

Bu Proje, Avrupa Birliği ve Türkiye Cumhuriyeti tarafından ortaklaşa finanse edilmektedir.

#### MUNI | RECETOX SCI



# Effectiveness evaluation, long-term monitoring studies Selected case studies

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## Target

### Examples of long-term monitoring programmes. Effectiveness evaluation of remediation and bioremediation.











### **Contents**

Groundwater monitoring – definitions, approaches

Global and regional long-term monitoring

Monitoring under Stockholm Convention

Using of passive sampling for the monitoring of contaminated sites - passive sampling

**Case studies** 











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## **Groundwater** monitoring

**Objectives groundwater monitoring:** 

- ✤ To assess/understand general groundwater quality of the groundwater (ambient + operational monitoring)
- Finding major pollution sources (ambient/effluent monitoring)
- Compliance with regulations/ standards (effluent monitoring)
- Impact of an accidental pollution (early warning monitoring)

## **Groundwater** pollution

- ✤ Input of untreated domestic wastewater (BOD, Suspended solids, nutrients, bacteria and viruses, *etc.*)
- **Industrial spills; mining (BOD, SS, micropollutants)**
- $\Leftrightarrow$  Agriculture (NO<sub>3</sub><sup>-</sup>, pesticides, Cl<sup>-</sup>....)
- **b** Pit latrines and other on-site sanitation systems
- **Waste dumps (domestic and hazardous wastes)**

Treatment: slow, difficult and very expensive --> prevention!

## Groundwater-surface water relationships



## **Groundwater flows**



May take decades-millenia between recharge  $\rightarrow$  discharge In arid/semi arid zones often poor quality, *e.g.* high salinity

## Unsaturated zone



Contains network of plant roots; usually < 2m thick;

Absent in humid areas, but with large thickness in arid areas;

Zone directly above groundwater table; water pressure is less than atmospheric (tension). Thickness ranges from 1-50 cm, dependent on rock type.

Zone with (saturated) groundwater. Pressure at the groundwater table is atmospheric.

### Process in the unsaturated zone



**\_\_\_** groundwater table

Water in unsaturated zone is prone to evapotranspiration and/or downward flow or 'groundwater recharge from precipitation'.

Assuming a precipitation event with groundwater recharge, then after the event stopped, downward flow will continue until field capacity is reached (curve 1). At field capacity, gravity forces acting on water equal surface tensions exterted by the pore structure, and downward flow terminates. Field capacity depends on type of soil. The one shown here is typical for silty loam.

During dry periods, when there is no downward flow, there may be upward flow or capillary flow. When wilting point is reached, roots are not able to extract sufficient moisture for plant survival. Curve 2 shows wilting point conditions for a silty loam.

## The structure of rocks: porosity

Porosity of rock is the ratio of the volume of open space in the rock and the total volume of rock (including the open space):



- *n* rock porosity
- $V_O$  volume of the open space (m<sup>3</sup>)
- $V_{T}$  total volume of the rock including open space (m<sup>3</sup>)



In <u>consolidated rocks</u>, openings are primarily present at fractures, joints, bedding planes, and solution holes. This type of porosity is referred to as secondary porosity.

In <u>unconsolidated rocks</u>, openings or pores are present between individual grains. This type of porosity is referred to as primary porosity.

## The structure of rocks: porosity

The structure of rocks: porosity

In unconsolidated rocks, (total) porosity ranges from 0.2-0.7.

Rock type	Range of porosities
Unconsolidated rock	0.2-0.4
Gravel	0.2-0.5
Sand	0.3-0.5
Silt→clay	$0.3., -0.7 \rightarrow > 0.95$



## **Groundwater Terminology**



# Classifying aquifers: a quite complicated example

From left to right, aquifer B is phreatic, confined, leaky, confined, and finally, leaky again. Please note that, when the piezometric surface is above ground surface, the aquifer is called 'artesian'.



## Regional flow and groundwater head contour maps



For shallow aquifer: flow towards river.

For lower aquifer: flow towards the city. Here, a cone of depression is present, caused by excessive pumping below the city.

There is also flow from the upper to the lower aquifer through the aquitard.

105 groundwater head contour line

flow direction

Left figure: upper aquifer; right figure: lower aquifer (separating aquitard is not shown)

## Groundwater sampling/ analysis

**Piezometer nests** 

in Exfiltration area



Holocene Cover

## Groundwater sampling/analysis







Karst spring, Mount Hermon area, Syria



Hidden in the little hill, a public supply drinking water well, Brixen, Italy



Groundwater seep (with very low electrical conductivity!!) South-Pare mountains, Tanzania



Dug well in Yemen highland



Artesian well, Strijbeekse beek, The Netherlands

## Groundwater sampling/analysis



### Classical contaminant conceptual model



# LNAPL (light non-aqueous phase liquid; e.g. petrol, benzene)



# DNAPL (Dense non-aqueous phase liquid, e.g. heavy oils)



## Fate of pollutants on groundwater

### Groundwater flow cm's/day (much less in clay)



- Solution Adsorption (but for *e.g.*  $NO_3^-$  unhindered flows)
- **Microbiological degradation (***e.g.* **BOD; also die-off of bacteria)**
- ♦ Complexation, redox reactions, *etc.* (*e.g.*  $Fe^{2+} \rightarrow Fe^{3+} \rightarrow Fe(OH)_{3\downarrow}$ )

## Number, locations, frequency

- Number of stations much dependent on objectives; in The Netherlands: *ca.* 1 per 100 km<sup>2</sup> (near drinking water extractions)
- In many (large and/or less developed) countries: much lower density.
- Location of stations: After surveys. Look at groundwater
  flows and directions; geology, *etc.* Often special boreholes
  have to be constructed.

Piezometers installed in a drillhole



## Number, locations, frequency

Sampling frequency: about 1-4 times per year; much more for:

- **Specific research (see figure hereunder)**
- Rapid groundwater flows; high permeability (sand)



Figure 4: Aerial view (left) and profile (right) of the recommended lay out to monitor point pollution, using reference wells upstream (A) and monitoring wells downstream (B) of the potential source.



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# **Global monitoring of POPs**



## Need for regional monitoring programmes

- 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"**

## **Regional monitoring of POPs**



## Existing monitoring programmes

- European Monitoring and Evaluation Programme (EMEP)
- The Arctic Monitoring and Assessment Programme (AMAP) and the Northern contaminants programme (NCP)
- **Norwegian Arctic and Antarctic stations**
- The Toxic Organic Micropollutants (TOMPS) air monitoring programme
- **Monitoring (MONARPOP)**
- **Integrated Atmospheric Deposition Network (IADN)**
- **The National Air Pollution Surveillance (NAPS)**
- **Global Atmospheric Passive Sampling (GAPS) network**
- MONitoring NETwork (MONET) of POPs in ambient air using the PUF passive samplers

## Regional monitoring programmes

- UN-ECE LRTP POPs protocol includes measurements of several PTSs in air
- Solution AMAP is collecting data on PTSs levels in the Arctic region
- Marine conventions in Europe (OSPAR, Helsinki, Barcelona and Bucharest Conventions) are collecting data from the marine environment
- Solution States Stat
- **DG Environments initiative "Health and Environment"**

## **Regional approches**

### **Regional:**

- UN ECE Convention on Long Range Transboundary Air Pollution – POPs Protocol
- **EMEP** Activities

Co-operative Programme for Monitoring and Evaluation of the Long-Range Transmission of Air Pollutants in Europe



## **EMEP** - Regional approches





## Water Framework Directive

- Water Framework Directive (WFD) 2000/60/EC
- Environmental Quality Standards (EQS) Directive 2008/105/EC
- Directive 2013/39/EU amending Directives 2000/60/EC and 2008/105/EC as regards priority substances in the field of water policy
- Directive 2009/90/EC on technical specifications for chemical analysis and monitoring of water status (QA/QC)

## Water Framework Directive

- **Protection of aquatic ecosystems**
- **No deterioration principle**
- **Water management based on river basin districts**
- **Environmental quality standards and emission controls**
- **%** "Phasing out" of priority hazardous substances
- **Integration of other directives related to water issues**
- Objective: To achieve good water status (ecological and chemical) by December 2015

# Environmental Quality Standards (EQS) Directive 2008/105/EC and its update 2013/39/EU

- Sets out environmental quality standards (EQS) of certain pollutants and substances or groups of substances identified as priority on account of the substantial risk they pose to or via the aquatic environment
- AA-EQS the average value or concentration of the substance concerned calculated over a one-year period. The purpose of this standard is to ensure the long-term quality of the aquatic environment;
- MAC-EQS the maximum allowable concentration of the substance measured specifically. The purpose of this second standard is to limit short-term pollution peaks.
- Member States must ensure compliance with these standards. They must also verify that the concentration of substances concerned does not increase significantly in sediments and/or the relevant biota.

## Priority Substances according to 2008/105/EC

#### **Priority Hazardous Substances**

**Priority Substances** 

Other specific pollutants

Anthracene Brominated diphenylethers Cadmium and its compounds C10-C13-Chloroalkanes Di(2-ethylhexyl)phthalate (DEHP) Endosulfan Hexachlorobenzene (HCB) Hexachlorobenzene (HCBD) Hexachlorocyclohexane Mercury and its compounds Nonylphenols Pentachlorobenzene Polyaromatic Hydrocarbons (PAHs) Tributyltin compounds

Toxic, persistent, liable to bioaccumulate

Alachlor Atrazine **Benzene** Chlorfenvinphos Chlorpyrifos (ethyl) **1,2-Dichloroethane Dichloromethane** Diuron Fluoranthene Isoproturon Lead and its compounds Naphthalene Nickel and its compounds **Octylphenols** Pentachlorophenol Simazine **Trichlorobenzenes Trichloromethane** 

DDT / p,p<sup>c</sup>-DDT Aldrin Dieldrin Endrin Isodrin Carbontetrachloride Tetrachloroethylene Trichloroethylene
## New Priority Substances: 2013/39/EU

- **4** 10 additional Priority Substances (PS)
- **Pesticides and biocidal products**
- ✤ Industrial chemicals (POPs)
- Solution States States States (Second States Sta
- **Stricter EQS for some existing PS**
- **Biota standards for several substances**

## Water Framework Directive

### All surface waters

- **k** Rivers, lakes, artificial waters
- Solution Transitional waters (partly saline)
- Solution Coastal waters (up to one sea mile)

## **Types of Chemical Monitoring**

- Surveillance (12 samples per year )
- **Operational**
- **b** Investigative

## Available water data

- European environmental agency holds a database
- http://www.eea.europa.eu/#tab-datamaps
- And so does AMAP <u>http://www.amap.no/data</u> from the marine environment there is little water data as monitoring is mostly focused on biota
- For **OSPAR** the data are accessible at ICES <u>www.ices.dk</u> ICES seems to allow passive sampling data, but not much is uploaded yet.
- Dome portal has all sediment data up to 2011 available ofline
- http://ices.dk/marine-data/data-portals/Pages/DOME.aspx
- In the UK <u>http://data.gov.uk/</u> On request they also deliver data on specification <u>http://data.gov.uk/odug</u>
- The Netherlands data accessible through <u>http://live.waterbase.nl/waterbase\_wns.cfm?taal=en</u>, but can be delivered in database format through <u>https://www.rijkswaterstaat.nl/formulieren/contactformulier\_servicedesk\_da</u> <u>ta.aspx</u>

The Marine Strategy Framework Directive EU's legal instrument for the protection of our seas Overall objective: achieve or maintain <u>Good Environmental Status</u> (GES) of the EU's marine waters <u>by 2020</u>.

Adoption of an <u>ecosystem-based</u> <u>and integrated approach</u> to the management of all human activities which have an impact on the marine environment.

Regional approach to implementation, and establishment of European Marine Regions





Aegean-Levantine sea

SOUTH ATLANTIC

## Good Environmental Status (GES)

"The environmental status of marine waters where these provide ecologically diverse and dynamic oceans and seas which are clean, healthy and productive" (Art. 3(5)).

- Marine resources are used at a sustainable level, ensuring their continuity for future generations.
- Ecosystems are fully functioning and resilient to humaninduced environmental change;
- Biodiversity is protected and biodiversity decline caused by human activities is prevented;
- Substances and energy introduced in the marine environment by human activities do not cause pollution effects.

## National Atmospheric Observatory Košetice – the core part of ACTRIS-CZ



# Atmospheric Station, CzechGlobe



## Atmospheric Station, CzechGlobe

- ✤ 250 m tall atmospheric tower
- **b** ground based technological containers
- technological container at 230 m
- sir-conditioned cabinets at 8, 50, 125 m
- ♦ elevator (230 m)



AS is focused on the investigation of the background temporal trends, vertical concentration gradient and long-range transport of GHGs and selected atmospheric pollutants.

This is complemented by the monitoring of basic meteorological characteristics.

## Atmospheric station Křešín u Pacova





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## **Stockholm Convention**

The objective of the Convention is to protect human health and the environment from POPs with the ultimate goal to eliminate them, where feasible.

An obvious way to evaluate the effectiveness of the Convention (pursuant to Art. 16) is to measure (to monitor) the concentration of the POPs listed in annexes A, B, and C of the Convention in relevant matrices.

## **Global Monitoring - Air**



**UNEP - Stockholm Convention on POPs** "Effectiveness Evaluation"

**Other Biota** Human Milk

Passive air samplers to complement active air samplers.

- no pump; no electricity
- small and cheap
- simple

Ø

## **Recommendations for POPs to be monitored**

Because it may not be necessary or even possible to analyse all individual congeners present in the POPs mixtures, such as PCBs, PCDDs, PCDFs, Toxaphene, the following substances, incl. some transformation products are recommended for monitoring analysis:

Chemical	Parent POPs (Transformation Products)	
Aldrin	Aldrin	
Chlordane	cis- & trans-chlordane (cis- & trans-nonachlor, oxychlordane)	
DDT	4,4'-DDT, 2,4'-DDT (4,4'-DDE, 2,4'-DDE, 4,4'-DDD, 2,4'-DDD)	
Dieldrin	Dieldrin	
Endrin	Endrin	
НСВ	НСВ	
Heptachlor	Heptachlor (heptachlorepoxide)	
Mirex	Mirex	
PCBs	SPCBs: # 28, 52, 101, 105, 118, 138, 153, and 180	
	PCBs with TEFs: # 77, 81, 105, 114, 118, 123, 126, 156, 157, 167, 169, and 189	
PCDDs	2,3,7,8-substituted congeners	
PCDFs	2,3,7,8-substituted congeners	
Toxaphene	Congeners # 26, 50, 62	

## GAPS, Environment Canada





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## Superstation concept - Observatory Košetice, CR

#### **EMEP POPs Network** Integrated POPs monitoring - Observatory Košetice



# POPs ambient air monitoring programmes until 2006





# **Global/national POPs monitoring - MONET**

### **RECETOX Monitoring Network**





MONET – MOnitoring NETwork		
MONET-CZ =	MONET-PIs =	
Czech Republic	Pacific islands -	
	Fiji	
MONET-CEECs	MONET-Africa	
= 20 CEE	= 17 African	
countries + 2 CA	countries	
countries		







MONET-EUROPE – 55 sampling sites round whole Europe





# POPs Monitoring in ambient air – selected POPs sources



# Distribution of PAHs in DEZA vicinity, 19/03-16/04/2004 - Biggest circle represents the total amount of 0.533 mg of PAHs sequestered



# MONET-CZ - Monitoring of POPs in ambient air – passive sampling - $\Sigma$ 16 PAHs [ng/filtr], January - December 2006





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# Local Monitoring











Spolana Neratovice, Czech Republic Chemical factory – former producer of organochlorinated pesticides

## POPs problems in Spolana - Ghost of the past

The Spolana Neratovice chemical site is a large chemical complex based on chlorine chemistry.

- During the 1960s, the production unit called PCP (pentachlorophenol) produced insecticides and herbicides.
- № 1961 production of HCHs (13% γ) → pesticides + production of TrCBz → production of TeCBz and HCB
- $\forall HCB \rightarrow pentachlorophenolate Na \rightarrow PeCP$
- $\forall$  TeCBz  $\rightarrow$  trichlorophenolate Na  $\rightarrow$  245-T  $\rightarrow$  Agent Orange
- **High contents of PCDDs/Fs**











## Spolana Neratovice







## Protection of environment

- **Enclosure of contaminated buildings A 1420 a A 1030**
- **Treatment of all waste inside the building with concrete soil**
- **Maintain of negative air system**
- **Anti flood protection**
- **Anti noise protection and its monitoring**
- **Monitoring emissions and ambient air**
- **Monitoring health of workers**
- **RECETOX research and monitoring activities**













SF3



# Long term monitoring of ambient air using the passive samplers (RECETOX 2004 – 2008)

















**70** 

# Monitoring of remediation – case of Spolana Neratovice – relative levels of HCHs in ambient air (ng/filtr)




# **Remediation in Spolana**



# **240 000 000 €**

# And what 8 ??

Spolana Neratovice, CR Former producer, highly contaminated site effective, successfull, but not complete Remediation - by using of BCD technology -What we know about this site ??? What happens under surface ??? F 28 ρ ø 100000 120000 140000 160000 180000









Košetice in this time -Country background below 10 ng filter<sup>-1</sup> SEHİRCİLİK BAKANLIĞI çevre ve ikilm Eylemi Sektör Operasyonel Programı Ľ .v .v Kalıcı Organik Kirleticiler 

#### MONET-CZ/Spolana – log term trends – HCHs – 2004 – 2008 [ng/filter]

AN LONG











#### Distribution of HCHs in SPOLANA vicinity, 16/02-15/03/2004 Biggest circle represents the total amount of 445 ng of HCHs (a sum of α, β, γ, δ-HCH) sequestered on the filter



# Monitoring of remediation – case of Spolana Neratovice – relative levels of HCHs in ambient air (ng/filtr)



# EU Project APOPSBAL Former Yugoslavia – environmental consequences of Balkan wars

# **EU Project APOPSBAL**

Assessment of the selected POPs (PCBs, PCDDs/Fs, OCPs) in the atmosphere and water ecosystems from waste materials generated by warfare in former Yugoslavia



- Klanova, J.; Kohoutek, J.; Cupr, P.; Holoubek, I. Are the residents of former Yugoslavia still exposed to elevated PCB levels due to the Balkan wars? Part 2: Passive air sampling network. Environ. Int. 2007, 33, 727-735
- Skarek, M.; Cupr, P.; Bartos, T.; Kohoutek, J.; Klanova, J.; Holoubek, I. A combined approach to the evaluation of organic air pollution a case study of urban air in Sarajevo and Tuzla (Bosna and Hercegovina). Sci. Tot. Environ. 2007, 384, 182-193

# **APOPSBAL – RECETOX** sampling sites



# APOPSBAL – passive sampling – identification of hot spots



Klanova, J.; Kohoutek, J.; Cupr, P.; Holoubek, I. Are the residents of former Yugoslavia still exposed to elevated PCB levels due to the Balkan wars? Part 2: Passive air sampling network. Environ. Int. 2007, 33, 727-735

Skarek, M.; Cupr, P.; Bartos, T.; Kohoutek, J.; Klanova, J.; Holoubek, I. A combined approach to the evaluation of organic air pollution - a case study of urban air in Sarajevo and Tuzla (Bosna and Hercegovina). Sci. Tot. Environ. 2007, 384, 182-193 Boršov u Kyjova, Czech Republic Fire of pesticide storehouse

# Boršov u Kyjova





#### Site history

- **Solution** Former pesticides storage used in 1980s
- **Damaged in 1988 by huge fire; 20 000 people evacuated**
- HW generated by fire temporary deposited at the site in a underground sarcophagus

# Boršov u Kyjova – basic information





#### **Basic information**

- Temporary sarcophagus was constructed as a double wall reinforced concrete construction; 31 x 10,5 m x 5,5 m.
- Nearly 700 tons of waste partially burnt agrochemicals and other polluted waste



# Monitoring

Before entering the sarcophagus: Monitoring of the ambient air

- field measurements of CH<sub>4</sub>, HCN, NH<sub>3</sub>, H<sub>2</sub>S, C<sub>x</sub>H<sub>y</sub>, CO<sub>2</sub>, CO a  $O_2$
- ambient air sampling for lab analyses (PM10, hydrogen cyanide,

pesticides (organochlorinated, triazins and acid pesticides)

Sarcophagus check by microcamera

- Findings: above limits (atrazin, prometryn, MCPA a MCPP);
  - acceptable exposure limits not exceeded; need of full protection

of workers (masks, filters, disposable suit)





d<mark>eko</mark>nta

Contamination of the Baroque Theater at the Castle in Český Krumlov with organochlorine and organotin pesticides and its solution

# Český Krumlov



Historic Centre of Czech Krumlov is an excellent example of a small central European medieval town whose architectural heritage has remained intact for more than five centuries.

# Baroque castle



Czech Republic - Český Krumlov, historic center, UNESCO heritage, historic site with exceptional value.

## **Baroque theatre**











Mašinérie, jevištní technika zámeckého divadla, je po letech soustředěného zájmu z nejpodstatnější části obnovena. Některé funkce barokní jevištní techniky v provazišti a v krovu především rumpály létacich strojů, rumpály na sufitové osvětlení, rumpál v krovu (snad rumpál na mraky nebo alegorie) a také principy vedení lanovodů sufit a prospektů ještě nejsou dostatečně poznány a pochopeny. Musíme doufat, že při dostatečné pily a vytrvalosti najdeme odpovědí a řešení v archivních zdrojích nebo v samotné jevištní technice krumlovského divadla či konstrukčních principech divadel jlných. Je nepochybné, že obnovená barokní jevlštní technika snese nejpřísnější srovnání a je vzorem pro vetšinu pracovišť v celém divadelním světě.















## Theatre contamination

# Reasons of contamination

Improper application without proper preparation: přípravky typu Lastanox ( $Sn_{org}$ ), Pentalidol (5% PCP, 2% DDT, 0,1%  $\gamma$ -HCH) and methylbromid



Suspicion of technological discipline: uniform application and application to a dust layer deposited on horizontal surfaces



Effects: in the early 1990s, a longer stay in the theater resulted in irritation of the eyes, mucous membranes and skin

Decontamination: during the 1990s the amount of contaminated dust and rubble was removed (approx. 5 tons + 500 kg in the second stage)

## Extent of contamination of the truss structure





# Air sampling



Air sampling in 2001: in the auditorium, on the stage, in the upper rope yard and in the theater floor Sampling in the years 2003 to 2005: in parallel at two sampling points - the stage and the floor of the theater

Sampling of POPs (OCPs): according to US EPA methodology TO-13 (sampling time 12 hours; collected volumes approx. 200 m<sup>3</sup>) Sampling of organotin substances (Snorg): according to the NIOSH methodology (sampling time 8 hours; collected volumes approx. 0.4 m<sup>3</sup>)

# Testing of passive samplers

 2004 - 2006 - the attic space of the chateau theater was used as a test chamber for testing the effectiveness of POPs capture from the open air within the preparation of monitoring of POPs in the open air within the MONET program of the RECETOX center.



# Two sampling campaigns in 2017



### **Results of measurements**



### **Planned measures**



Závažná degradace prostředí krovu aplikací insekticidních látek na bázi polychlorovaných bifenylů (PCBs), organochlorových pesticidů (DDT, Lindan) a jiných organocíničitých látek.

# Free deposition of pesticide dust





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# TEŞEKKÜR EDERİM...







