Final Workshop

Enhanced knowledge in mercury fate and transport for Improved Management of Hg soil contamination

29th November 2013

Online conference in combination with National hotspots

SNOWMAN NETWORK
Knowledge for sustainable soils

Organised with the financial support of:

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Wetterauw	Matthijs	Arcadis
Zijderlaan	Diane	SKB

Final Programme

Welcome 8.00-8.30

8.00-8.20	Arrival at venue - Coffee
8.20-8.30	Word of welcome – at national meeting points

Setting the scene

8.30-8.40	Word of welcome - Background to IMaHg [P-F. Berrier ADEME for SNOWMAN network]
8.40-8.55	Presenting the "Hg contaminated land issue": regulator and industrial points of view [D. Darmendrail COMMON FORUM and R. Jacquet SOLVAY]

Fate and Transport & Characterisation of Mercury

8.55 -9.10	Modelling of Hg fate and transfer [Diederik Jacques SCK-CEN]
9.10 -9.20	IMaHg survey results [Corinne Merly BRGM]
9.20-9.35	Characterisation of mercury contaminated site [Valérie Guérin BRGM]
9.35-10.00	*Discussions on introductory presentations, IMaHg survey, geochemical modelling and characterization (plenary)*
10.00-10.25	*National discussion on implementation of IMaHg outcomes on geochemical modeling and characterization (national meeting points) –* *Coffee break*

Risk assessment & Remediation of Mercury

10.25-10.40	Risk Assessment of mercury contaminated site [Yvonne Ohlsson SGI]
10.40-10.55	Remediation of mercury contaminated site [Daniel Hubé BRGM]
10.55-11.10	*Discussions on risk assessment and remediation*
11.10-11.35	*National discussion on implementation of IMaHg outcomes on risk assessment and remediation (national meeting point)*

Lunch at each meeting point 11.35-12.15

Conclusions and closure

12.15-12.45	Results of national discussions – plenary
12.45-13.05	Wrap up of the workshop & closure (plenary)
13.05-13.10	Closure & thank you – at national meeting points

SNOWMAN network:

Knowledge for sustainable soils

IMaHg, a SNOWMAN project

Paris, 29 November 2013

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GOALS

- Presentation SNOWMAN Network
- Future Investigation SNOWMAN Network
- IMaHg, a SNOWMAN Projet : Aims of the project

2

SNOWMAN, What is it?

- **What is the Snowman Network ?**

  A Transnational group of research funding organizations and administrations in the field of Soil and Groundwater in Europe

- **What is the objective of the Snowman Network?**

  To develop and share knowledge for sustainable use and management of soil and groundwater:

  "knowledge for sustainable soils"

- **How the Knowledge for "sustainable soil" is developed?**

  through the funding of "SNOWMAN Network Research Program" (SNRP)

  four calls for projects have been done until June 2013.

3

SNOWMAN, What is it?

- **Who are the actual partners of the Snowman Network ?**

Full members:

Affiliate members:

Cooperation from:

4

SNOWMAN, What is it?

- **What are the Snowman Network themes?**

✓ **A**griculture and Forestry
✓ **B**iobased economy
✓ **C**limate change (adaptation, mitigation) and energy
✓ **D**egradation (soil threats: water and wind erosion, organic matter decline, compaction, salinization, landslides, **contamination**)
✓ **E**cosystem Services
✓ **F**unctions: biomass production; biodiversity pool; carbon pool; storing, transformation and filtering of nutrients, substances and water (Soil Strategy)
✓ **G**overnance & socio-economics
(law, economics, valuation, sociology, spatial planning, antropology, etc)

→ "ABC" for sustainable rural & urban development

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SNOWMAN Network and H2020

- To develop a shared strategic research agenda (SRA) on sustainable soil and land management to address the H2020 **Societal Challenges**:
  - **importance of** sustainable soil and land management to address SCs
  - active **transnational collaboration**: viable network, experienced in joint calls
  - communication and knowledge dissemination to improve science-policy-practice interfaces
  - cross-disciplinary interaction, especially between socio-economic and environmental sciences
  - broad scope: "**ABC" for sustainable rural & urban development**

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SNOWMAN Network: knowledge development and dissemination

- **How is Knowledge dissemination performed?**
  - Website, Newsletter, Webinars , conference on SNOWMAN projects
  - “SNOWMAN Landscape” : a database to link SNOWMAN projects with each other and with national programmes

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SNOWMAN “LANDSCAPE” ?

- Create a mindmap: “landscape” of existing knowledge by labeling projects with the research questions (SNRP)
- For researchers: overview where similar research is done
- For funders: access to information and research results (ROI)
- For service providers: acces to what is new

So, the landscape
- Helps to find information
- Helps to find partners & to stimulate collaboration
- Helps to define research gaps
- Helps to disseminate knowledge

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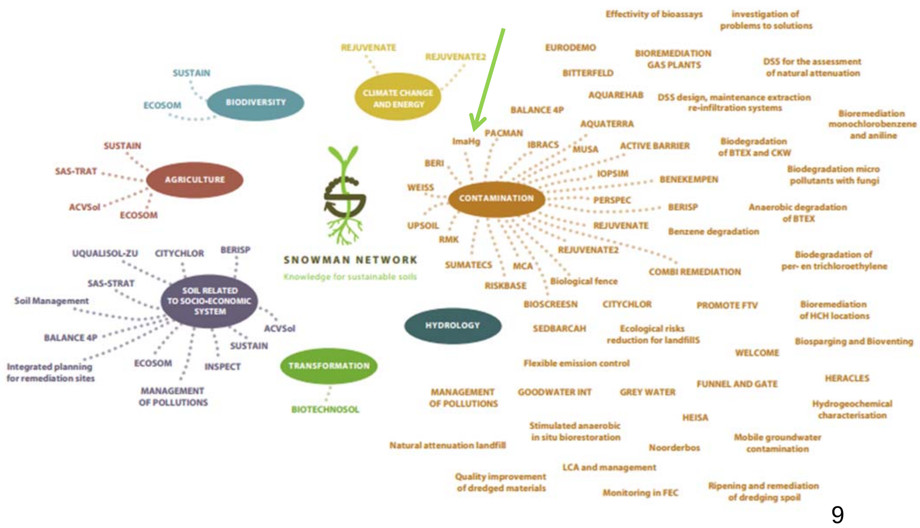
SNOWMAN + NATIONAL PROJECTS



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IMaHg, a SNOWMAN research project.

Enhanced knowledge in mercury fate and transport for Improved Management of Hg soil contamination

Partners: SCK•CEN, brgm, CL:AIRE, SGI

Funders: OVAM, ADEME, Naturvårdsverket

Start	End	Duration (months)	Total Funding (k€)	Dissemination cost (k€)
October 2011	February 2014	29	287	34,6

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Aims of the project IMaHg

- Improving the understanding of mercury speciation (chemical forms) and partition (physical forms) in the vadose zone, by:
  - Compiling physical, chemical and thermodynamic constants of mercury forms,
  - Checking mercury geochemical modelling capabilities
- Give recommendations for characterisation, assessment and remediation of mercury contamination in the vadose zone, by
  - Comparing available and currently used practices in characterisation, risk assessment and remediation of mercury,
  - Highlighting needs to improve management of mercury contaminated sites.
- Identification of further research needs for mercury

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You are a European key player in the soil use, land use and land management…

- funding organizations or knowledge dissemination funding organization , what about joining SNOWMAN network?
- Other key players (university, institute, non profit organization, services providers..) be aware about the Snowman Events.

More information about Snowman?

www.snowmannetwork.com

info@snowmannetwork.com

Thank you for your attention.

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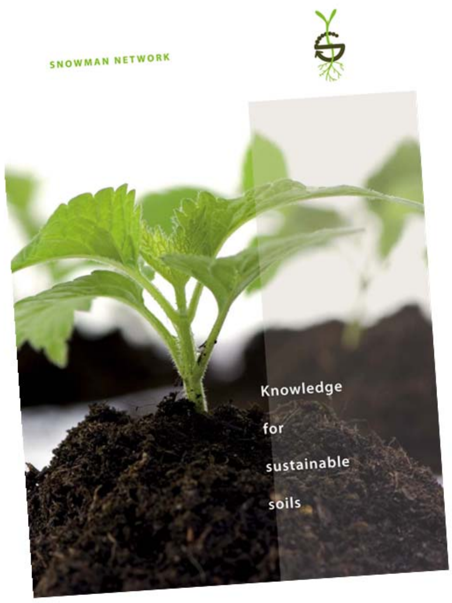

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COMMON FORUM ON CONTAMINATED LAND IN EUROPE

Common Forum

Hg contamination/ EU legislation

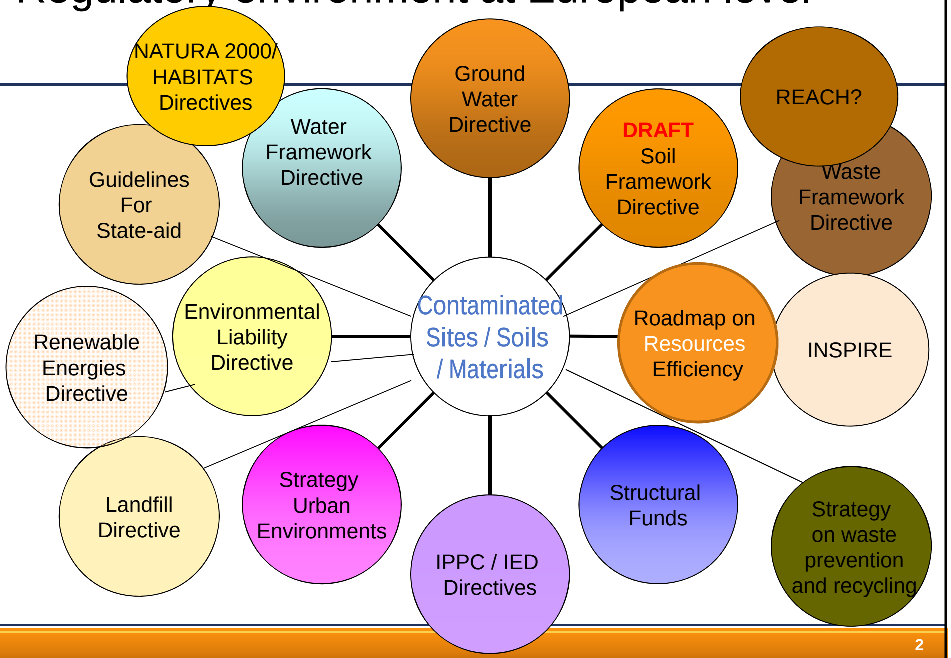
Dominique DARMENDRAIL

ImaHg
Paris, November 2013

ICCL / Common Forum networks

- Network of contaminated land policy experts and advisors dealing with contaminated land management:
  - International scale (since 1993), Europe (since 1994)
- Mission:
  - Being a platform for exchange of knowledge and experiences, for initiating and following-up of international projects among members,
  - Establishing a discussion platform on policy, research, technical and managerial concepts of contaminated land,

Regulatory environment at European level



Hg/ The most important EU Directives

- The Industrial Emissions Directive:
  - Reducing the Emissions at the source
  - Provisions on soil monitoring and actions at site closure
  - BREFS documents :
    - Chlor-alkali industry, Cement, Waste incineration (revision), Large combustion plant (up coming)
- The « Products » directives: prohibition or restriction of the use of Hg in batteries, electrical and electronic equipments, pesticides, wood preservatives, ….
- The 2007/61/EC Directive on marketing of measuring devices containing Hg (thermometers)
- REG 1102/2008 on safe storage of metallic Hg from major sources

Hg / The International Conventions

- The Basel Convention / transboundary transfer of waste
- The new Minamata Convention – specific to Hg

Minamata / Article 12 : Contaminated sites

- 1. Each Party shall endeavour to develop appropriate strategies for identifying and assessing sites contaminated by mercury or mercury compounds.
- 2. Any actions to reduce the risks posed by such sites shall be performed in an environmentally sound manner incorporating, where appropriate, an assessment of the risks to human health and the environment from the mercury or mercury compounds they contain.

Minamata / Article 12 : Contaminated sites

- 3. The Conference of the Parties shall adopt guidance on managing contaminated sites that may include methods and approaches for:
- (a) Site identification and characterization;
- (b) Engaging the public;
- (c) Human health and environmental risk assessments;
- (d) Options for managing the risks posed by contaminated sites;
- (e) Evaluation of benefits and costs; and
- (f) Validation of outcomes.

Minamata / Article 12 : Contaminated sites

- 4. Parties are encouraged to cooperate in developing strategies and implementing activities for identifying, assessing, prioritizing, managing and, as appropriate, remediating contaminated sites.

Thanks for your attention!

More information on:

www.commonforum.eu

www.iccl.ch

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ImaHg
Mercury contaminated land issues
Industrial perspective

Mechelen (B) – 29 Septembre 2013

General approach

- Not different from other contaminations
  - risk based land management
  - site specific
  - sustainable remediation

What makes it different from other metals

- Metallic mercury
  - non wetting very dense liquid
    - nugget effect
    - does it flow in porous media?
      - in dry or wet soil?
      - is the water table a barrier to its flow
  - significant vapour pressure at ambient T°
  - Empirical site experiences
    - Hg° plume short vs Cl^-, CVOC
    - sharp decrease in concentration in the vertical profile
    - Hg° found below, above the water table

SOLVAY asking more from chemistry®

What do we (all) need

- Understanding the behaviour of Hg°
  - transfer of liquid Hg in soil
    - experimental lab and on site work (before or in parallel to modelling)
  - transfer of vapour in soil
    - can vapour condense as droplet outside the source zone
  - transfer in water
    - can it transfer in water as micro droplet (e.g. after condensation of vapour)?
- RA/ERA
  - Hg fate in the terrestrial environment
    - fewer data than on the aqueous environment
    - available data show
      - little uptake from the root,
      - uptake by the leaves is the major route
      - little bioaccumulation in comparison with the aqueous environment

SOLVAY asking more from chemistry®

Have an fruitful event

SOLVAY
asking more from chemistry®

SNOWMAN NETWORK
Knowledge for sustainable soils

Call 3 SNOWMAN projects

Modelling of Hg fate and transfer

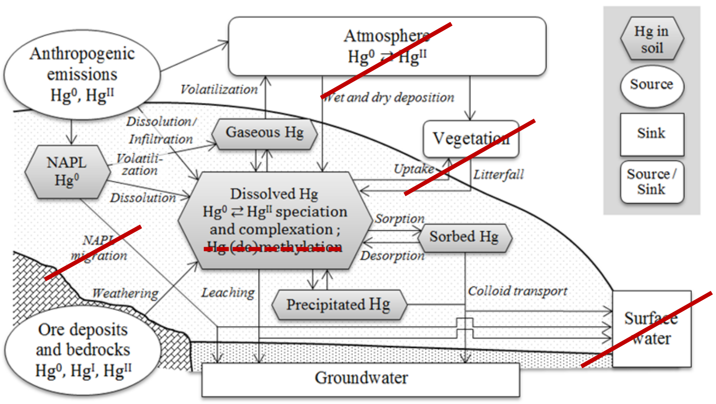
Bertrand LETERME and Diederik JACQUES (SCK-CEN)

SCK•CEN STUDIECENTRUM VOOR KERNENERGIE CENTRE D'ETUDE DE L'ENERGIE NUCLEAIRE
brgm Géosciences pour une Terre durable
CL:AIRE
SGI

Introduction

Conceptual model

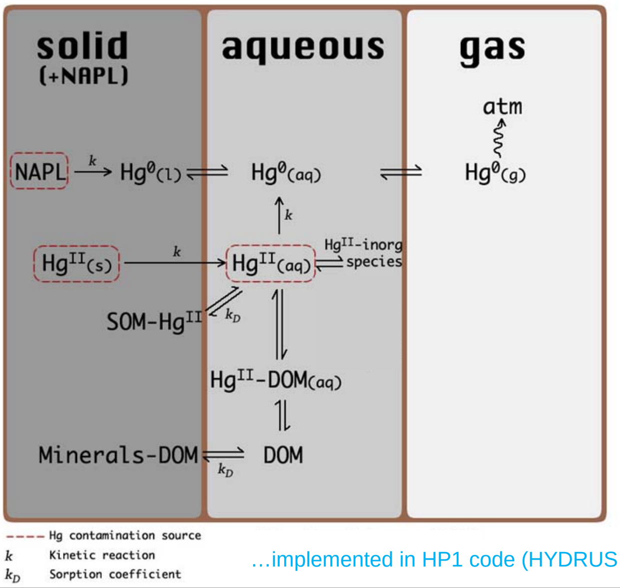
- Objective : improve prediction of Hg fate in soils
- Literature review



Anthropogenic Hg contamination :
some processes can be neglected

Introduction

Conceptual model



…implemented in HP1 code (HYDRUS – PhreeqC)

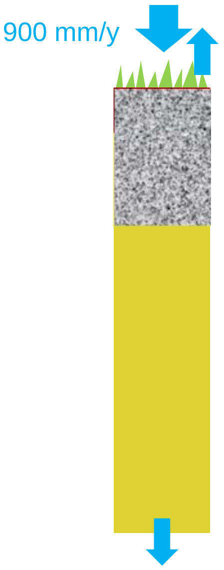
Introduction

Parameterization

- THERMODDEM (BGRM)
  - updated for inorganic Hg species
    $HgCl_2$, HgOHCl, $Hg(OH)_2$…
  - verification with predominance diagrams
- literature
  - Hg interactions with solid- and dissolved organic matter
  - DOM sorption to soil minerals
  - $HgS_{(s)}$ kinetic dissolution
  - …

Virtual simulation cases

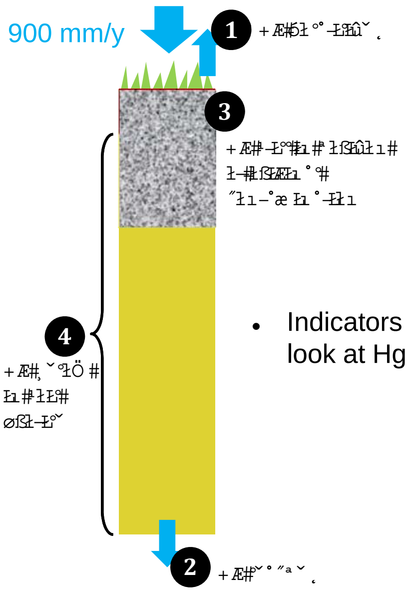
1-m sandy column



- 3 contamination forms (+combinations)
  - $HgS(s)$, $Hg^0(l)$ (NAPL), $HgCl_2(aq)$
- Aqueous reactions : THERMODDEM
- Dissolved and solid organic matter :
  - humic and fulvic acids
  - thiols (less abundant but higher affinity)
- Indicators : 5, 25, 50-year model runs and look at Hg fate

Virtual simulation cases

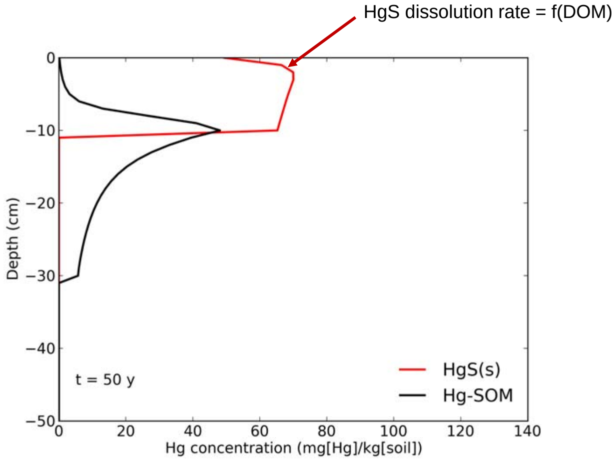
1-m sandy column



- Indicators : 5, 25, 50-year model runs and look at Hg fate

Example (I)

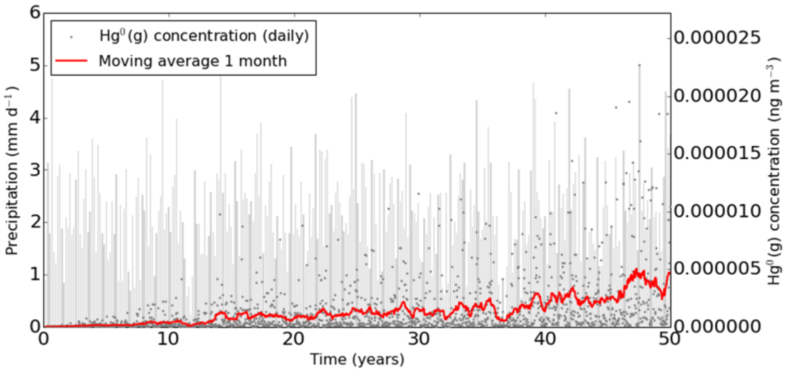
Cinnabar and Hg-SOM over 50 yrs



Example (II)

Hg^0(g) conc. at the surface

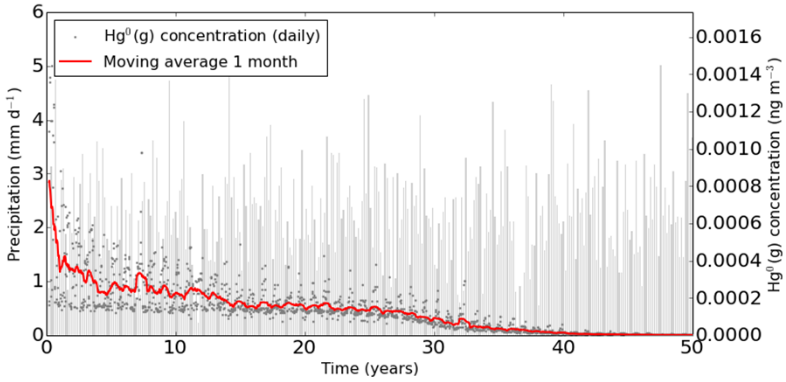
Source : HgS(s)



Example (II)

$Hg^0(g)$ conc. at the surface

Source : $HgCl_2$(aq)



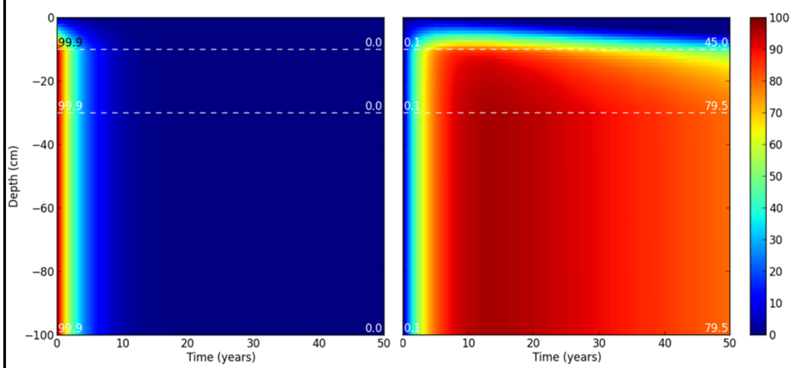
Hg immediate release and availability for transport

Example (III)

Hg^0(l) NAPL

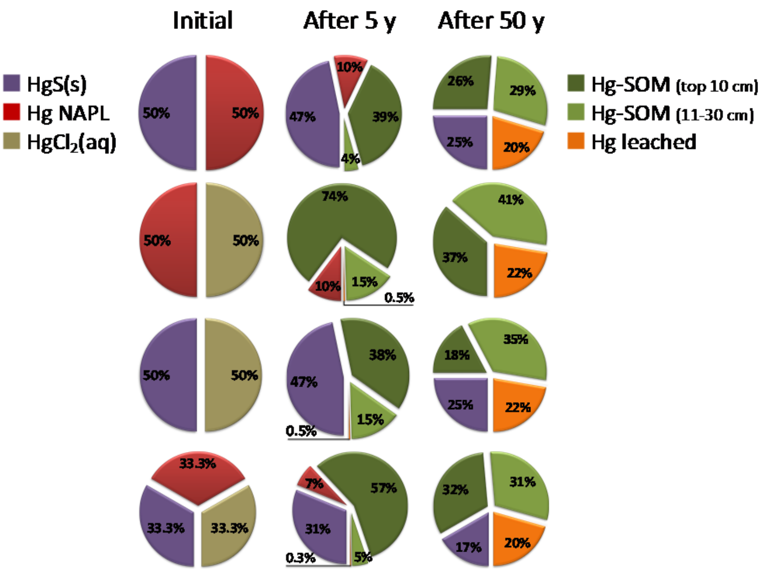
Hg NAPL

Hg-SOM, Hg-DOM…



~20% Hg leached after 50 yrs
~45% Hg still in originally contaminated horizon as Hg-SOM

Combinations of Hg sources



Sensitivity analysis

Main results

- Most important processes and parameters are
  - DOM concentration
  - parameters related to Hg sorption to SOM (HA and FA)
  - initial concentration
- Results depend on the type of initial contamination and on time

Potential applications

Risk management and remediation studies

- Investigate likely transport pathways on (very) long term
  - e.g. Hg volatilization delayed due to slow kinetics
- Identify parameters for which site-specific information is important
- Simulate possible remediation strategies
  - additional confidence in cost-benefit analysis of remediation

Final words

- Model appropriate for oxic conditions, anthropogenic pollution
- Hg (de)methylation can be implemented for more reducing conditions
- No calibration / validation

Best technologies versus current practices in mercury contaminated land management: Results of the IMaHg survey

Enhanced knowledge in mercury fate and transport for Improved Management of Hg soil contamination

IMaHg final workshop, 29th of November

C. Merly, V. Guérin, Y. Ohlsson, D. P.-E. Back, Berggren Kleja, D. Jacques, B. Leterme, R. Sweeney

SCK•CEN STUDIECENTRUM VOOR KERNENERGIE CENTRE D'ETUDE DE L'ENERGIE NUCLEAIRE — brgm Géosciences pour une Terre durable — CL:AIRE — SGI

IMaHg Survey – Current management practices

Objectives & Methodology

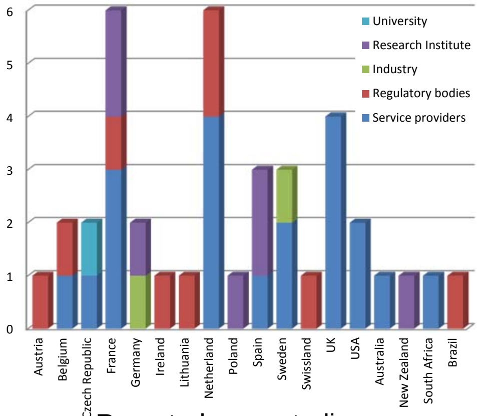
- Objectives: To compare available and currently used practices in mercury contaminated land management
- EU wide consultation based on a questionnaire designed in four sections
  - Characterisation
  - Risk assessment
  - Remediation
    - References of national technical guidance
    - Feedback on current practices – "interesting" case study
    - Difficulties faced & needs for future R&D
  - Regulatory aspects
    - Implementation of Hg regulation
    - Development of guidelines for Hg management
- Targeted audience: Service providers, problem owners, regulators and researchers
- Dissemination through national contacts points and CL networks such as SNOWMAN, Common Forum, Heracles, NICOLE Hg Working group and Eurodemo+, International Committee on Contaminated Land.

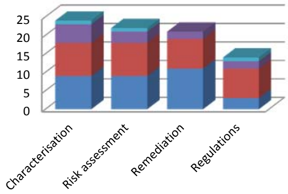
SCK•CEN — brgm — CL:AIRE — SGI

IMaHg Survey – Current management practices

Results – overview on participation

- 39 answers
- 18 countries: 13 EU countries, 5 non EU countries



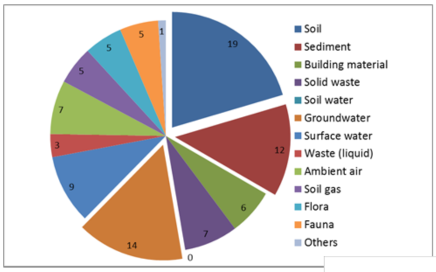


- Reported case studies: 1/3 Chloroalkali-plants, mining activities, “other” industrial activities, measurement equipment industry, electric industry and wood treatment plant industry.

IMaHg Survey – Current management practices

Results – Characterisation

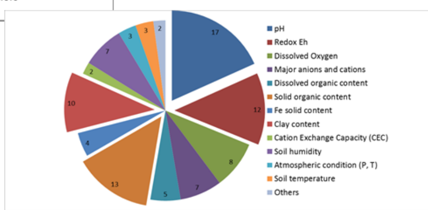
- 24 answers



Sub-surface compartments

- Soil
- Sediment
- Groundwater

- pH, E_H
- Clay content
- Solid organic content

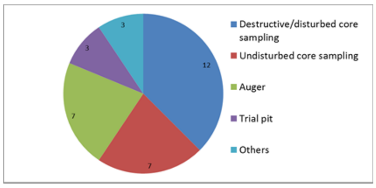


Other parameters

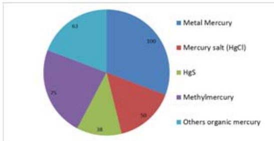
IMaHg Survey – Current management practices

Results – Soil Characterisation

- Soil sampling technologies
  - Issue of volatilisation
  - Downwards migration



- Soil screening was performed in 30% of the cases
- Analyses of speciation in 42% of the case
  - 100% Hg0
  - 75% Methylmercury
  - 38% Cinnabar

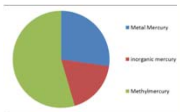


- Four types of solid speciation methods: extraction, thermal desorption, spectroscopic and EXAF
- Need for method standardisation and development to provide reliable solid speciation at reasonable price

IMaHg Survey – Current management practices

Results – Water & Gas Characterisation

- Characterisation of Hg speciation - Water
  - 1/3 cases reported speciation



  - Need for reliable analytical method $HgCH_3$
- Water Passive samplers and specific probes gave bad reproducibility

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- Gas analysis were performed in 1/5 of the reported cases in order to determine:
  - 1. Ambient air (73%)
  - 2. Soil gas (36%)
  - 3. Indirect Source identification (45%)
- Systematic characterisation of Hg^0 and organic mercury half of the reported case study
- Need for better qualified operators for better data acquisition and interpretation

IMaHg Survey – Current management practices

Results – Characterisation

- Pitfalls (1 is very important and 5 is the least important)

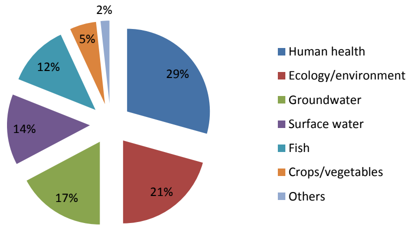
Representativeness	2,1
Knowledge of mercury species fate and transport	2,1
Loss of mercury associated with sampling protocol	2,8
Change of in-situ conditions, while sampling	3,0
Matrix effect	3,0

- Technologies exist but must be used more systemically
  - Solid: Speciation (Speciation analysis and Solid Phase Thermo Desorption), Standardization of sampling strategy
  - Water: Speciation
  - Flora: Assessment of mercury deposition

IMaHg Survey – Current management practices

Results – Risk assessment

- 21 answers



Protection targets for mercury contamination

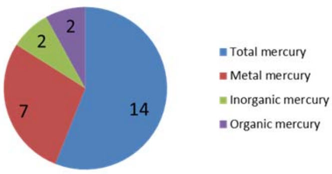
- Mercury species:
  - Total mercury was usually considered in the RA
  - Organic mercury was considered in 10% of the cases
- Human Health RA:
  - 40% comparison with generic guidelines values
  - 40% site specific RA
  - 20% combination of both generic and specific

IMaHg Survey – Current management practices
Results – Risk assessment

- Exposure pathways depend on phase partitioning:
  - Kd approach
    → Measurements of pore gas and pore water concentrations
      → Geochemical modelling
- Improvement for risk assessment
  - Oral intake pathways – bioavailability tests
  - Vapor intrusion pathways - pore gas measurements
  - Development of Hg-specific transfer model (vapor exposure in particular)
  - Better understanding of the MeHg bioamplification and accumulation in the foodchain
  - For ecosystems, measurements of methylmercury apart of total Hg
  - By more systematic definition and application of toxicological dose-effect-values (RfD, RfC, UR, etc.) for all Hg-Species

IMaHg Survey – Current management practices
Results - Remediation

- 20 answers
- Types of remediation thresholds

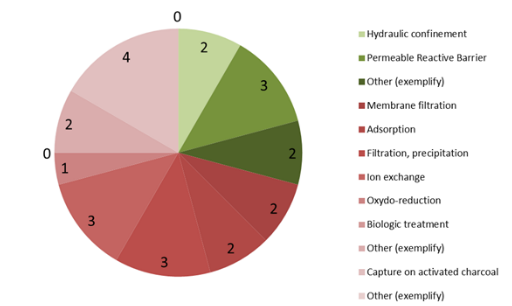


- Did you look at mercury forms to select the remediation technology?
  - Yes: 42% ; No: 58%

IMaHg Survey – Current management practices

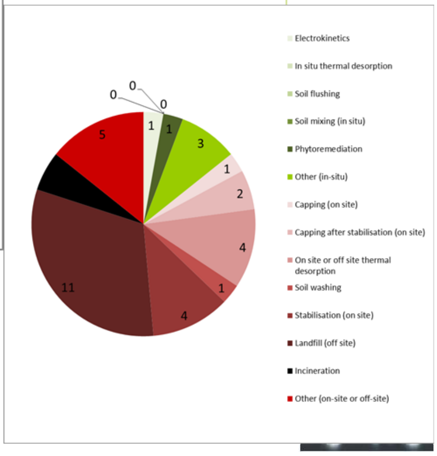
Results - Remediation

- Type of remediation technologies used (in-situ vs ex-situ)



For contaminated water

For contaminated soil



For contaminated gas: capture on activated carbon

IMaHg Survey – Current management practices

Results – Remediation difficulties

- Main difficulties encountered

Remobilisation of Hg during the remediation process	1,9
Insufficient knowledge in Hg fate and transport	2
Lack of Hg contamination characterisation	2,3
Matrix effect	2,6
Achievement of the remediation goal	2,6
Lack of efficient remediation technologies	2,8
Presence of cocktail of Hg species having very different fate in the environment	3,1
Interaction of mercury with other contaminants	3,2

- “Solutions”
  - Only ex-situ method used
  - By prior technical-economic feasibility study and field pilot tests
  - Good and Enough sampling and quick measurement

IMaHg Survey – Current management practices

Results – Remediation

- Technology development and implementation
  - Re-inforce passive & in-situ treatments for cost reduction
  - More cost effective techniques for element mercury recovery from soils as opposed to segregation, solidification and disposal
- Management / Guidelines
  - Spread of mercury by earthmoving equipment during excavation work is a concern that must be managed
  - Importance of a very good characterisation
  - Development of a guideline for BAT selection
  - Further education and understanding on fate, transport of mercury species

Thank you for your attention

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CHARACTERISATION of Mercury Contaminates Sites: State of the Art, Recommendations and Improvements

Enhanced knowledge in mercury fate and transport for Improved Management of Hg soil contamination

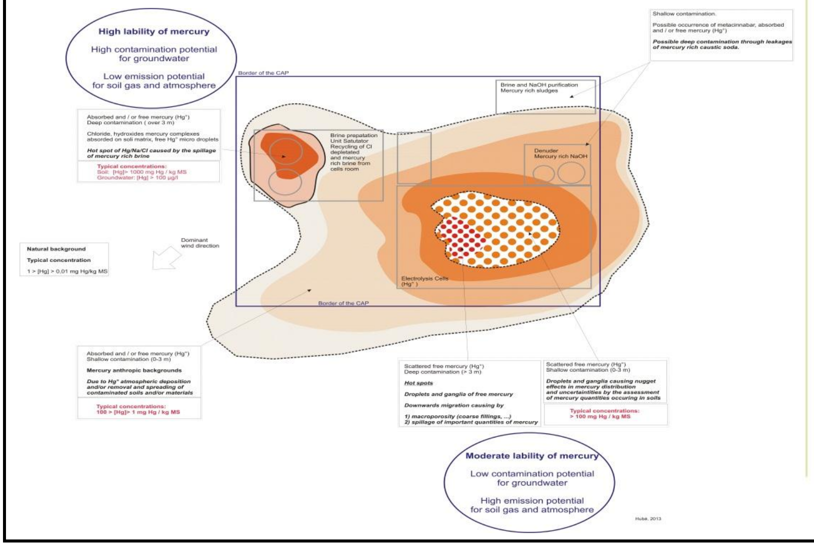
V. Guérin, D. Hubé, V. Laperche, S. Grangeon

Elaboration of characterisation plan

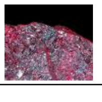
- Main principles in mercury contaminated land characterisation:
  - Historical study:
    - Mercury has been used in many processes and areas of activity in various forms : Hg° , HgCl2, HgNO2, HgS
    - All forms of Hg & waste management practices must be identified
  - Once relased into the environment, the speciation of Hg is controlled by a number of reactions including:
    - Oxidation and reduction
    - Methylation and demethylation
    - Formation of complex inorganic
    - Formation of complex organic

Example of historical study:

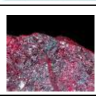
- Link between forms of mercury, potentially affected media and associated risks



Consequences of speciation on the media to investigate

	Compound	Physical state	Solubility µg/L	T° C	Saturated Vapor concentration mg/m³
	Hg° metal mercury	liquid	20-60	0	2
				20	13,2
				30	29,5
				40	62,4
	HgCl2 mercuric chloride	crystalline solid	600-700	11	0,28
				23	0,81
	HgS mercuric sulfide	crystalline solid	0,01	20	0

Consequences of speciation on the media to investigate

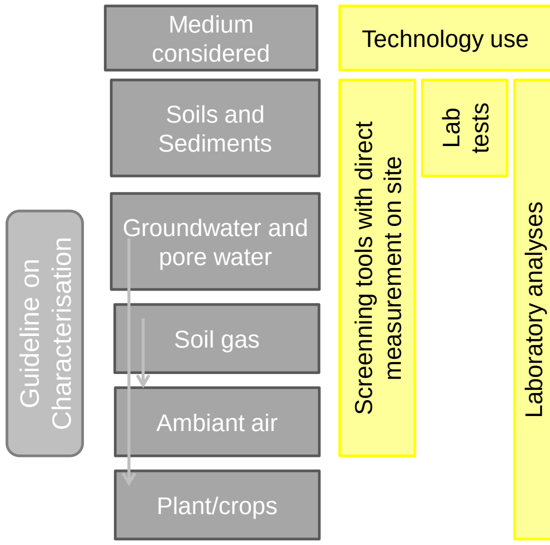
	Compound	Physical state	Solubility µg/L	T °C	Saturated Vapor concentration mg/m³
	Hg° metal mercury ➡	Mobile to groundwater and to the air			
	HgCl2 mercuric chloride ➡	Mobile to and into groundwater			
	HgS mercuric sulfide ➡	**Stable motionless, low bioavailable Hg**			

Elaboration of characterisation plan

- Fit to the objectives
  - Baseline characterisation
  - Risk assessment: on site / off site characterisation:
    - ✓ Hg ° → direct exposure by inhalation, ingestion of soil, water and plants,
    - ✓ MeHg → indirect exposure through the consumption of fish,
    - ✓ Hg2 + → direct exposure by ingestion of water
  - Remediation: on site characterisation
    - ✓ Evaluate forms of mercury that require the implementation of management measures from the ones that do not pose a problem due to geochemical context, land use and mercury properties
    - ✓ Assess the evolution of / characterise residual pollution

Characterisation technologies

Rapport content



Characterisation technologies

Main findings

- Technologies to approach speciation exist for solid matrices and water
- There is no universal method that allows to answer all the questions : the use of several complementary techniques provides the best guarantees of a reliable and usable result
- The techniques are mature and can be offered by specialized institutions to non prohibitive costs
- Some simple measures on site can give a first approach to identify certain mercury species (Hg0)
- The choice must be made according to the specificity of the site (hydro-geo-chemical context) and the advantages and limitations of the technology

Characterisation

Progressive approach

- Step 1: Measurement of total mercury according to standards :
  - To find and identify a mercurial impact

➡ If there is an impact: As the measurement of total Hg is necessary but not sufficient to manage a site issue

- Step 2: Is mercury a problem?
  - Characterize mercury and its various forms in different environmental compartments: Speciation analysis on a reduced set of targeted samples.
  - In addition, characterisation of:
    - Soil / solid: pH and redox, organic matter, particle size, presence of other compounds, soil type.
    - Water: pH, EH presence of other contaminants.

Selection of characterisation options

Recommandations for soils

Aim	Characterisation	Remediation	Risk assessment	Modelling
Tier 1	Total Surface Depth, XRF (depending on historical study form of Hg, site characteristics)	Total: Surface, Depth XRF, lumex	Ingestion : surface, total Inhalation (gas): Hg0 (Lumex or other screening tool) : 1-2 m Risk towards groundwater: surface, depth, total Plant : total, direct measurement If no plant: total in soil Animal : Hgtot	pH, EH, water chemistry : anions cations TOC, DOC
Tier 2	Total Surface Lumex (start of a speciation)	Total: Surface, Depth MTD (Biester)	Ingestion: surface, bioavailable fraction-selective extraction Risk towards groundwater: surface, depth, water extraction	XRD,
Tier 3		Total: Surface + depth Chemical extractions	Specific lixiviation test for bioavailability assessment: mimic of digestive system Specific lixiviation for risk toward groundwater (adapted to the hydrochemical context) or column test	

Selection of characterisation options

Recommandations for waters

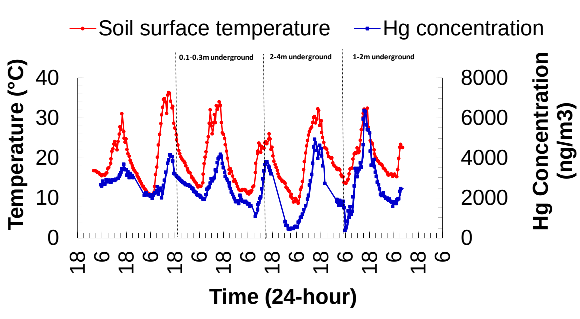
Aim	Characterisation	Remediation	Risk assessment	Modelling
Tier 1	Total	Lumex for Hg0 estimation	Total + Dissolved	pH, EH
Tier 2	Particulaire Dissolved and particulate fraction Si EH<0 MeHg	Speciation (Hg° , HgCl2)	Speciation MeHg for ingestion Hg in pore water	pH, EH, water chemistry : anions cations
Tier 3	Speciation			

Selection of characterisation options

Recommandations for gas

Aim	Soil gas for ambiant air estimation	Soil gas for source characterisation	Ambiant air
Tier 1	Lumex Passive sampling	Lumex	Lumex
Tier 2	Flux chamber	Lumex after purging at different flow rate	Canistair – passive sampling

NB : to be done several times, measurements above and under soil P and T, soil humidity



Challenges of mercury characterisation

Presence of various species of mercury in one or several media

Interaction of mercury with other contaminants

Complex mercury behaviour

Loss and changes of mercury during sampling and analysis

Capability to estimate its mobility

Capability to estimate toxicity

Improvement of characterisation, and geochemical modelling

Sufficient knowledge in mercury fate and transport

Decrease uncertainties associated with remediation technologies and risk assessment

Promising characterisation technologies

- **Use of vegetal as indicator of atmospheric deposition**
- **In situ sensor deployment**
- **Use of Isotopes for Tracking Environmental Changes**
- **Use of passive samplers for water monitoring**

Mercury contamination in water can be detected with a mobile phone

Thank you for your attention

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Risk Assessment

Yvonne Ohlsson

Risk assessement

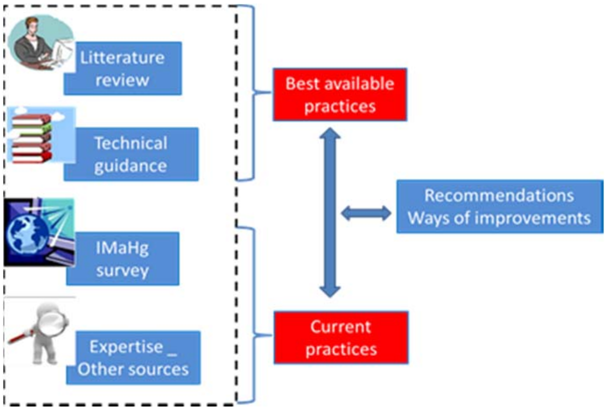
Objectives and methods

Objective: identify practices used for mercury risk assessment and propose improvements

Focus:

- on **assessment models** for soil, **guideline values** and the **assumptions behind the values**.
- on **strategy** that can be used to **optimize RA**

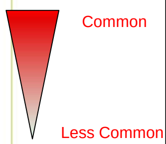
Strategy



<u>Means</u>: litterature review ; european wide consultation ; partners experience

Survey results in short

- Speciation often not accounted for
- More likely that Hg forms are analysed/assessed if there are generic guideline values for these.
- Human health most important protection target *and* the target at risk at mercury contaminated sites.
- Inhalation of vapour, ingestion of crop/vegetables and ingestion of soil specifically mentioned
- phase partitioning estimated/measured in several ways
  - *based on the Kd-concept*
  - *direct measurements of pore gas concentrations or pore water concentrations (instead of modelling)*
  - *geochemical modelling using site specific measured data*



Hg - metal, inorganic, organic form

Differ in

- physico/chemical properties
- toxicity
- bioavailability
- **Dominating exposure pathways**

Generic guideline values

The Netherlands and England/Wales:

- metal, inorg and organic

Sweden:

- Total mercury

Risk: Chem analysis based on what Generic Guideline values there are

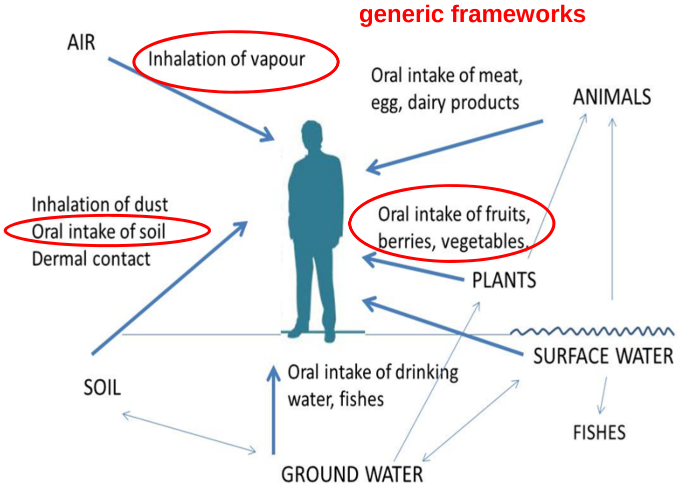
TDI – different sets in different frameworks

National framework	Elemental	Inorganic	Methylmercury	Inorg/org
England and Wales	NR	$2.0 \cdot 10^{-3}$	$0.23 \cdot 10^{-3}$	9
Sweden	NR	**$0.3 \cdot 10^{-3}$**	$0.23 \cdot 10^{-3}$	1,3
the Netherlands	NR	$2.0 \cdot 10^{-3}$	$0.1 \cdot 10^{-3}$	20
the United States[4]	(NR)	$(0.3 \cdot 10^{-3})$	$(0.1 \cdot 10^{-3})$	3

Effect of addressing different forms depends on which country you are in ☺

Exposure pathways of potential significance

Dominating pathways in generic frameworks



Oral ingestion of soil

- 100 % of Hg in soil bioavailable in generic guideline values
- No country has included, or recommend the use of, *in vitro* bioavailability tests for mercury into their frameworks.

- If inorganic Hg predominant – Oral ingestion may be most important pathway and bioavailability <<100%

Oral Bioavailability MeHg>inorg Hg>>Metal-Hg

Often reported: >99% <1%

E.g. guidance in Shoof (2003) including parts on Hg

- Test protocols (*in vitro*-tests, *in vivo*-tests)
- Guidance on soil analysis (speciation) etc

Schoof, R.A, (2003) Guide for Incorporating Bioavailability Adjustments into Human Health and Ecological Risk Assessments at US Department of Defense Facilities

Vapor intrusion pathway

Most complex exposure route

- common to measure total mercury in soil + simple Kd approach to estimate mercury concentrations *in pore gas* and pore water.

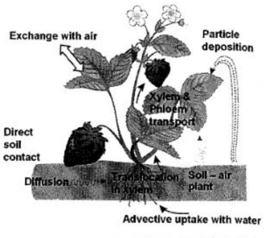
Problem

- Several biogeochemical and physical processes involved – complex modelling to predict risk
  - Direct volatilization of Hg(0) + reduction of Hg (+2) (redox and microorg)
  - Moist can increase and decrease volatilization
  - T important
  - Etc

Best Practice Vapor Intrusion, e.g.

- Geochemical modelling option to a simple generic model for estimating pore gas concentrations (partitioning).
- Use of measured pore gas concentrations instead of measured concentrations in soil.
- Measuring mercury-conc closer to the risk target could reduce uncertainty from soil to indoor air.
- Measurements AND modelling can reduce uncertainties and need for large time-series of measurements
- For future buildings – Modelling in combination of carefully selected measurements
- Potential other effects may control long-term human risk e.g.
  - variability in climate conditions
  - potential future changes in the building (cracks etc)
  - potential influence from other indoor sources

Fruit, vegetables etc?



Trapp and Legind, 2011

Contradictory results, e.g.

Patra and Sharma (2000):

- Higher uptake in plants of organic Hg, direct uptake of organic *and* inorganic mercury from soil by plants is *in general low*.
- A barrier to mercury translocation from plant roots to tops
- Fraction of mercury retained in the roots is about 20 times that observed in the shoots.

⇒ ***High conc in soil induce only small increases in plant mercury conc.***

⇒ ***Hg(g) more easily taken up through the leaves than mercury in soil and thus mercury concentration in aboveground parts of plants appears to depend largely on foliar uptake.***

On the other hand

Environment Agency, 2009

Mercury is found in green, root and tuber vegetables and also in herbaceous and shrub fruits in different concentrations

In some of the studied investigations:

mercury was mainly retained by the soil.

In other:

plant concentrations of mercury similar or higher compared to the soil concentrations.

Still…

Often governing pathway in generic models or in using generic models for site specific assessments.

- ”Good” chance that Hg has limited uptake at a site.
- Could ”pay off” to verify little or no uptake

What about fish?

Not included in generic models

- Usually weak connection between conc in fish and conc in soil
- Hg in fish often due to atmospheric deposition
- If soil intake, oral ingestion or vapor intrusion considered these commonly result in lower cleanup values than the fish ingestion pathway = cleanup due to other pathways also affect the fish ingestion pathway.
- Indirectly taken into account by not allowing full TDI-use as basis for cleanup values (e.g. in Sweden)

But

- Could be the risk driver at heavily polluted sites.
- Can become important patway if above pathways are ignored

Simple ”tool” – example soil ingestion

	Hg in:	Common practice	Improvement options	Best Practice	Potential impact	Comment
Conc in organs	Humans	Not commonly considered	Blood test, hair test Hg-species specific modeling.	-	-	Not commonly relevant in contaminated land investigations. Relevant only if assessing current exposure situation.
Intake and uptake		100% Hg uptake/bioavailability is generally assumed	Determining the water-soluble and exchange-able Hg fraction. *In Vitro* bioavailability test. *In Vivo* bioavailability test.	*In-Vitro* bio availability tests	Intermerdiate/high	Lirerarture reports 2-38 % available fraction. Risk reduced by 2-50 times resulting in a guideline value at a maximum 50*GV(100%). No in vitro oral bioavailability test has been validated for Hg
Conc in soil	Vadose zone	Measurement of total Hg in soil or of inorganic and organic mercury	Measure Organic Hg, inorganic Hg	Measure Organic Hg & inorganic Hg-conc	Intermediate/High	Uptake of inorganic Hg less than of organic Hg

Thank you for your attention

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Remediation of mercury contaminated sites: State of the Art & Recommendations & Future needs

Enhanced knowledge in mercury fate and transport for Improved Management of Hg soil contamination

IMaHg final workshop, 29th of November

D. Hubé, C. Merly

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Challenges of mercury remediation: its complex environmental behaviour

→ Like organic pollutant (DNAPL), mercury is present as mobile free phases (dense gas and fluid),
→ Behaviour of metals with a low redox potential,
→ Complexation both with organic matter and inorganics (elements and minerals (oxi (hydroxides) ,…)

→ **Mercury spilled in the soil could affect all the environmental compartments through different pathways,**

→ **Mercury is present as a non weatable liquid in the soil (disseminated droplets) → masses in presence are difficult to assess / quantify → how to evaluate the mercury / soil masses that have to be remediated?**

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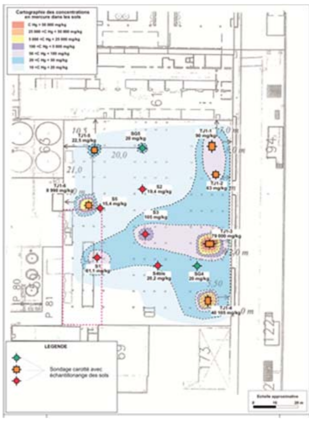
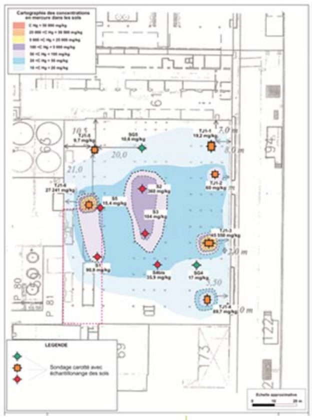
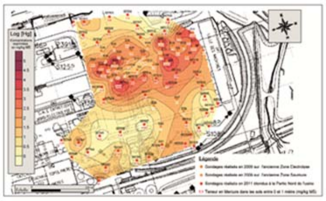
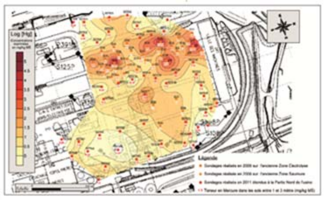
Total mercury distribution in soils underneath former electrolysis cells





→ **Shallow pollution through free Hg° with nuggets effect.**





Elaboration of remediation plan

Main principles / recommendations in mercury contaminated land remediation

Step 1

- Accurate and complete site conceptual model
- Approach tailored to typology of the contaminated sites → site specific approach

Step 2

- Needs of lab scale essays for preliminary treatability study,

Step 3

- Needs of field scale pilots for preliminary technically and economically feasability study

Step 4: during operation

- Management of Mercury residue produced by the remediation
- Protection of workers' health and the environment during remediation / specific measures,
- Incertainties on masses and Hg concentrations have to be taken into account → technical / financial adaptation

Elaboration of remediation plan

Key Step : preliminary treatability and technically and economically feasability studies

- Vertical and horizontal **distribution of masses and concentrations** of total mercury,
- **Speciation** → what is the mercury that really needs to be remediated? for which media (groundwater, soil gas and ambient air)? for which exposure?
- Hydrological, physico chemical settings and contexts,

Effects of the soil/ solid characteristics on the mercury remediation process

Soil /Solid Characteristic	Effects on remediation technologies		
	Solidification / Stabilisation(1)	Soil Washing / Acid extraction(1)	Thermal Treatment(1)
pH – redox potential	+ +	+ +	-
Organic matter and Total Organic Carbon	-	+ +	-
Particle Size	+	+ +	+
Presence of other compounds	+	+	+
Soil type	-	+ +	+

- **Proven and existing technologies in balance to 1) remediation goals and 2) costs**

Speciation and the choices of remediation strategies: example

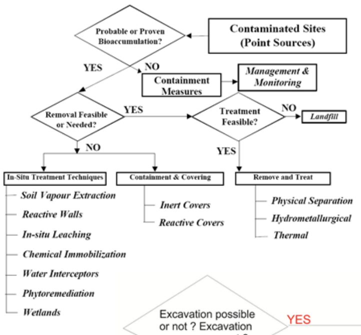
Total mercury concentration in soils: 500 mg/kg

1) **Screening of remediation technologies**
2) **Traitability with technically / economically balance**
3) **Best remediation strategy → excavation with stabilisation and off-site landfilling: 500 tons of Hg-rich gravels and sands**

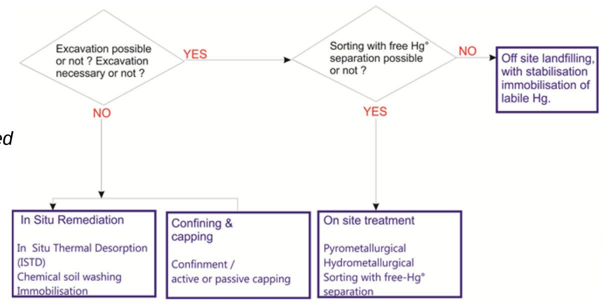
~ 700-1000 € /T

Elaboration of remediation plan

Examples of remediation selection approach



Hilton (2001)



Hubé (2013) adapted from Hilton (2001)

Remediation technologies

Report content

- For soils and waters: presentation of the different technologies
  - Proven technologies
  - Emerging and potential alternative remediation technologies
- Remediation technologies summary table

Technology	Principle	Key advantages	Main disadvantages	Targeted mercury	Status
Source removal with excavation	Excavation of the polluted materials on the whole contaminated area	**Provide total remedy, radical with no residual concentrations to manage**	Could be expensive due to health and safety constraints for workers and surrounding. Risk of remobilization of labile elemental mercury. **Treatment of material required** Geotechnical limitation due to groundwater level and/or existing infra-structures	Total labile mercury	☺ demonstrated technology but with difficulties inherent to the occurrence of mercury
Hot spot removal with excavation	Excavation of the polluted materials on the hot spots where the mercury masses are concentrated	**Provide total remedy on hot spots**, radical with no residual concentrations to manage in hot spots	Could be expensive due to health and safety constraints for workers and surrounding. Risk of remobilization of labile elemental mercury Management with other technologies of residual non excavated soils. **Treatment of material required** Geotechnical limitation due to groundwater level and/or existing infra-structures	Total labile mercury	☺ demonstrated technology but with difficulties inherent to the occurrence of mercury
In situ Containment	Isolation of existing contaminated areas	• Relatively simple and rapid to implement, • Uses standard construction equipment, • can be more economical than excavation and removal of waste, and thermal treatment, • can be applied to large areas or volume of	**Mercury remains on site** and there is no reduction of toxicity and masses; this represents a potential risk should containment fail.		☺ Commercially available and

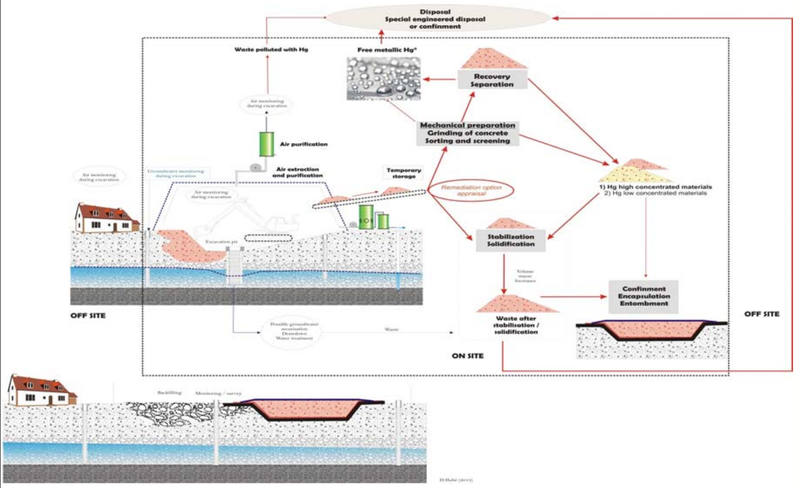
Remediation technologies

Soil Remediation technologies with or without excavation	
Proven	Emerging
•**Soil flushing** •**Thermal treatment:** ETD, Batch retorting, Incineration •**Immobilisation** •**In-situ isolation / containment:** capping or vertical barrier	•**Electrokinetics** •**Phytoremediation** •**In-situ thermal treatment** •**Other technologies:** ultrasound, nanotechnologies, solar treatment, soil flushing with L-cistéine..

Water Remediation technologies with or without Pump and Treat	
Proven	Emerging
•**Reactive barriers**	•**Amalgamation** •**Pump & stripping** •**Nanotechnologies** •**(Bio)-adsorption** •**Coagulation / Floculation** •**Bio-remediation**

Remediation technologies

scheme for soils



Recommendations / conclusions

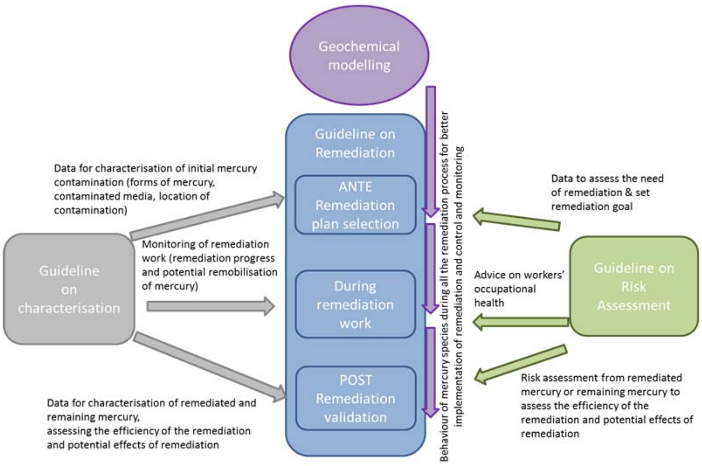
- **Remobilisation of mercury**: protection of workers 'health, organisational constraints, additional costs
- **Technologies train often required**
- **Soil remediation technologies**: Only a few of them are applied (excavation and on-site treatment of the soils; excavation and immobilisation and in-situ containment)
- **Need to develop implementation of innovative in-situ technologies**.
- **Barriers for emerging technologies implementation:**
  - **Uncertainties on efficiency**: characterisation (Fate & transport, Toxicity) of remediated and remaining forms of mercury; longevity
  - **Lack of knowledge in the effects of the implementation on the environment**
  - Mainly laboratory or pilote scale.

Research needs

- **Development of in-situ technologies** (eg thermal)
- **Assessment of longevity of the remedial technologies** (stabilisation, containment, etc..)
- **Improvement of treatment of high rate of Mercury polluted air** - to secure excavation.
- **Increase of sorption and filtration capacities** - to remediate mercury contaminated groundwater with flow rate and extraction rate adapted to P & T?
- **Improvement of treatment of Hg in heavily polluted groundwater under high pH / ionic strength and presence of co-contaminants** (chloralkali sites),
- **For emerging / innovative technologies**: Assessment of efficiency, potential for full scale application and effects on the environment,
- Tools for the assessment of remediation efficiency.

Conclusions

- **Improvement of characterisation, risk assessment and geochemical modelling to decrease uncertainties associated with remediation technologies**



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To go further…

Enhanced knowledge in mercury fate and transport for Improved Management of Hg soil contamination

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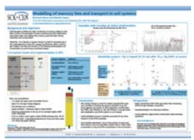
IMaHg outcomes

Already available

- Aquaconsoil (2013): **www.aquaconsoil.org**
  - Presentation of the IMaHg survey results
  - Poster on **Modelling of mercury fate and transport in soil systems**
- Goldschmidt (2013)
  - Modelling the migration of mercury in a column experiment: biotic against abiotic mechanisms
- Wide audience publication in Environment Industry Magazine (UK): Mercury contaminated land management in EU context



IMaHg Outcomes

To come

- Reviewed paper: A reactive transport model for mercury fate in soil – Application to different anthropogenic pollution sources (B. LETERME, P. BLANC and D. JACQUES, paper submitted)
- Final workshop IMaHg presentations: very soon at http://www.snowmannetwork.com
- IMaHg technical reports – February 2014
  - Report on fate and transport of Hg in vadose zone
  - Report on geochemical modelling of Hg
  - Best available practices & recommendations in:
    - Mercury characterisation
    - Mercury risk assessment
    - Mercury remediation
- Brief note on recommandations and Needs for mercury contaminated land management: characterisation, risk assessment, remediation – February 2014

Thank you for your participation