounts
- can be measured.
- Stable isotope-labeled internal standards can be employed.





HRMS/LRMS-SIM chromatogram from the analysis of 2378-TCDD

Flow chart of a clean-up procedure for stack emission samples



Quality assurance/quality control

Quality assurance

Preventive measures (quality of facilities, personnel and education, equipment and service, calibration, internal and recovery standards)

Quality control

Control measures (internal – blank and reference material analyses, external – interlaboratory comparison, audit)

Reasons

- repeatibility of measurements
- comparison of results between laboratories
- political and economical importance of results

Terminology

Calibration
Limit of detection and quantification
Sensitivity and specificity
Accuracy, trueness, precision
Method validation and verification
Internal standards
Recovery and surrogate recovery standards
Certified reference materials
interlaboratory calibration tests,
GLP

Examples

Mokrá - půdy 2002 - 4

vyhodnoceno: 25.4.2003

Koncentrace ng/g

Číslo vzorku	toluen	02-753	02-752	02-740	02-741	02-742	02-743	02-744	02-745	02-746	02-747	02-748	02-749	02-750	02-751	
Lokalita	GC blank	Lab. blank	RM	454 Hosten	Čihálky	332 Vodojem	Velká Bata1	Velká Bata2	Prostřed kopec	420Vel Bata	Chlumek 1	Chlumek 2	Horák mysl.	Nové pole	jižní CVM	LOQ
Číslo zadav				303S	304S	305S	306S	307S	308S	309S	310S	311S	312S	313S	314S	
Datum odbě				14.11.02	14.11.02	14.11.02	14.11.02	14.11.02	14.11.02	14.11.02	14.11.02	14.11.02	14.11.02	14.11.02	14.11.02	KALIB30
Navážka (g)	5.0	5.0	5.0	5.0	5.0	5.0	5.0	5.0	5.0	5.0	5.0	5.0	5.0	5.0	5.0	5.0
Ředění	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1
Naftalen	0.10	1.86	26.74	12.5	6.6	7.5	5.2	5.5	11.8	13.5	7.1	6.6	8.6	5.9	8.5	0.10
Acenaftyle	-	0.02	0.58	0.8	0.3	0.7	0.4	0.5	2.2	1.8	0.6	0.5	1.2	2.4	0.8	0.10
Acenaften	-	0.04	1.22	1.4	0.3	1.4	1.6	0.6	5.3	3.4	2.5	0.8	2.0	5.4	1.2	0.10
Fluoren	-	0.04	2.26	1.7	0.6	1.4	1.3	0.7	4.9	3.8	2.0	1.0	2.2	4.7	1.5	0.10
Fenantren	-	0.12	23.96	24.9	6.4	20.5	18.8	8.4	69.1	59.4	14.2	13.6	29.5	109.3	16.8	0.10
Antracen	-	-	1.12	2.0	0.4	1.9	3.4	1.1	6.1	5.2	2.1	1.4	2.9	16.9	1.8	0.10
Fluoranten	-	-	27.78	68.2	13.7	58.0	42.0	24.2	213.0	162.5	40.7	37.6	82.5	450.2	42.9	0.10
Pyren	-	-	19.38	50.5	9.7	45.6	35.4	20.2	159.3	123.6	32.0	28.6	63.8	377.2	33.0	0.10
Benz(a)ant	-	-	4.60	17.9	2.9	14.4	14.7	9.1	61.5	49.3	18.3	13.1	26.3	206.3	13.6	0.10
Chrysen	-	-	11.50	32.4	7.3	25.6	18.4	12.2	102.6	75.9	22.3	16.8	41.2	204.2	20.0	0.10
Benzo(b)flu	-	-	18.30	61.0	11.7	32.2	23.6	20.4	169.5	128.2	28.0	29.4	67.7	261.1	31.2	0.10
Benzo(k)flu	-	-	6.04	18.1	3.8	14.4	11.0	7.9	56.4	41.9	13.0	11.2	22.4	134.8	11.6	0.10
Benzo(a)py	-	-	8.34	27.6	3.5	23.6	20.3	13.3	92.8	71.6	24.2	18.4	38.4	285.9	21.3	0.10
Indeno(123	-	-	8.22	33.1	6.4	21.4	14.8	11.1	98.7	72.0	22.6	19.6	41.0	216.1	20.7	0.10
Dibenz(ah)	-	-	0.82	2.7	0.6	2.4	1.6	0.9	7.1	8.3	1.8	2.3	4.1	25.8	1.8	0.10
Benzo(ghi)	-	-	11.26	29.7	5.3	20.6	14.8	11.4	83.9	61.4	19.4	16.3	36.0	181.8	18.5	0.10
Suma PA	**0.10**	**2.08**	**172.12**	**384.5**	**79.5**	**291.6**	**227.3**	**147.5**	**1144.2**	**881.8**	**250.8**	**217.2**	**469.8**	**2488.0**	**245.2**	**1.60**
100% D-PA	2 000	2 000	2 000	2 000	2 000	2 000	2 000	2 000	2 000	2 000	2 000	2 000	2 000	2 000	2 000	
ředění	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	
D8-naftaler	0%	0%	88%	72%	79%	66%	65%	80%	62%	66%	21%	61%	75%	81%	81%	
D10-fenant	0%	0%	90%	77%	91%	68%	72%	86%	77%	79%	88%	79%	85%	94%	92%	
D12-peryle	0%	0%	86%	74%	34%	67%	73%	86%	83%	83%	89%	82%	93%	101%	96%	

GC blank ..... slepý vzorek přístroje GC-MS - nástřik čistého rozpouštědla do plynového chromatografu

Lab. blank ..... laboratorní slepý vzorek - analyzovaný celým analytickým postupem s čistými rozpouštědly a všemi použitými materiály

GPC blank ..... slepý vzorek GPC chromatografu

blank, GF blank ..... terénní slepé vzorky - pasivní odběr na polyuretanovou pěnu a skleněné vlákno

CRM ..... analýza certifikovaného referenčního materiálu

RM ..... analýza laboratorního referenčního materiálu

NQ ..... nekvantifikováno - analyt byl překryt interferentem

LOQ ..... meze stanovitelnosti

Monitoring

- is a long-term consistent observation or measurement of precisely defined indicators well described in the space and time

- is performed in the monitoring network representative for the region

- consists of the observations and measurements, evaluation of the current status, changes as well as future perspectives.

Environmental monitoring is at the very beginning of the environmental information chain:

- it is the basis of environmental data collection,
- environmental reporting and environmental research,
- the basis of understanding of environmental problems and trends.

Measurement of substances in the environment

Screening - is it possible to detect the substance in environmental samples?

Survey - how big is the problem?

Monitoring -long-term measurements of the temporal trends and/or

-large scale measurements of the spatial distribution

Modeling - where is the substance ?

Need for regional monitoring programs

UN ECE **Convention on Long Range Transboundary Air Pollution** – POPs Protocol – includes the measurements of several PTSs in the air

EMEP Activities

AMAP collects data on PTS levels in the Arctic region

Marine conventions in Europe (OSPAR, Helsinki, Barcelona and Bucharest Conventions) collect data from the marine environment

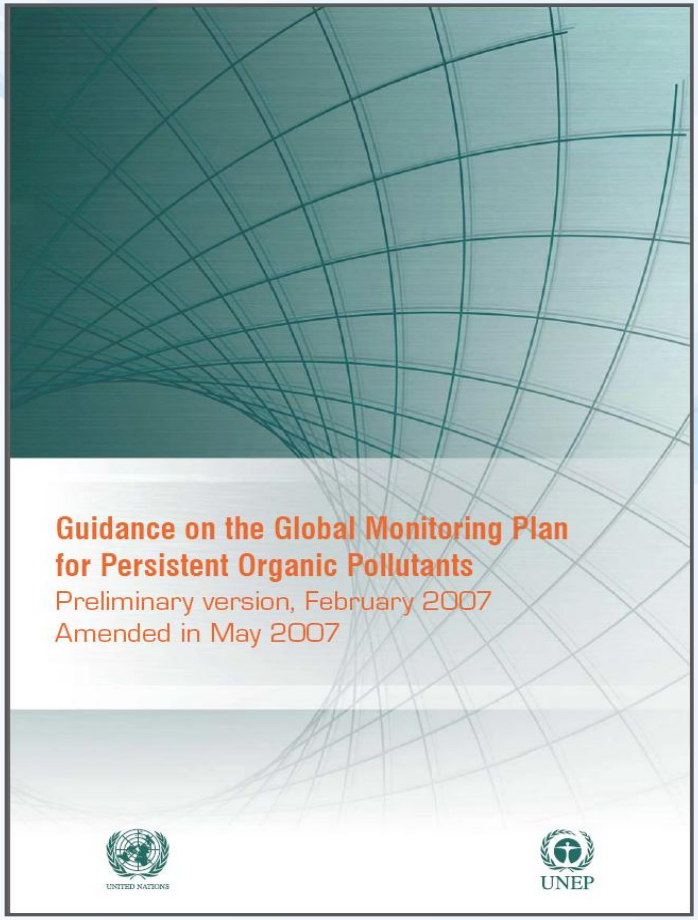
The **Water Framework Directive** demands a large amount of new data to be produced in EU

DG Environments initiative "**Health and Environment**"

Guidance to the Global Monitoring Plan

Core matrices

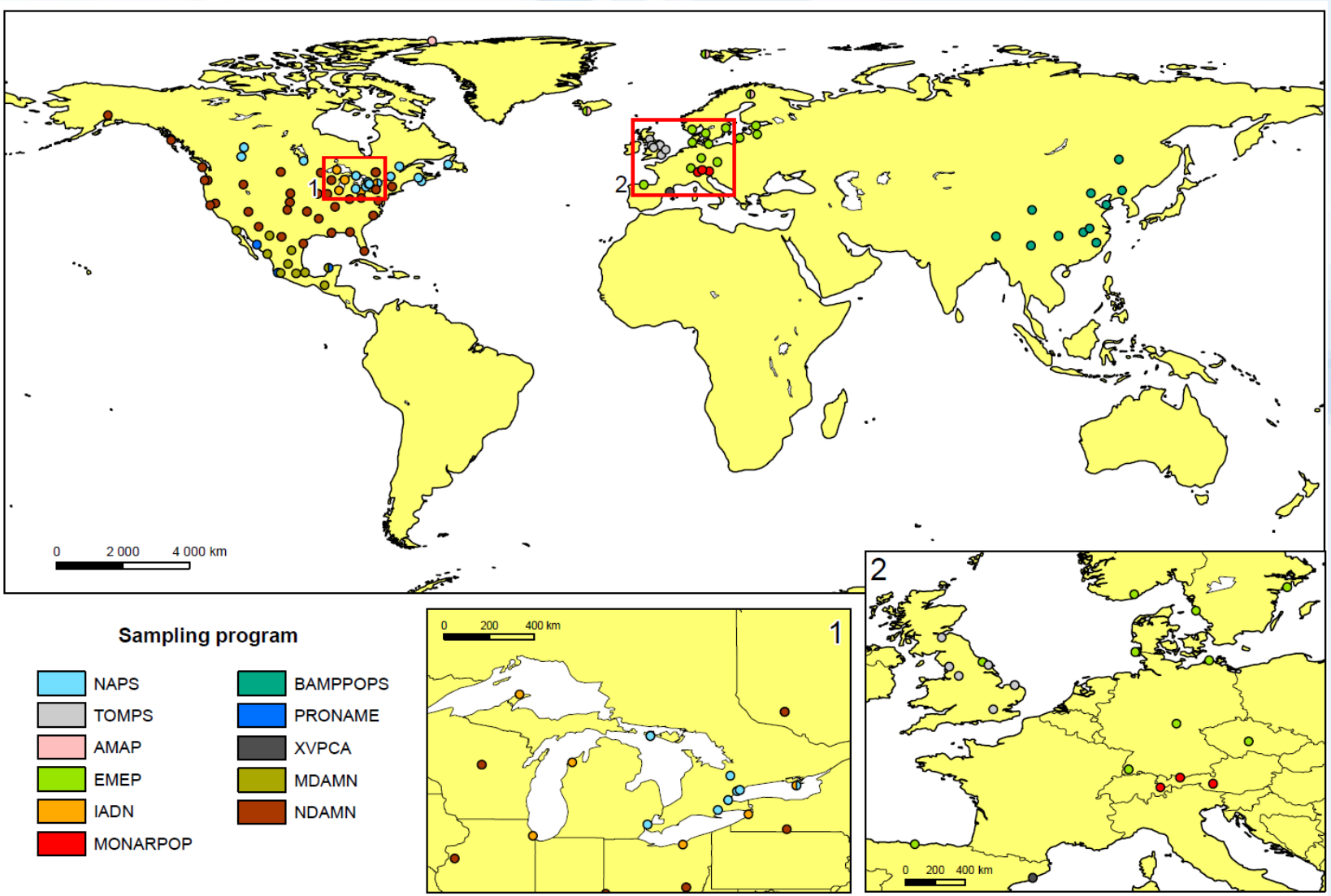
- Air
- Human Milk and blood



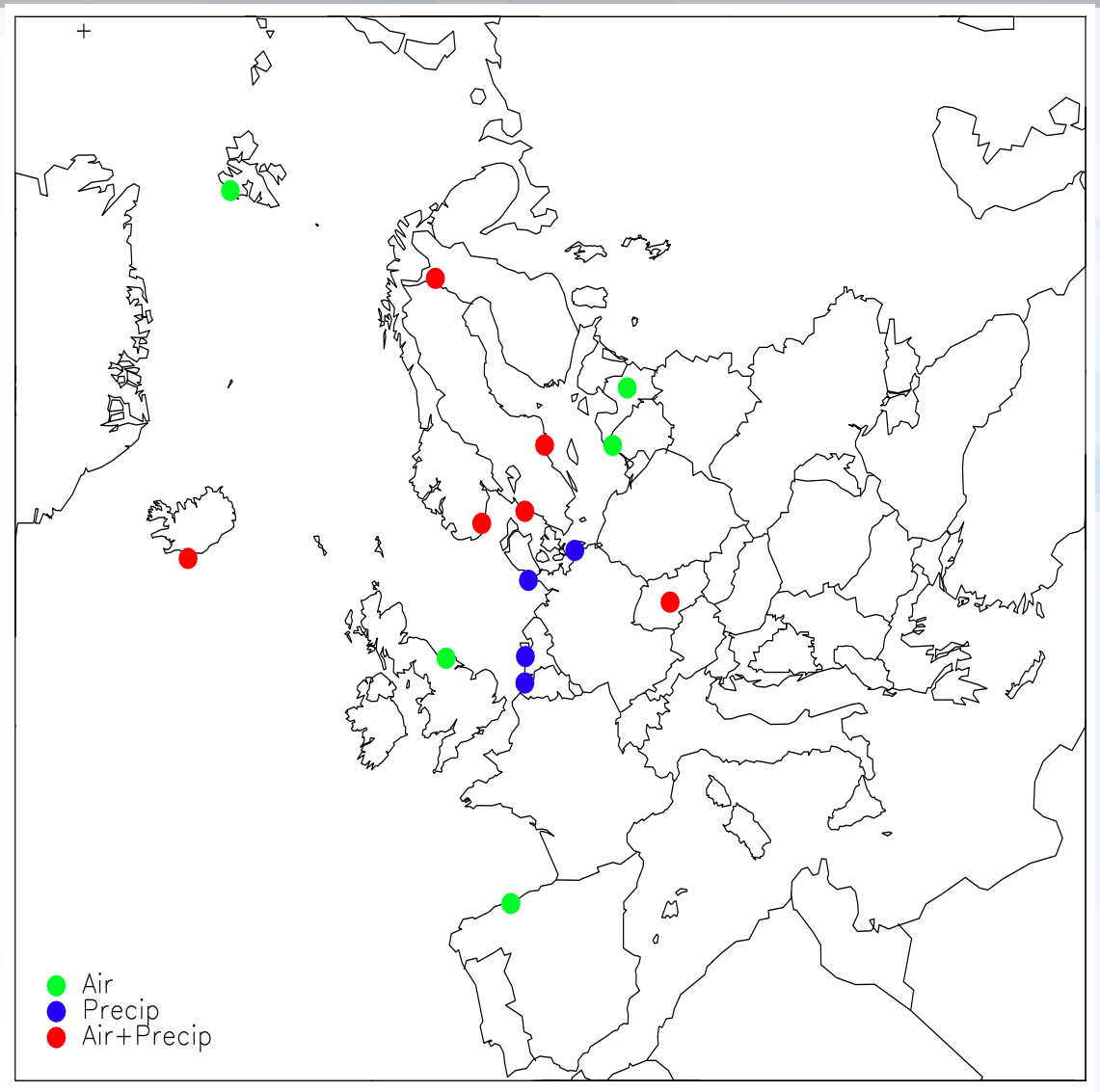
1st GMP report presented at COP4 in May 2009

and every 6 years thereafter

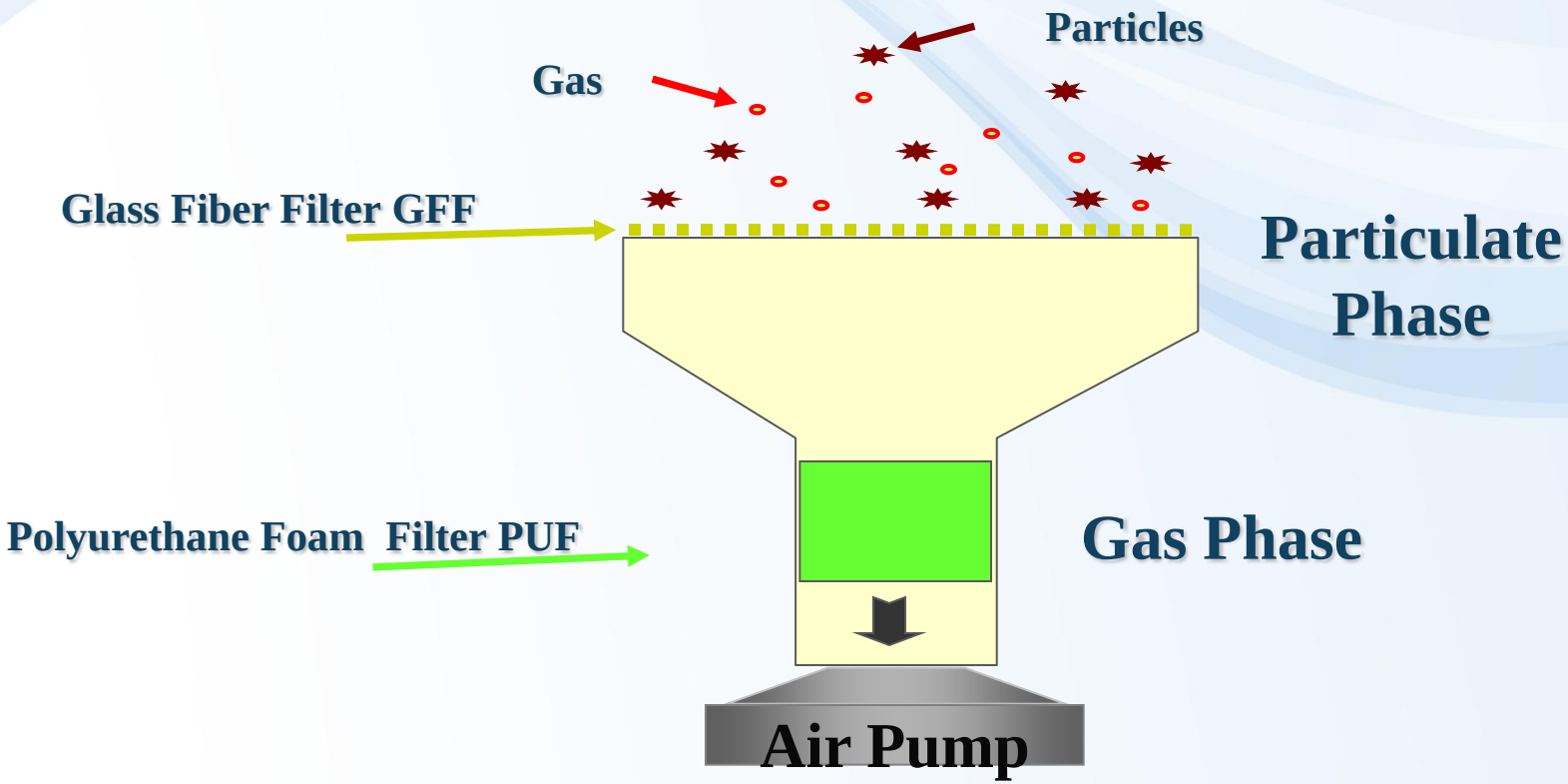
Long-term active air sampling networks



EMEP active air monitoring network

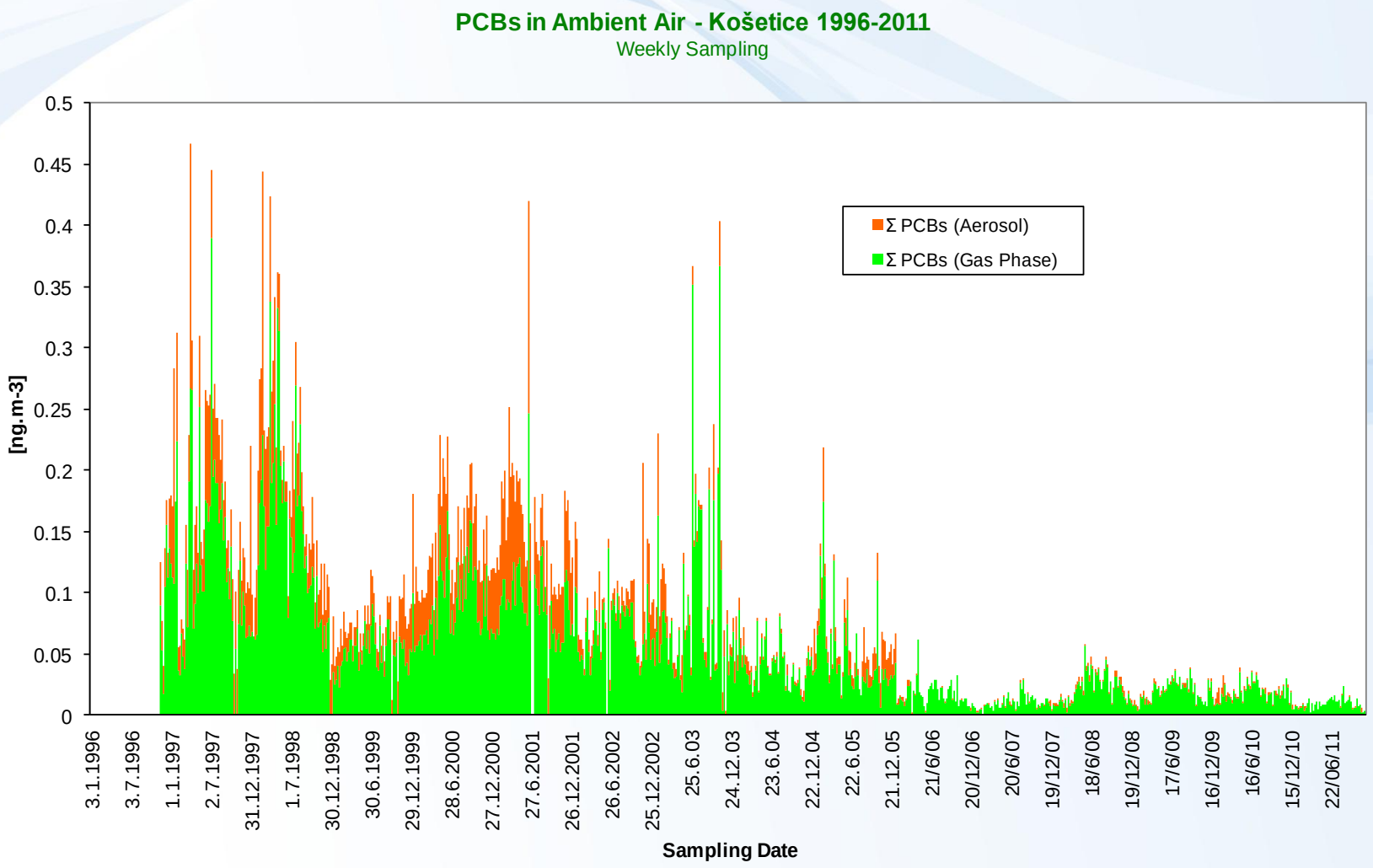


Sampling Techniques

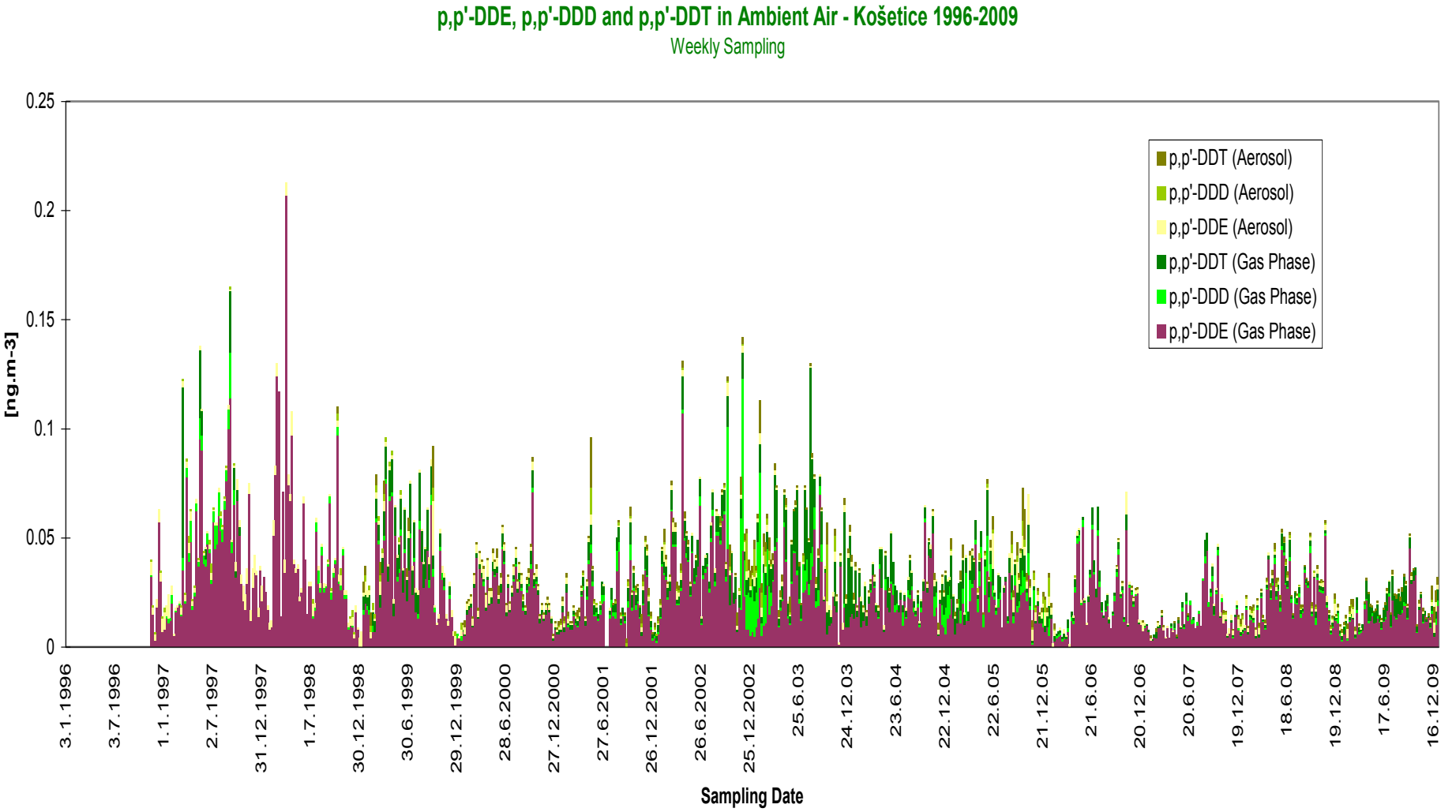


High-Volume sampler

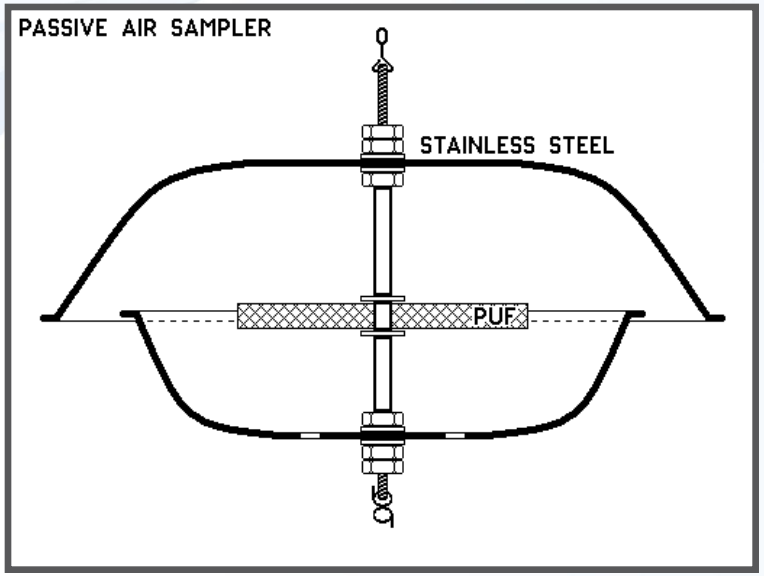
PCBs in the ambient air, Kosetice observatory, 1996-2009



DDTs in the ambient air, Kosetice observatory, 1996-2009



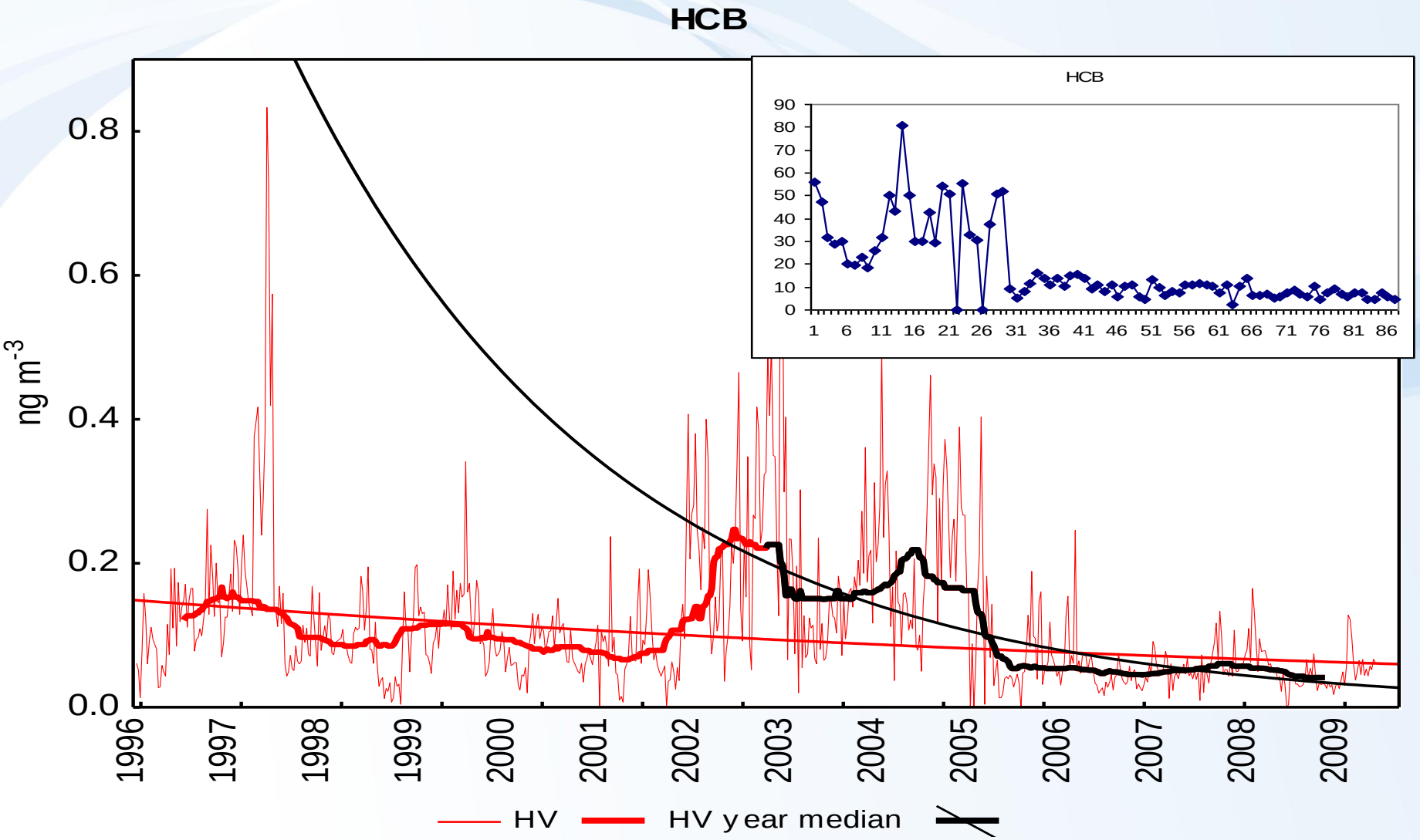
Passive air sampling technique



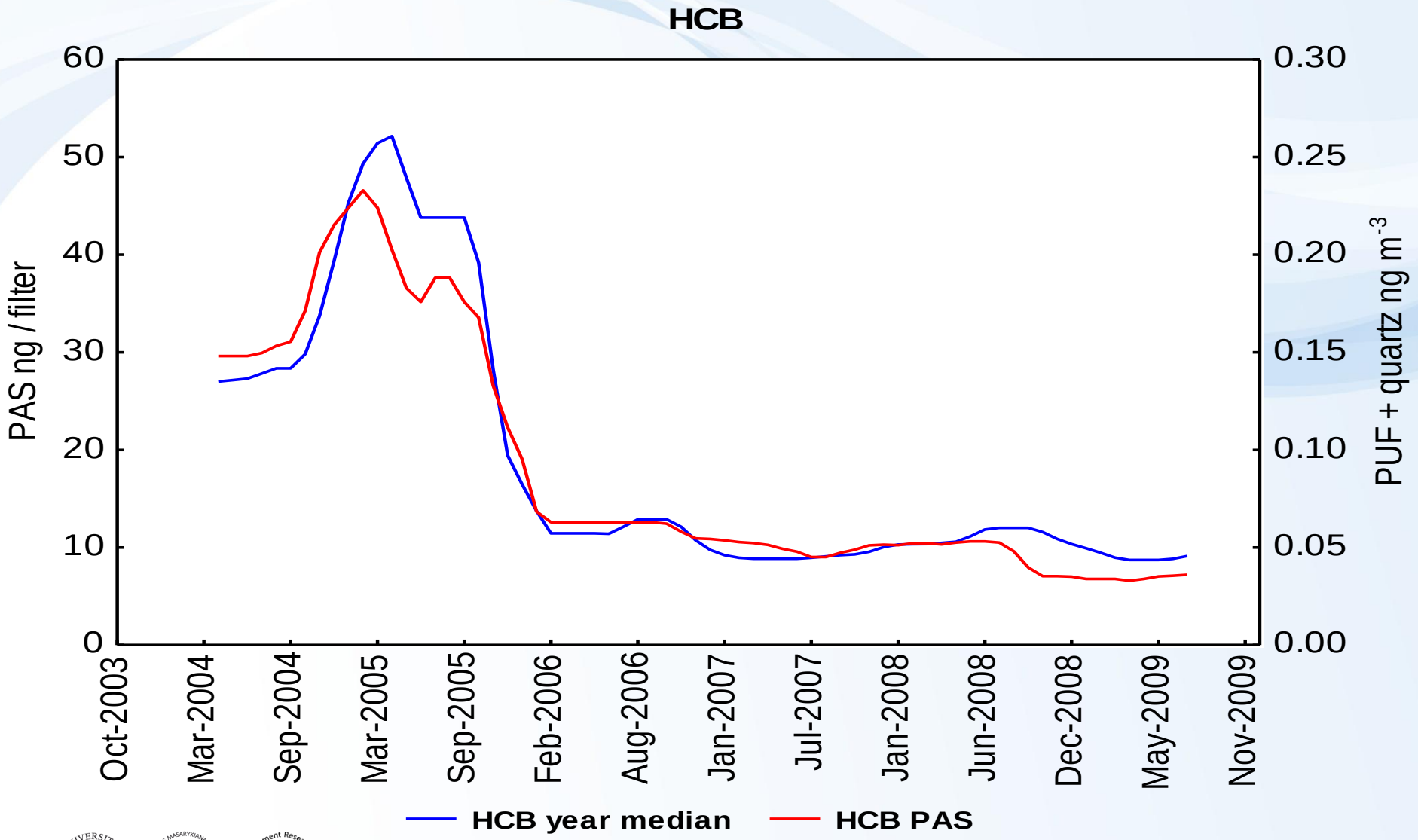
- **filter (polyurethane foam)** – captures pollutants from the surrounding air

- **sampler body** – filter protecting chamber (wind, rainwater, solar radiation)

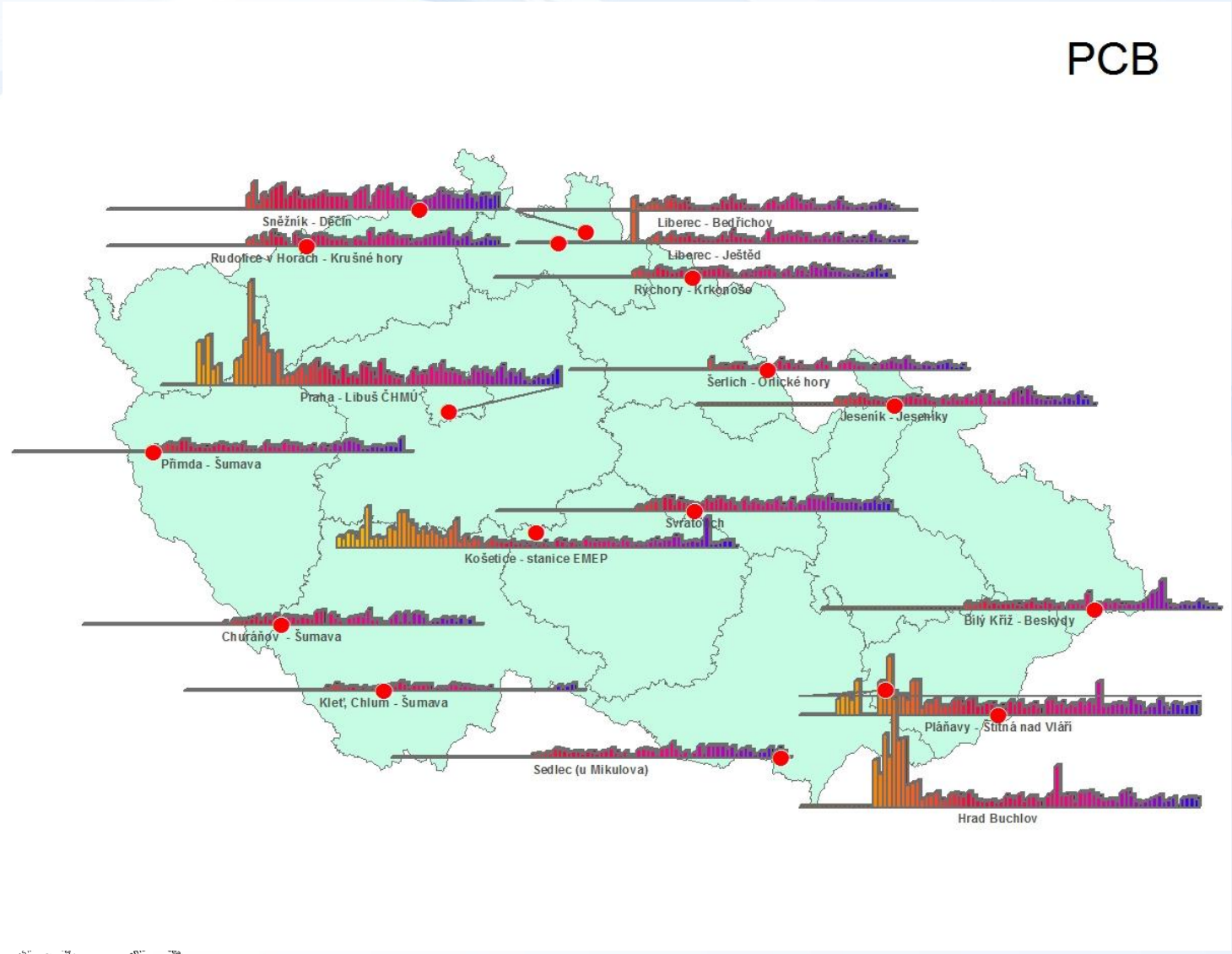
HCB and PeCB in the air, Kosetice, 1996-2009



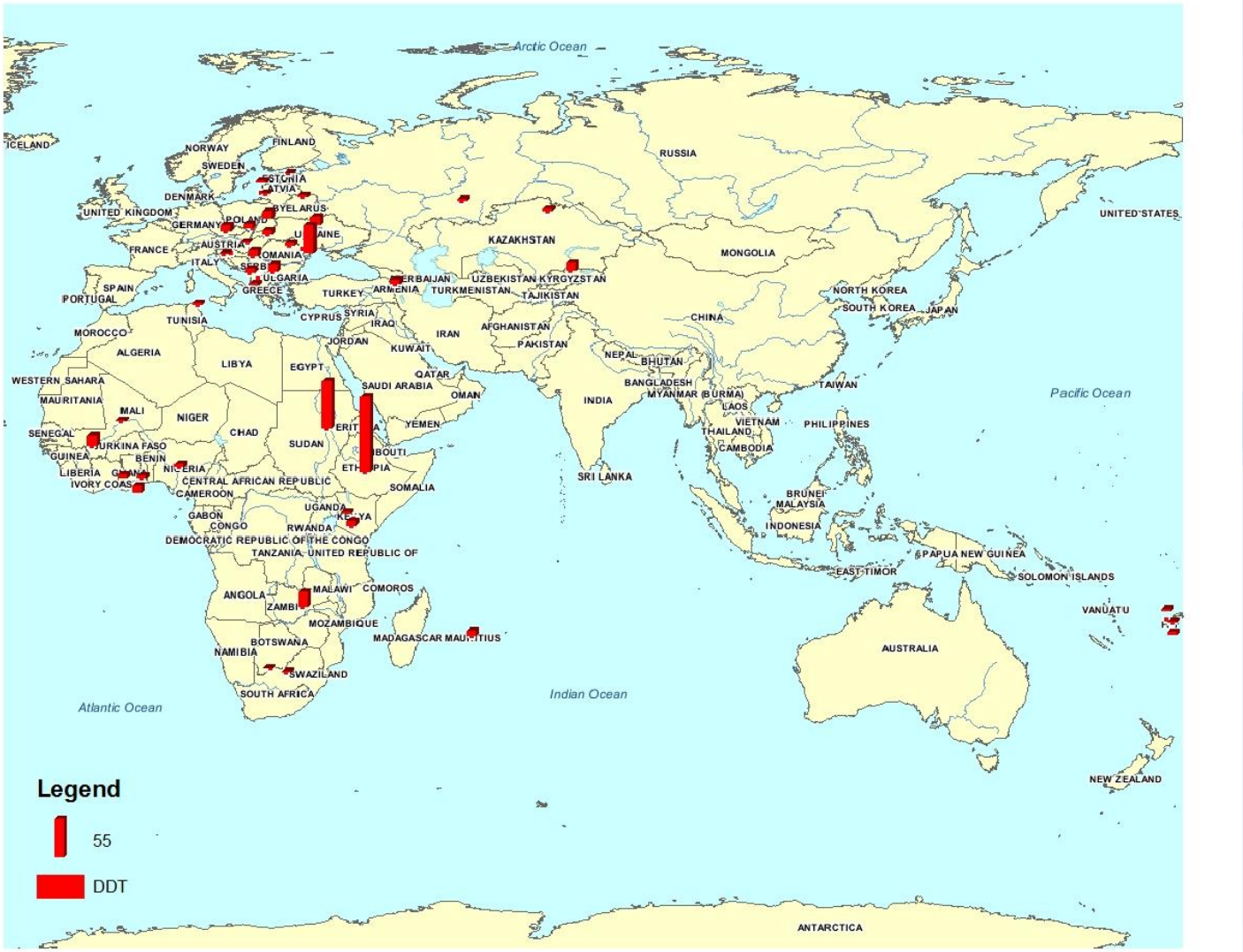
Corelation of passive and active air sampling data, HCHs



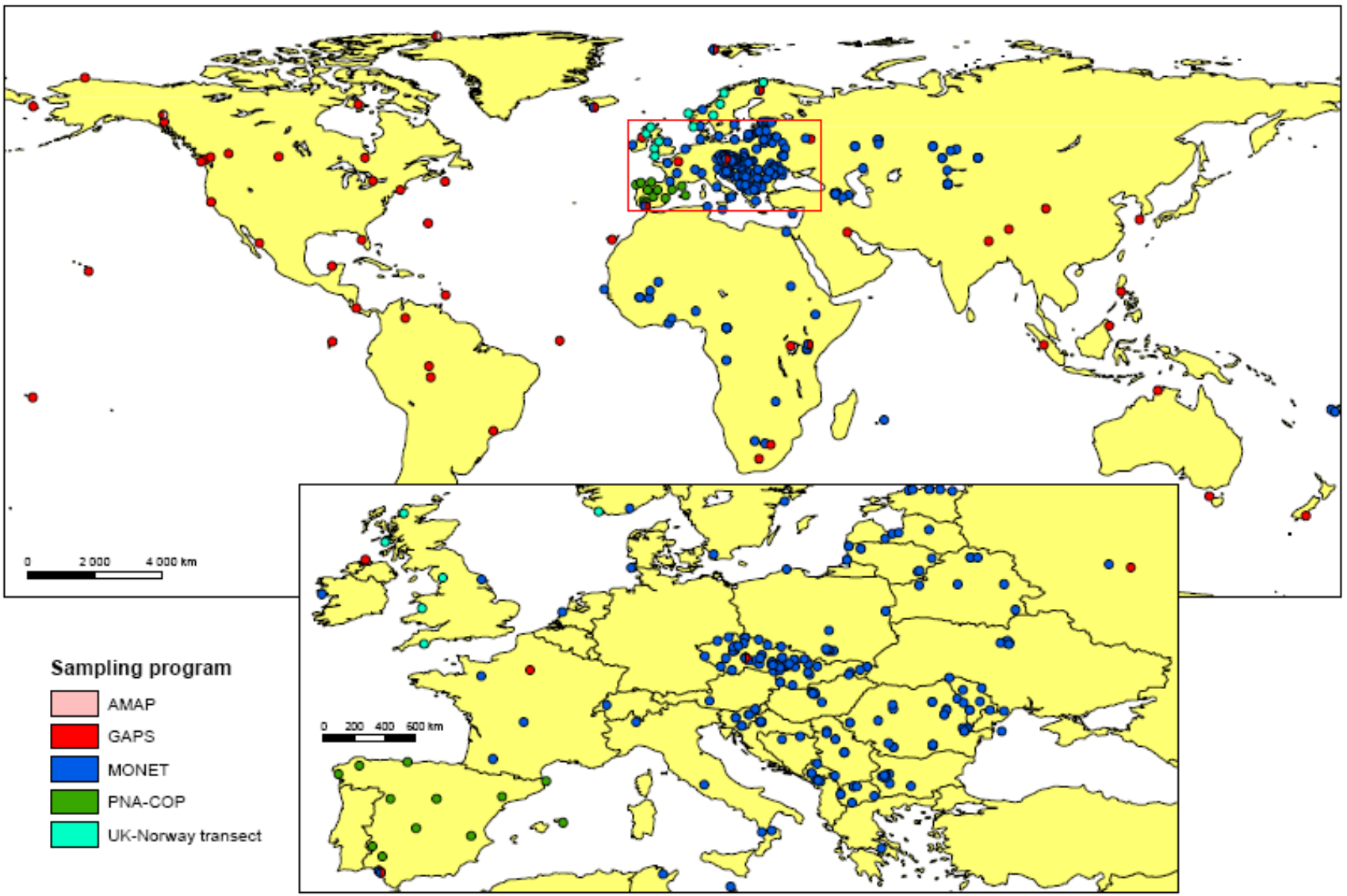
PCBs in the ambient air, Czech Republic, 2003-2010



MONET monitoring networks



Passive air sampling networks globally



Questionnaire for mothers donating breast milk

QUESTIONNAIRE FOR POTENTIAL HUMAN MILK DONORS

Fourth WHO-Coordinated Survey of Human Milk for Persistent Organic Pollutants

CONFIDENTIAL!

Section 1: Personal Information

Name	Phone number	Today's Date (dd/mm/yyyy)
	e-mail	
Address		

Section for National Coordinator

Individual Identification Code		Pool Identification Code	

Is the participant eligible? Yes ☐ No ☐

What is the status of donor in regard to the survey?

Selected ☐ Alternate ☐ Not Selected ☐

If this mother has been pre-selected to donate a sample (or is designated as an alternate), the top of Section 4 should be completed and detached from this questionnaire. Section 4 should be sent to the clinic to be completed at the time of sample collection.

Section 2: Screening Questionnaire

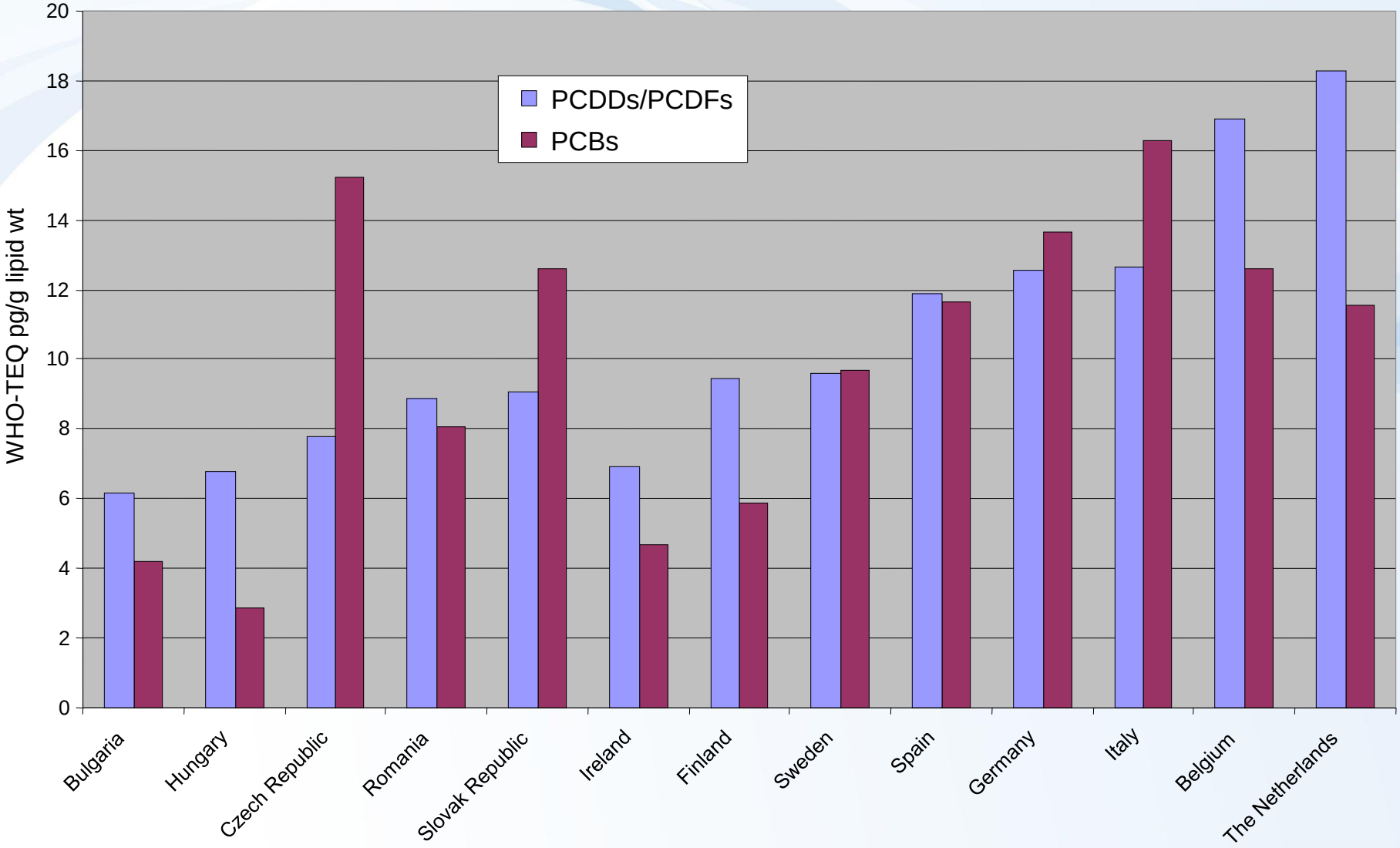
Name of Interviewer:	Date of interview (dd/mm/yyyy):

Place of interview:

1. Are you planning to breastfeed your child?
   Yes ☐ No ☐
2. Is this your first child?
   Yes ☐ No ☐
3. Are you expecting a single child? (not twins)
   Yes ☐ No ☐
4. Are you having a normal healthy pregnancy?
   Yes ☐ No ☐
5. Have you lived in your current area for 10 years?
   Yes ☐ No ☐ Actual _____
6. Are you under 30 years of age?
   Yes ☐ No ☐
   If yes, date of birth _____
7. Do you live near incinerators, pulp and paper industries, metal industries or where chemicals are produced
   Yes ☐ No ☐

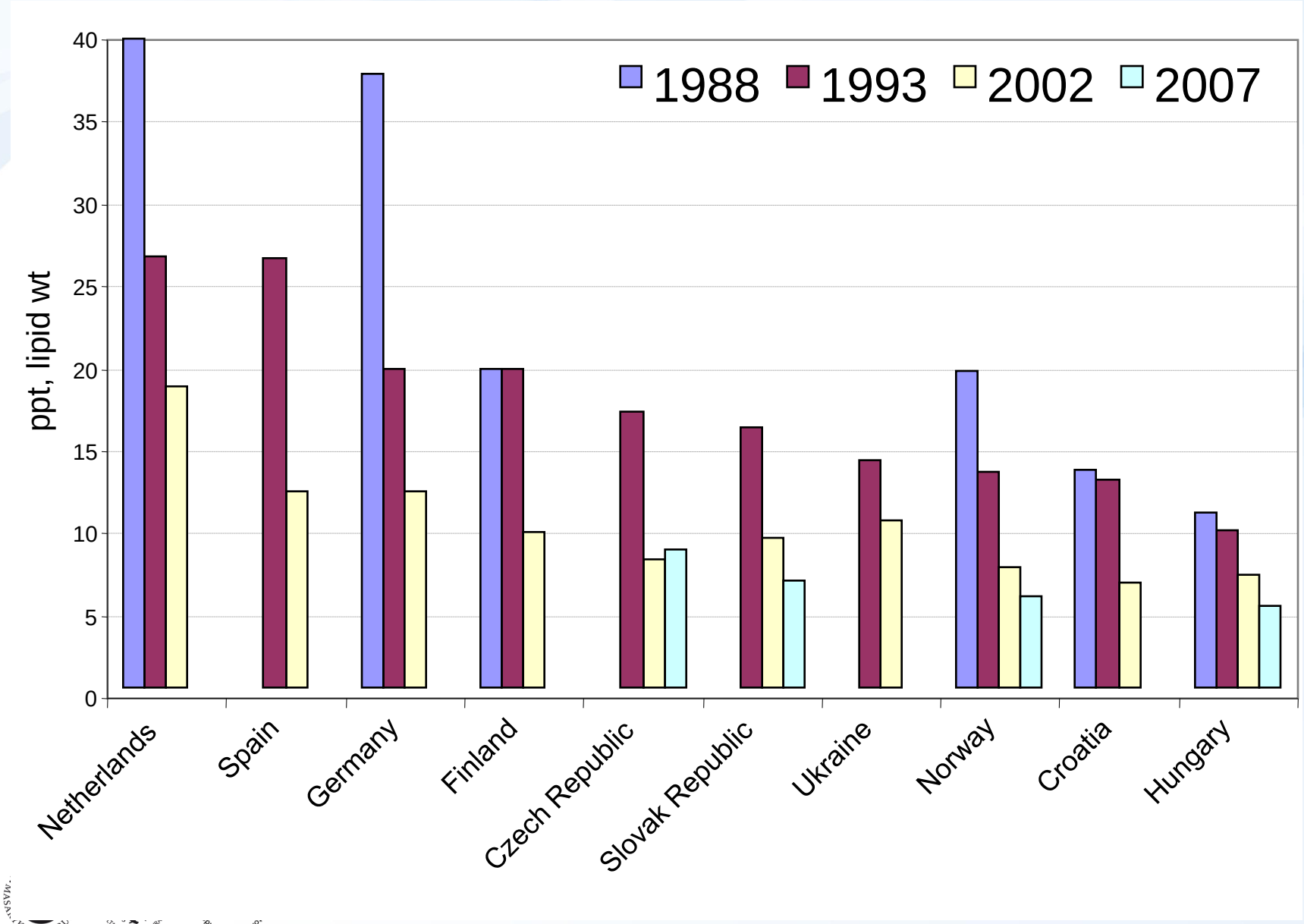
European PCDD/F and PCB levels in human milk

(WHO Exposure Study 2001/2002)

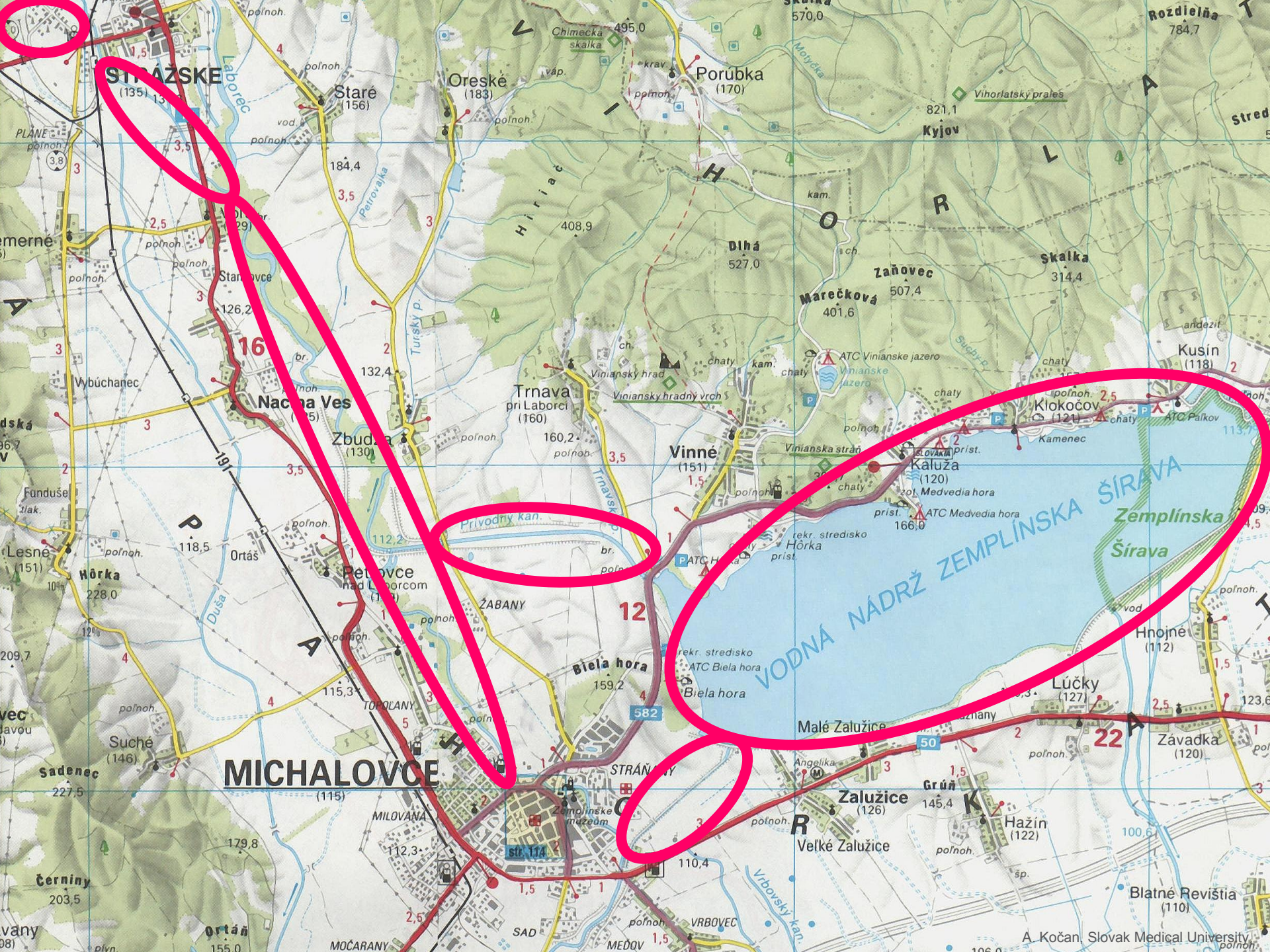


Source: Van Leeuwen, Malisch 2002 "WHO exposure study on the levels of PCBs, PCDDs and PCDFs in Human Milk" 3rd round

Time trends in PCDD/F levels in human milk (WHO Exposure Studies)

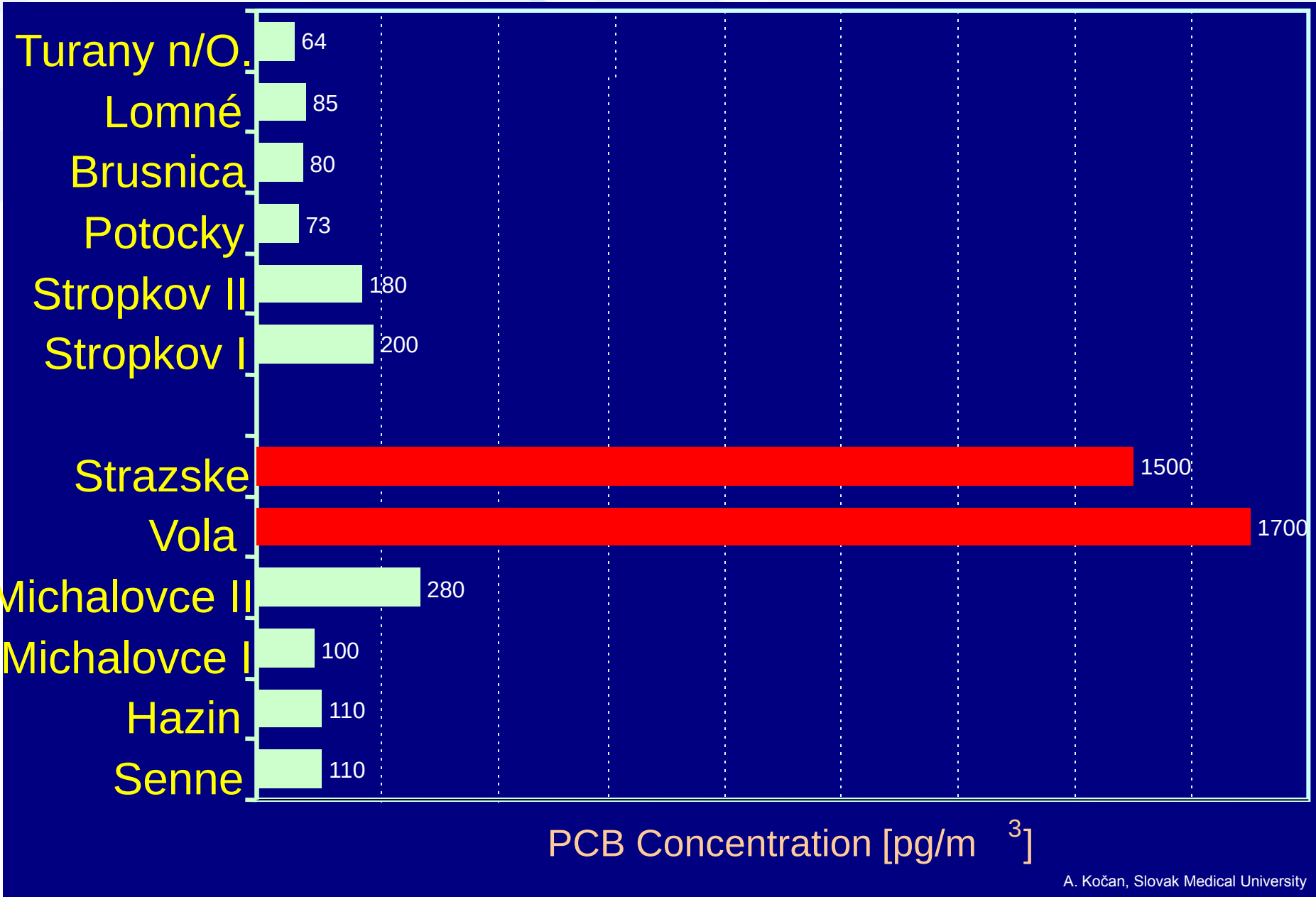


Slovakia‘s districts chosen for exposure studies



PCB Concentrations in Ambient Air

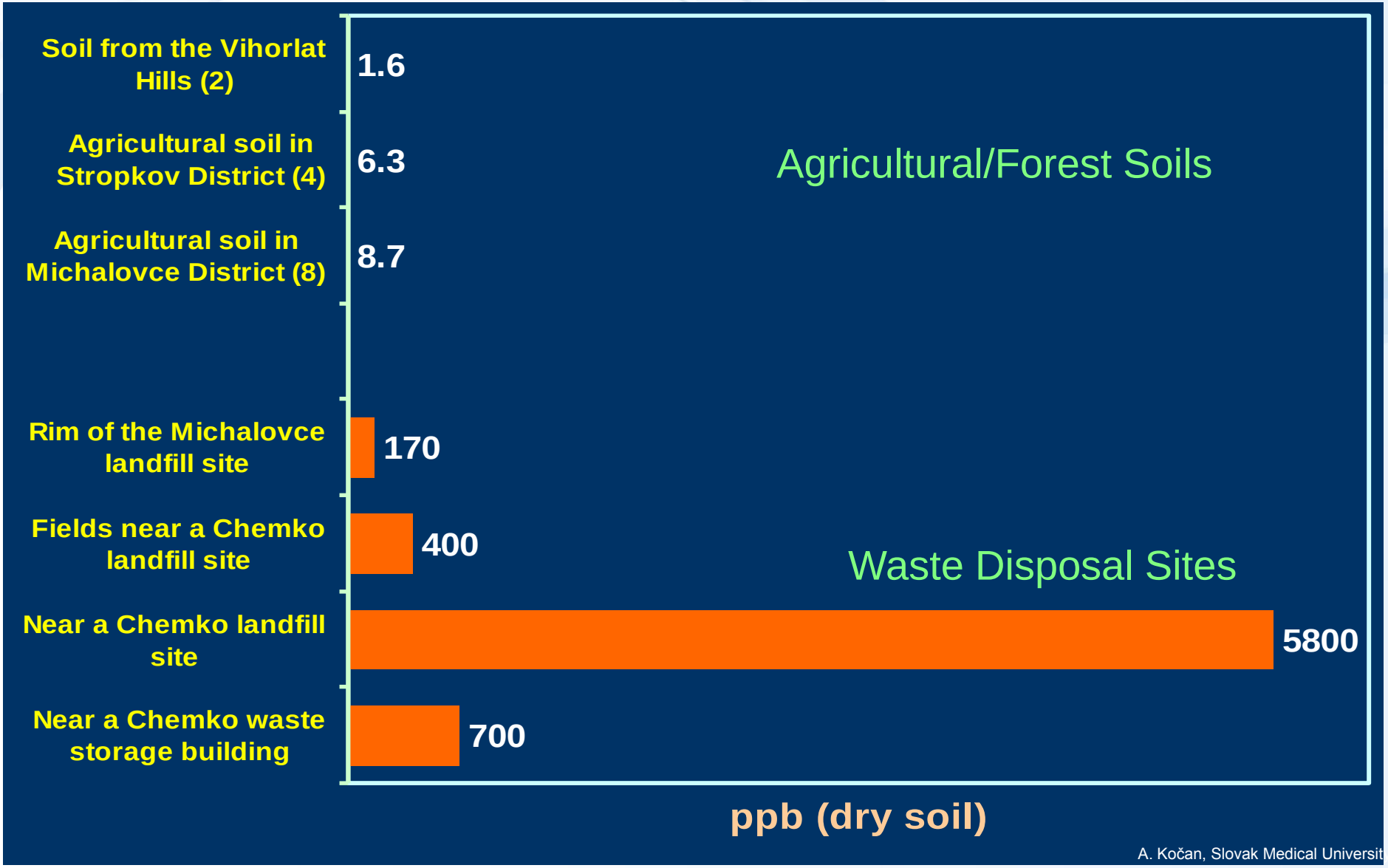
Michalovce (polluted district) vs Stropkov (control district)



A. Kočan, Slovak Medical University

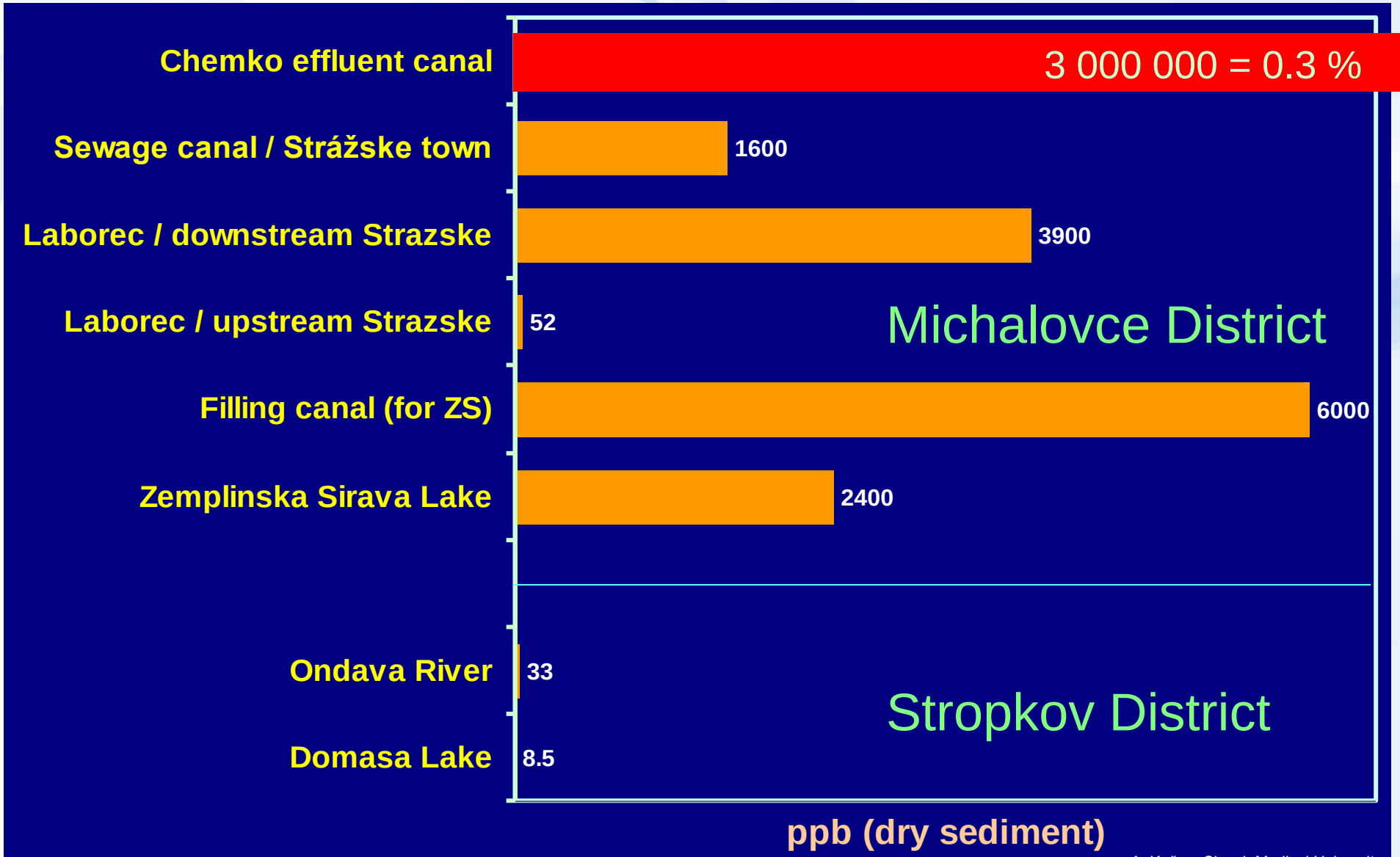
PCB Concentrations in Soil

Vicinity of Chemko disposal sites and agricultural fields



PCB Levels in Sediment Samples

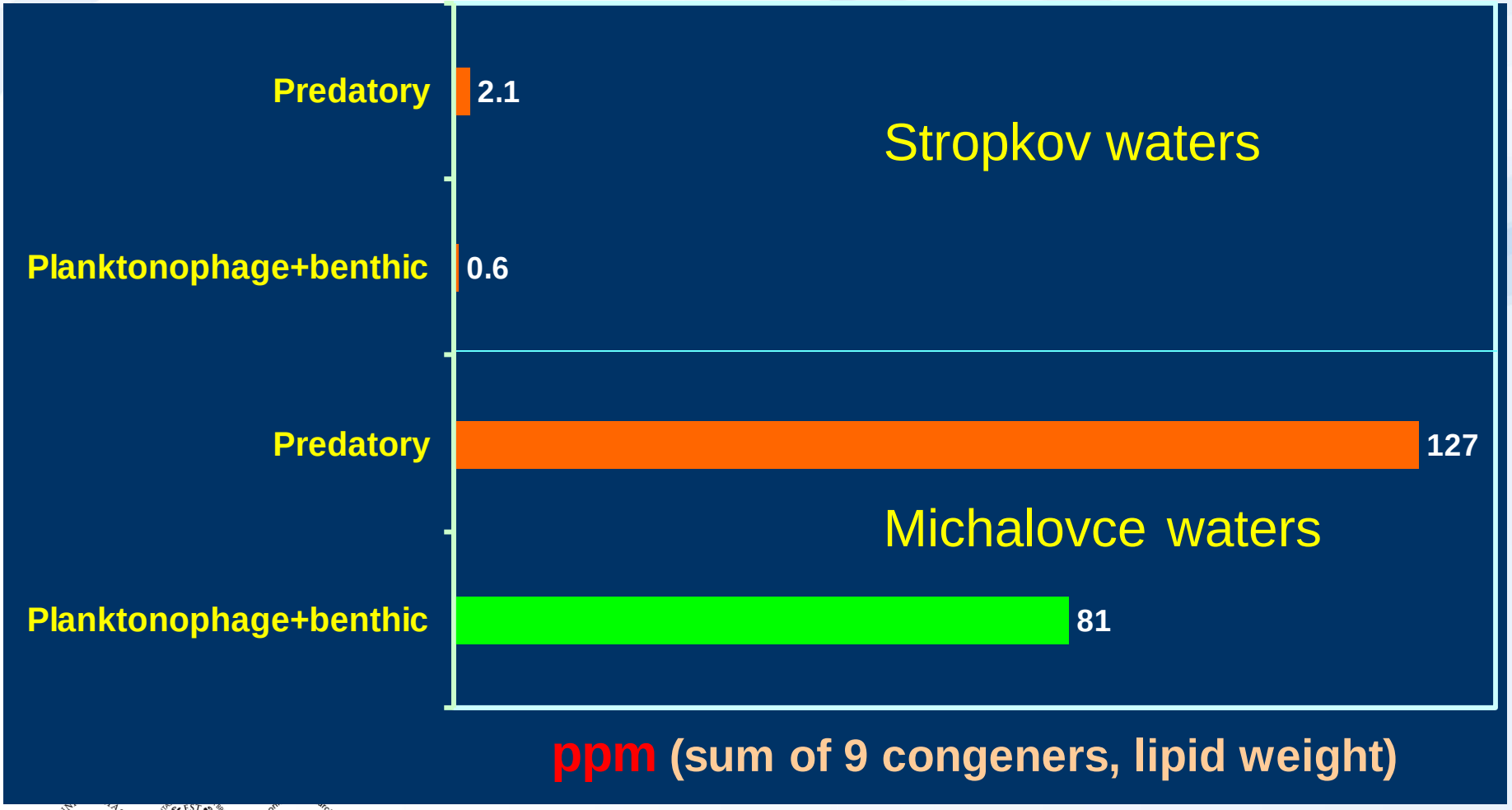
Michalovce (polluted district) vs Stropkov (control district)



A. Kočan, Slovak Medical University

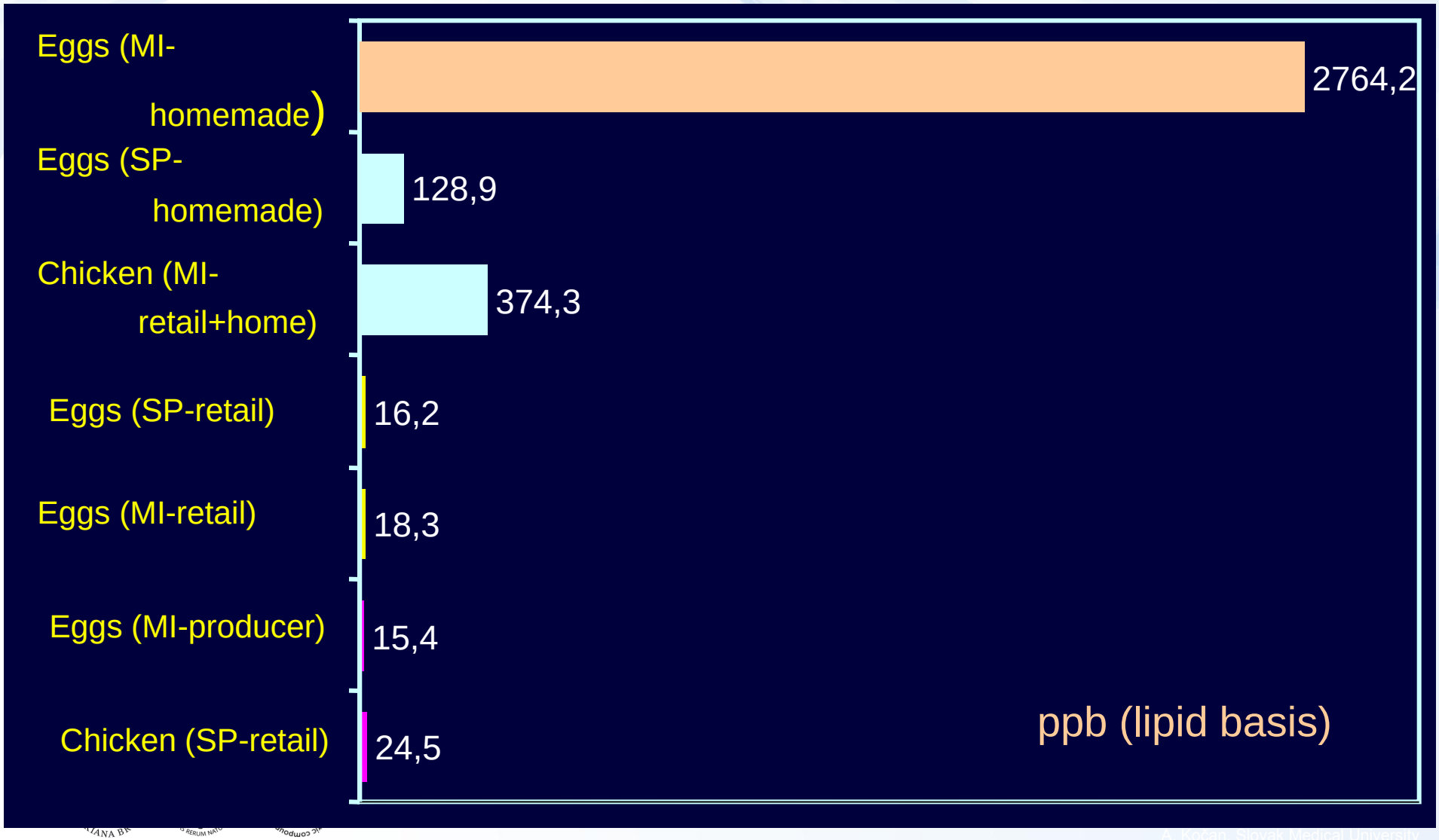
PCB Levels in Fish

Michalovce (polluted district) vs Stropkov (control district)

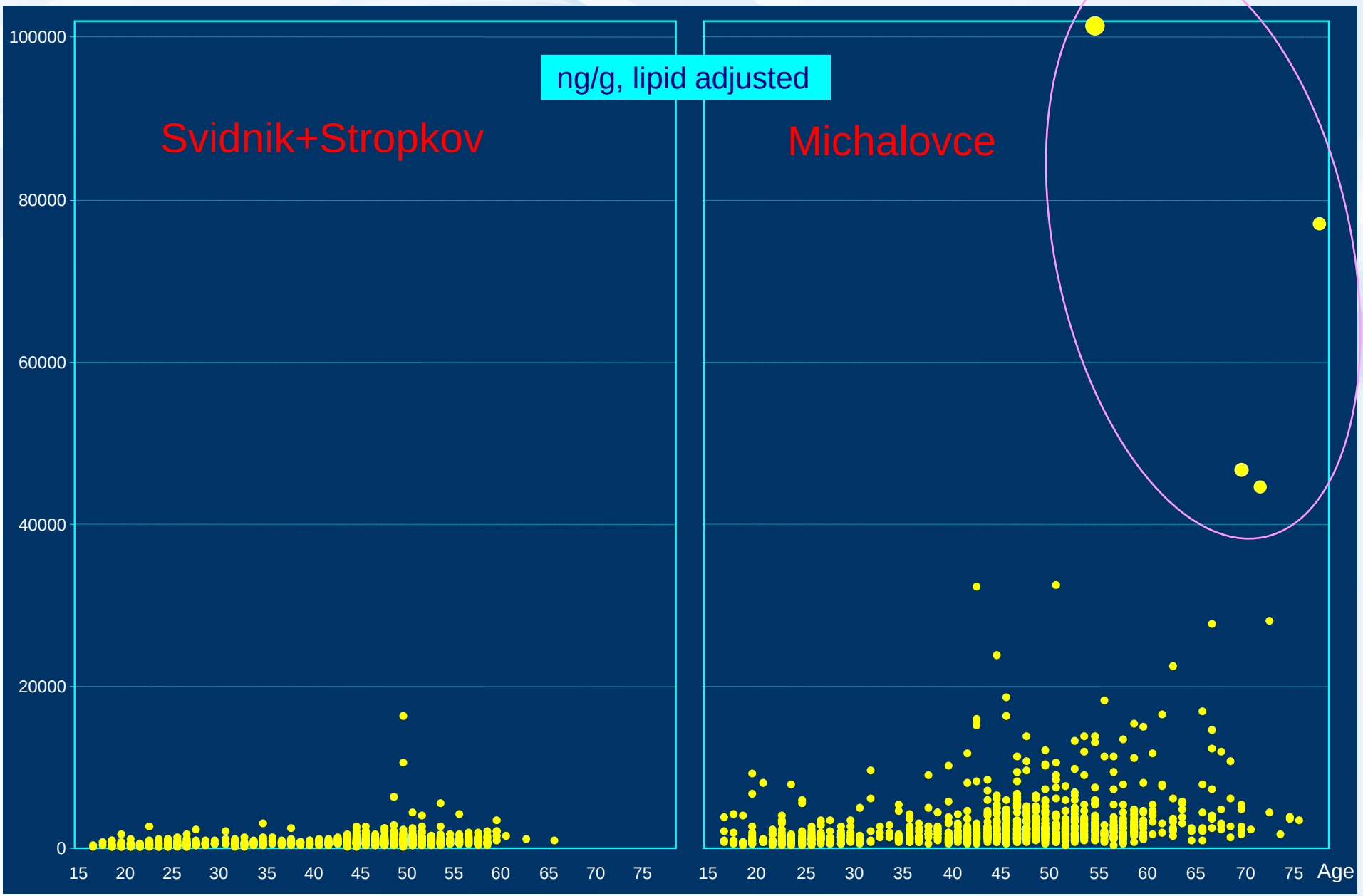


Average PCB Levels in Eggs and Chicken Collected in Michalovce and Stropkov Districts

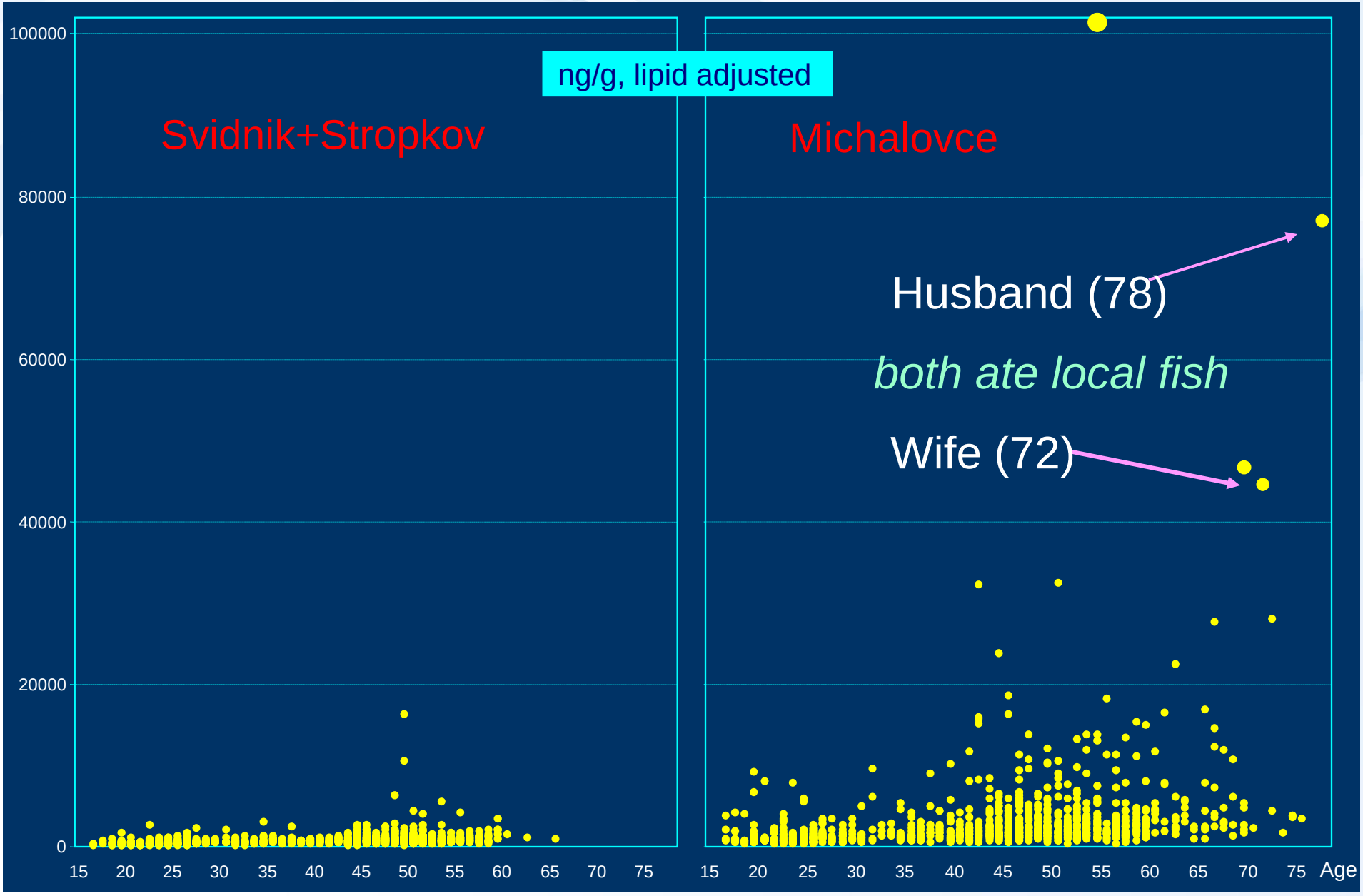
Sum of 28, 52, 101, 118, 138, 153, 156, 170 and 180 congeners



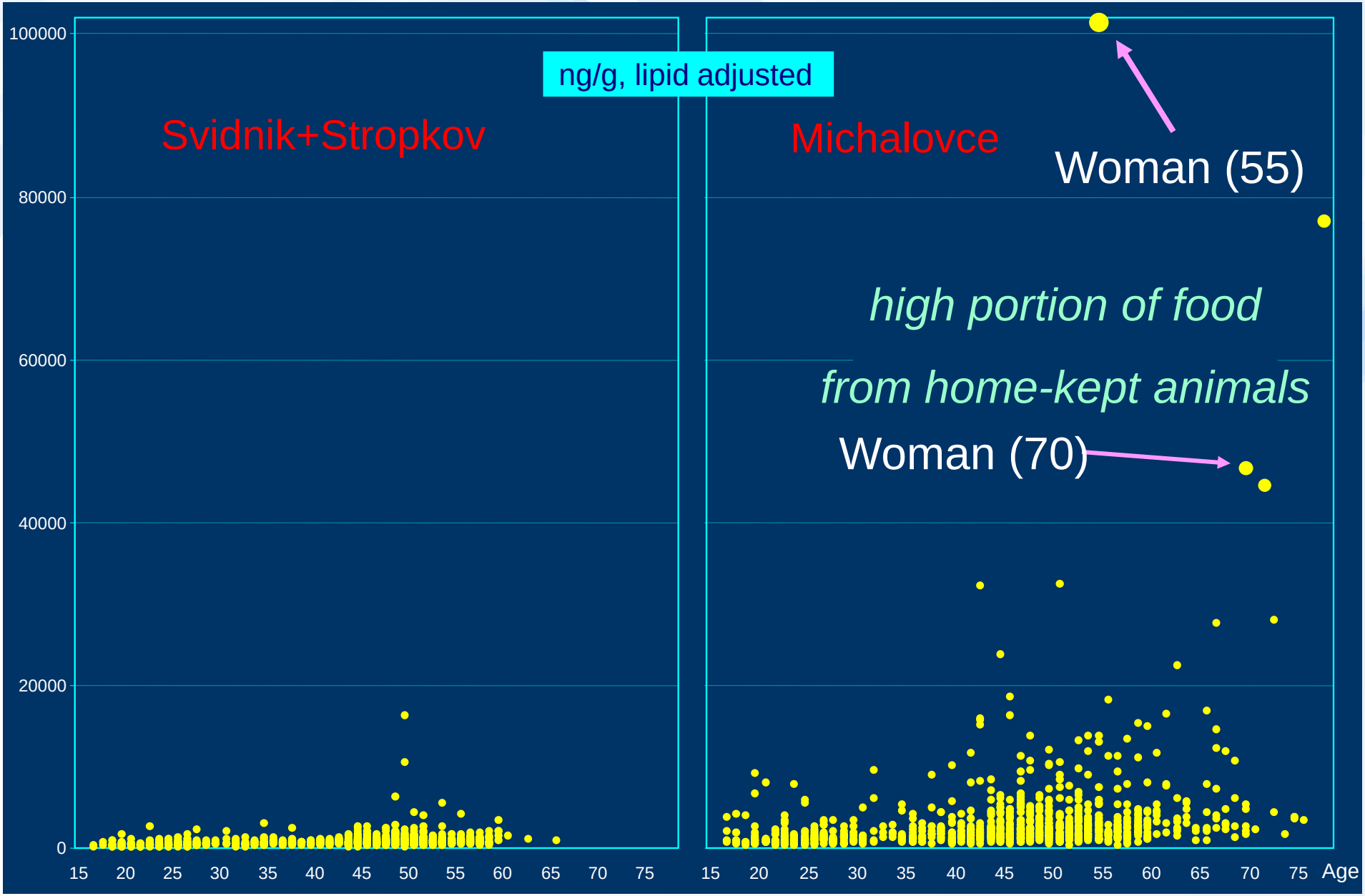
PCB Levels - Adults



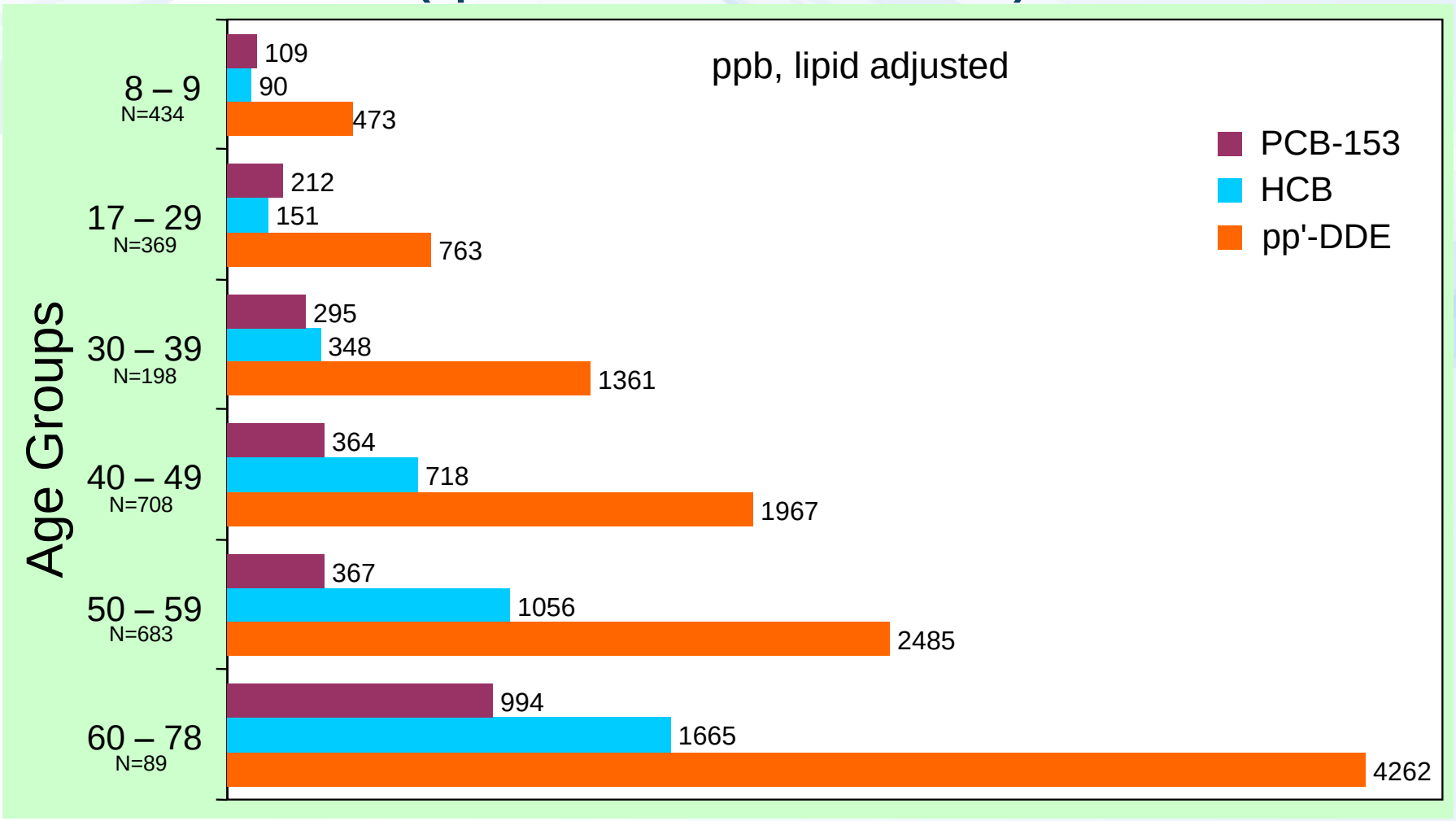
PCB Levels - Adults



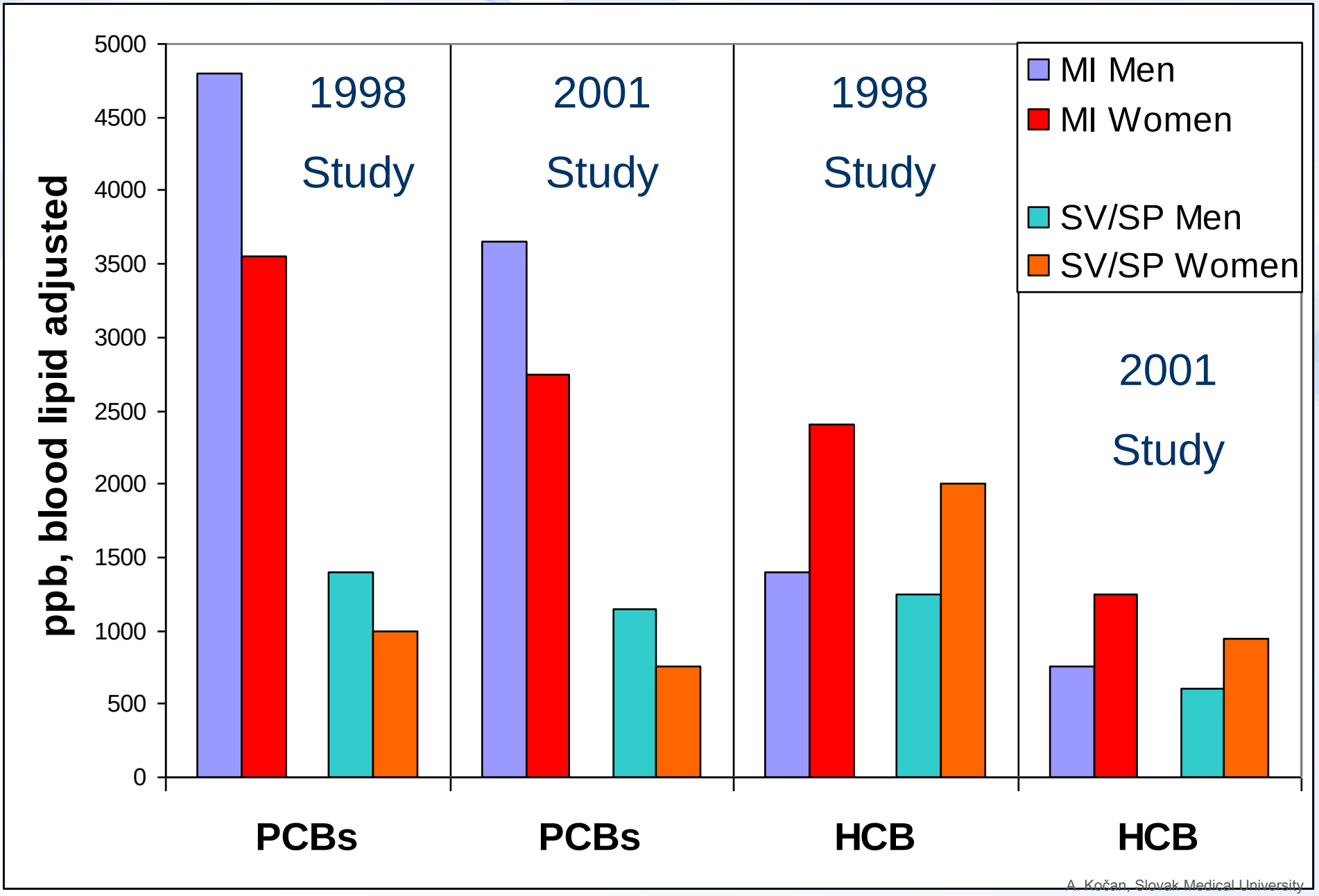
PCB Levels - Adults



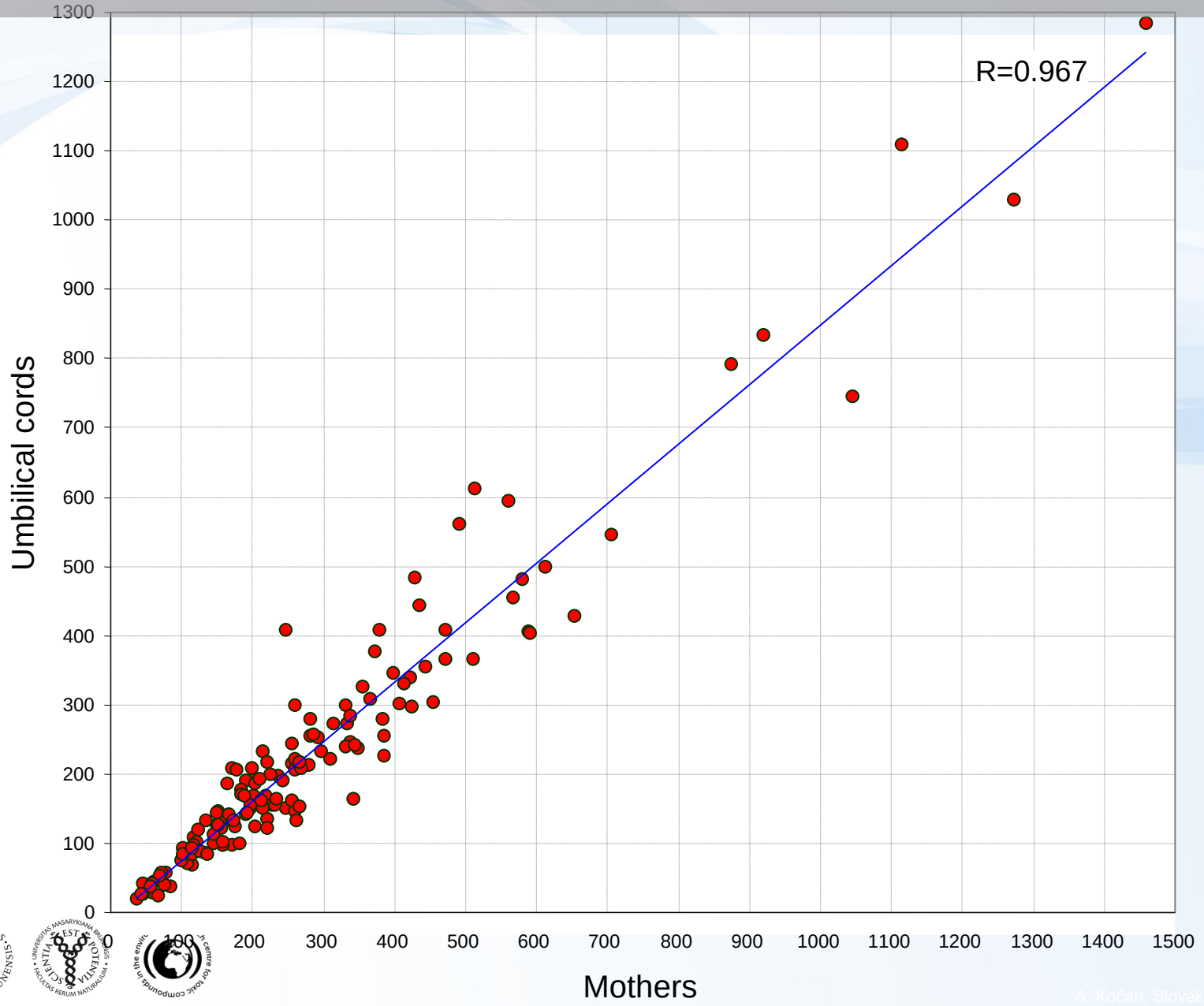
Median PCB-153, HCB, and p,p'-DDE levels in blood serum vs age groups (specimens collected in 2001)



Comparison of POP levels in men and women and time trends



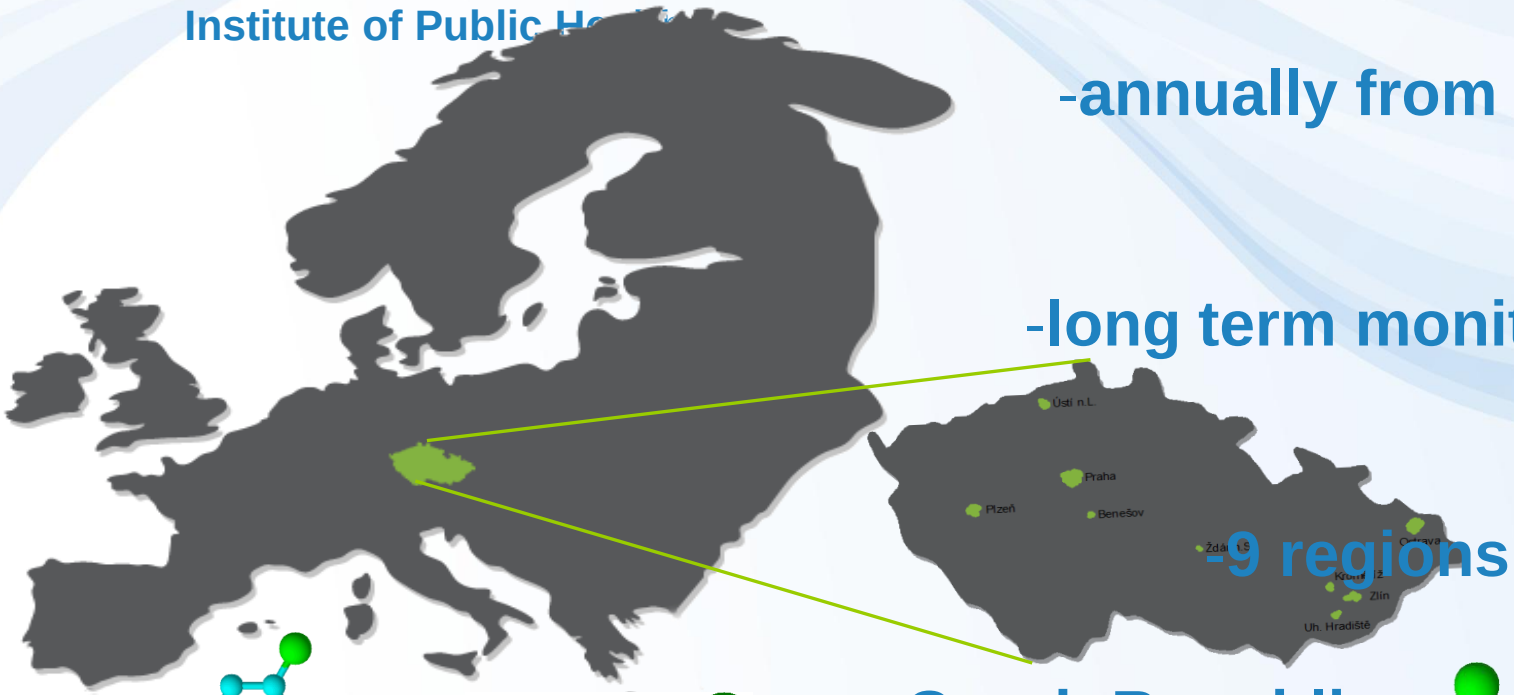
PCB-153 in blood serum from mothers and umbilical cords



POPs content in breast milk (Czech Republic)

- long term trends – background results for Central Europe

Monitoring sites map NIPH - National Institute of Public Health

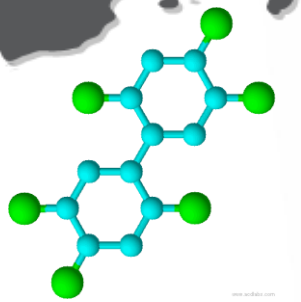


-annually from 1994

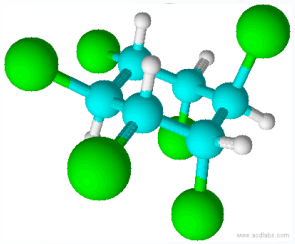
-long term monitoring

-9 regions

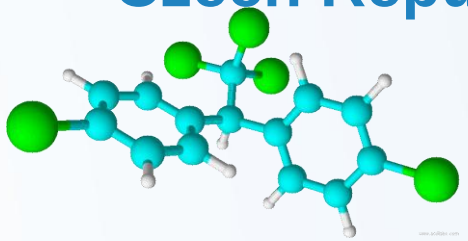
Czech Republic



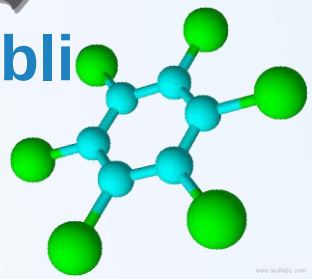
PCB 153



Gama-HCH



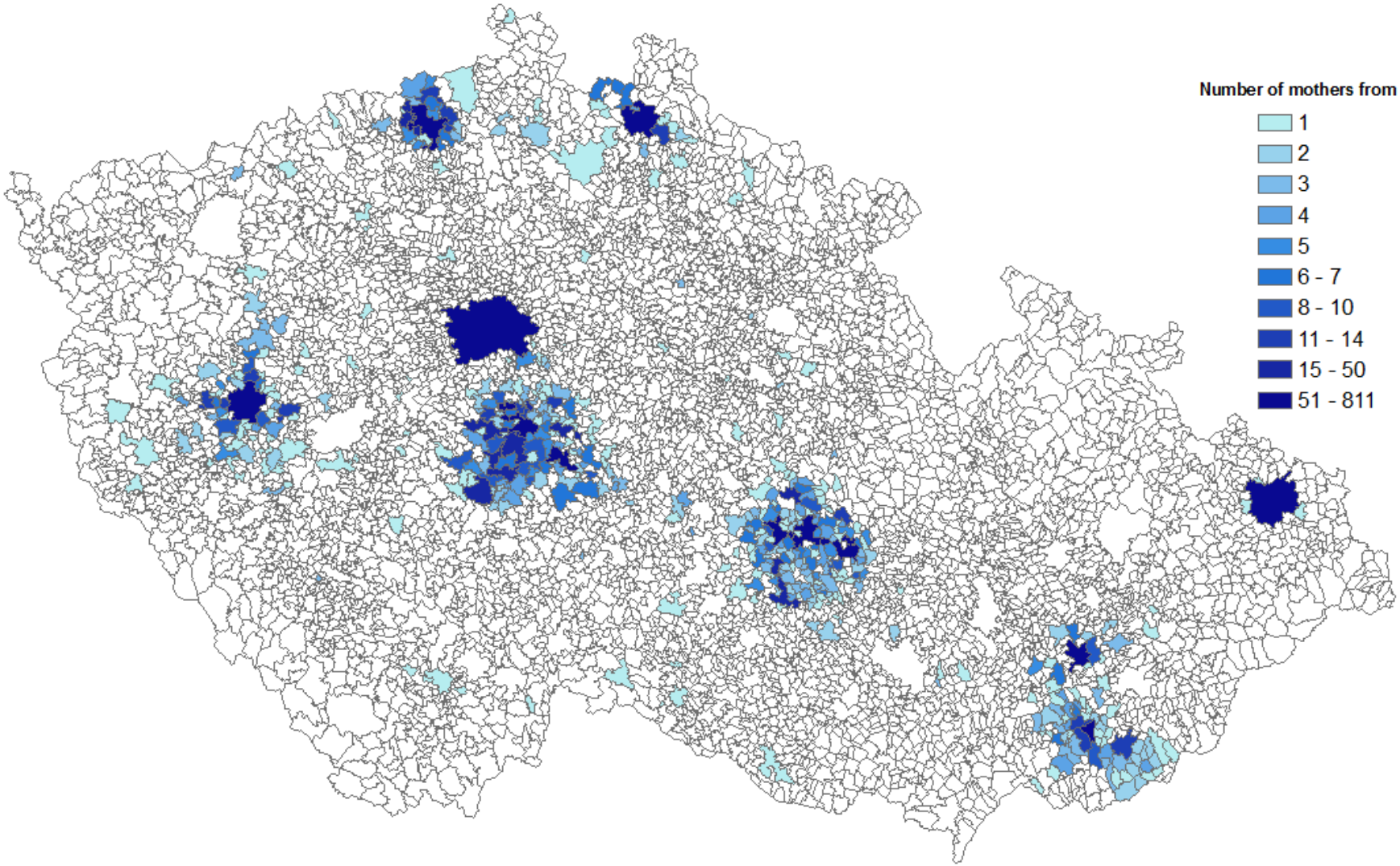
DDT



HCB

selected chlorinated pesticides

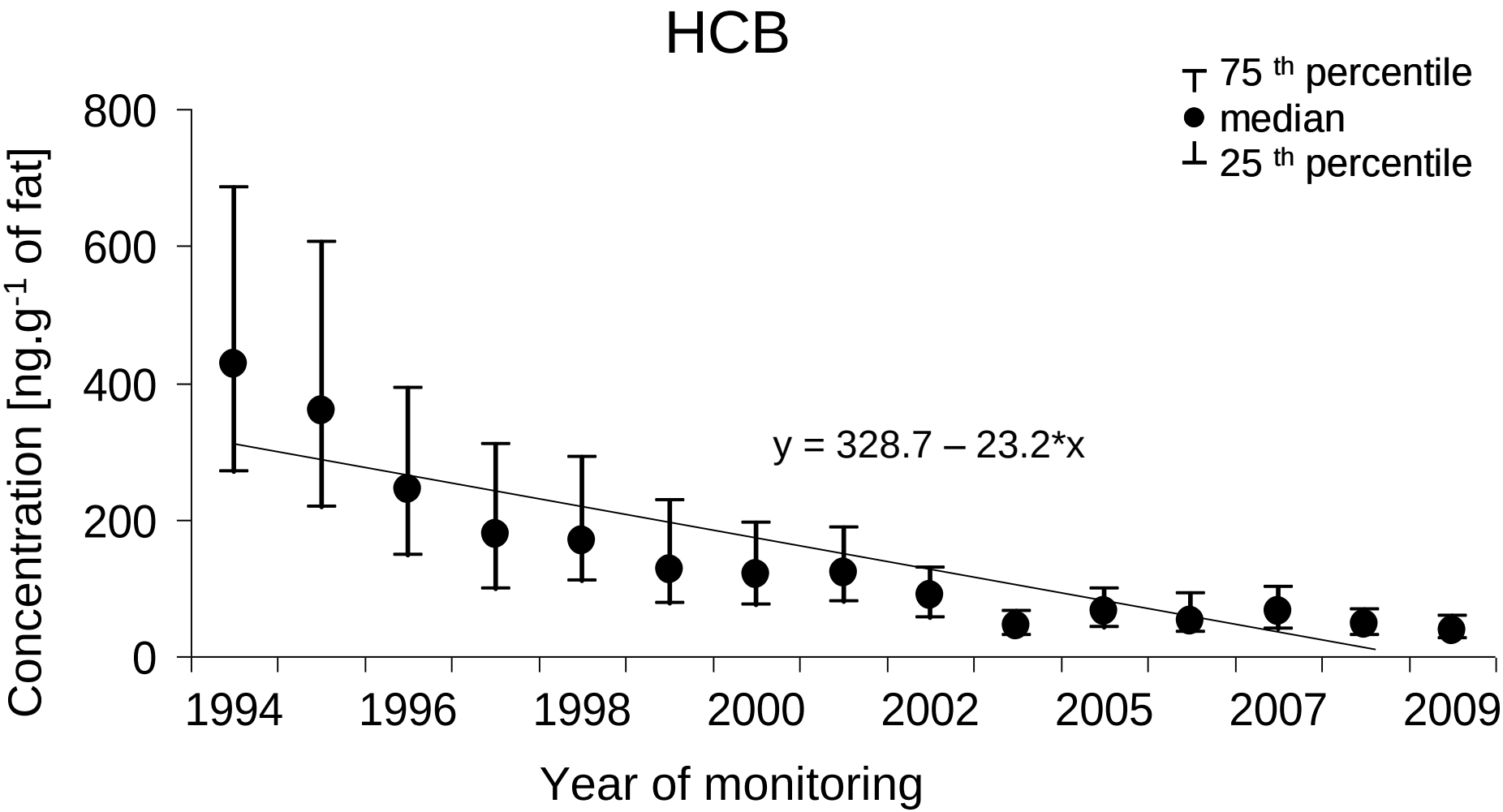
Breast Milk POPs
PCB28
PCB52
PCB101
PCB118
PCB138
PCB153
PCB180
HCB
alfaHCH
betaHCH
gamaHCH
DDT
DDE
DDD

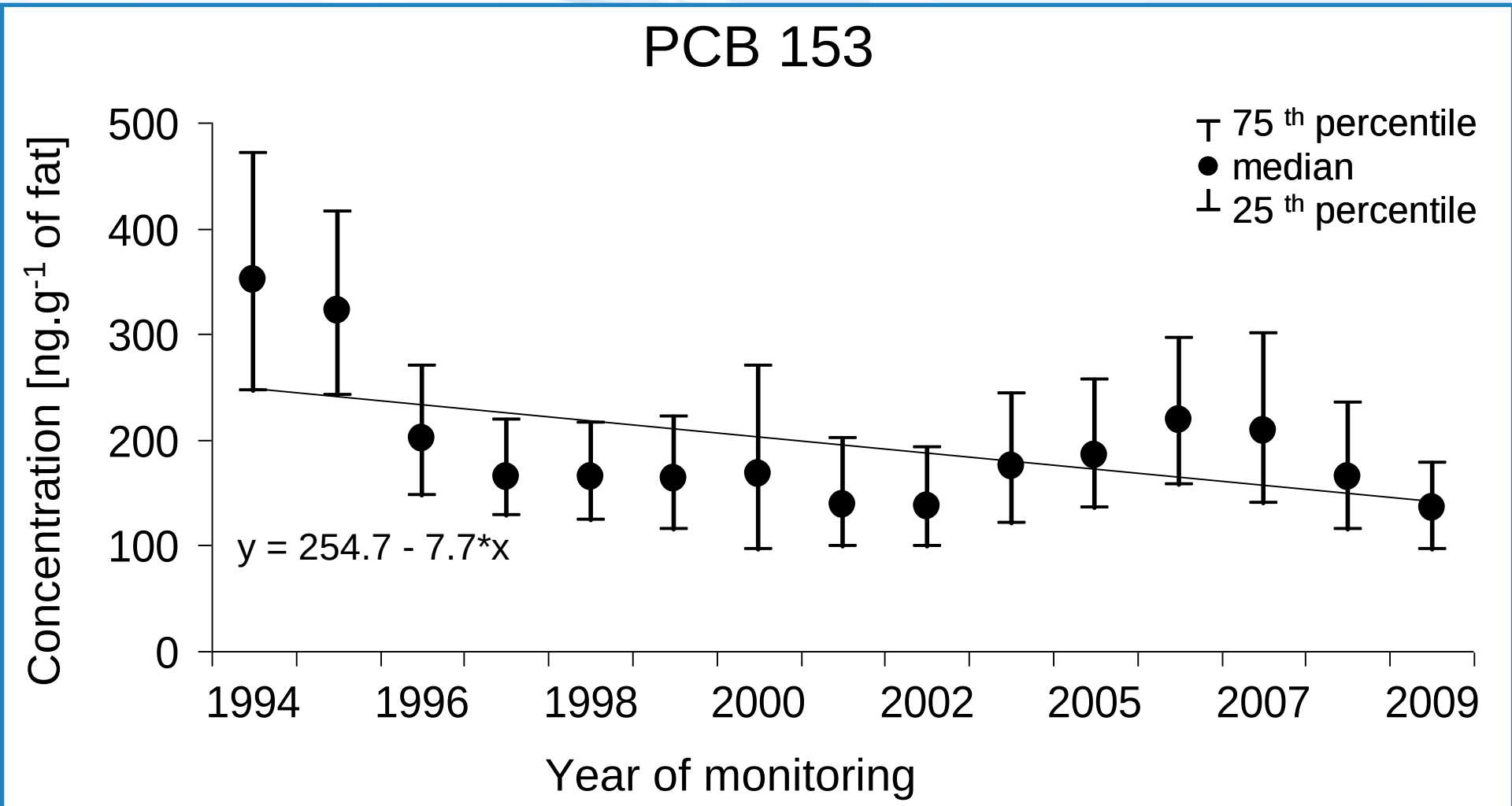


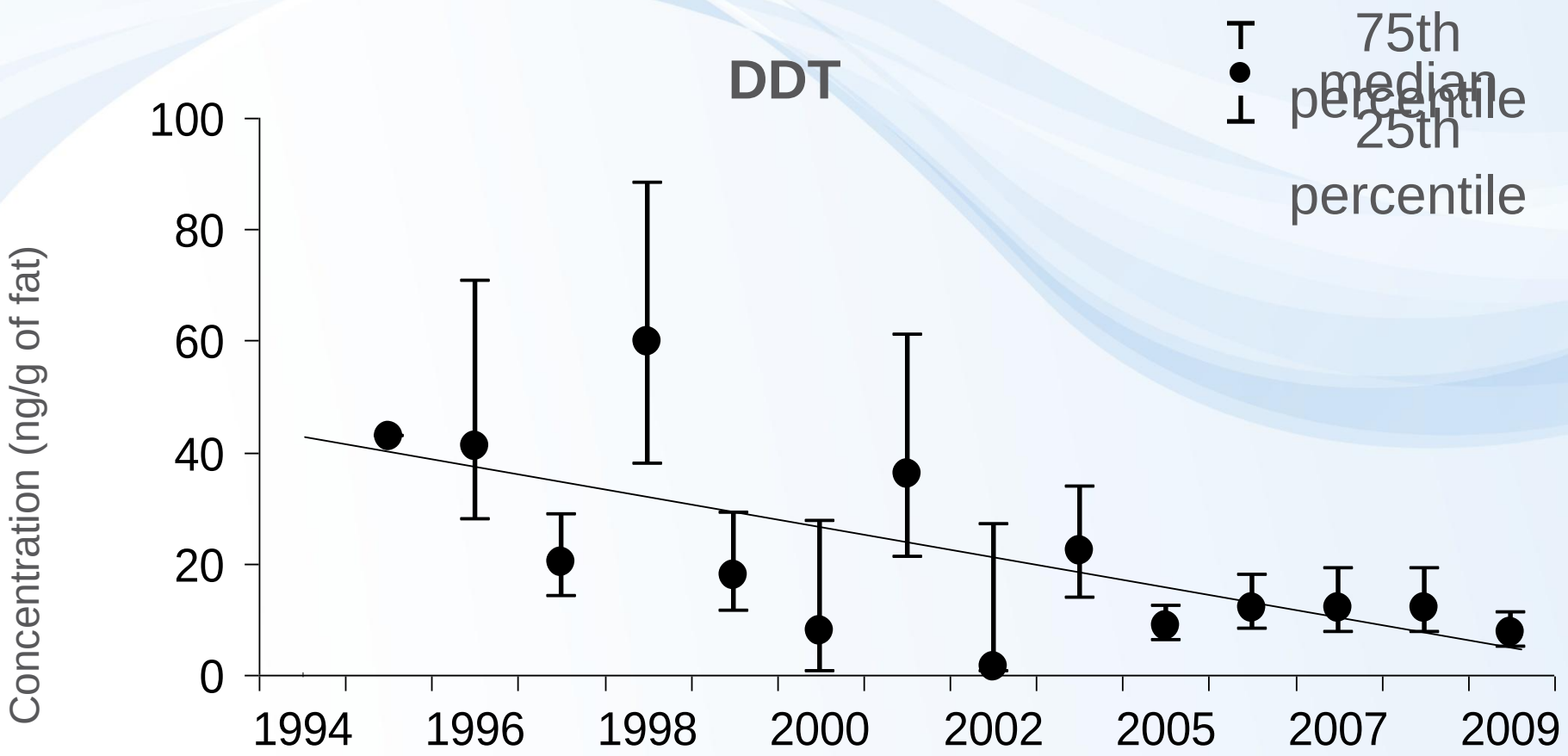
4700 samples

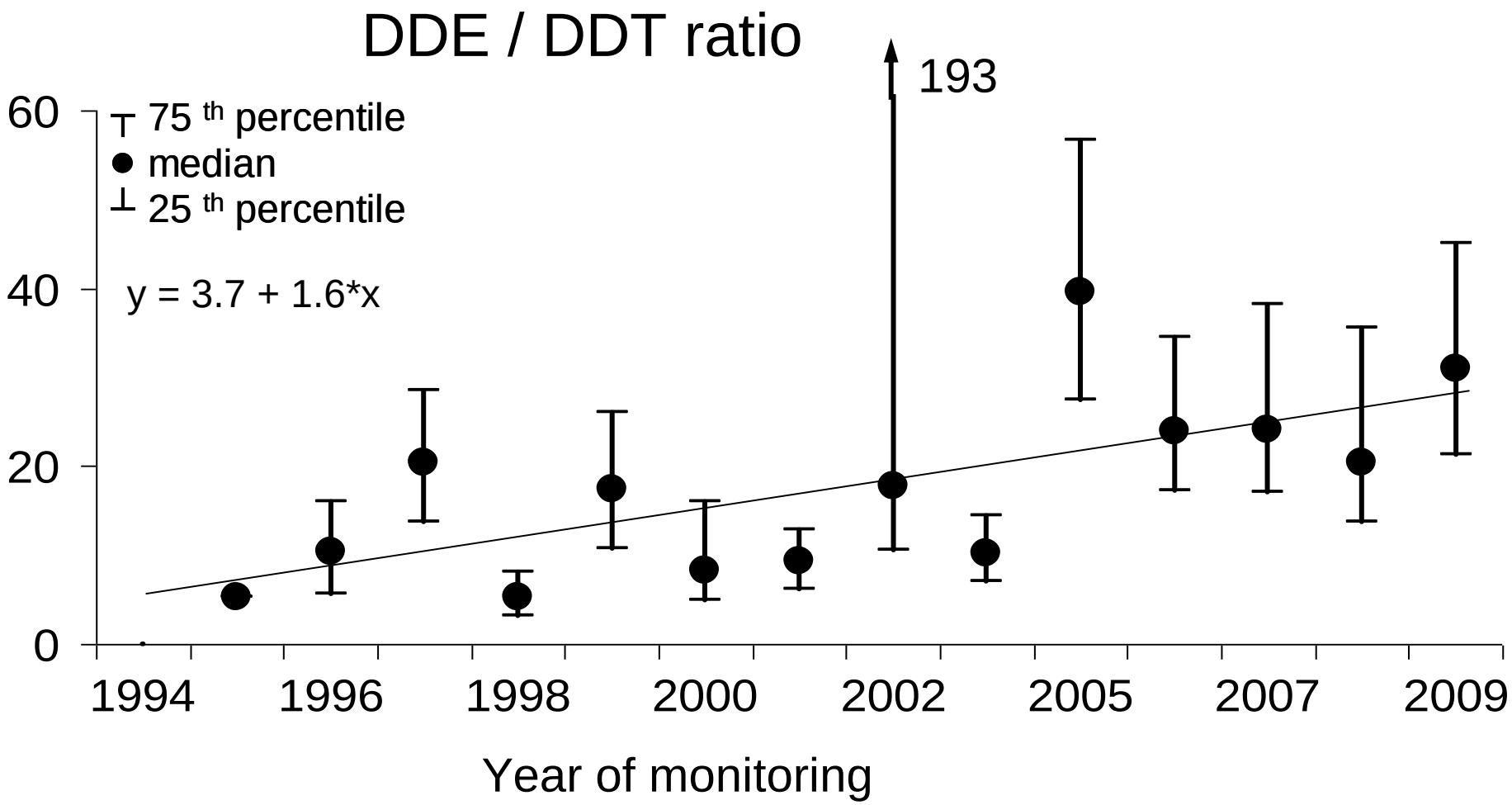
HCB long-term trends

- POPs content in breast milk (Czech Republic)

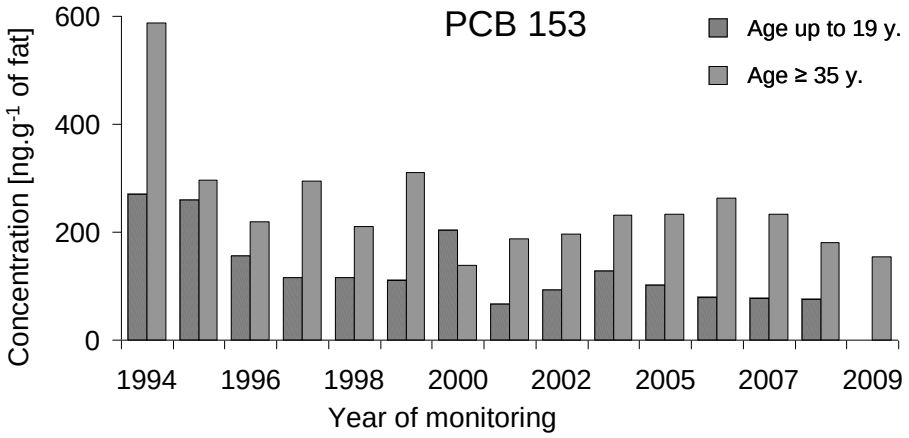


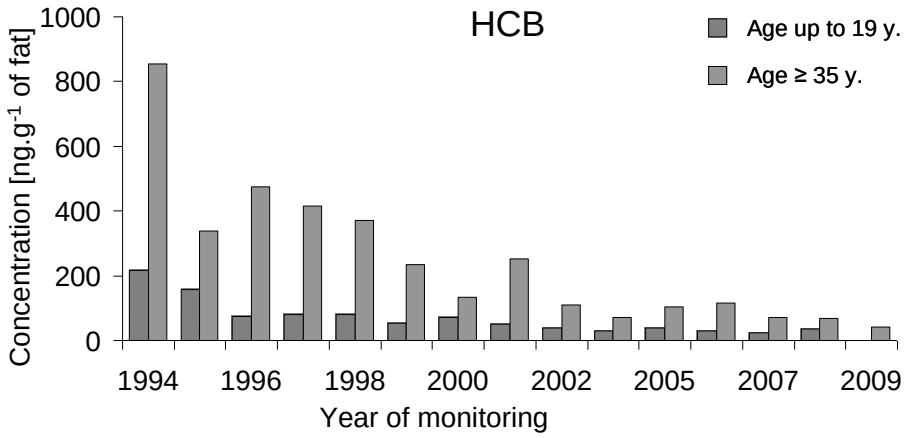

PCB 153
Concentration [ng.g-1 of fat]
500
400
300
200
100
0
75 th percentile
median
25 th percentile
y = 254.7 - 7.7*x
1994
1996
1998
2000
2002
2005
2007
2009
Year of monitoring


DDT
75th percentile
median
25th percentile
Concentration (ng/g of fat)
100
80
60
40
20
0
1994
1996
1998
2000
2002
2005
2007
2009

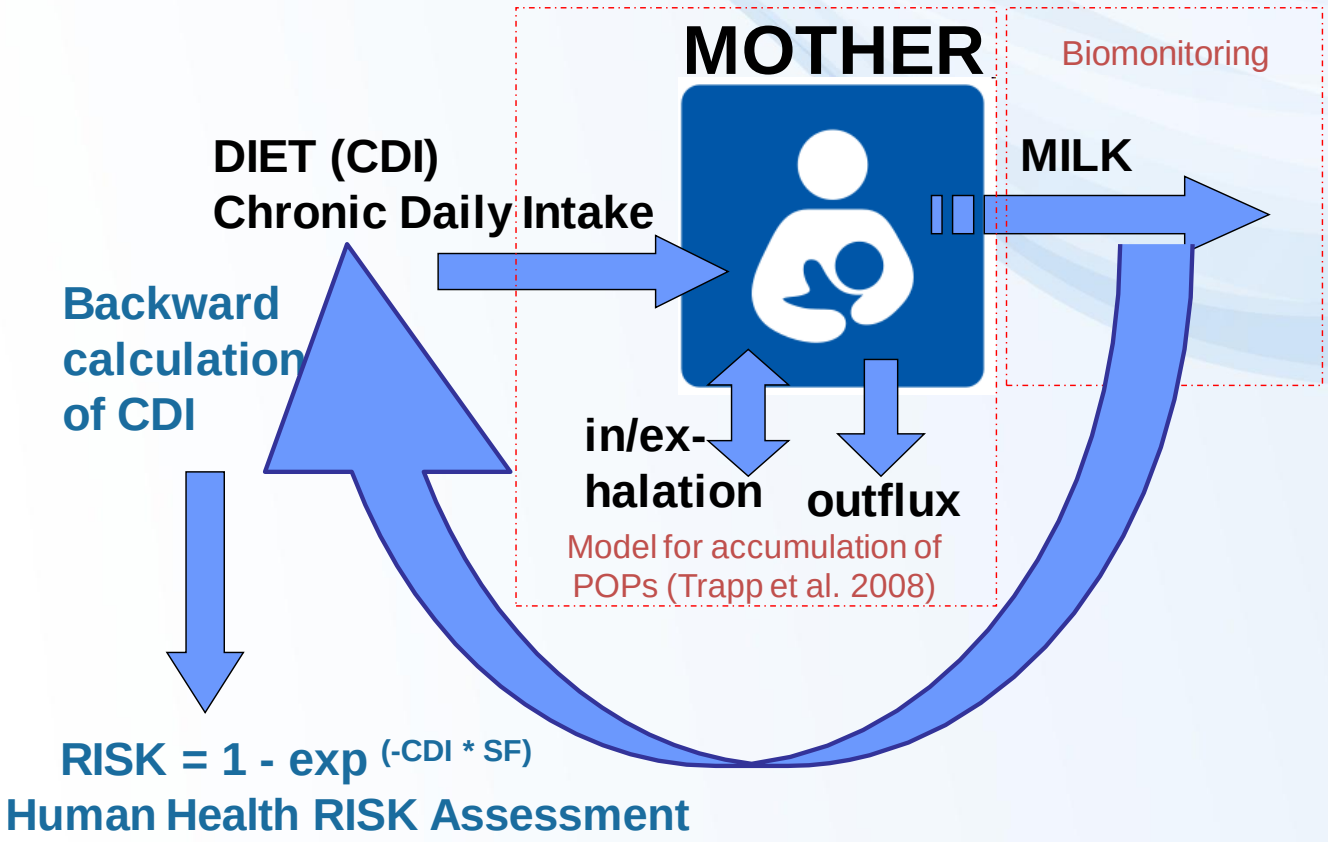

DDE / DDT ratio
193
75 th percentile
median
25 th percentile
y = 3.7 + 1.6*x
60
40
20
0
1994
1996
1998
2000
2002
2005
2007
2009
Year of monitoring

Age specific comparisonfor the oldest and youngest mothers



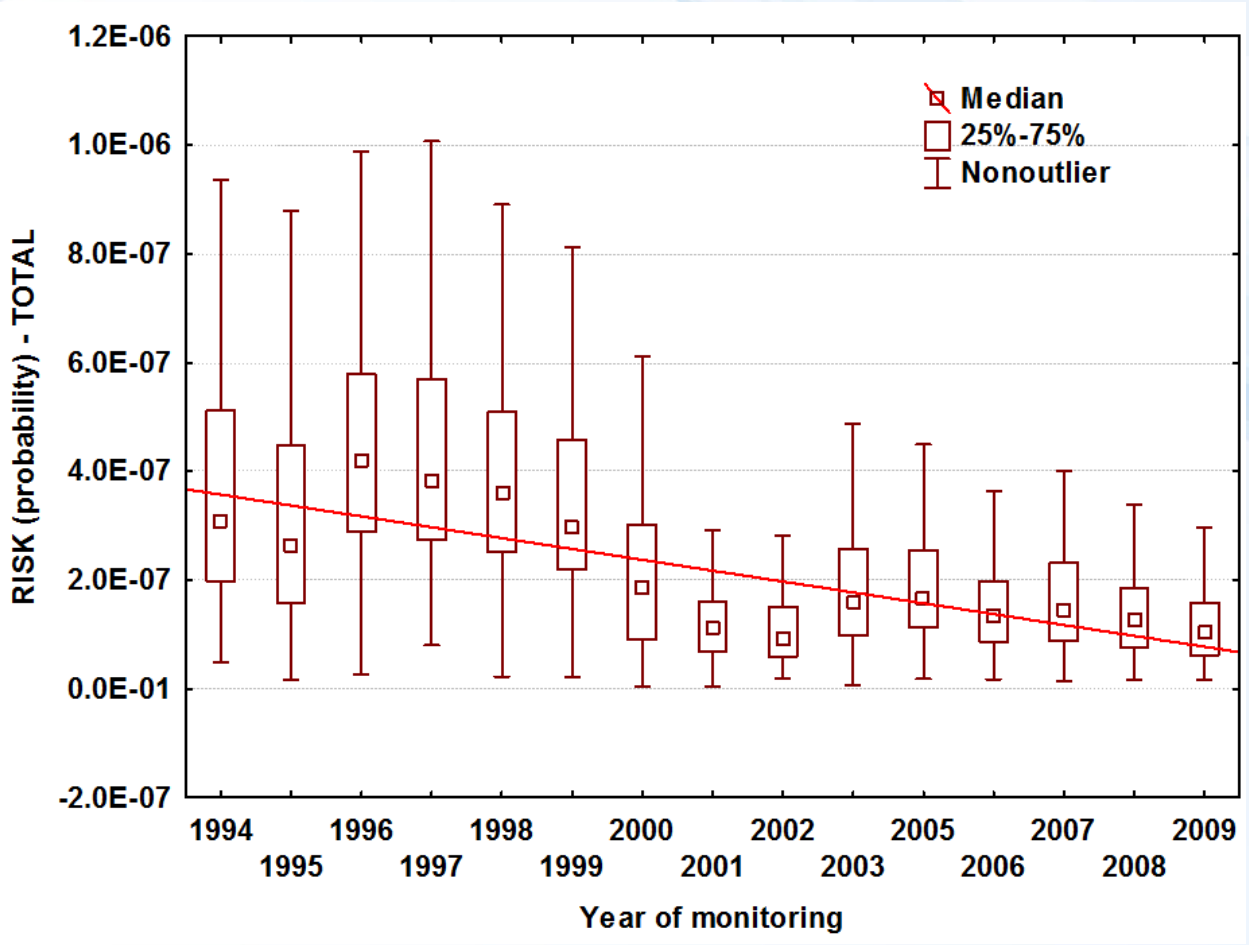


APPLICATION FOR HUMAN HEALTH RISK ASSESSMENT



APPLICATION FOR HUMAN HEALTH RISK

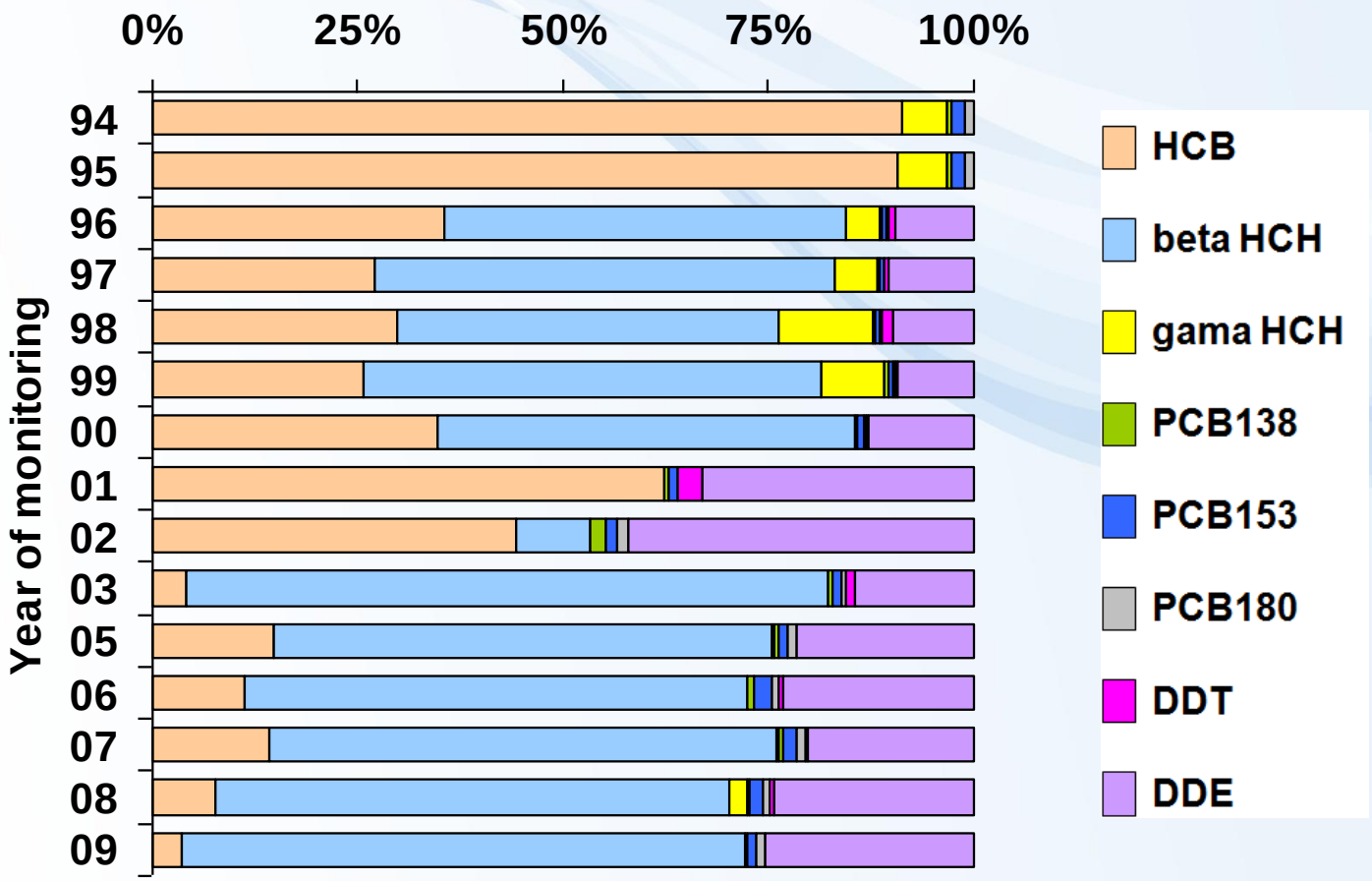
Čupr et. al 2013: (in preparation/unpublished) LONG-TERM TRENDS OF POPs IN HUMAN MILK IN CZECH REPUBLIC & APPLICATION FOR HUMAN HEALTH RISK ASSESSMENT



Total RISK sum for all chlorinated chemicals (probability).

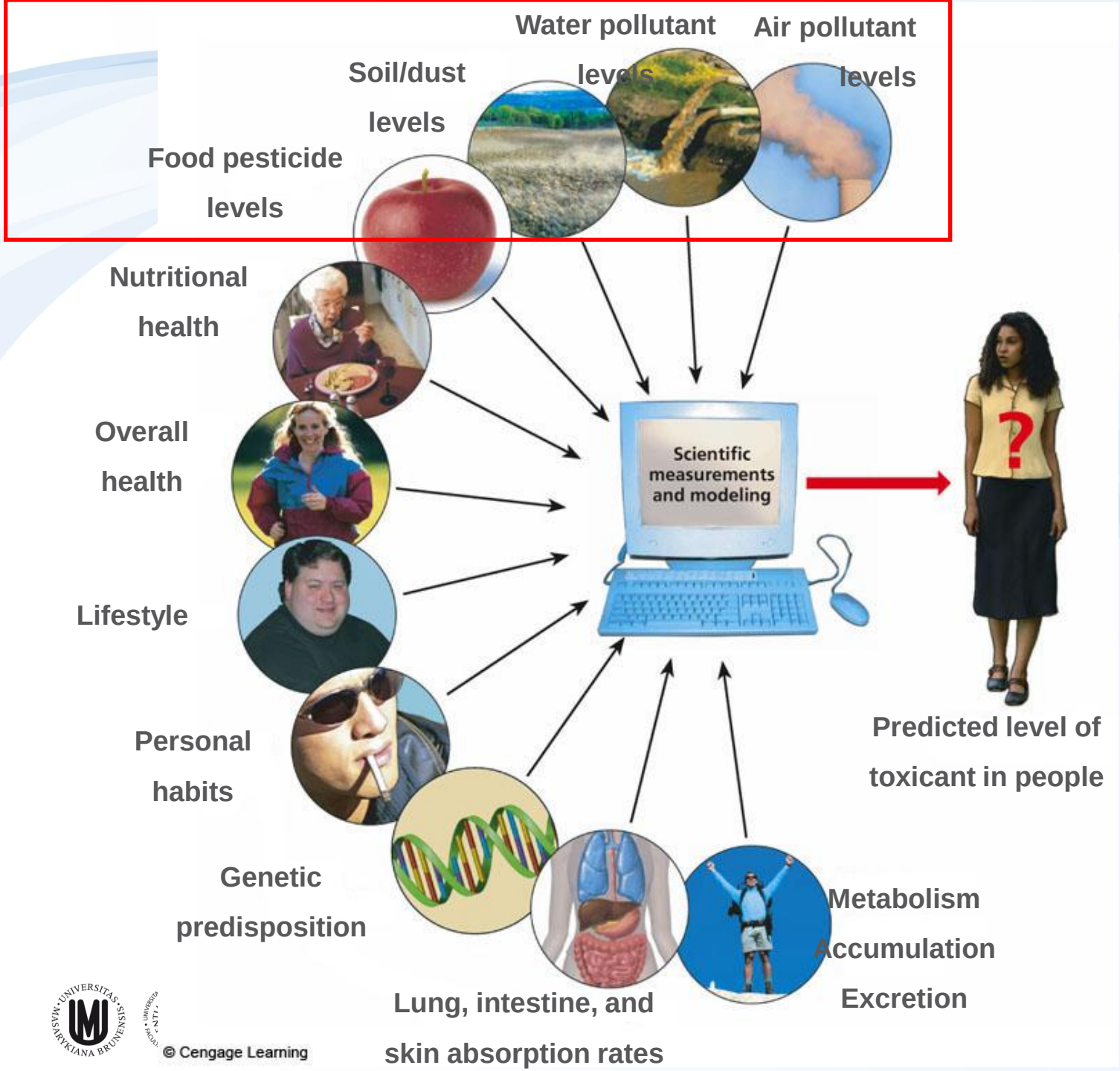
APPLICATION FOR HUMAN HEALTH RISK

Čupr et. al 2013: (in preparation/unpublished) LONG-TERM TRENDS OF POPs IN HUMAN MILK IN CZECH REPUBLIC & APPLICATION FOR HUMAN HEALTH RISK ASSESSMENT



Contribution of individual POPs to total risk.

This presented new method for Human Health Risk Assessment of breast-feeding mother is useful tool for results interpretation of long-term biomonitoring



GENASIS portal

Selection of the analytical tool

Menu options

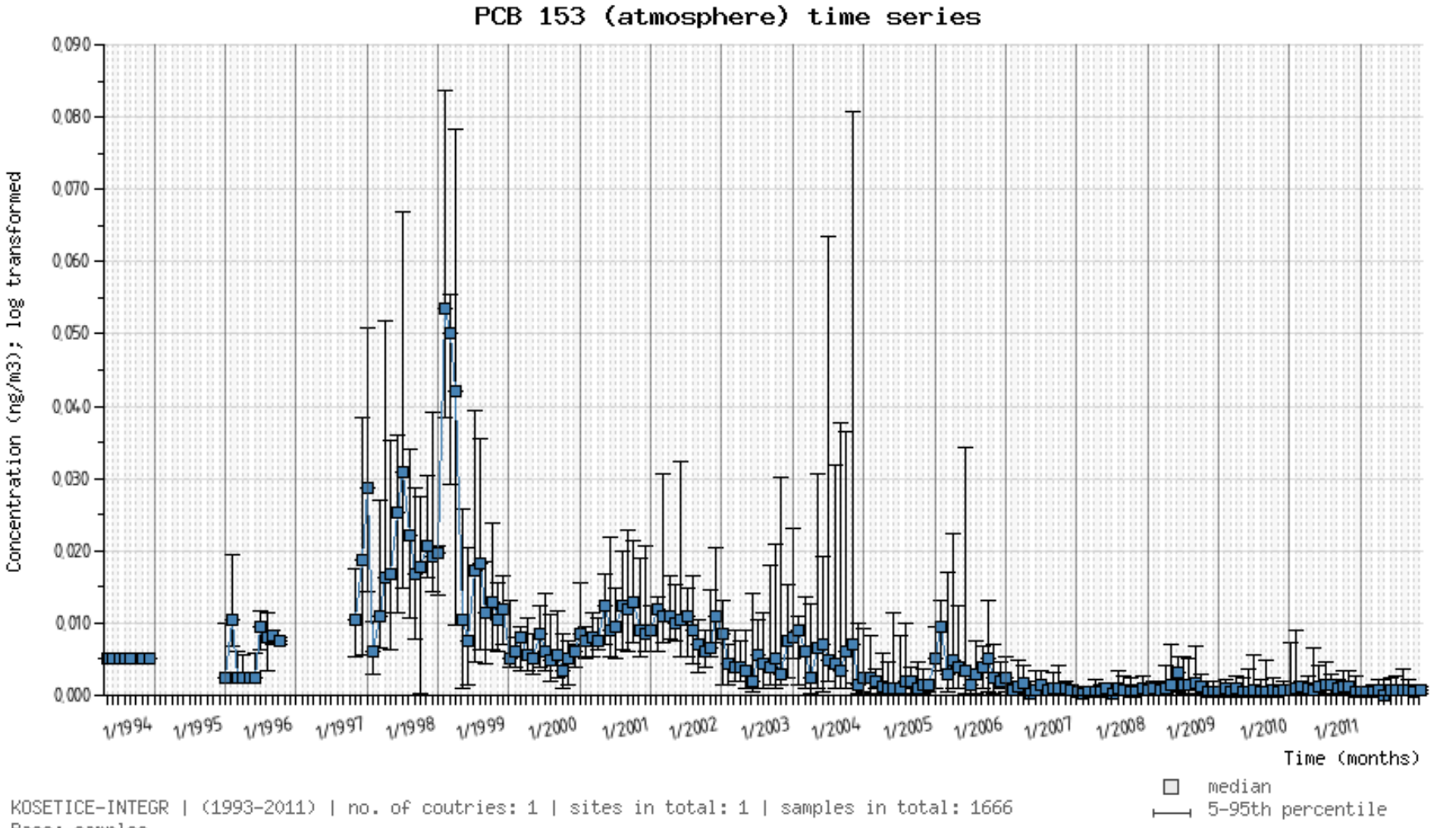
Description of project aims and importance

Survey of data sources

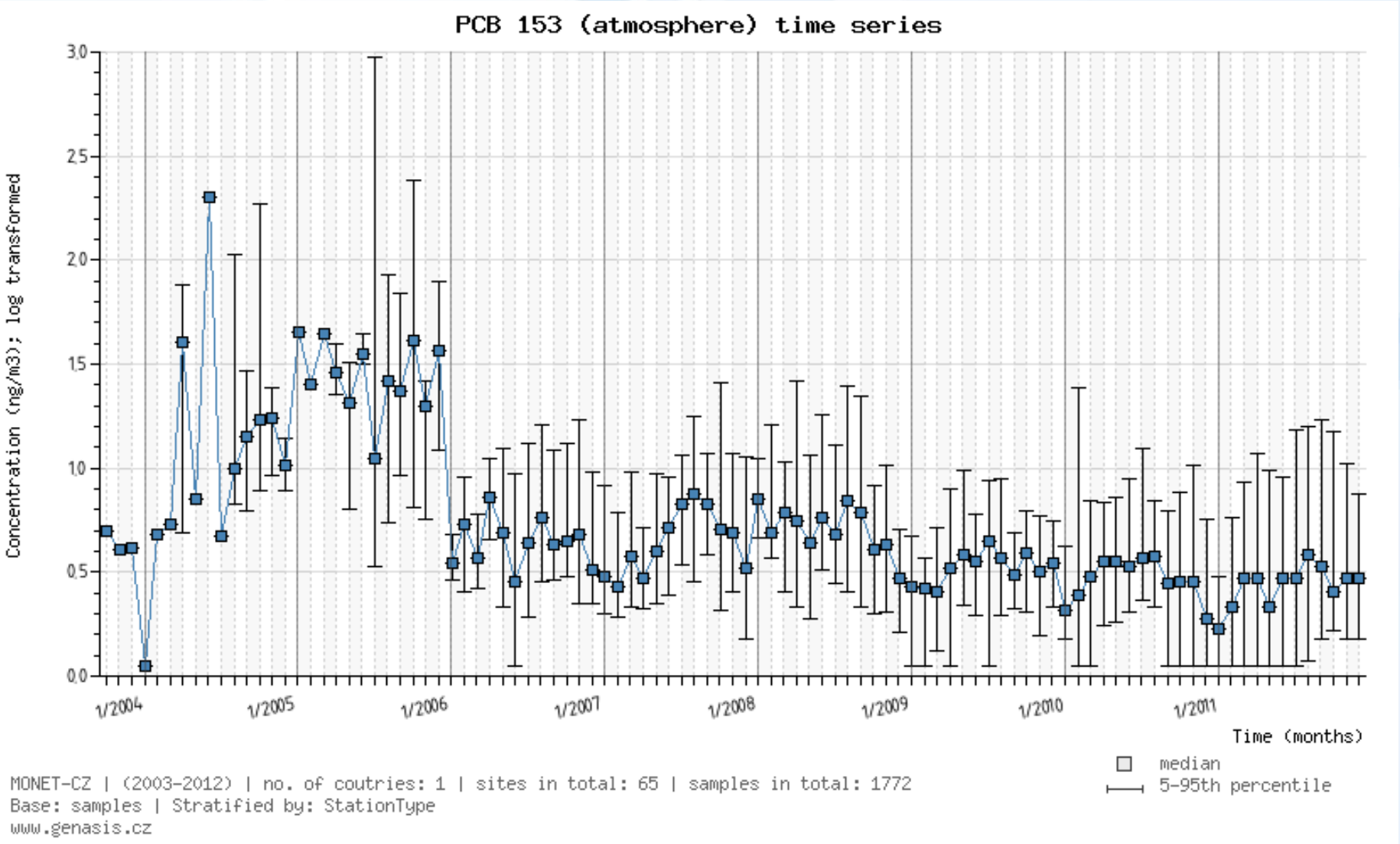
- User-friendly access to main system functions
  - Main functions are directly accessible from the title page:
    - Analytical tools
      - With selection of the tool, the user runs software window and selects data for the appropriate analysis.
      - There are exceptions: 1) tool of Box models, where the Czech Republic box model window is opened directly and 2) module comparing substances.
    - Survey of data sources – opens table and map survey of all data sources.
    - Menu – access to all system functions.
    - Project aims – access to the detailed description of the project
  - Other options
    - CZ/ENG language switch
    - RSS channel with news

www.genasis.cz

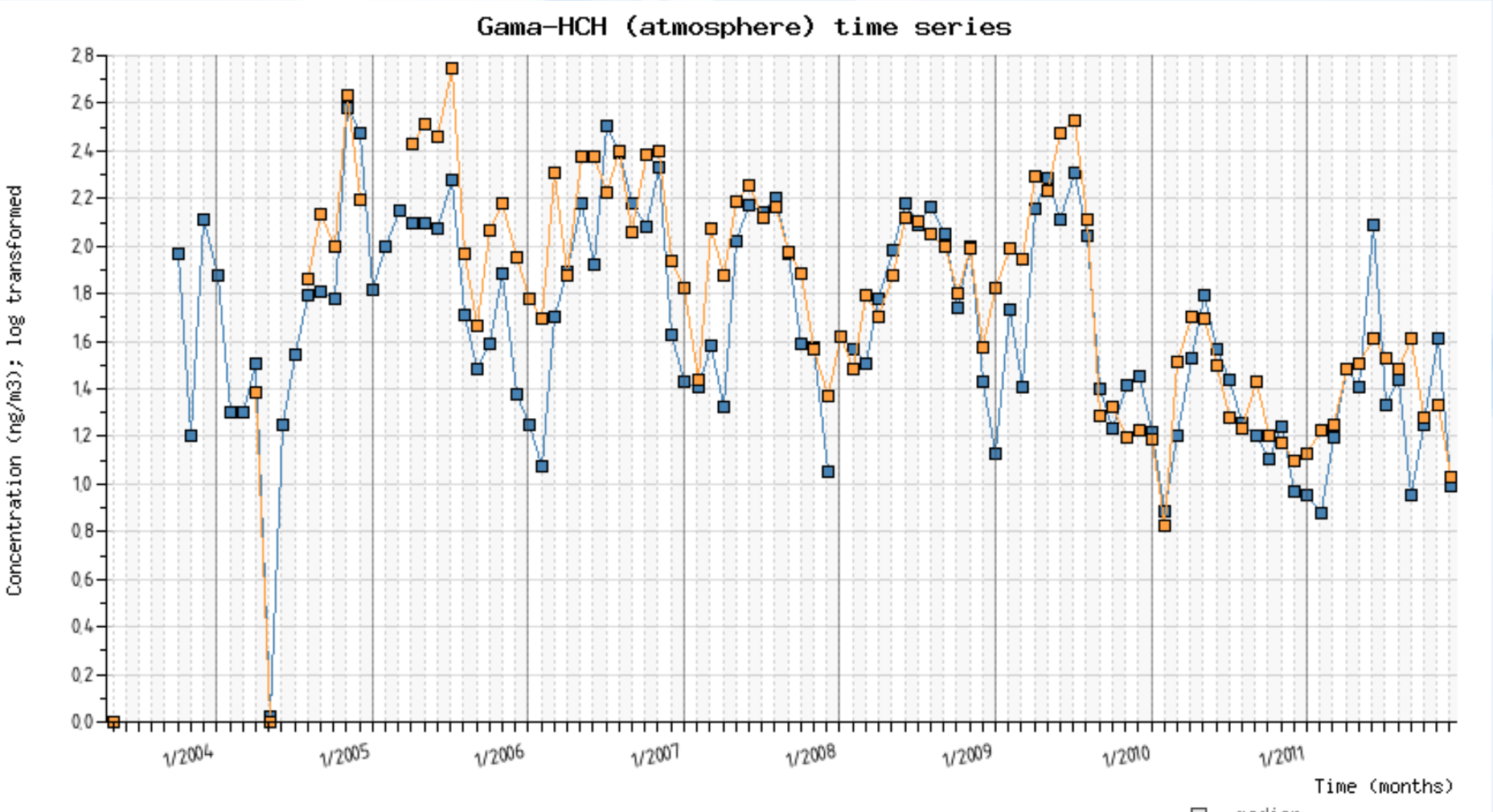
Time series, sumary



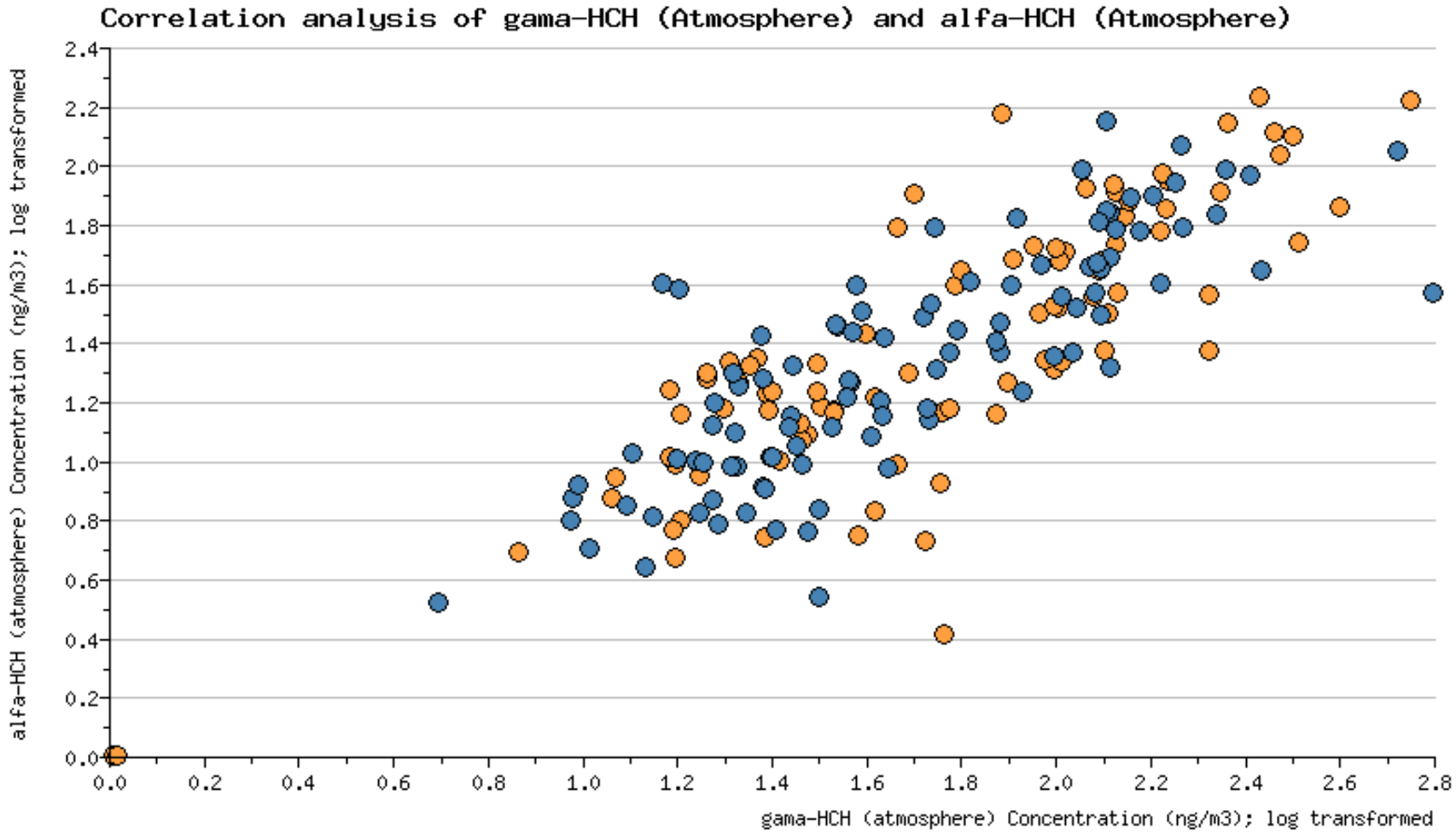
MONET CZ time series, summary



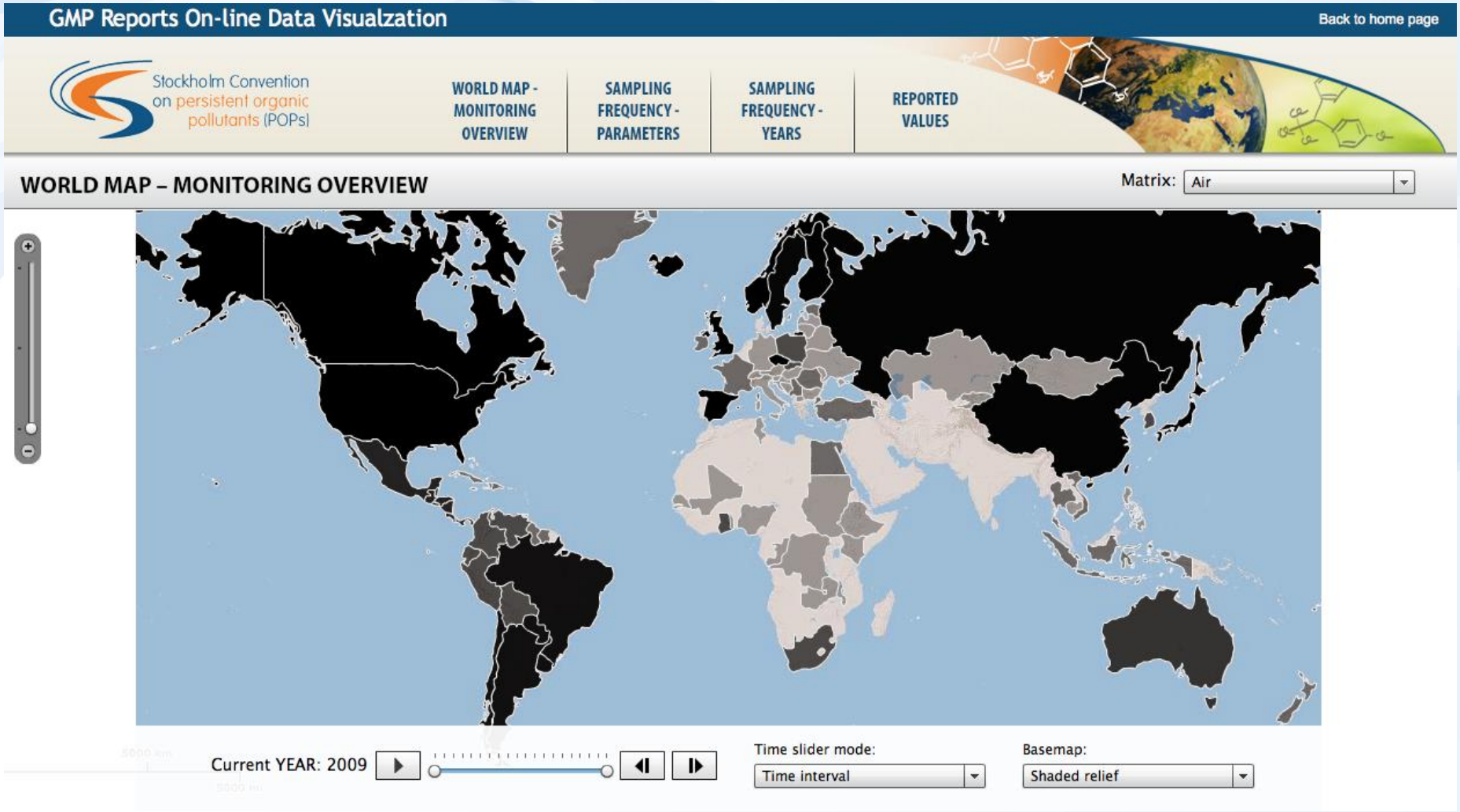
MONET EUROPE (APOPSBAL, CZ, CEE, EU)



MONET EUROPE (APOPSBAL, CZ, CEE, EU)



APOPSBAL, MONET-CEEC, MONET-CZ, MONET-EU | (2003-2012) | no. of coutries: 30 | sites in total: 130 | samples in total: 3132
Base: samples | Stratified by: SettlementType
www.genasis.cz

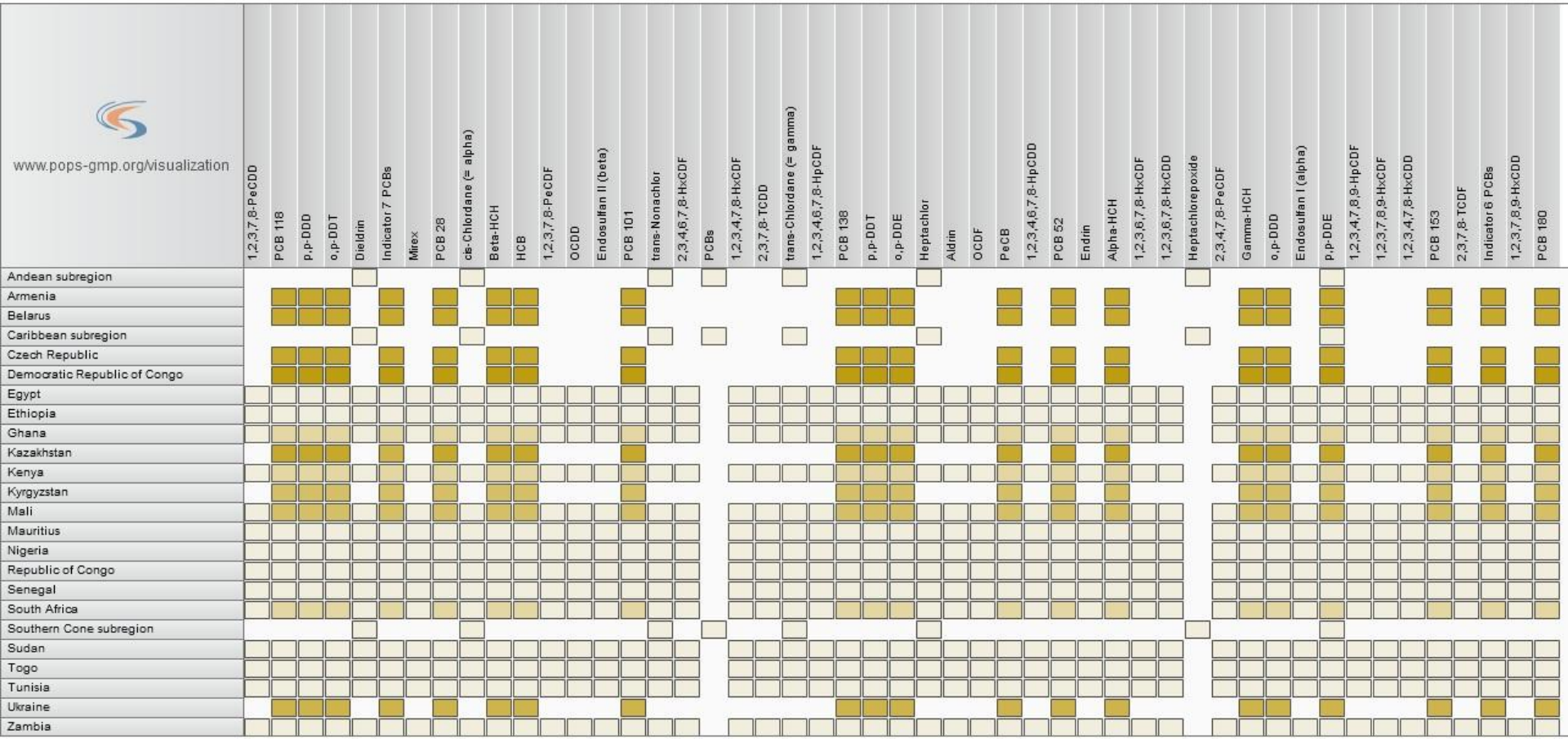


www.pops/gmp.org

GMP Reports On-line Data Visualization

AVAILABLE DATA – PARAMETERS

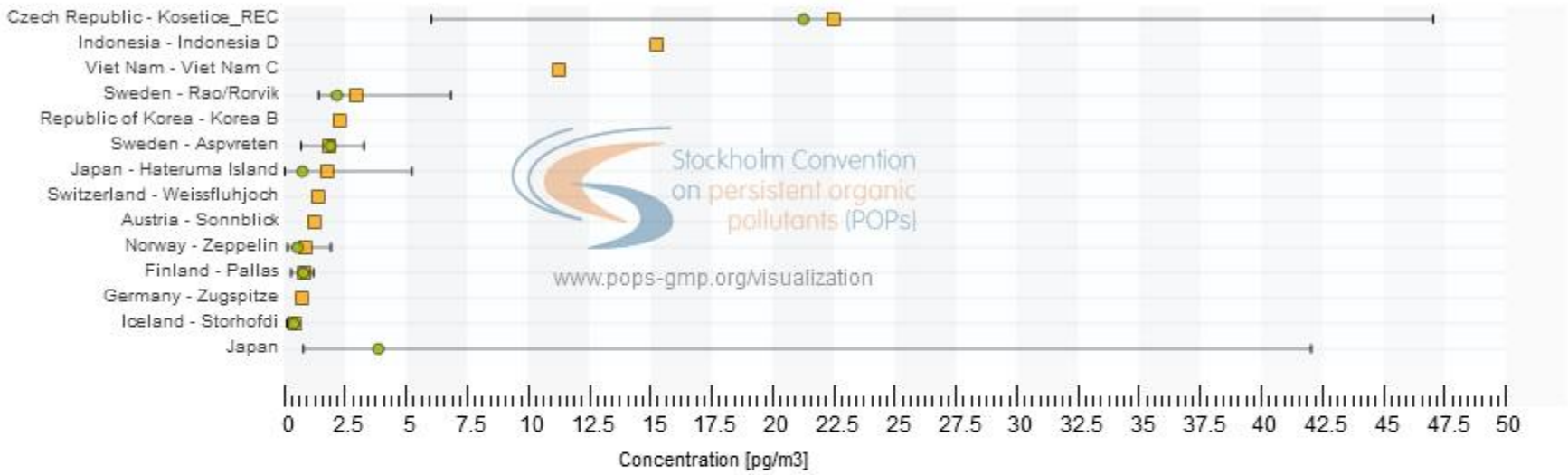
Matrix: **Air** | Sampling method: **passive** | UN region: **null** | Compound: **null** | Year: **2008**



GMP Reports On-line Data Visualization

REPORTED VALUES - backgroud sites only

Matrix: **Air** | Sampling method: **active** | Compound: **Alpha-HCH** | Parameter: **Alpha-HCH** | Unit: **pg/m3** | Year: **2005**



Legend

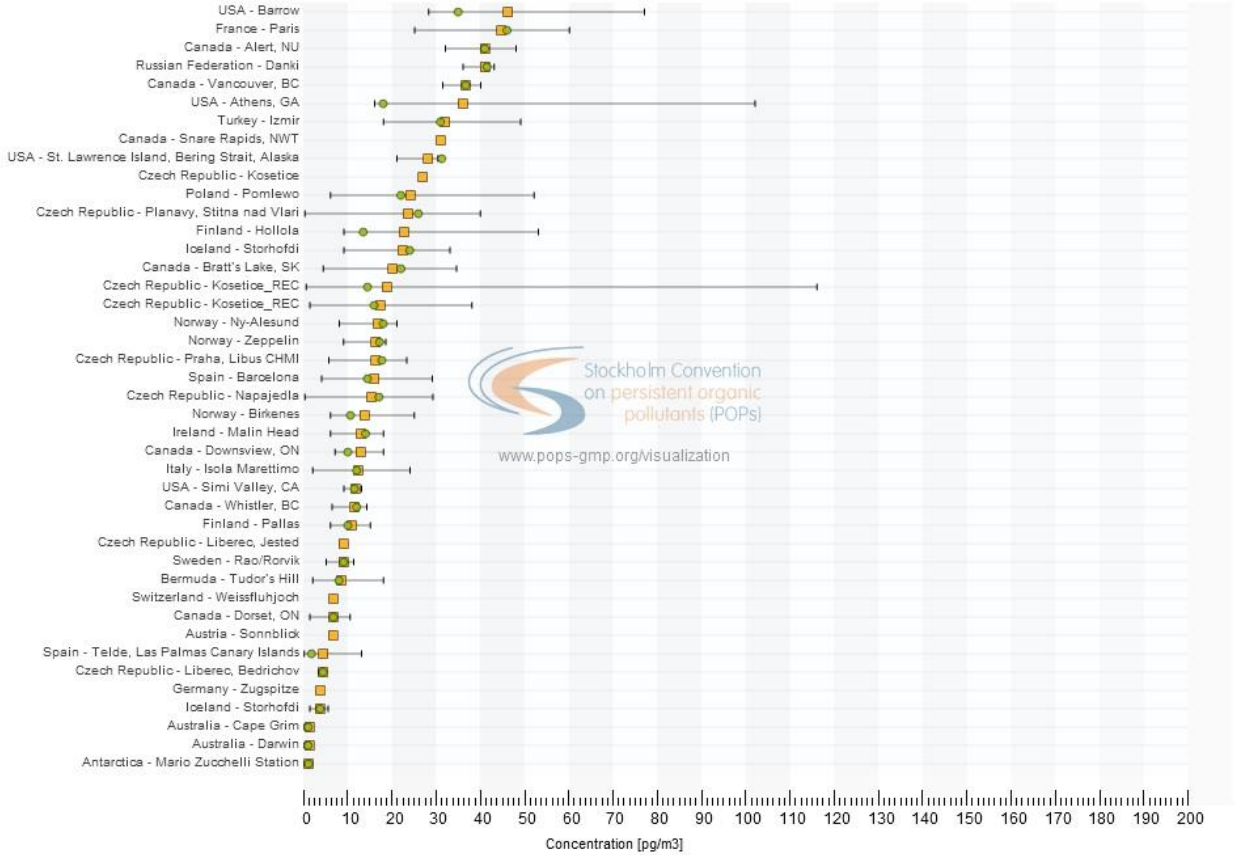
** - Records marked with the asterix are taken from multiple-year aggregation.*

(LoQ/N) - Values in paranthesis indicate proportion of records under limit of quantification (LoQ) and total number (N) of records.

GMP Reports On-line Data Visualization

REPORTED VALUES - backgroud sites only

Matrix: **Air** | Sampling method: **active & passive** | Compound: **Alpha-HCH** | Parameter: **Alpha-HCH** | Unit: **pg/m3** | Year: **2005**



Legend

Min *Mean* *Median* *Max*

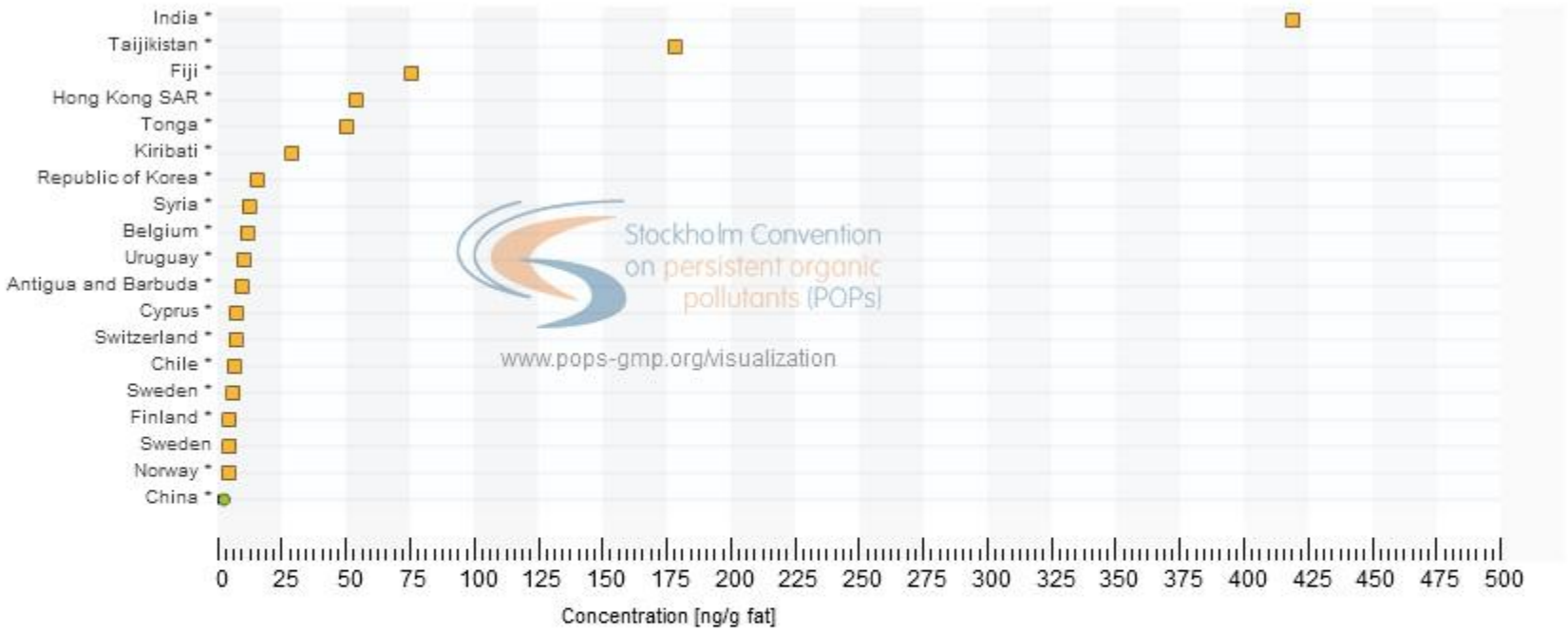
** - Records marked with the asterix are taken from multiple-year aggregation.*

(LoQ/N) - Values in paranthesis indicate proportion of records under limit of quantification (LoQ) and total number (N) of records.

GMP Reports On-line Data Visualization

REPORTED VALUES - backgroud sites only

Matrix: **Breast milk** | Sampling method: **null** | Compound: **DDT** | Parameter: **p,p-DDT** | Unit: **ng/g fat** | Year: **2007**



Legend

** - Records marked with the asterix are taken from multiple-year aggregation.*

(LoQ/N) - Values in paranthesis indicate proportion of records under limit of quantification (LoQ) and total number (N) of records.

Thank you for your kind attention