## **Environmental Sampling**

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## Introduction

#### Sampling

Proces of taking or constitung of sample Sampling is a part of testing program

An estimate of the proportion of errors:Sampling85%Transport10%Laboratory analysis5%

#### **Program of testing**

Total sampling operation, from the first step in which the objectives of sampling are defined to the last step in which data is analysed against the objective

## Testing program

- 1. Defining the objectives of the testing program (comparison of sample quality with limits defined in legislation, health risk assessment, environmental risk assessment...)
- 2. Preparation of sampling plan
- 3. Sampling according to sampling plan and sample treatment on site
- 4. Create a sampling protocol
- 5. Storage / transport to laboratory
- 6. Preparation of the test sample
- 7. Sample pretreatment
- 8. Performing the test
- 9. Sampling summary report
- 10. Compare results with program objectives

## Sampling documentation

# The documentation should comprise at least:

- Sampling plan
- Sampling protocol
- Laboratory report

# Sampling methods

#### Sampling with judgment

A sampling method in which the sampling site selection is based on the subjective judgment of the person making the sampling (modification – **tergeted sampling**)

#### **Probabilistic sampling**

Sampling method based on statistical sampling principles The basic principle is that each part of the tracked set has the same probability of being selected as a sample.

**Probability sampling should be used preferentially** 

## **Technical equipment**

(working with samplers is part of the tutorial video)



## Sampling on site

- Sampling is the process by which we obtain information about the sampled unit by selecting characteristics.
  - Sample a portion of material selected from a larger quantity of material

Sub-sample – individual portion of material collected by a single operation of a sampling device

Composite sample – two or more subsamples mixed together in appropriate portions from which the average value of desired characteristic may be obtained

Representative sample – sample that can be expected to reflect adequately the properties of interest in the parent population

# Sample size

Sample - it must be large enough to take account of the limits of determination of the method and at the same time only large enough to be manipulated and treated

Sample - this shall include all particle sizes in the same proportion as they occur in the sampled unit. The particle size determines the total sample size

|                  | Material characteristic                    |                  |                        |                      |  |  |  |  |
|------------------|--|------------------|------------------------|----------------------|--|--|--|--|
| Particle<br>size | very mostly mostly homogeneous homogeneous |                  | mostly<br>heterogenous | very<br>heterogenous |  |  |  |  |
|                  | R  | epresenattive am | ount of sample         |                      |  |  |  |  |
| mm               | g  | g                | g                      | g                    |  |  |  |  |
| 0,010            | 0,015                                      | 0,010            | 0,006                  | 0,003                |  |  |  |  |
| 0,100            | 0,951                                      | 1,000            | 1,012                  | 1,012                |  |  |  |  |
| 1,000            | 60,000                                     | 100,000          | 180,000                | 320,000              |  |  |  |  |
| 10,000           | 3786                                       | 10000            | 32009                  | 101193               |  |  |  |  |

If it is not of the stated size - it is necessary to carry out tests on more samples and use statistical estimates of the monitored parameters

Homogenity / Heterogenity – the degree to which a propety or constituent is uniformly distributed throughout a quantity of material

#### Sample

There must be no change in the monitored parameters from the time of collection until the transfer to the laboratory

#### **Sampling container**

The material must not affect the original properties of the sample (sorption, chemical reactions, leaching of material) The sampling container must avoid leakage of the sample into the environment and prevent the health and safety of persons

To determine inorganic parameters - recommended PE sampling container

To determine organic parameters – recommended glass sampling container with teflon closures

#### Labeling sampling container

Clearly readable, unambiguous codes for each sampling container

Label directly to the sampling container with a permanent marker or sticker (preferably both!)

Alternatively, place sampling containers in a plastic bag and seal it tightly

#### **Preservation of samples**

Any method used to stabilize the sample in such a way that the properties to be tested remain stable from sampling to analysis

Losses or changes may be caused, for example, by:

Microbiological activity

Oxidation with air oxygen, CO2 reaction, reaction with water (humidity)

Loss of volatile ingredients

Photochemical reactions, chemical transformations (temperature)

#### **Common methods of sample conservation:**

Storage without air access (or directly nitrogen atmosphere)

Storage in the dark

Storage at temperatures <4 ± 2 ° C (may result in precipitation) or freezing

Drying (watch out for volatile componds)

Chemical preservation (addition of preservative, extraction on site)

#### **Chemical reagents:**

sodium hydroxide, nitric acid, sodium thiosulfate ...

## Sample analysis

- Storage
- Preparation of test sample
- Pre-treatment of test sample
  - Analysis
  - Comparison of results with defined limits



# Laboratory results

Uncertainty of the result – the range of values in which the actual value lies with a certain probability

- Random errors affect the accuracy of the result
- Systematic errors affect the veracity of the result

Accuracy - the tightness of agreement between measurement results repeated under predefined conditions

Truthfulness - the tightness of the agreement between the arithmetic mean and the reference value

## Work safety

Safety precautions - an integral part of the sampling plan

Safety and health hazards - due to sampling (eg release of toxic gases), hazardous environment

Identifying important safety measures to protect the sampler

Particular attention should be paid to:

- Organizational responsibility
- •Staff training in health and safety
- Working with hazardous substances (especially inhalation risks)
   Hazardous biological factors
- •Checking the working environment at the sampling site
- Application of PPE and first aid principles

•Specific risks!

### Sampling of sediments and water





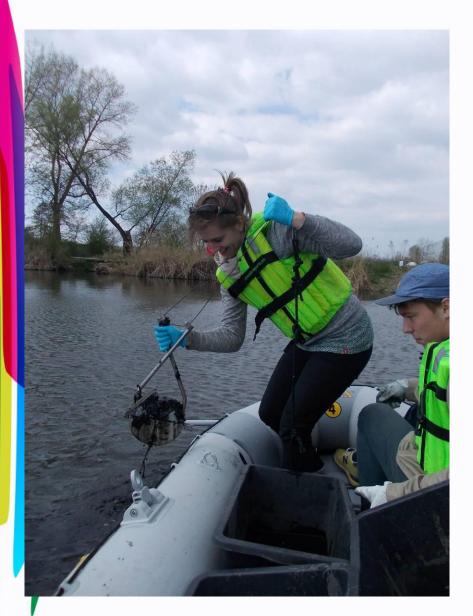


Grab sampler

Piston dril sampler

Peat probe

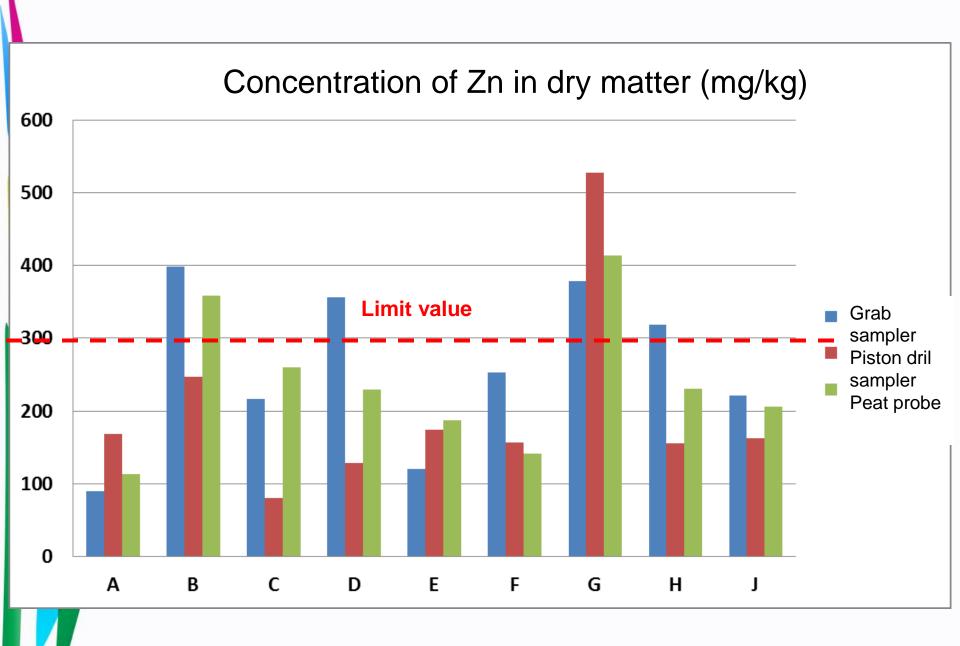
### Case study

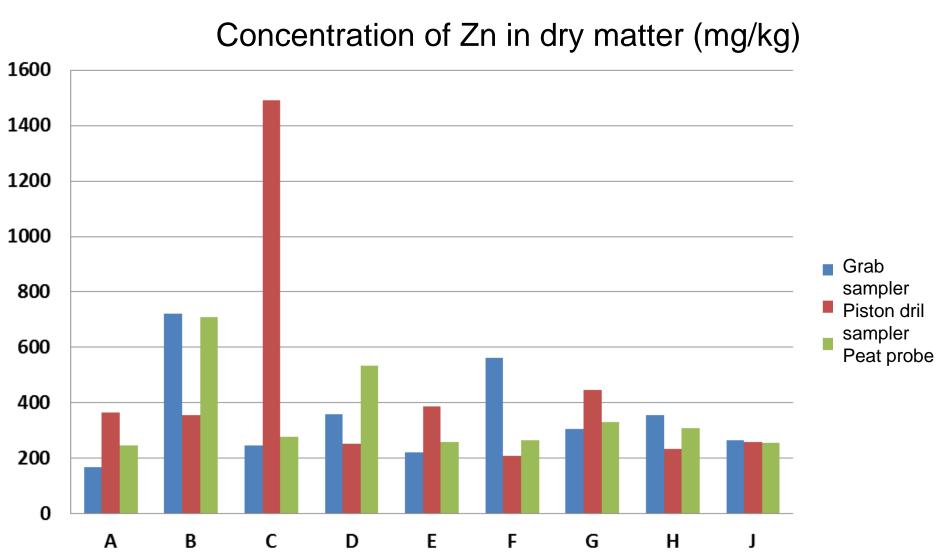




## Decree No. 257/2009 Coll.

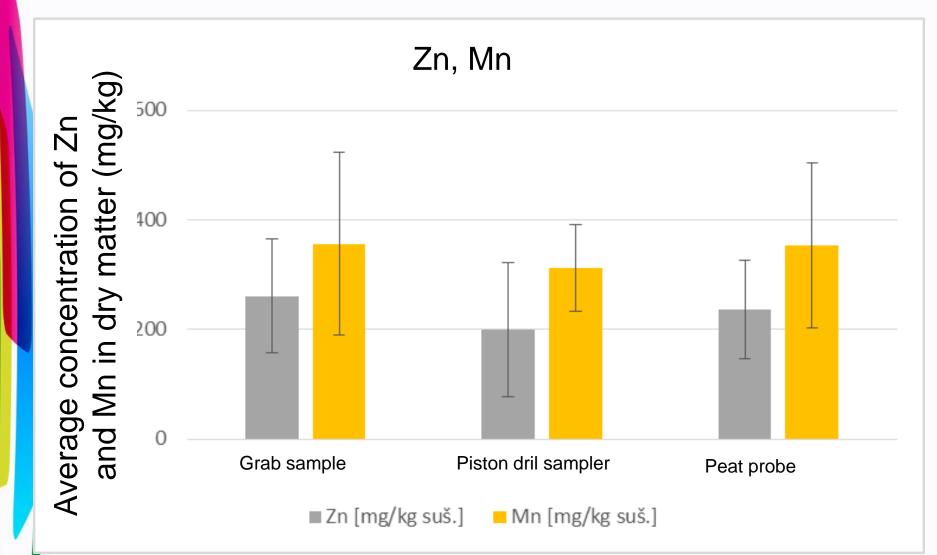
| Parameter                   | Limits (mg.kg <sup>-1</sup> dry matter) |
|-----------------------------|---|
| As                          | 30                                      |
| Be                          | 50                                      |
| Cd                          | 1                                       |
| Со                          | 30                                      |
| Cr                          | 200                                     |
| Cu                          | 100                                     |
| Hg                          | 0.8                                     |
| Ni                          | 80                                      |
| Pb                          | 100                                     |
| V                           | 180                                     |
| Zn                          | 300                                     |
| BTEX                        | 0.4                                     |
| PAH                         | 6                                       |
| PCB                         | 2                                       |
| hydrocarbons C10-C40        | 300                                     |
| DDT (including metabolites) | 0.1                                     |





Uncertainty of the result - an interval of values in which the actual value lies with a certain probability

Accurasy = Trueness + Precision



## Sampling of playgrounds

 Decree No. 238/2011 Coll., Laying down hygiene requirements for swimming pools, saunas and hygiene limits for sand in sandboxes of outdoor playing areas.

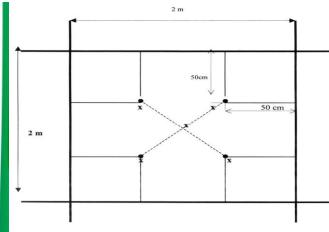
| Parameter | Limits [mg/kg of dry<br>matter] | Parameter | Limits [mg/kg of dry<br>matter] |
|-----------|---------------------------------|-----------|---------------------------------|
| As        | 10                              | Hg        | 0.3                             |
| Ве        | 1,5                             | Мо        | 0,8                             |
| Cd        | 0,5                             | Ni        | 60                              |
| Со        | 50                              | Pb        | 60                              |
| Cr        | 100                             | V         | 80                              |
| Cu        | 0,3                             | Zn        | 150                             |

## Sampling of playgrounds

Exposure pathways– dermal contact, ingestion of dust, ingestion of soil

EPA – exposure factors Children: Ingestion of soil: 50 mg/day Ingestion of dust: 60 mg/day





# Risk analysis of contaminated sites - objectives

The objective of the risk analysis is to describe the existing and real potential risks arising from the presence of pollution in a comprehensive way. These risks may be a current threat to human health or to individual environmental components (eg natural resources and ecosystems)

Or potential threats in the future can be described, eg in the event of further widespread pollution or changes in the use of the site. Based on the assessment of the severity of these risks, remediation measures are set, (or risk management strategy are set)

1) Survey of available data and survey of the state of pollution of the site

The survey is usually carried out in several follow-up stages (preliminary risk analysis can be prepared at the level of the preliminary conceptual model or the first stages of the survey)

2) Assessment of health risks and risks for individual components of the environment resulting from the identified pollution

3) Design of objectives and final parameters of the remediation measures and how to demonstrate their achievement, including the design of post-remediation monitoring

4) Propose remediation measures or compare alternative risk reduction or elimination procedures, or Proposal for the feasibility study
- assessment of the practicality of a proposed project or system.

Technical, legislative, financial (cost-benefit analysis of the risk reduction) and time aspects must be taken into account

5) Risks are assessed with respect to the existing, anticipated or possible way of use of the contaminated site and the surrounding area to the extent possible of migration and the effects of contamination.

# Design of the risk analysis

Comprehensive processing of risk analysis implies sufficient and up-to-date exploration of the contaminated area and knowledge of all transport routes through which pollution can spread beyond the original contamination.

At first - **preliminary conceptual model** of the contaminated area is processed which comprises:

the character of the area information on sources and hot spots of pollution information on real transport routes risk recipients

## Risk analysis - conceptual model

The conceptual model defines the expected exposure routes from source to risk recipient

#### Exposure path = source of contamination + transport pathway + exposure scenario of the risk recipient

## Health risk assessment

- 1) Identification of chemical substances in the contaminated area in terms of possible health risks
- 2) Comparison of concentrations of identified harmful substances in the contaminated area with defined concentration limits according to the legal regulations or with recommended standards or specific values for each of the environmental and working environment factors
- 3) Estimation of health risks based on real exposure scenarios

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## Environmental risk assessment

In particular in these cases:

- Contaminants threat underground and surface water

   in particular protected areas of natural water
   accumulation, groundwater and surface water
   sources and their buffer zones
- 2) Surface water is used or suitable for the life and reproduction of fish and other aquatic animals
- 3) If there is a social demand for environmental risk assessment for a specific case

# Risk analysis - validity

Risk analysis is based on facts verified or known at the time of its processing and therefore has a limited validity.

If there are changes that significantly affect the conclusions of the risk analysis (eg changes in land use, changes in the development or extent of pollution, new scientific knowledge about the effects of the contaminant, new remediation technologies), it is necessary to follow the updated risk analysis, which is mainly focused on the evaluation and the assessment of the consequences of these changes

# **Risk analysis - limitation**

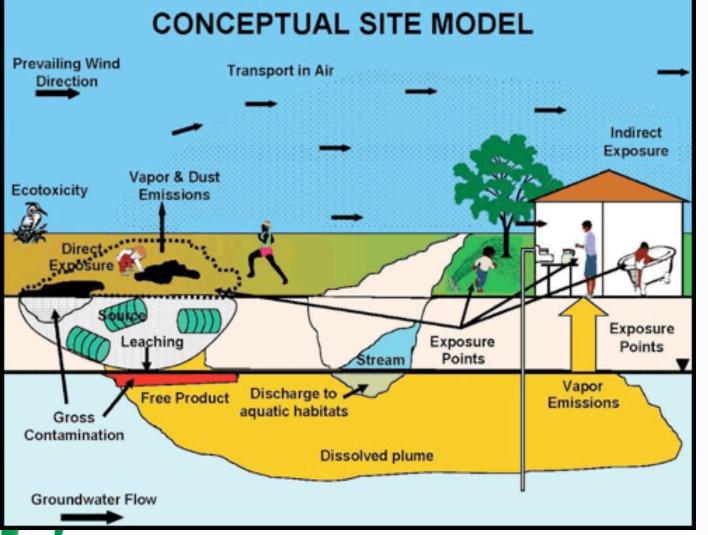
Lack of information on the amount of contamination in the underground

Lack of information on background concentrations of substances or background pollution

Insufficient geological and hydrogeological survey of the site

The results of exploratory work are no longer up to date

# **Conceptual model**



•Conceptualize the relationship between contaminant sources and receptors through consideration of potential or actual migration and exposure pathways

• Presents the current understanding of the site

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| Soil   | <b>▼ ∨</b>  | egetable ingestion                       |                         |
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#### Choose Chemical: HCB

| Chemical: HCB                |          | 1st Title Line: 780 2nd:                     | ND     |
|------------------------------|----------|--|--------|
| Chemical Parameters          | Value    | Toxicity Parameters                          | Value  |
| CAS Number                   | 118-74-1 | EPA Carcinogenic Clasification               | B2     |
| Molecular Weight [g/mole]    | 284.4    | 284.4 Ingestion Slope Factor [1/(mg/kg-day)] |        |
| Density [g/cm^3]             | 2        | Inhalation Slope Factor [1/(mg/kg-day)]      | 1.6    |
| Vapor Pressure [mmHg]        | 1.09E-5  | Dermal Slope Factor [1/(mg/kg-day)]          | 3.2    |
| Solubility [mg/l]            | 6.2      | Oral Reference Dose [mg/kg-day]              | 8E-4   |
| Henrys Law [(mg/l)/(mg/l)]   | 5.41E-2  | Inhalation Reference Dose [mg/kg-day]        | ND     |
| log Kow                      | 5.89     | Dermal Reference Dose [mg/kg-day]            | 3.2E-4 |
| Koc [cm^3/g]                 | 5.5E+4   | Oral-Soil Abs. Adjust. Factor [-]            | 1      |
| Kd [(mg/L)/(mg/kg)]          | ND       | Oral-Water Abs. Adjust. Factor [-]           | 1      |
| Diffusion in Air [cm^2/s]    | 5.42E-2  | Dermal-Soil Abs. Adjust. Factor [-]          | 1      |
| Diffusion in Water [cm^2/s]  | 5.91E-6  | Dermal-Water Abs. Adjust. Factor [-]         | 1      |
| Vegetable Uptake Factor [-]  | use Kow  | Inhalation Abs. Adjust. Factor [-]           | 1      |
| Degradation (high-end) [1/d] | ND       | Skin Permeability Coefficient [cm/hr]        | 0.25   |
| Degradation (low-end) [1/d]  | ND       | MCL (Maximum Contaminant Level) [mg/l]       | ND     |

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| Information                                 |                     |                              |    |
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| Enter Red                                   | ceptor Specific Dat | ta                           |    |
|   | Adult Resident - Ty | pic Child Resident - Typical |    |
| Lifetime [yr]                               | 70                  | 70 🔺                         |    |
| Body Weight [kg]                            | 70                  | 15                           |    |
| Exp. Freq. for Soil [events/yr]             | 40                  | 130                          |    |
| Exp. Duration for Soil [yr]                 | 9                   | 6                            |    |
| Ingestion rate for soil [mg/day]            | 40                  | 90                           |    |
| Total Skin Surface Area [cm^2]              | 18400               | 6800                         |    |
| Fraction Skin Exposed to Soil [-]           | 0.11                | 0.13                         |    |
| Soil/Skin Adherence Factor [mg/cm^2]        | 0.2                 | 0.2                          |    |
| Exp. Freq. for Vegetable Intake [events/yr] | 350                 | 350                          |    |
| Exp. Duration for Vegetable Intake [yr]     | 9                   | 6                            |    |

#### Enter Bioavailability in Soil for Each Chemical [fraction]

1.0

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# SEKM

The system for the evidence of contaminated sites

SEKM database and a set of its software application utilities for the acquisition, management and presentation of information about contaminated sites

The SEKM system is available at <a href="http://www.sekm.cz/">http://www.sekm.cz/</a>

## **Environmental sampling**

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