



MERCURY SEMINAR 2015

Bioavailability and bioaccessibility of the chemical species of mercury in soils in Northern France

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Structure of our university



Department of Chemistry and Biochemistry

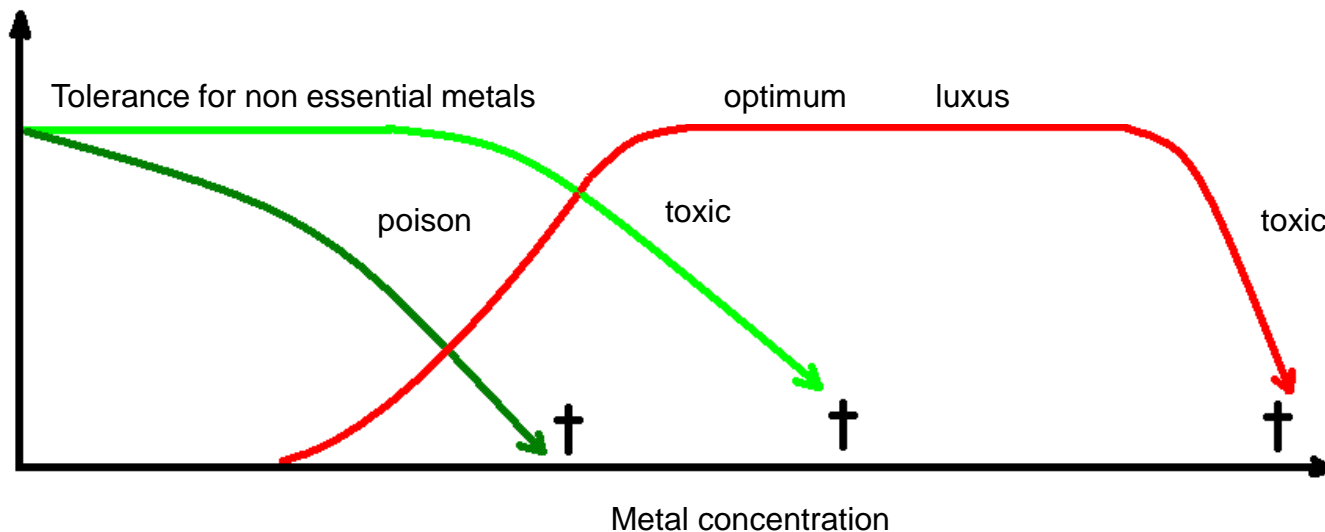


Toxicity of heavy metals

($\rho > 5 \text{ g} \cdot \text{cm}^{-3}$)

metals - Cd, Zn, Pb, Hg, Cr, Ni, Cu ...

Heavy metals ↗
↘ Essential heavy metals
Toxic heavy metals



Biological Availability

(Bioavailability)

Definition can be based on either the percentage of a nutrient **ingested** or the percentage of a nutrient **absorbed** that becomes useful to the organism

The percentage ingested is preferred by some because the percentage absorbed is difficult to determine and relies on an indirect analysis

Bioavailability x Bioaccessibility

Bioavailability (*in vivo* studies)

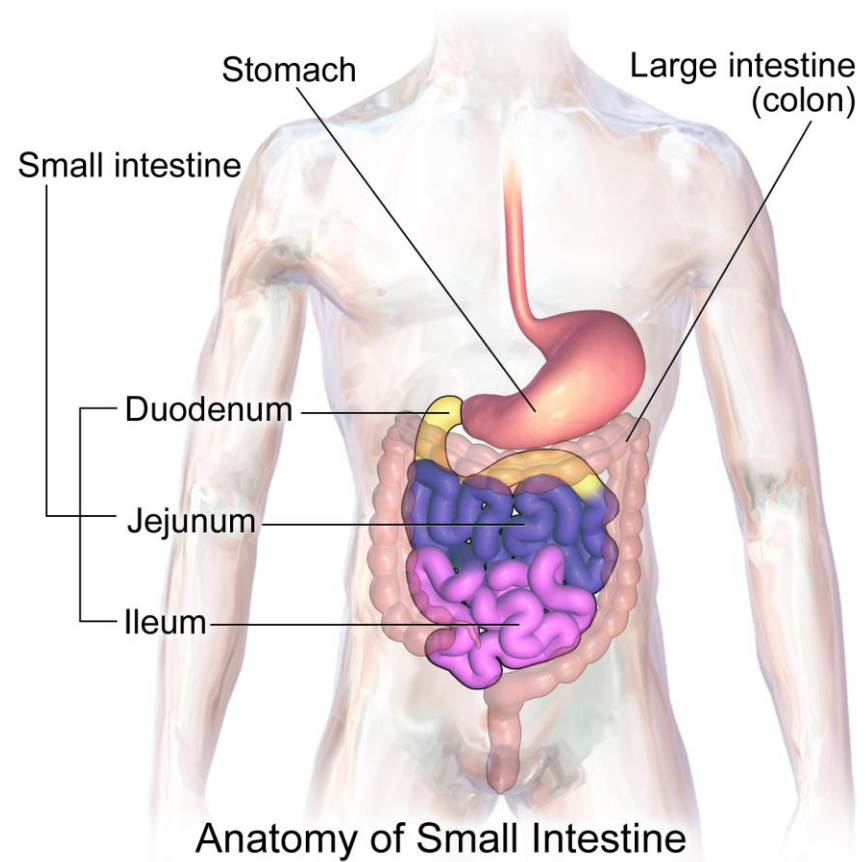
Fraction of a contaminant in the blood compartment
Time-consuming, variable, ethical problems
Release/complexation processes are a black box

Bioaccessibility (*in vitro* studies)

Fraction of a contaminant which releases from soil and which becomes available for intestinal transport
Important precursor to bioavailability

What happens to ingested contaminants?

- **Stomach**
 - Low pH, pepsin
- **Small intestine**
 - Absorption across epithelium
 - Breakdown of sugars, fats proteins
- **Large intestine (colon)**
 - Absorption of water
 - Microorganisms



Comparison study for metal bioaccessibility?

- Bunker Hill soil (USA)
- 6 European *in vitro* models!
 - BGS: PBET
 - RIVM
 - Bochum Universität : DIN
 - TNO : TIM
 - LabMET: SHIME
 - UBM Barge
- Assess bioaccessibility
- Relate to *in vivo* bioavailability
- FASTED versus FED conditions

Our questions, plans and information

- Bioaccessibility should always be higher than Bioavailability
- Role of separation method in bioaccessibility
- Every *in vitro* method has its value: proper interpretation needed
- Contaminant speciation in the GIT



Our experiment

Part 1: Initial studies – D. experiments (Cu,Cd,Pb,Hg)

Part 2: Initial studies – M+S studies (Cu,Pb,Zn)

Part 3: New project – MERCURY M+S

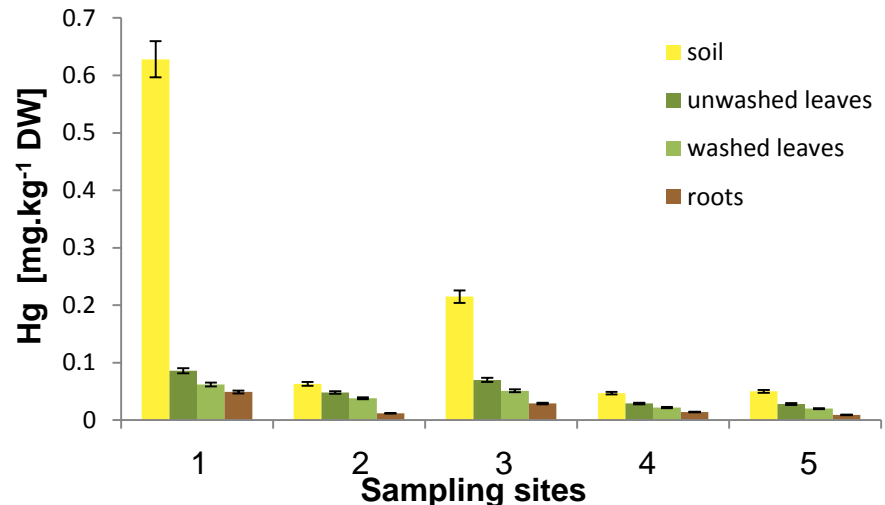
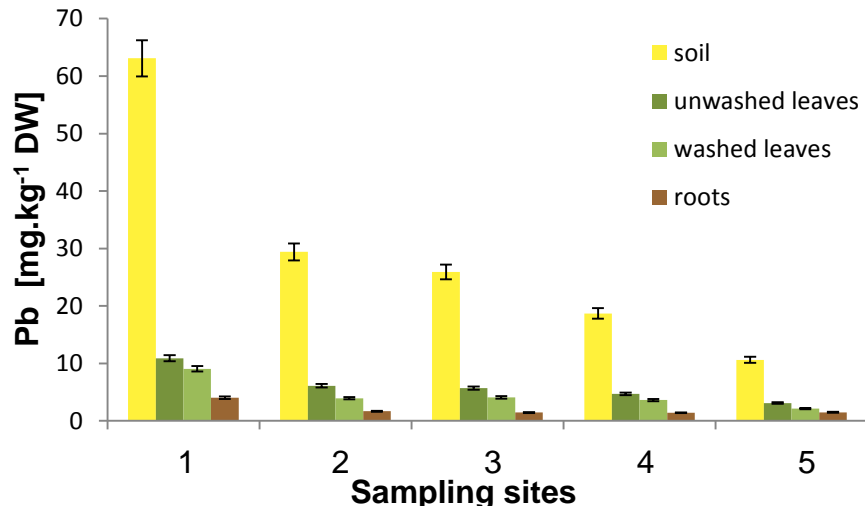
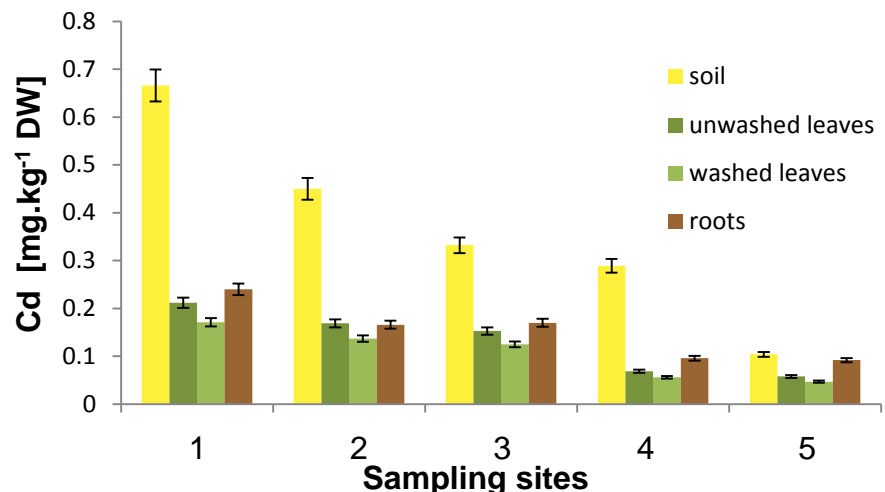
Part 1: Initial studies

Dandelion experiments (Cu,Cd,Pb,Hg)

- **total content of Cu, Cd, Pb, Hg in soil samples**
- **total content of Cu, Cd, Pb, Hg in plant samples**
- **single extractions**

RESULTS - Part 1: Initial studies – D. experiments (Cd,Pb,Hg)

Study of Cd, Pb, Hg content in leaves, roots and soil and study of the effect of washing plants at element content.

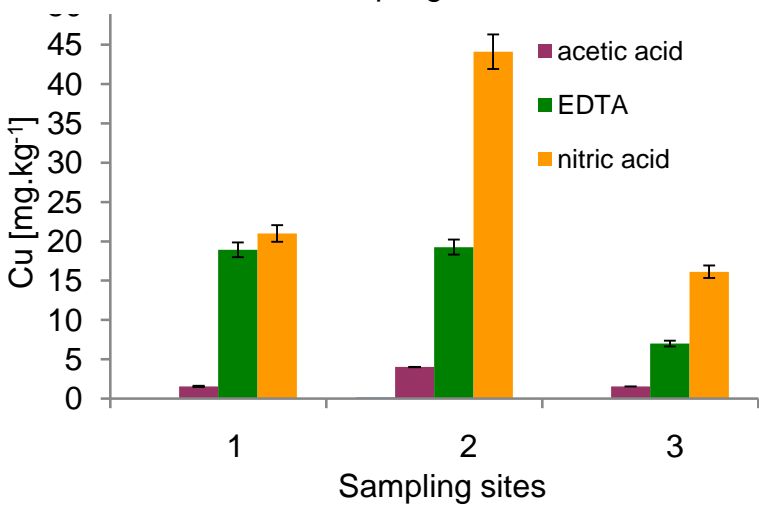
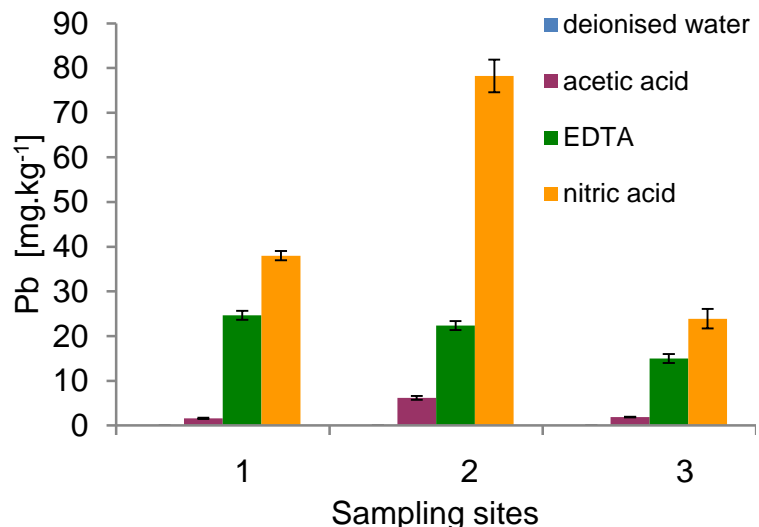
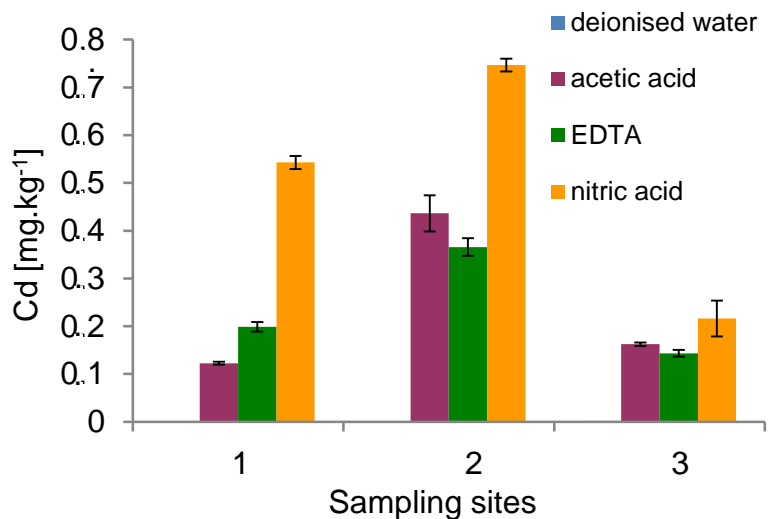


Correlations soil-roots, soil-leaves and roots-leaves

Pearson's correlation coefficient	Correlation soil-roots	Correlation soil-leaves	Correlation roots-leaves
Cadmium	0,953	0,919	0,992
Lead	0,665	0,910	0,890
Mercury	0,574	0,971	0,667

RESULTS - Part 1: Initial studies – D. experiments (Cd,Pb,Cu)

Study of Cd, Pb and Cu content in soil by using different leaching methods: 2M HNO₃, 0.43M CH₃COOH, 0.05M EDTA and deionised water



Regulation No. 13/1994
of the Czech Ministry of Environment :

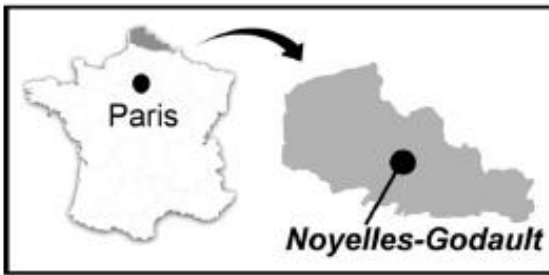
Cd: 1 mg.kg⁻¹
Pb: 70 mg.kg⁻¹
Cu: 50 mg.kg⁻¹
Hg: 0,8 mg.kg⁻¹









Part 2: Initial studies

Miscanthus experiments (Cd,Pb,Zn)

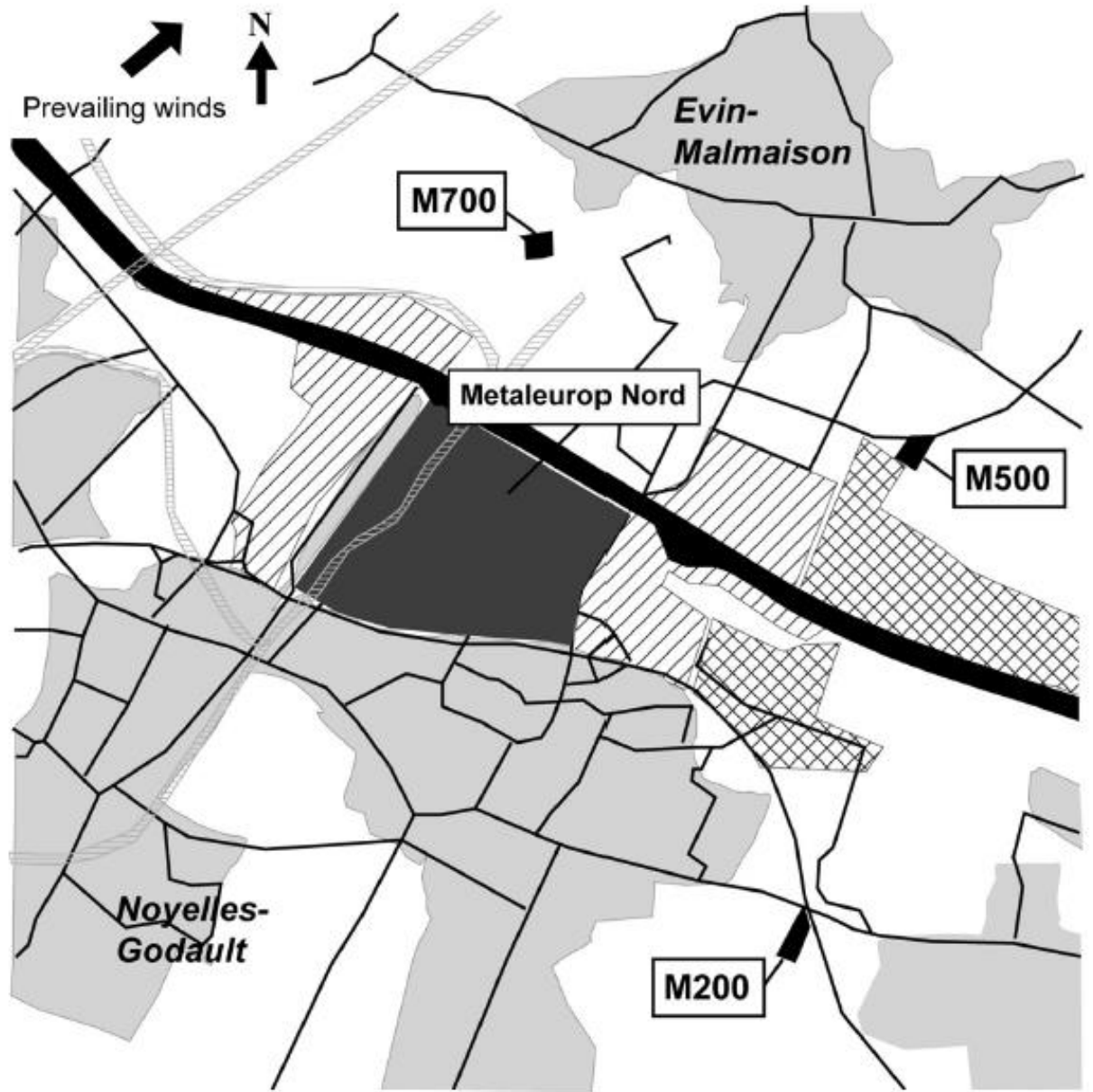
- **total content of Cd, Pb, Zn in soil samples**
- **total content of Cd, Pb, Zn in plant samples**
- **single and sequential extractions**
- **test for bioaccessibility and bioavailability**

Experiment - Part 2: Initial studies – M. experiments (Cd,Pb,Zn)

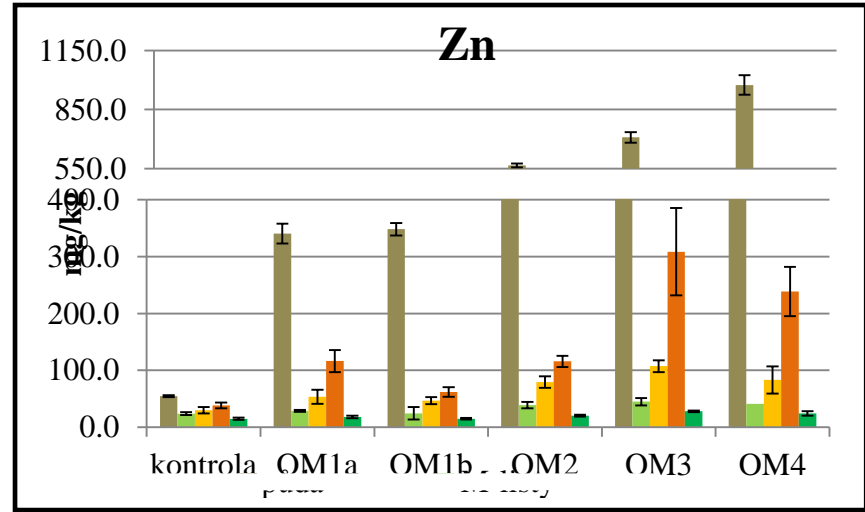
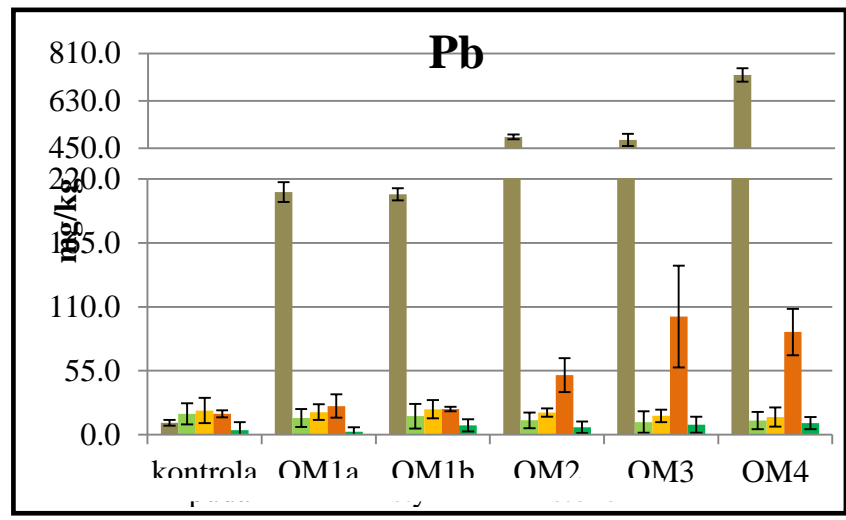
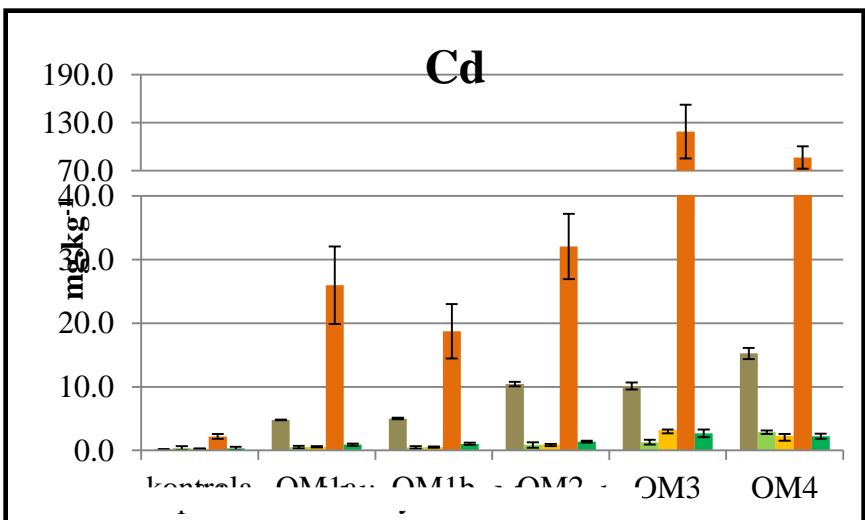


-  Agricultural area
-  Urban area
-  Highly anthropogenic area
-  Forested area
-  Smelter
-  Deule canal
-  Road
-  Railway

0 1,000 meters



RESULTS - Part 2: Initial studies – M. experiments (Cd,Pb,Zn)



- Soil
- Leaves
- Steam
- Root
- Rhizoderm

Part 3: New project

– MERCURY M+S

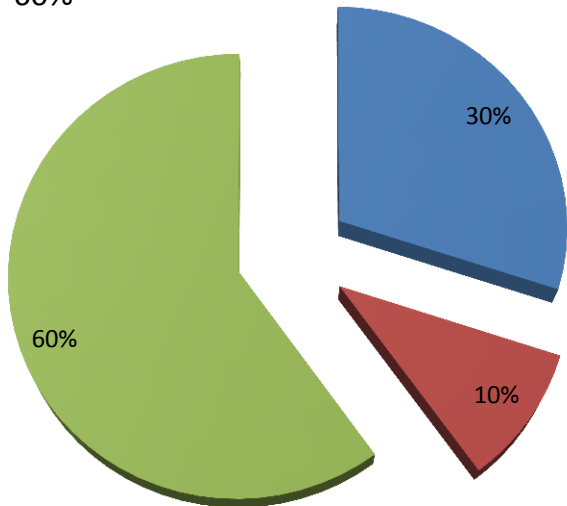
- **total content of Hg in soil samples**
- **total content of Hg in plant samples**
- **sequential extractions**
- **speciation analysis**
- **test for bioaccessibility and bioavailability**

Mercury in environment

- Inorganic mercury enters the environment from a variety of natural and anthropogenic sources
- Methylmercury is formed in the environment (in water bodies and wetlands) by micro-organisms that convert inorganic mercury to the organic (methylated) form.

Sources of mercury in the environment

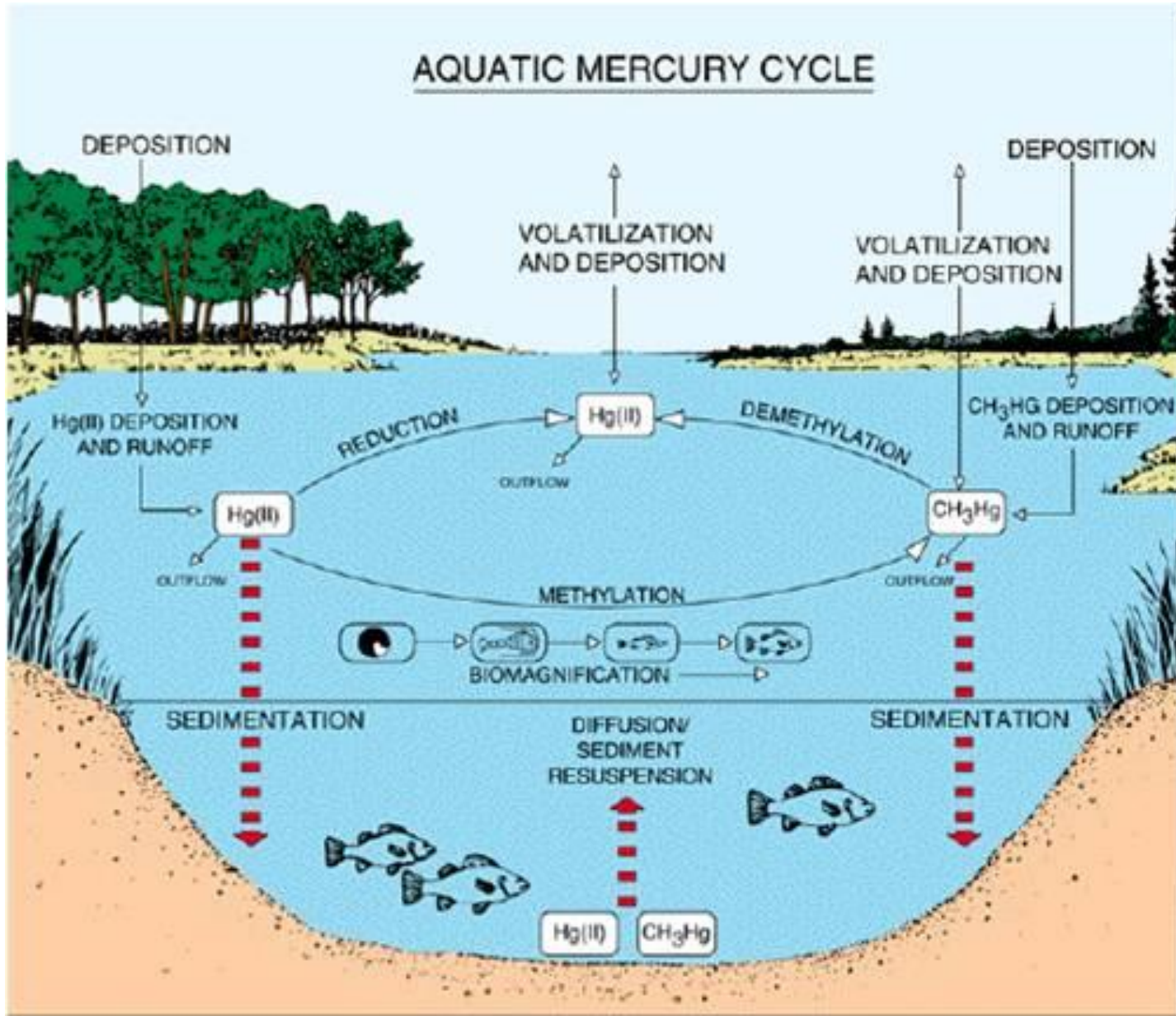
- Current anthropogenic sources, 30%
- Natural geological sources, 10%
- 'Re-emissions' of previously released mercury, 60%



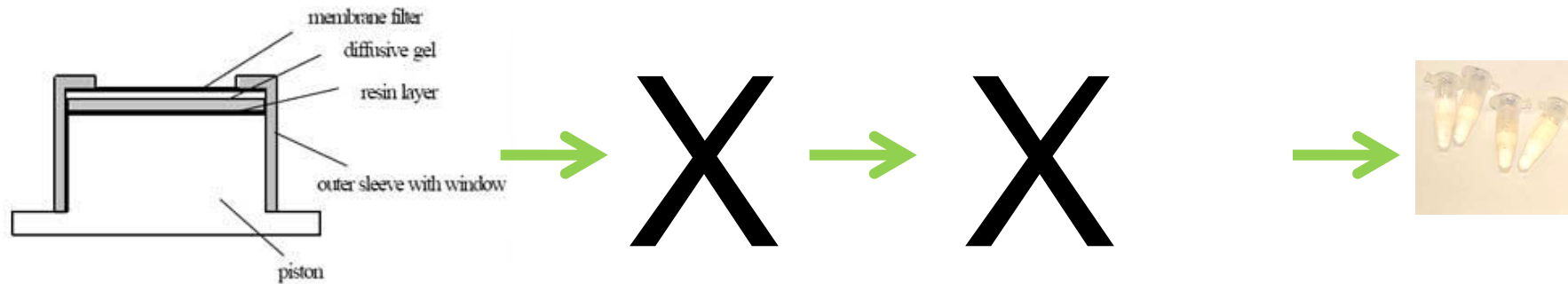
- Current anthropogenic sources are primarily from coal burning and artisanal gold mining
- Natural geological sources includes that from volcanoes
- Re-emission of previously released mercury includes both anthropogenic and natural sources that has built up over decades and centuries in soils and oceans.

Information from the United Nations Environmental Programme report Global Mercury Assessment 2013

Sources of mercury in the environment



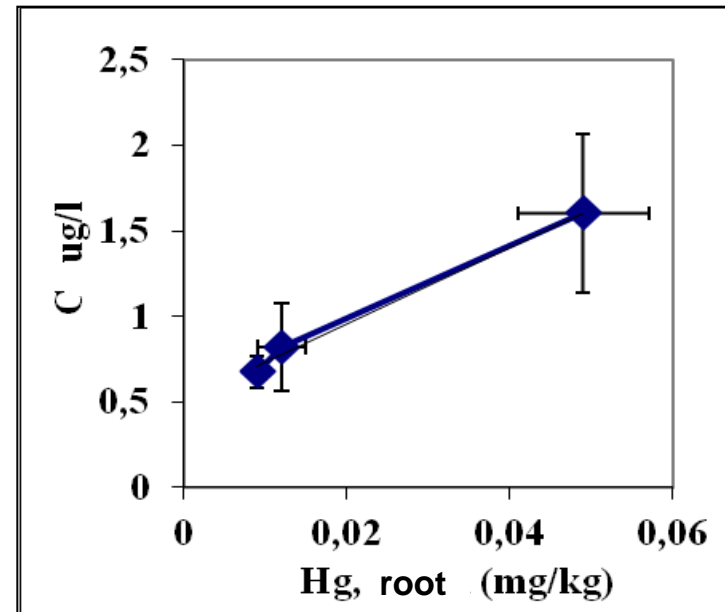
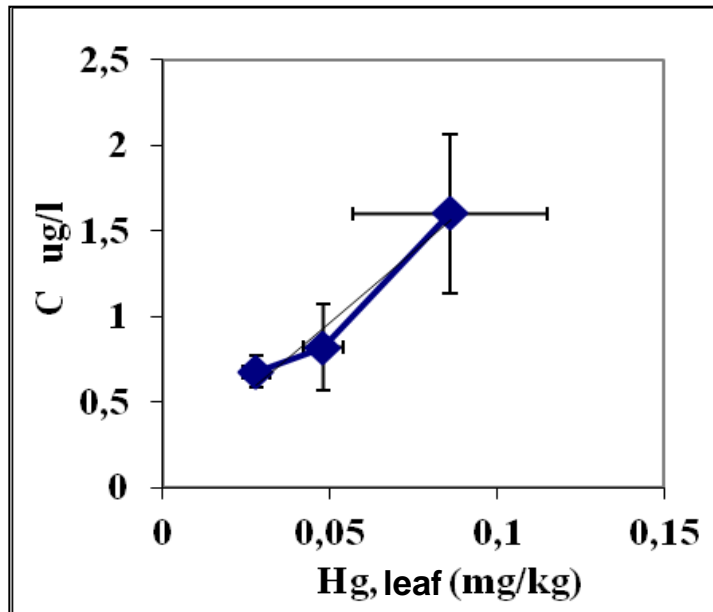
Assessment of mercury bioavailability in soil by using DGT technique



The dependence of the Hg amount recovered in gel sorption in exposure time (6, 12, 18, 24, 36, 48 and 72 hours).

Comparison of response techniques DGT with effective leaching by using some extraction reagents

RESULTS - Part 3: New project – Mercury M+S



Other new results and information are available at this address:

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Publications 2014/2015

Pelcová, Pavlína - Dočekalová, Hana - Kleckerová, Andrea. Determination of mercury species by the diffusive gradient in thin film technique and liquid chromatography - atomic fluorescence spectrometry after microwave extraction. *Analytica Chimica Acta*. 2015 in press

Pelcová, Pavlína - Dočekalová, Hana - Kleckerová, Andrea. Development of the diffusive gradient in thin films technique for the measurement of labile mercury species in waters. *Analytica Chimica Acta*. 2014. sv. 819, č. 819, s. 42-48. ISSN 0003-2670.

Pelfrene, Aurelie - Kleckerová, Andrea - Pourrut, Bertrand - Nsanganwimana, Florian, Douay, Francis. Effect of *Miscanthus* cultivation on metal fractionation and human bioaccessibility in metal-contaminated soils: comparison between greenhouse and field experiments. *Environmental Science and Pollution Research*. 2014. č. 9, ISSN 0944-1344.

Kleckerová, Andrea - Dočekalová, Hana. Dandelion Plants as a Biomonitor of Urban Area Contamination by Heavy Metals. *International Journal of Environmental Research*. 2014. sv. 8, č. 1, s. 157-164. ISSN 1735-6865.

Acknowledgment

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Thank you for your attention ...

