POPs
sampling and analyses in air and solid matrices

Prof. Dr. Ivan Holoubek, Ing. Katel Sottner

Provision of services related to training, assessment and reduction of PCDD/Fs releases from metallurgical industries in Turkey

Iskenderun Anemon Hotel, Turkey, 22 March, 2017

Content

Introduction to POPs

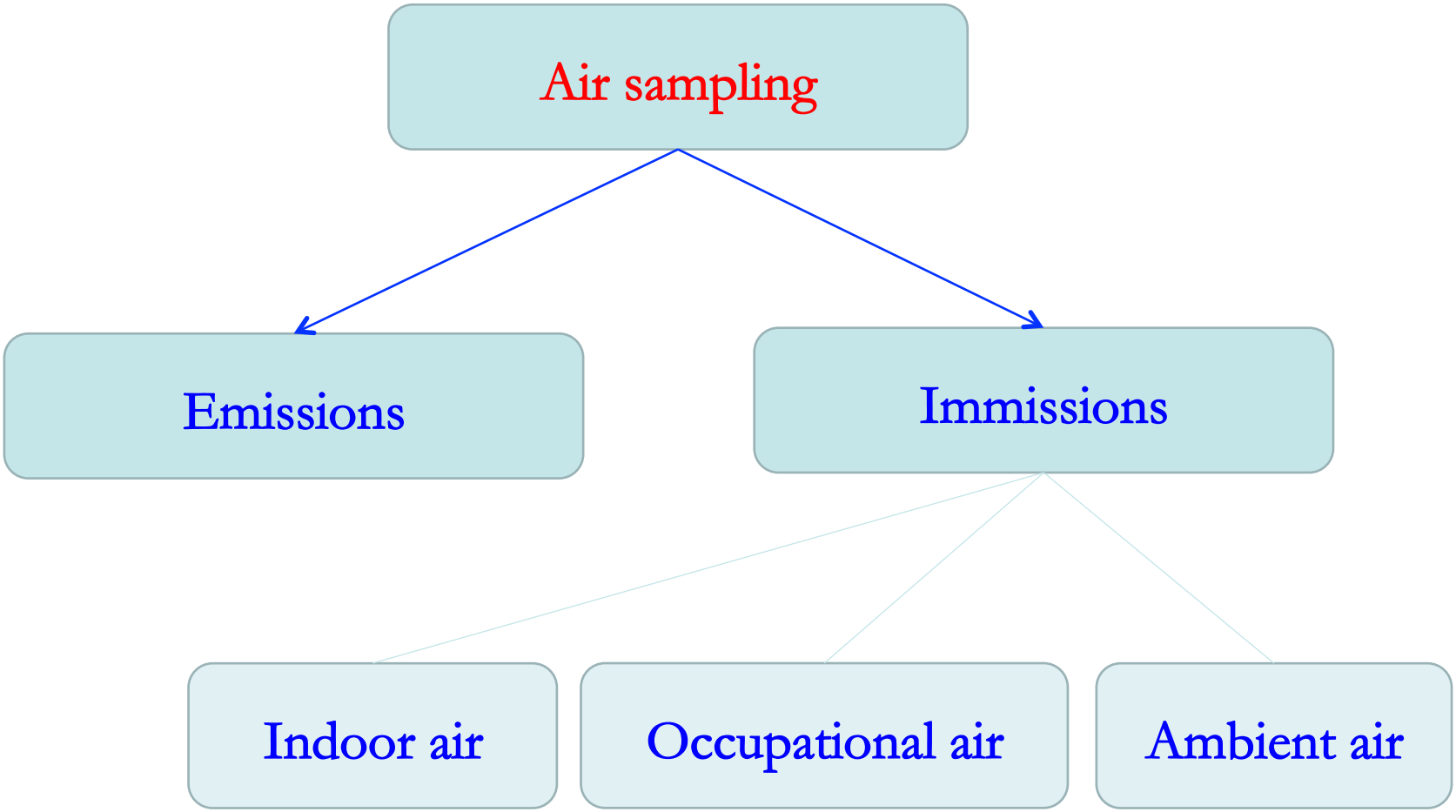
- Methods of sampling and monitoring of POPs in air;
- Methods of sampling of POP's in solid matrices;
- Methods of analyses and determination of PCDD/F in the samples.

Content

Introduction to POPs

- Methods of sampling and monitoring of POPs in air;
- Methods of sampling of POP's in solid matrices;
- Methods of analyses and determination of PCDD/F in the samples.

Air sampling



Methods of air sampling

Air sampling

Active sampling

Passive sampling

Continuous

Semi-continuous

Discontinuous

Air sampling

- Emissions (chimneys, ventilations,...) continuously

- Ambient air (environmental levels) sampling points, time period

Sampling strategy

What means sampling?

Sequence of activities for obtaining of representative sample from defined file and for defined purpose.

First step is **„Definition of the purpose“.** The one means formulation of target or reason what is necessary to take the sample (monitoring, survey. …etc.).

Second step is **„Definition of basic file“.** The one means what is the matrix which should be sampled.

Third step is **„Choosing of activities“.** The one means choice of methods and techniques which will be necessary for sampling so will be done the purpose.

On base above mentioned steps we are able to prepare:

SAMPLING PLAN

Sampling plan

Defined all procedures of sampling.

Sampling plane is possible to describe by :

Why?	Definition of the purpose and the aim;
What ?	What will be the matrix and which pollutants;
How ?	Which methods will be used;
By which?	By which apparatus and equipment ;
Where ?	In which locality and place;
When?	When the sampling will be carried out;
How long?	The sampling will be disposable, repeated, discontinuous continuous ….etc;
How ?	Who will be sampling, who will analyze and who will carry out evaluation;
According to?	According to result s will be evaluated;
Documentation?	Which documents will be in the report.

Problems of emission sampling

Sampling of emissions

- High pollutants concentrations
- High agresivity of sampling air
- Isokinetic sampling
- Sampling using the condense or dilution method

Method of manual sampling PCDDs/Fs

ČSN EN 1948-1

Stationary source emissions - Determination of the mass concentration of PCDDs/Fs

- Part 1 - sampling
- Part 2 - extraction and quantification
- Part 3 - identification and quantification

Developed to measure concentration about 0.1 ng m^{-3} I-TEQ

Method validated in range 0.03 až 0.13 ng m^{-3} I-TEQ

Methods of sampling of POPs in emisions

Method of manual sampling POP's

EN 1948-1 Stationary source emissions - Determination of mass concentration of PCDDs/PCDFs and dioxin-like PCBs

- Part 1 - Sampling of PCDDs/PCDFs;
- Part 2 - Extraction and clean-up of PCDDs/PCDFs;
- Part 3 - Identification and quantification of PCDDs/PCDFs;
- Part 4 - Sampling and analysis of dioxin-like PCBs;
- Part 5 - Long-term sampling of PCDDs/PCDFs and PCBs.

Group of Europe norm developed to measure concentration about 0.1 ng m^{-3} I-TEQ. Method validated in range 0.03 to 0.13 ng m^{-3} I-TEQ.

I-TEF and I-TEQ

- Toxic are only PCDD/F substituted by chlorine in positions 2,3,7,8
- The most toxic is 2,3,7,8-TCDD
- Are mixture together different chlorinated congeners of PCDD a PCDF
- I-TEF international toxic equivalent factor
- I-TEQ international toxic equivalent quantity
- I-TEQ = $\Sigma_i c_i * \text{I-TEF}_i$

Congener	I-TEF	WHO-TEF	Congener	I-TEF	WHO-TEF
2378-TCDD	1	1	2378-TCDF	0.1	0.1
12378-PeCDD	0.5	1	23478-PeCDF	0.5	0.5
123478-HxCDD	0.1	0.1	12378-PeCDF	0.05	0.05
123678-HxCDD	0.1	0.1	123478-HxCDF	0.1	0.1
123789-HxCDD	0.1	0.1	123789-HxCDF	0.1	0.1
1234678-HpCDD	0.01	0.01	123678-HxCDF	0.1	0.1
OCDD	0.001	0.0001	234678-HxCDF	0.1	0.1
			1234678-HpCDF	0.01	0.01
			1234789-HpCDF	0.01	0.01
			OCDF	0.001	0.0001

Sampling methods

- Isokinetic sampling in accordance with ISO 9096 or EN 13284-1

+

- filter/condenser method
- dilution method
- cooled probe method

Methods of sampling of POPs in emisions

The part of sampling o POPs must be measurement of:

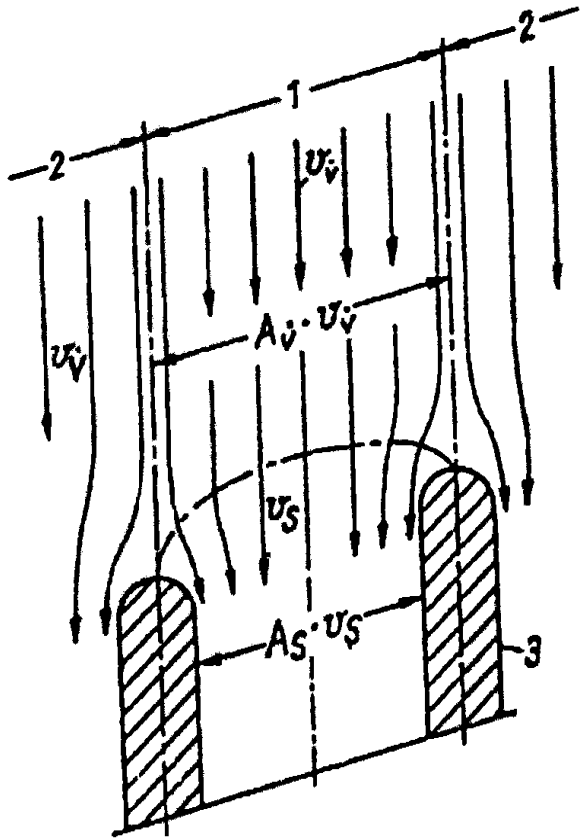
Emission-operational parameters:

- Gas velocity, gas flow rate, temperature, pressure; content of humidity, content of oxygen …..etc.

Meteorological parameters:

- Temperature, atmospheric pressure, wind velocity, wind direction …….etc.

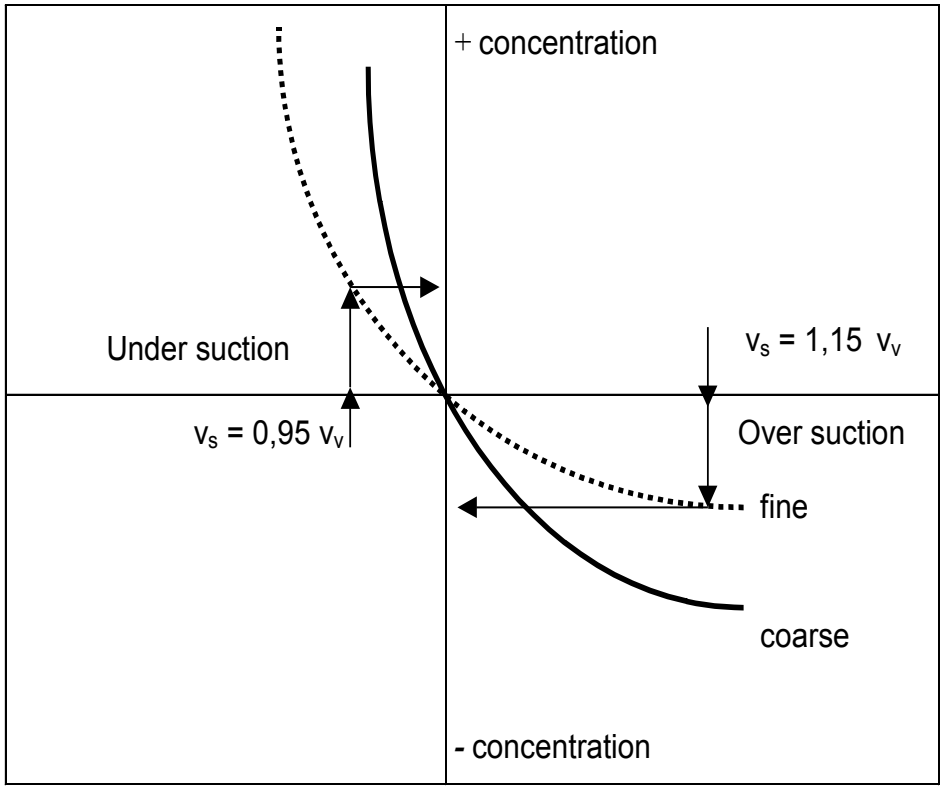
Isokinetic sampling



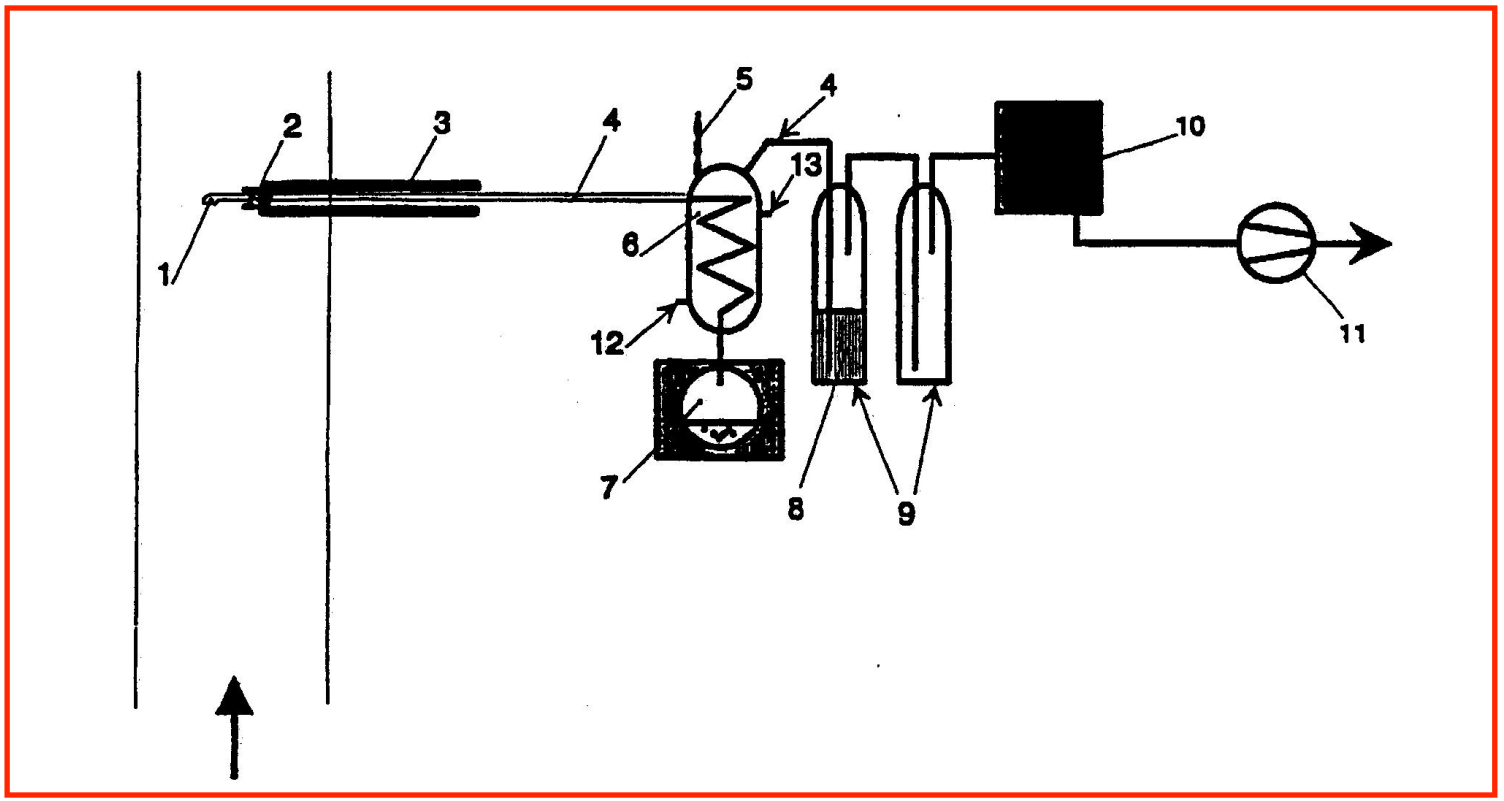
Measurement profile:

- collinearity of air flow till 15°
- no backward flow
- ratio of flow velocity in meas. points max. 1:3
- velocity in each point min. 3 m s^{-1}
- temperature difference between meas. points max. 5 %

Isokinetic ratio



Filter/condenser method

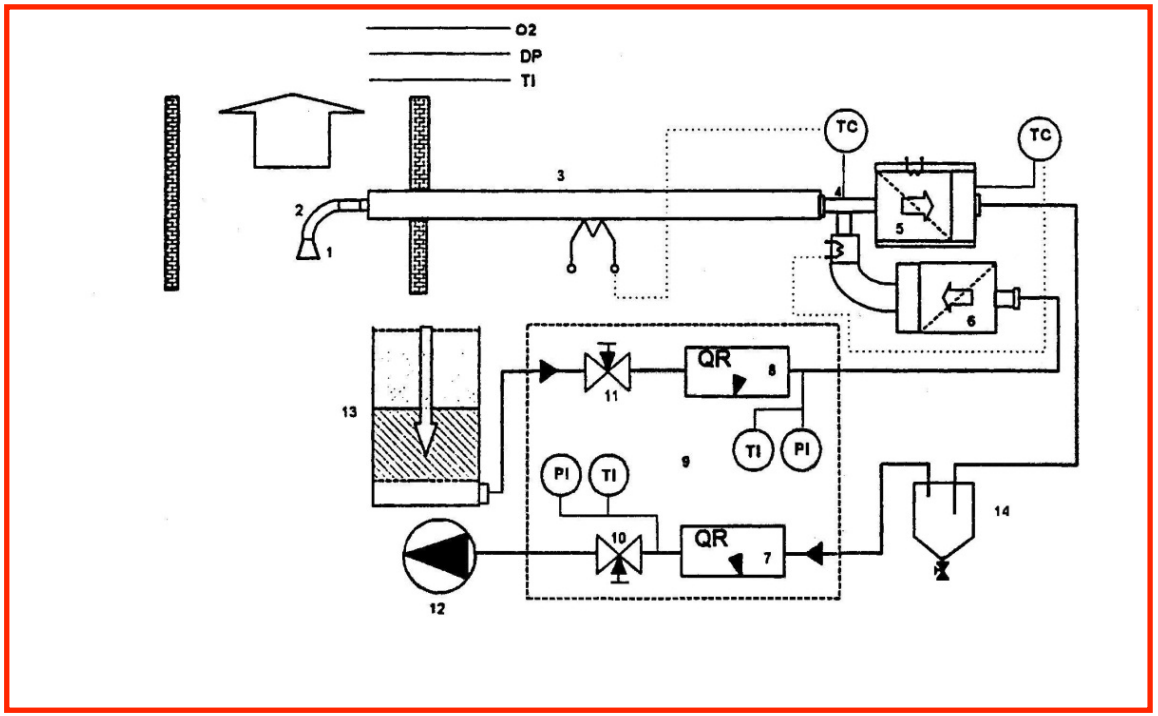


1 nozzle
2 thumble filer
3 heated probe
4 glass connections
5 temperature control
6 condenser
7 condensate flask
8 diethylene glycol
9 bubbler
10 drying tower
11 suction device
12-13 cooling water

Filter/condenser method

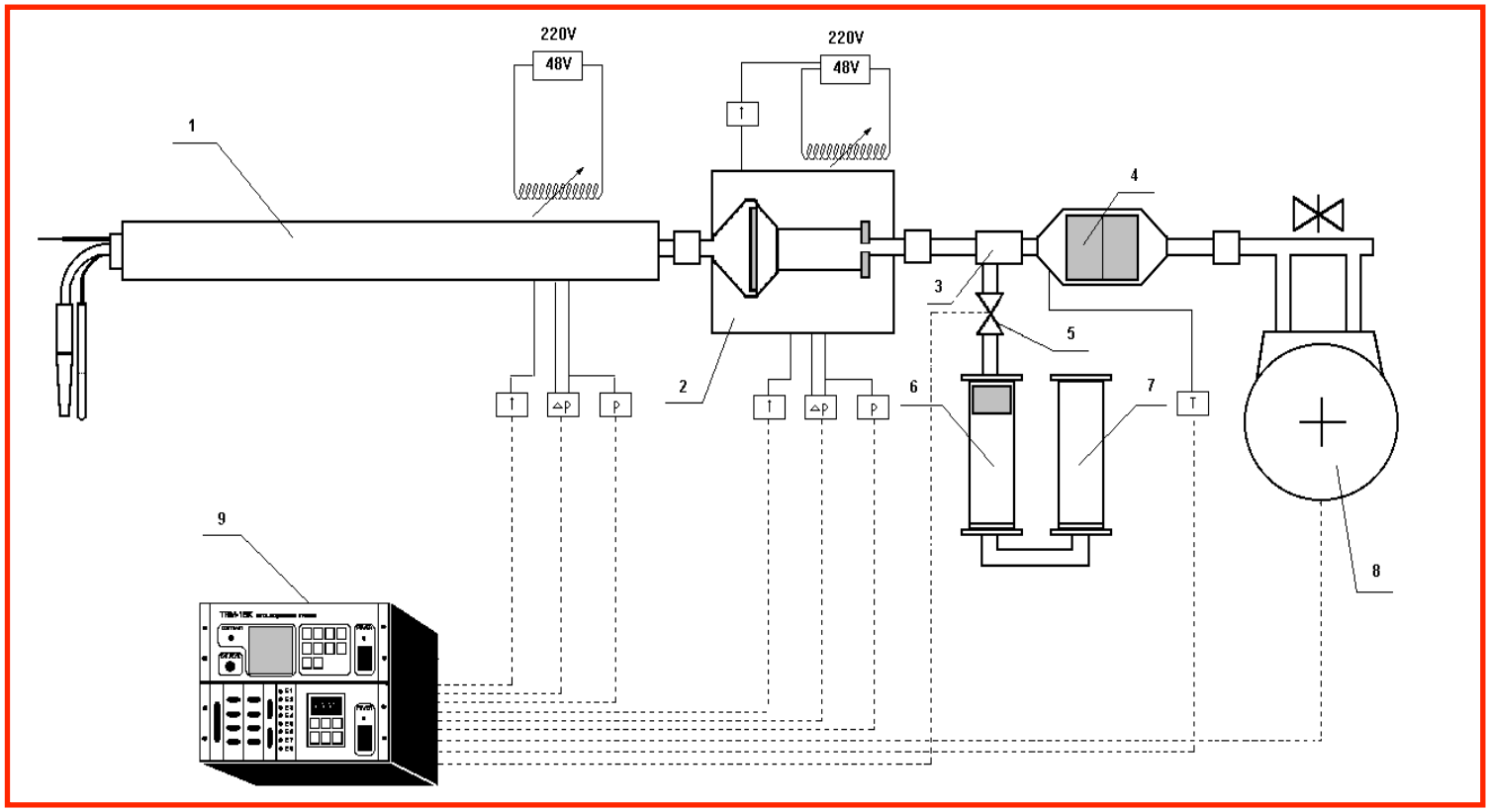
	item	conditions/requirements
1	in stack/out stack filter	dew point < t_{filter} < 125°C η_{filter} > 99,5 % (for PM 0,3 µm)
2	heated probe	dew point < t_{probe}
3	condenser	$t_{condensator}$ <20°C
4	ab/adsorber	impingers and/or solid adsorbents $\eta_{ab/adsorbents}$ > 90 % (for PCDDs/PCDFs)
5	flow division *(option)*	constant ratio main and side steams ± 10 %

Dilution method



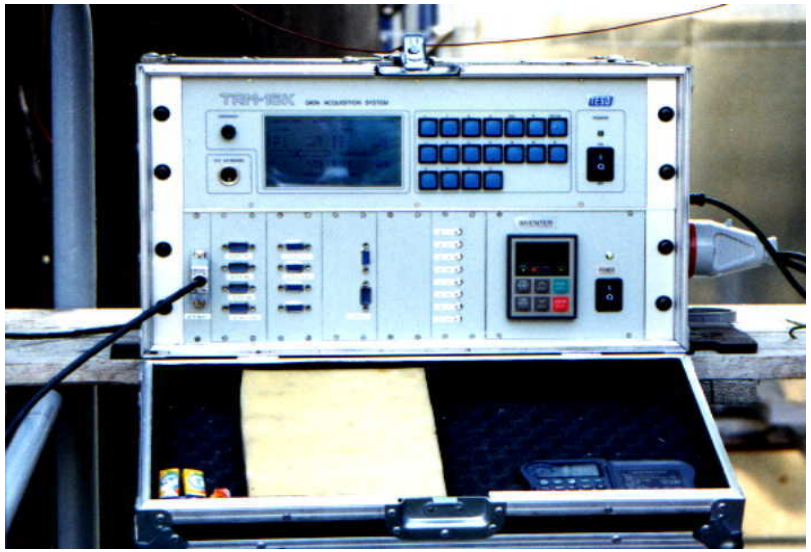
1 nozzle
2 elbow joint
3 heated probe
4 mixing channel
5 GF filter and PU foam
6 dilution air filter
7 flow measurement, diluted flue gas stream
8 flow measurement, dilution air
9 control unit
10 control valve, flue gas stream
11 control valve, dilution air
12 pump
13 silica gel bed
14 drying tower
TI temperature sensor
PI differential pressure gage
QR gas stream volume meter
TC temperature controller

The sample of dilution method IZOMAT-GTE



1 heated probe
2 heated filter and orifice
3 mixing channel
4 PU foam and control PU foam (validation)
5 control valve, dilution air
6 active coal bed and PU foam (control)
7 silica gel bed
8 frequency controlled pump
9 control unit

Automatic control of isokinetic sampling IZOMAT



000/00/000	0001	99-11-08	13:27:15
sonda		dýza	
ps	-1500	pc	-4825
pd	200	dpc	1800
t	282,4	tc	98
		kondenzátor	
IZO	1,007	pk	-5286
v	18,2	tk	18,3
		Vk	

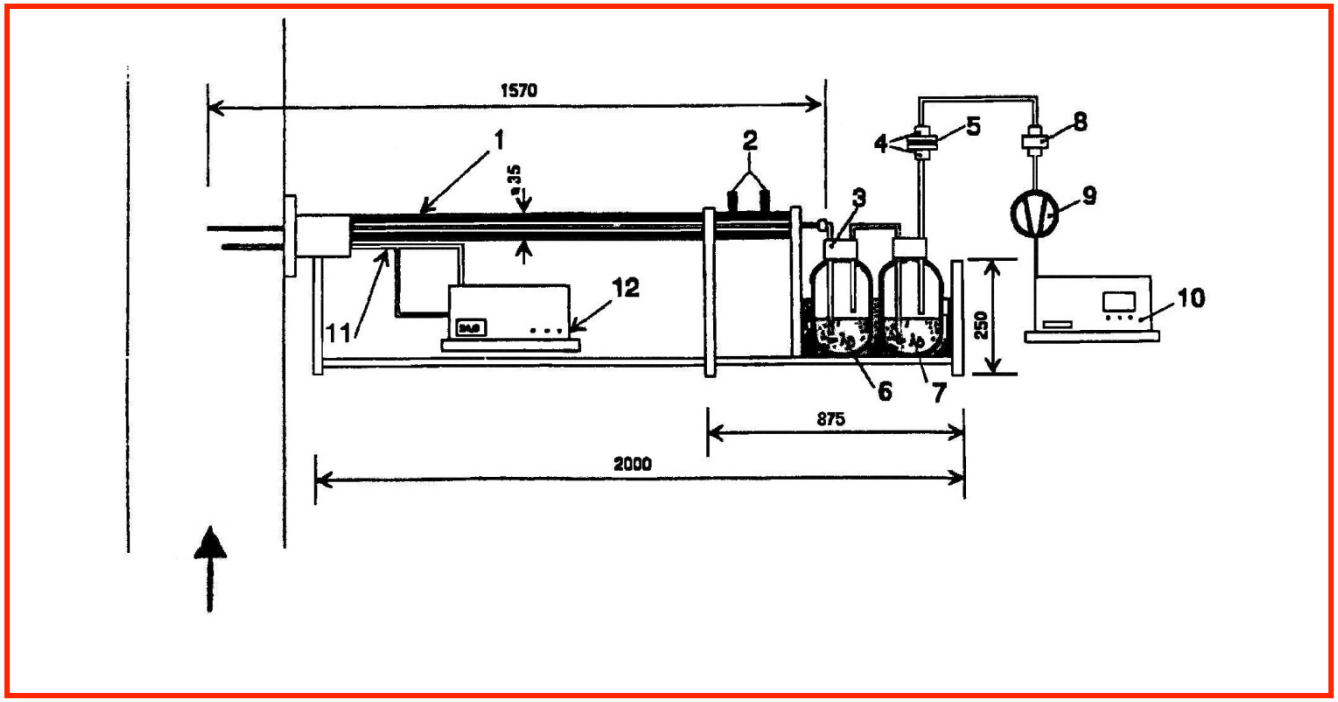
Měření bez závad

2,583 m³ (0%)

Dilution method

	item	conditions/requirements
1	heated probe	dew point < t_{probe}
2	mixing channel	dew point < $t_{channel}$ < 40°C
3	out stack filter	dew point < t_{filter} < 40°C η_{filter} > 99,5 % (for PM 0,3 µm)
4	adsorber	solid adsorbents downstream from the filter $\eta_{adsorbents}$ > 90 % for (PCDDs/PCDFs)

Cooled probe method



1 water cooled probe
2 cooling water
3 bubbler
PU foam
5 GF filer
6 condensate flask
7 organic solvent
8 drying agent
9 pump
10 volume regulation unit
11 Pitot tube
12 pressure measurement unit

Cooled probe method

	item	conditions/requirements
1	heated probe	dew point $< t_{probe}$
2	mixing channel	dew point $< t_{channel} < 40^{o}C$
3	out stack filter	dew point $< t_{filter} < 40^{o}C$ $\eta_{filter} > 99,5\ \%$ (for PM 0,3 µm)
4	adsorber	solid adsorbents downstream from the filter $\eta_{adsorbents} > 90\ \%$ for (PCDDs/PCDFs)

Requirements for characteristic of measurement device

Device	requirements
Pitot tube with a differential pressure gauge (alternatively a micromanometer)	for measuring the static and dynamic pressure in the waste gas channel (for calculating the gas flow velocity)
moisture measuring device	to determine the moisture in the waste gas, ± 1% (v/v), absolute
Micromanometer	to measure the flue gas pressure in the duct
oxygen measurement systém	to determine the oxygen content, ± 0,5 % (v/v), absolute
syringe (vial)	to add the $^{13}C_{12}$-labeled standard solution (sampling standards)
pressure gauge	± 1 kPa, absolute
Thermometer	± 2,5°C
volume measurement device	accuracy of the sampled gas volume ± 5 % of the value measured
flow rate measurement device	to measure the volume flow rate to allow isokinetic conditions to be maintained
isokinetism criteria (average) within	- 5 / + 15 %

Requirements for material of sampling device

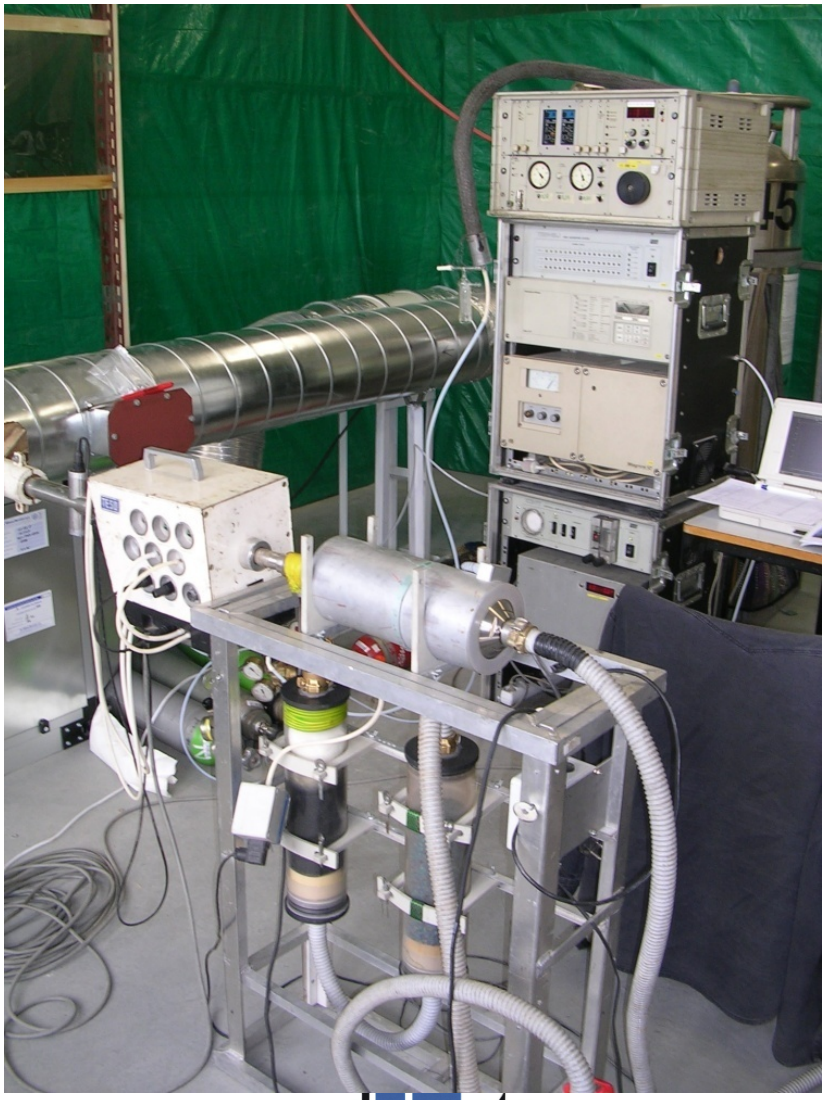
Device	material
inside parts of nozzle / elbow joint / probe / heated filter holder	titanium, quartz or glass PTFE (for temperatures below 180°C)
non heated filter holder, flow divider, mixing channel	corrosion-resistant material
condensate flask, bubbler, impinger	glass
ad/absorber	titanium, glass, PTFE
connection materials behind the last ad/absorber stage	corrosion-resistant stainless steel / plastics are allowed
drying tower	filled with moisture-adsorbing material, e.g silica gel, blue gel
solid adsorbent	XAD-2 / PU foam / Porapac PS / Florisil / or other solid adsorbents
liquid absorbent	methoxyethanol / ethoxyethanol / diethyl glycol

Continuous sampling of emissions for PCDDs/Fs determination

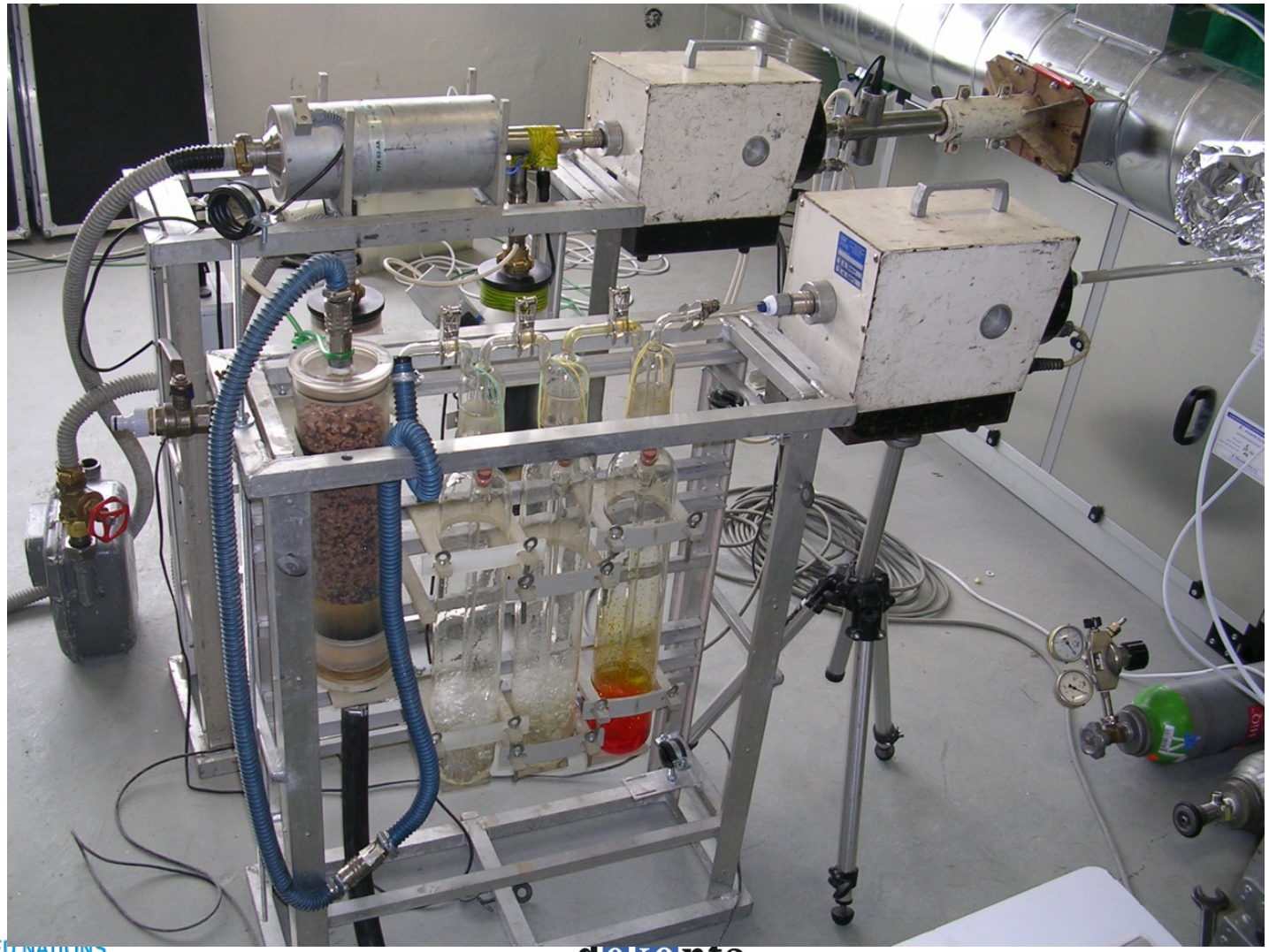
Sampling of occupational environment air for PCDDs/Fs, HMs and VOCs determination

Sampling of ambient air for PCDDs/Fs determination

One-off sampling of emissions for PCDDs/Fs determination



One-off sampling of emissions for PCDDs/Fs and Hg determination



Ambient air sampling

Aim air sampling:

Qualitative and quantitative detection of the presence and concentration of pollutants or groups of pollutants in the atmosphere at a given location

Specifics of air sampling:

- Low concentrations of pollutants
- Heterogenity of the sampled matrix
- Pollutants present in multiple forms

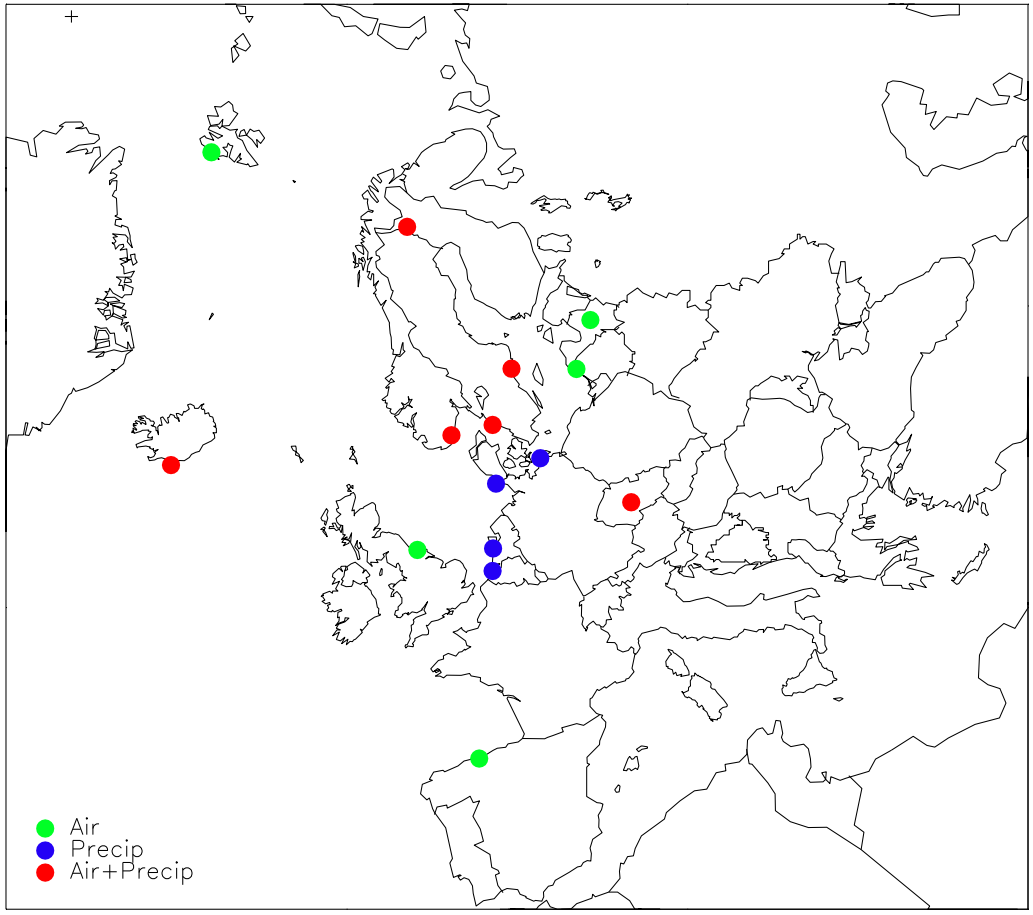
Sampling methodology

Factors affecting selection of sampling methods:

- Phase distribution of pollutants
- Stability of pollutants
- Time resolution considerations
- Analytical considerations
- Other physical-chemical properties of pollutants:
  - Termic stability
  - Volatility
  - Polarity
  - Ionic character
  - Chemical composition
  - Environmental-chemical properties

EMEP POPs monitoring network

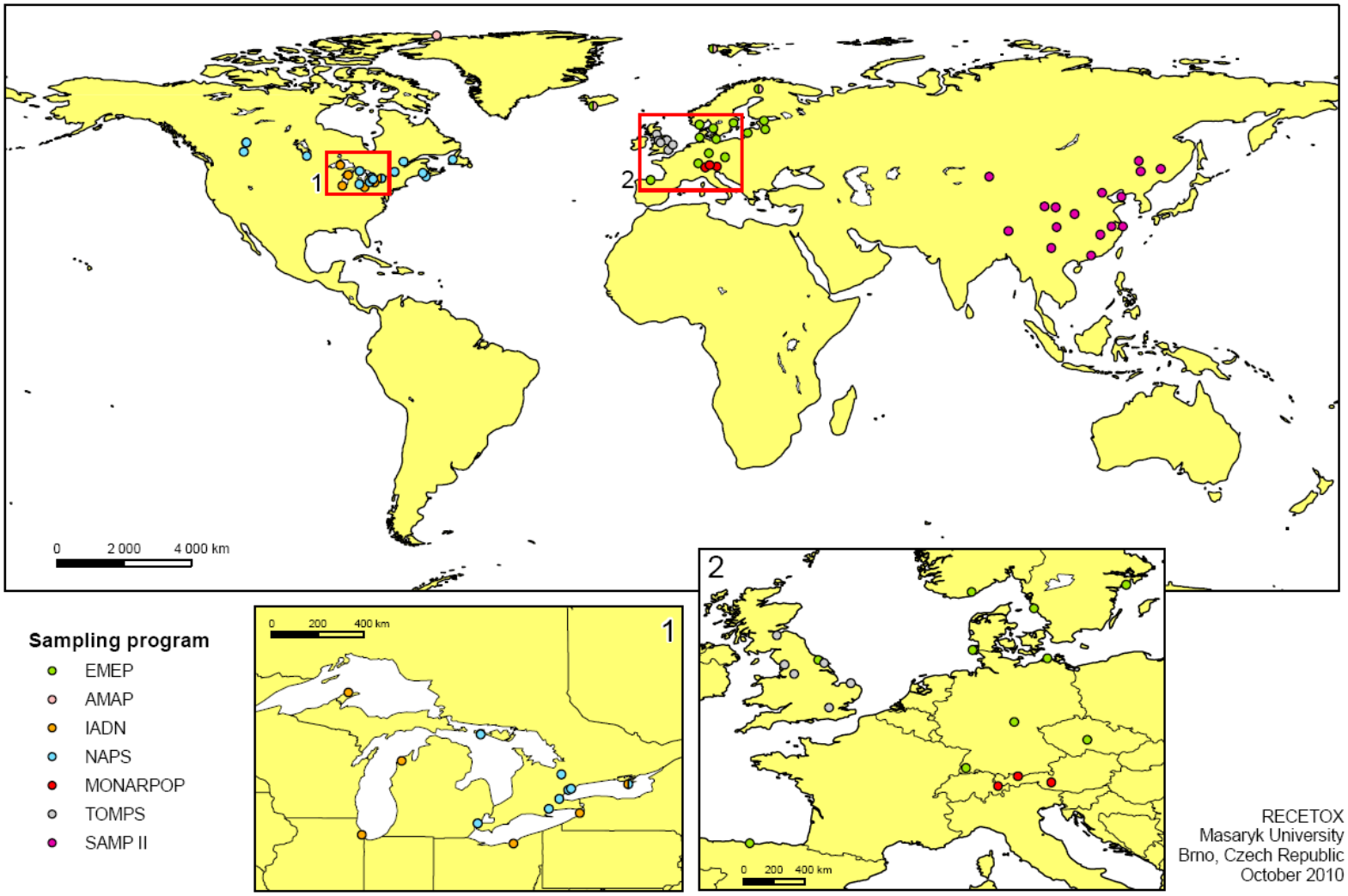
Only six (out of fifteen) EMEP sites reported POPs in both, air and wet deposition, in 2004



POP monitoring EMEP network, 2004

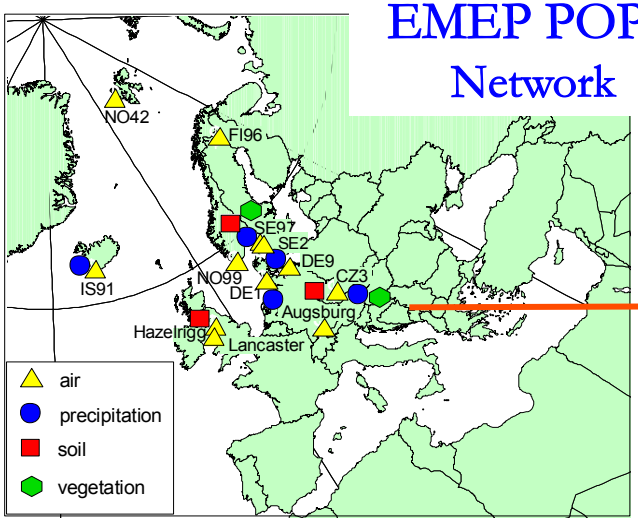
Monitoring of POPs

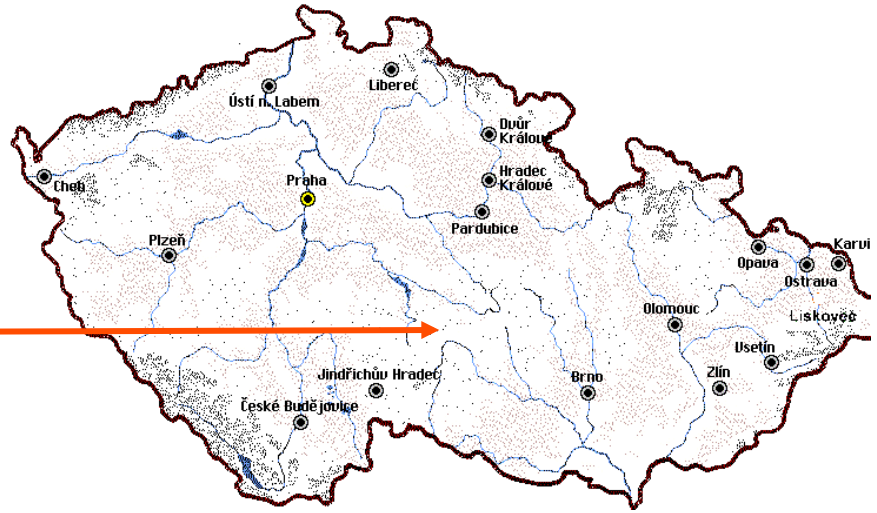
POPs ambient air monitoring programmes until 2006



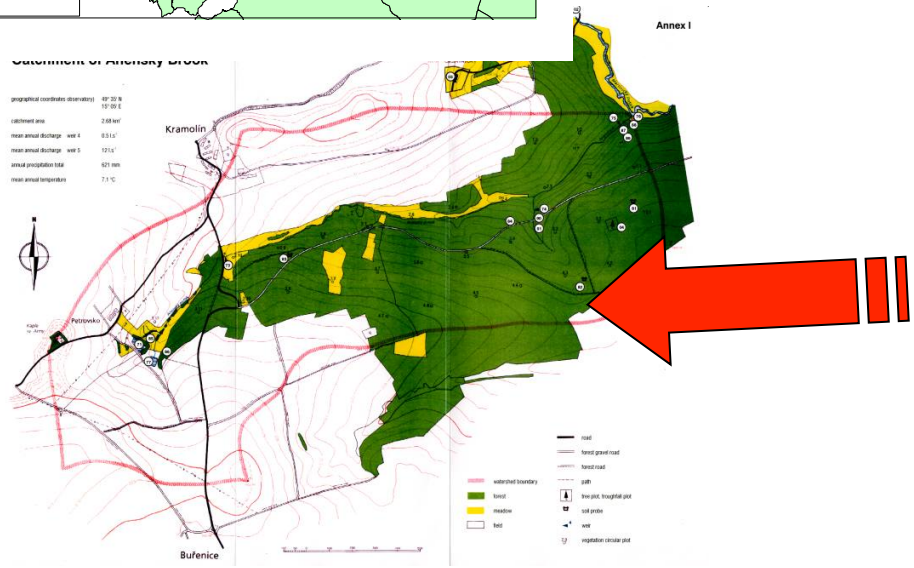
Regional monitoring of POPs

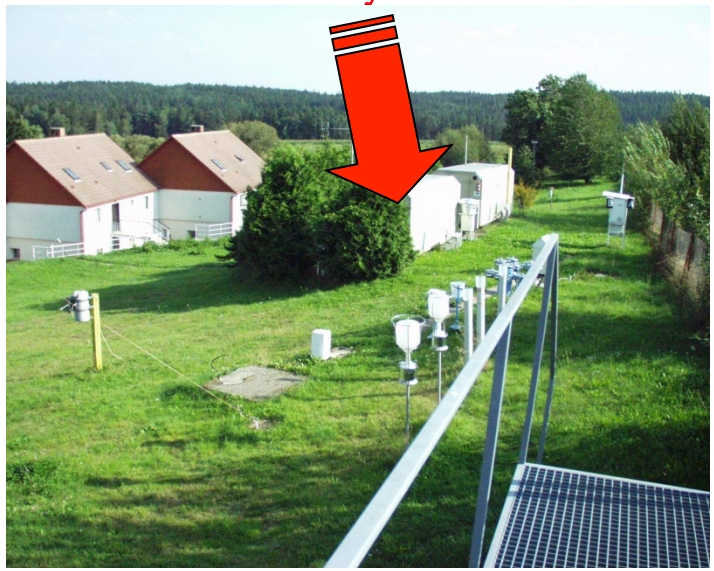
EMEP POPs Network





Observatory Košetice





Meteo – measurement of meteorological parameters

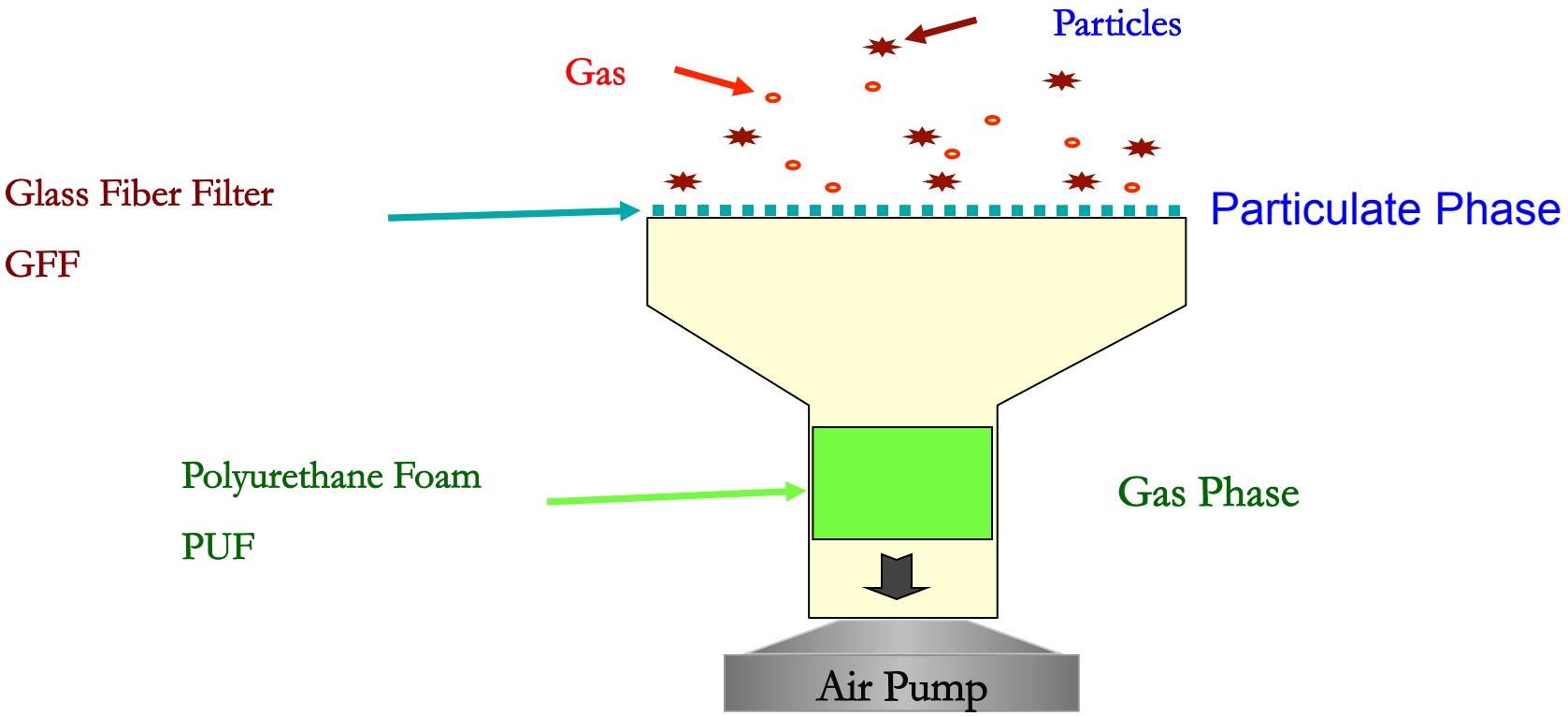
WV – wind velocity
WD – wind direction
p – atmospheric pressure
h – relative air humidity
RAIN – sum of precipitation
GLRD – sun irradiation
T – temperature (not specified)
T2m – temperature 2 m above terrain
T10m – temperature 10 m above terrain

Active sampling

- Active sampling – cost, training, power, supporting meteo data
- Establish regional 'super stations'?

Active sampling techniques

✓ AEROSOLS



High-Volume sampler

High volume samplers for active POPs sampling

Active samplers

Active samplers

PM-10 (Thermo Andersen, USA) flow more than 1 m^3 per minutes (1 500 m^3/24 hrs.)

PS-1 (Thermo Andersen, USA) flow more than 280 l per minutes (400 m^3/24 hrs.)

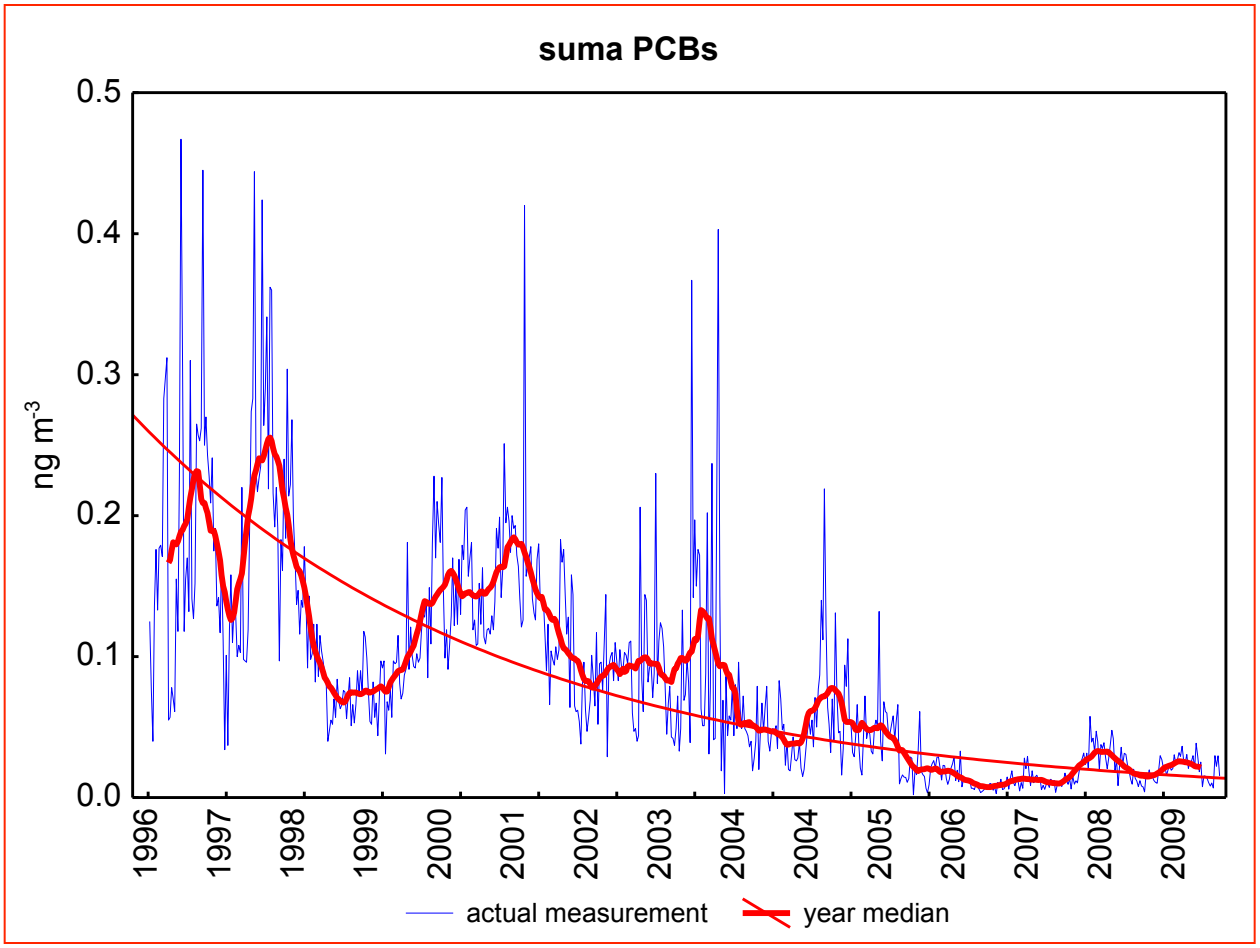
ENT ORGANIZATION

deko

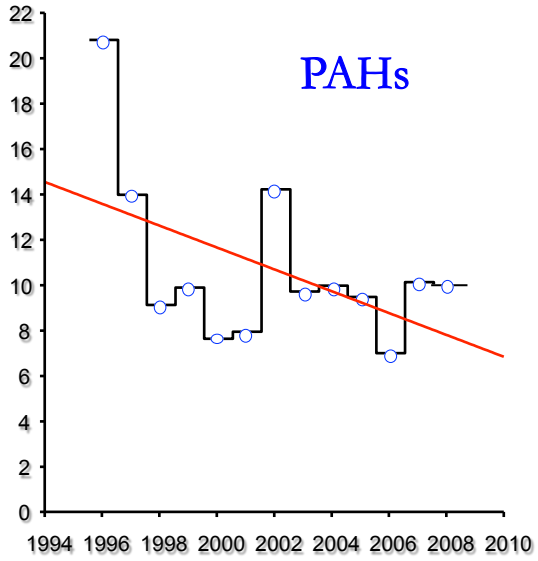
Active samplers

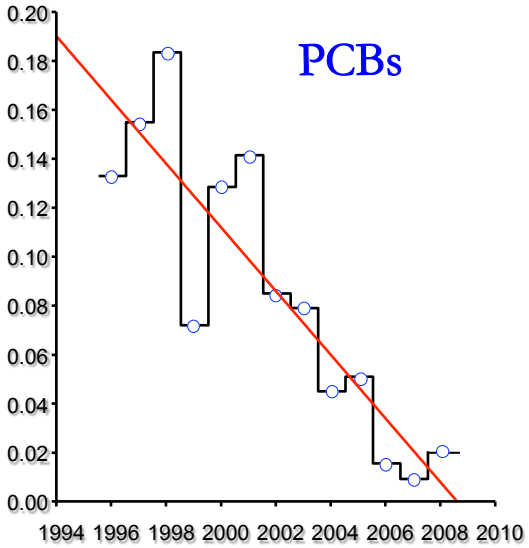
Leckel – sampling had - bio, PM1, PM2,5, PM10, PM+PUF, ozon denuder, TSP

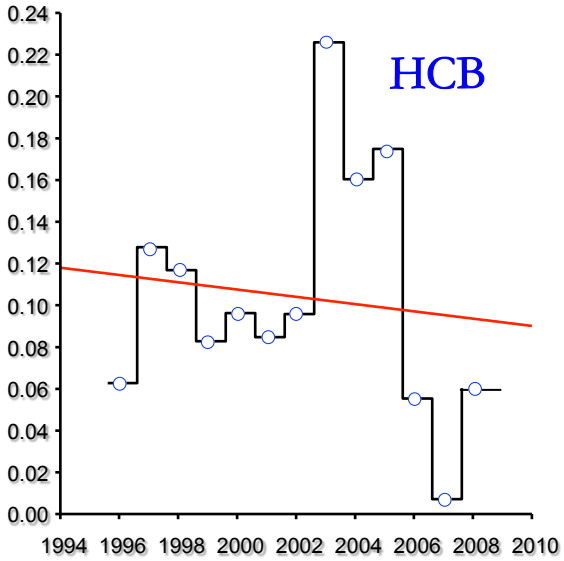
Long term trends of ambient air levels, Central European background site, observatory Košetice, CR, sum of 7PCBs [ng m^{-3}]

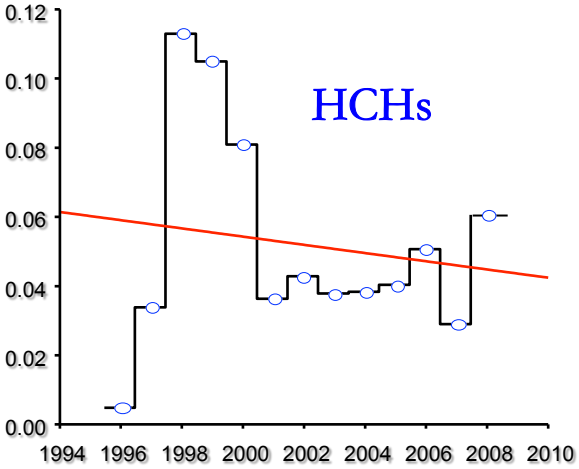


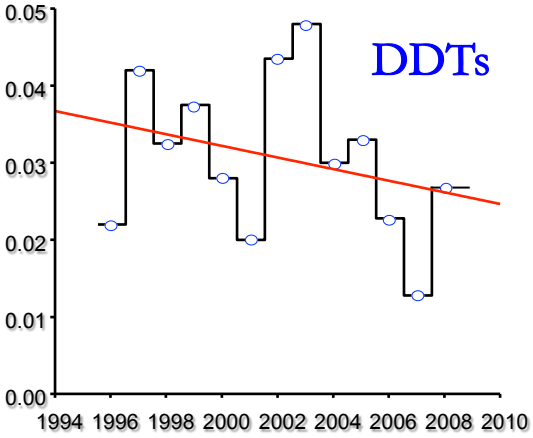
Long-term temporal trends of POPs in ambient air – observatory Košetice – 1996-2008 [ng.m^{-3}]



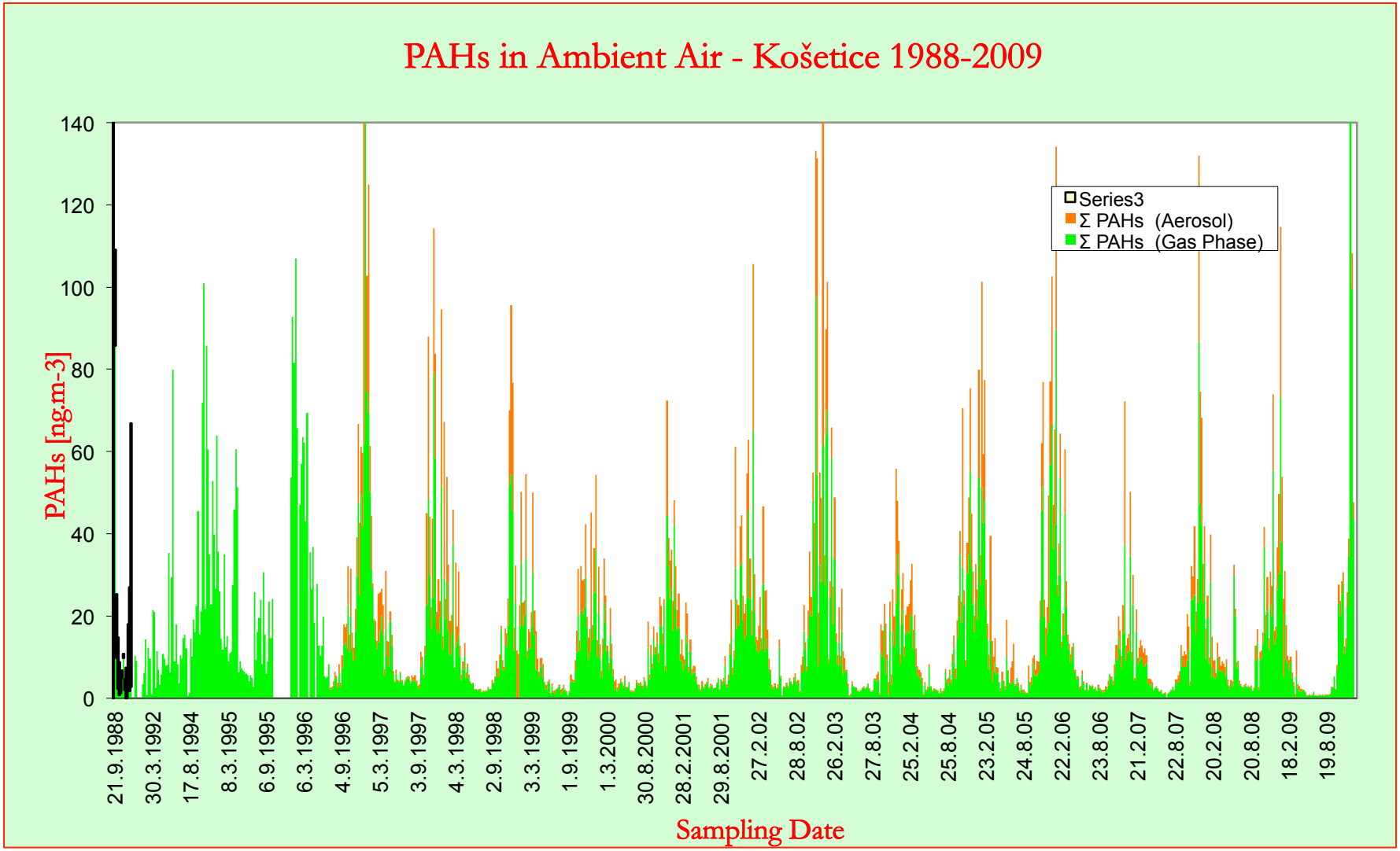




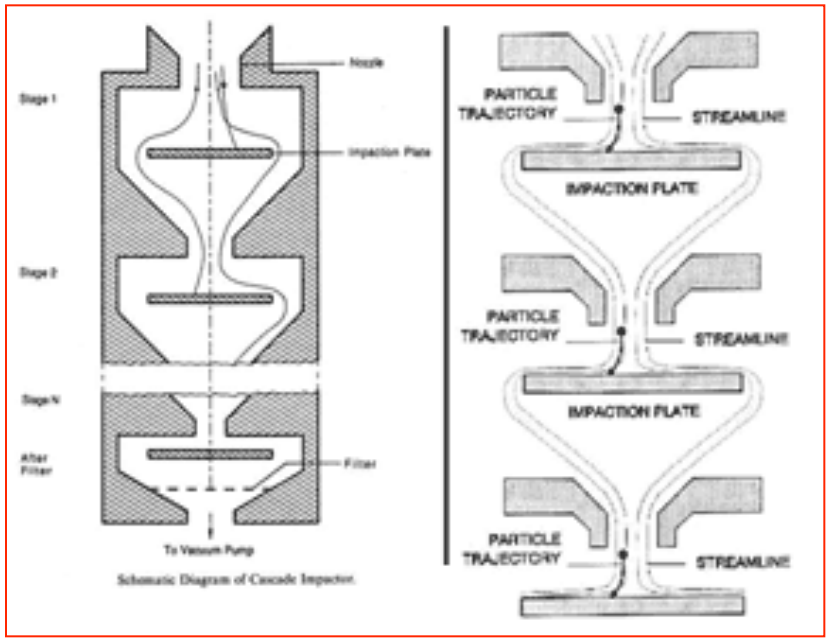




S 16 PAHs in air, observatory Košetice, seasonal variations, sampling every week, 1996 - 2009 [ng.m^{-3}]



Fractionation of PM



Passive sampling

The advantages/opportunities of passive air samplers are as follows:

- Low cost
- Excellent opportunities for high spatial and temporal sampling resolution data
- No power supply needed, easy deployment and little operator training required

Passive sampling

Their disadvantages/constraints are:

- Current techniques are still 'semi-quantitative', requiring knowledge of the sampling rate (m^3 air sampled/day) and the effects of temperature
- Optimisation of sampling requires further study, of the effects of wind speed, temperature
- Sampling is efficient for the gas phase component, but generally poorer for the particulate phase
- The time to reach gas phase-sampler equilibrium varies widely between POPs

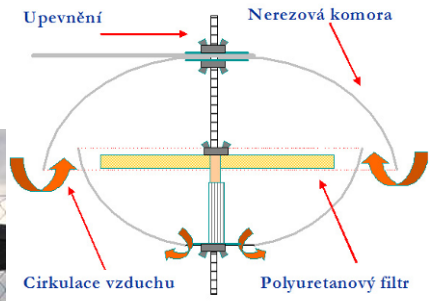
Passive sampling

- No pump – sampling air flows round exposed filter, membrane or other media (sorbents), which trapped determined pollutant(s)
- Mechanism of separation is based on the difference between pollutant concentration in air and sorbent
- Time of sampling is driven by time, which is necessary to establish the equilibrium state (saturation adsorption capacity)
- Samplers are less sensitive to random extreme changes in the actual concentration of pollutants - provide information on the long-term level of contamination

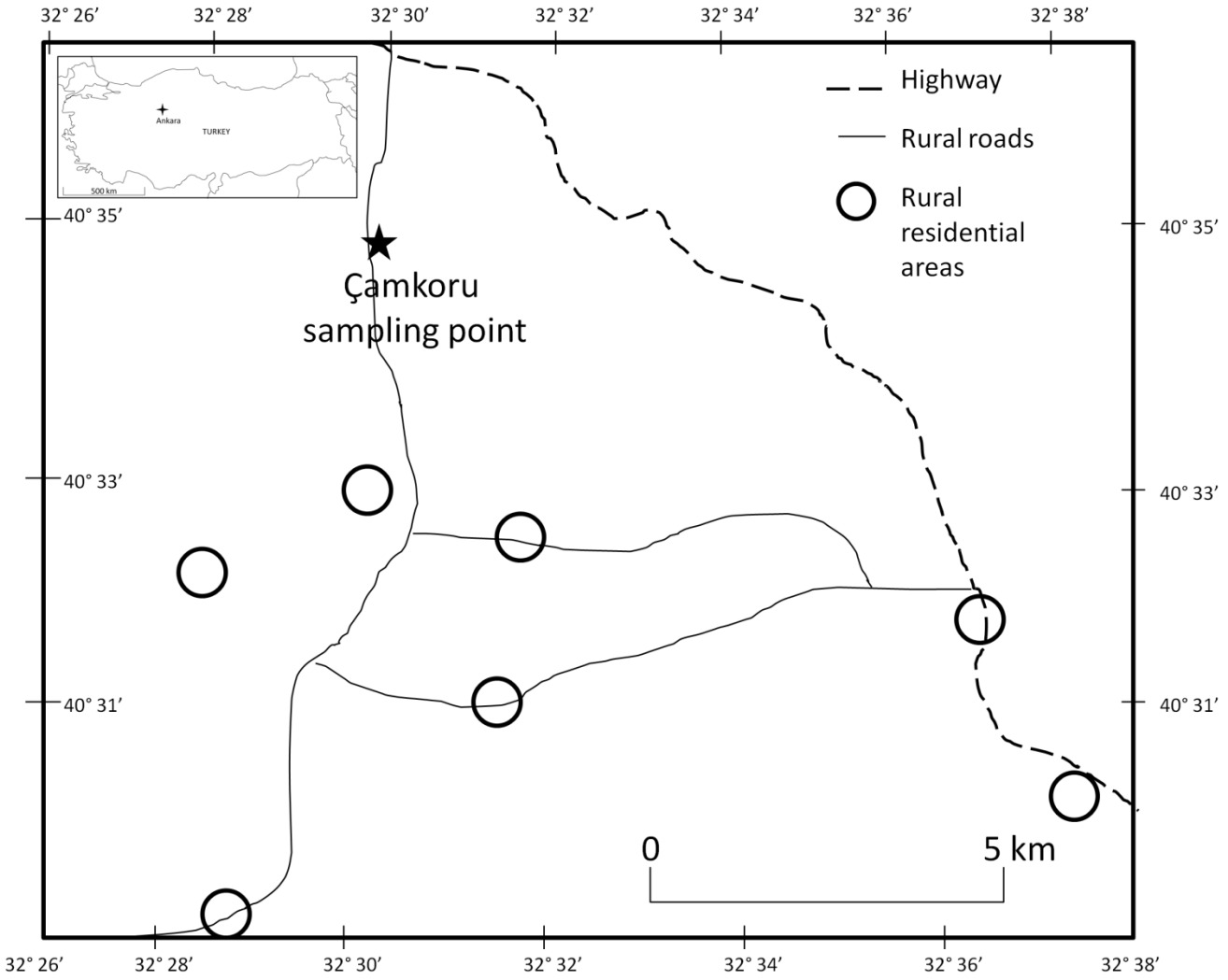
Passive sampling

Sorbents

- Biotic – mosses, needles, lichens
- Abiotic - SPMD, PUF, amberlit, ….



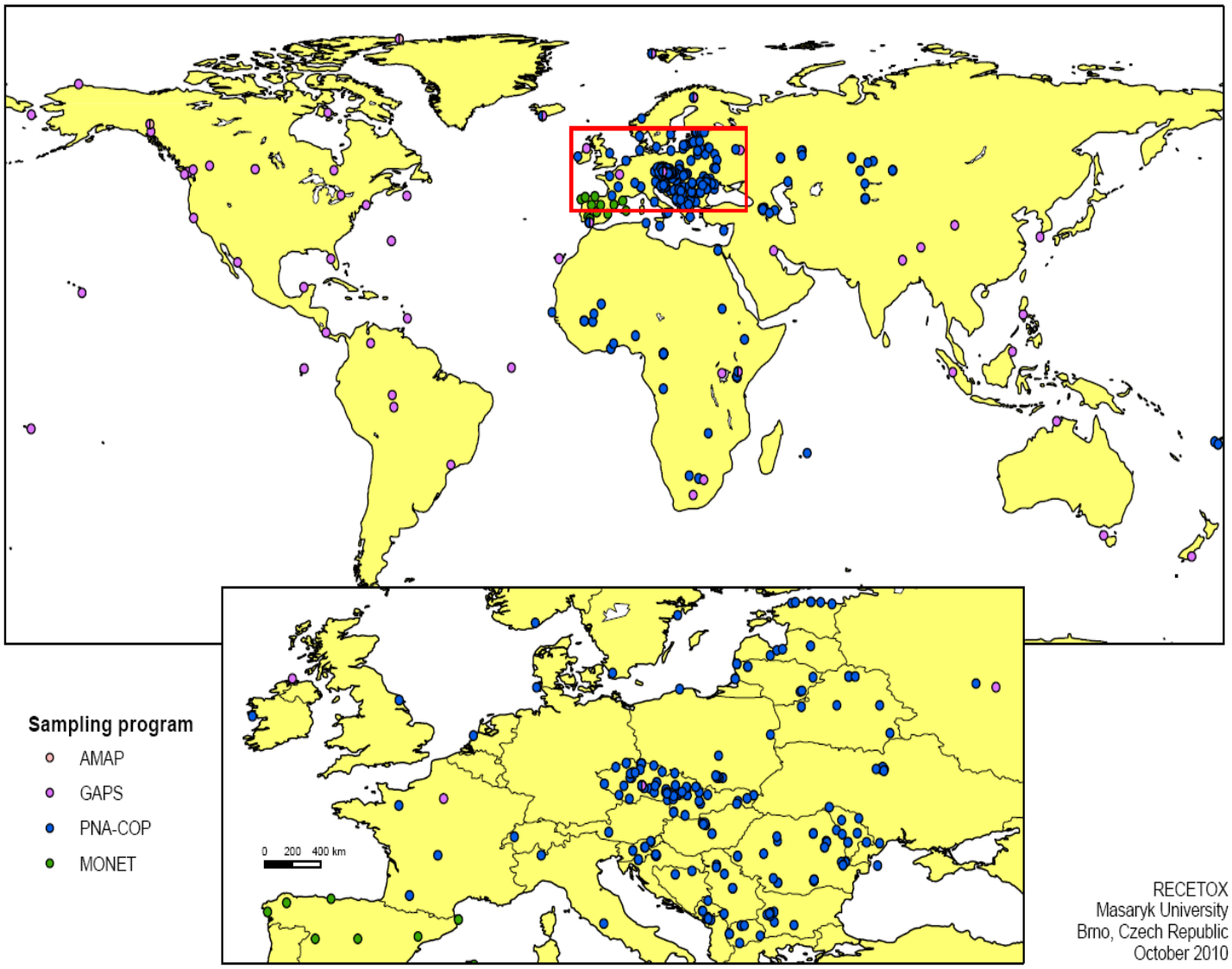
MONET – Turkey – begining
05 December, 2009



UNITED NATIONS INDUSTRIAL DEVELOPMENT ORGANIZATION

dekonta

POPs ambient air monitoring programmes 2010



Content

Introduction to POPs

- Methods of sampling and monitoring of POPs in air;
- Methods of sampling of POP's in solid matrices;
- Methods of analyses and determination of PCDD/F in the samples.

Methods of sampling of POPs in solid matrices

TNI CEN/TR 15310 Characterization of waste – Sampling of waste material

- Part 1 - Guidance on selection and application of criteria for sampling under various conditions;
- Part 2 - Guidance on sampling techniques;
- Part 3 - Guidance on procedures for sub-sampling in the field;
- Part 4 - Guidance on procedures for sample packaging, storage, preservation, transport and delivery;
- Part 5 - Guidance on the process of defining the sampling plan

Methods of sampling of POPs in soils

For the sampling of solid samples is possible to use the group of norm TNI CEN/TR 15310 Characterization of waste – Sampling of waste material.

- Samples for determination of POP‘s are taken common sampling techniques;
- In the case samples for determination of POP‘s is necessary to respect homogeneity and representativeness of samples.
- During the sampling of samples for POP‘s is necessary to heed on safety of workers.

Extraction and clean-up

- Isolation of PCDDs/Fs from the sample and collect in solvent
- Filter extraction procedure in Soxhlet extractor
- Liquid extraction of condensates and liquid adsorbents
- Purpose of cleaning is remove sample matrix component switch may:
  - overload the separation method
  - Disturb the quantification method
- Add of $^{13}C_{12}$- labeled standards for recovery quantification:
  - extraction standards
  - syringe standards

Content

Introduction to POPs

- Methods of sampling and monitoring of POPs in air;
- Methods of sampling of POP's in solid matrices;
- Methods of analyses and determination of PCDD/F in the samples.

Identification and quantification HRGC/HRMS

- Separation
- Gas chromatography with high resolution (HRGC)
  identification of isomers (position of Cl substituents)
- Identification
- Mass spectrometry with higher resolution (HRMS)
  identification of homologues (number of Cl substituents)
- Isotope dilution of sample

Requirements for the sampling quality control

Validation trial

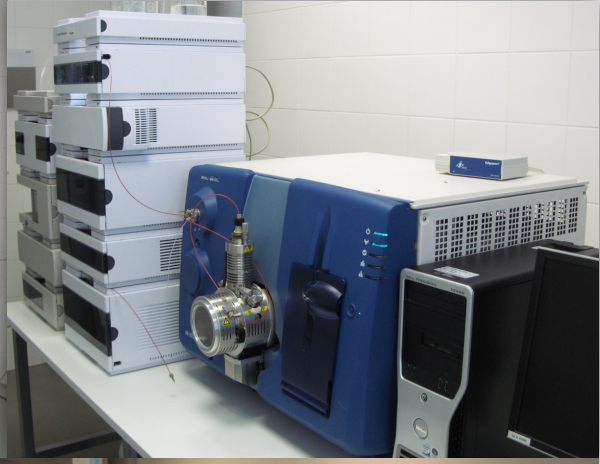
- Particles filtration efficiency (PM 0.3) min. 99.5 %
- PCDDs/Fs capture efficiency min. 90 % ($c_{PCDDs/Fs}$ min. 5% $EL_{I\text{-}TEQ}$)

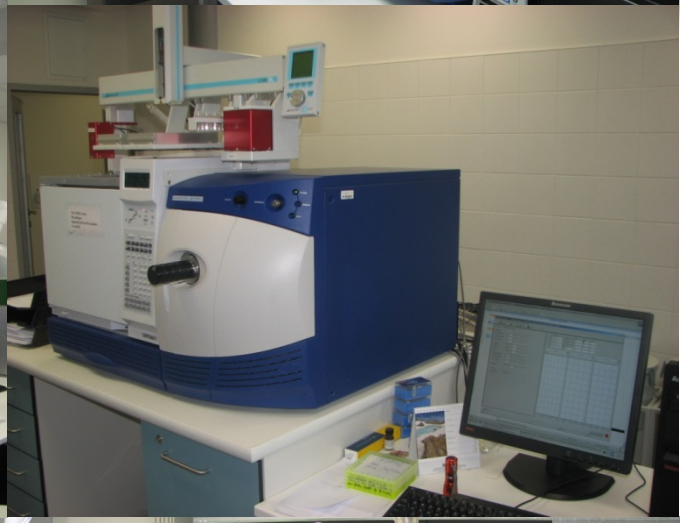
Sampling control

- Leak of sampling train till 5 % nominal output under max. load
- Average isokinetic ratio during sampling in interval 0.95 – 1.15
- Blank sample max. 10 % EL I-TEQ (result < blank sample)
- Control rising of the train before reused in sampling place ($c > EL_{I\text{-}TEQ}$)
- Required recovery of sampling standards min. 50 %

Added congeners	Annual quantity	pg
$^{13}C_{12}$-1,2,3,7,8-PeCDF	400	
$^{13}C_{12}$-1,2,3,7,8,9-HxCDF	400	
$^{13}C_{12}$-1,2,3,4,7,8-HpCDF	800	






Teşekkür Ederim