Mercury in soil – local vs. global implications

Milena Horvat, Jožef Stefan Institute, Ljubljana, Slovenia

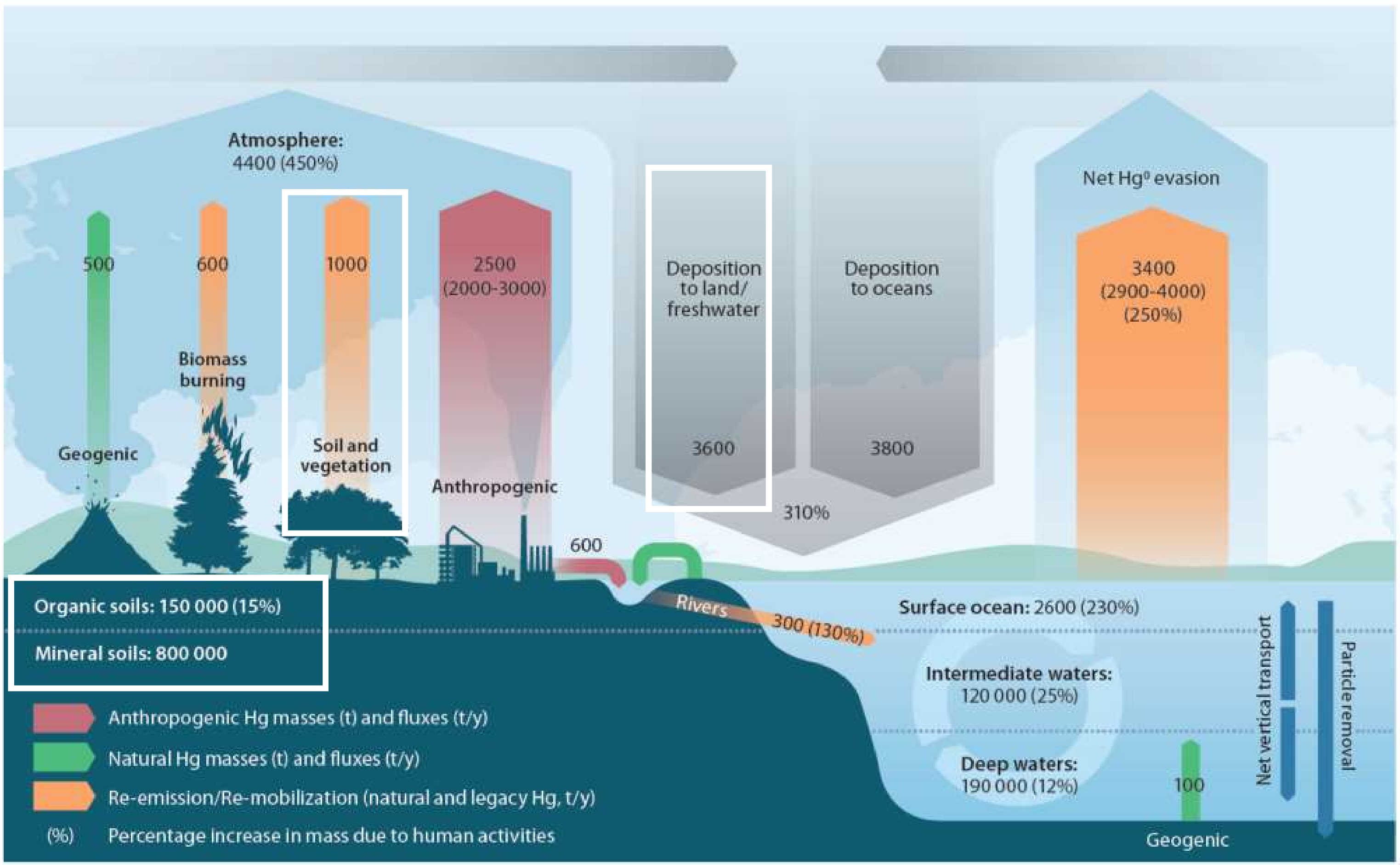
Department of Environmental Sciences

International Posgraduate School Jožef Stefan, Slovenia

Content

- Literature review of over 200 articles (emphesis on the last 5-10 years), GMA 2013, 2018
- Mercury sources and sinks and phases in soils
- Global vs. local implications
- What to measure in soils?
- Methodological challenges
- Conclusions

GMA 2018



Atmosphere:
4400 (450%)
500
600
1000
2500
(2000-3000)
Biomass burning
Geogenic
Soil and vegetation
Anthropogenic
Deposition to land/ freshwater
3600
Deposition to oceans
3800
310%
Net Hg⁰ evasion
3400
(2900-4000)
(250%)
600
Rivers
300 (130%)
Organic soils: 150 000 (15%)
Mineral soils: 800 000
Surface ocean: 2600 (230%)
Intermediate waters:
120 000 (25%)
Deep waters:
190 000 (12%)
100
Geogenic
Net vertical transport
Particle removal
Anthropogenic Hg masses (t) and fluxes (t/y)
Natural Hg masses (t) and fluxes (t/y)
Re-emission/Re-mobilization (natural and legacy Hg, t/y)
(%) Percentage increase in mass due to human activities

Global mercury cycle

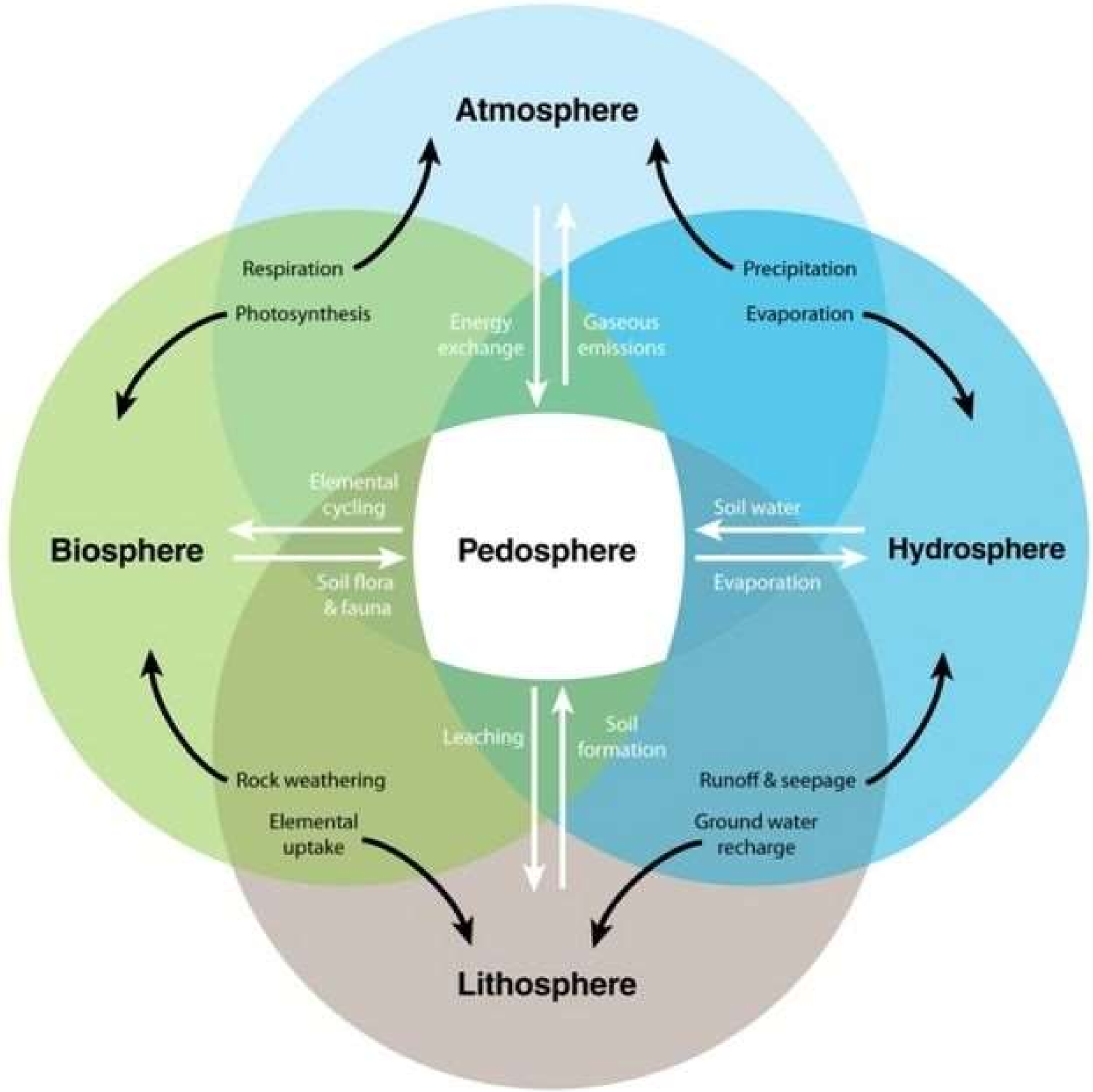
It is important to investigate the global and regional mercury fluxes. This includes:

- quantification of the mercury which is already or **potentially biologically available** in the ecosystem (e.g. sorbed to soils or sediments),
- the mercury which is released from **geological sources** (e.g. ore deposits and geothermal sources) and,
- the mercury which is released by **anthropogenic activity**.

A major question is the importance of anthropogenic mercury relative to the mercury content in pristine environment.

Pedosphere

O horizon
A horizon
E horizon
B horizon
gradational boundary
C horizon



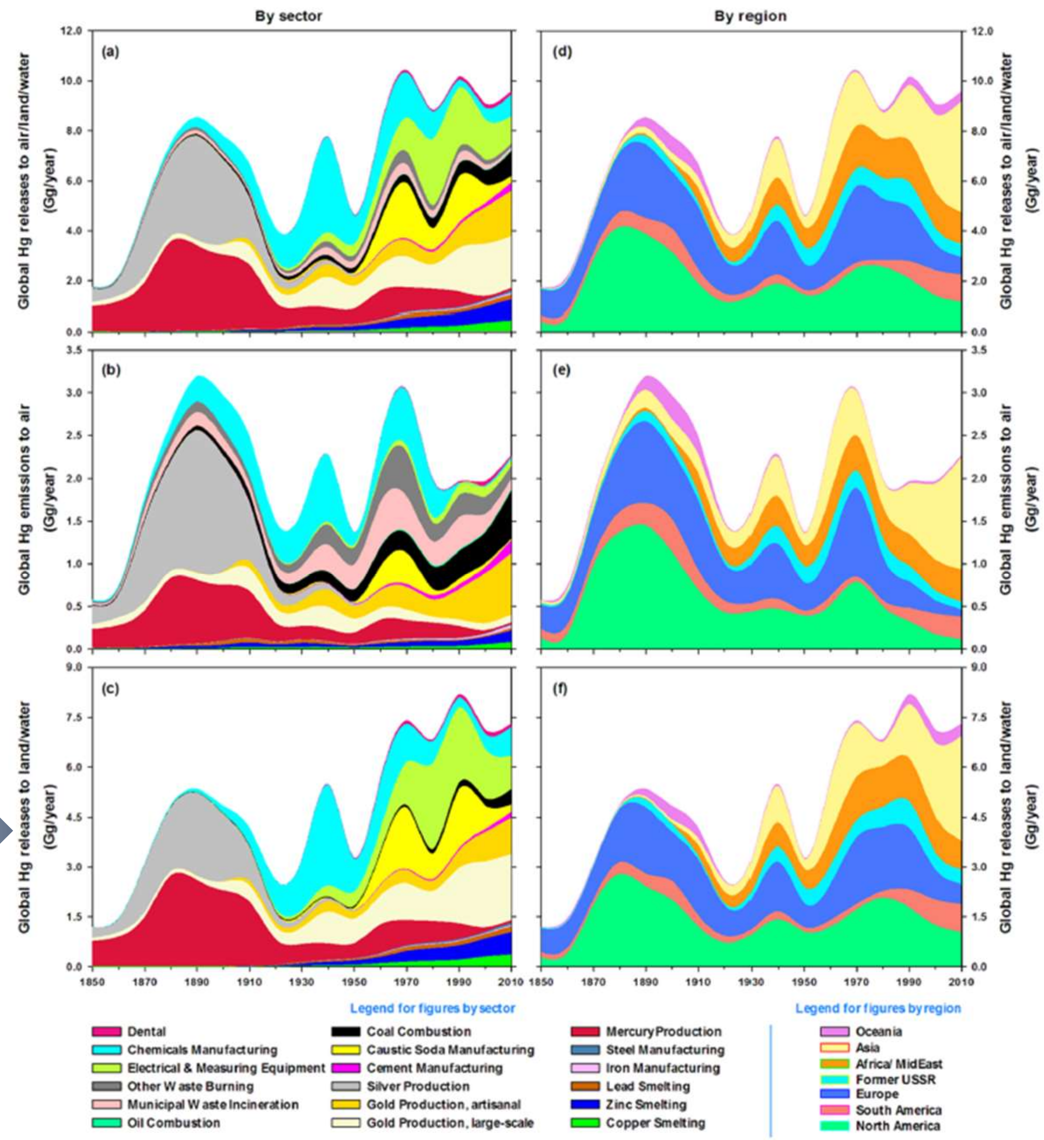
Atmosphere
Respiration
Photosynthesis
Energy exchange
Gaseous emissions
Precipitation
Evaporation
Biosphere
Elemental cycling
Soil flora & fauna
Pedosphere
Soil water
Evaporation
Hydrosphere
Leaching
Soil formation
Rock weathering
Elemental uptake
Runoff & seepage
Ground water recharge
Lithosphere

New evidence

Global Hg emission/release trends 1850−2010

,

- ***Inventories of all-time Hg releases*** *essential for the understandingof cumulative human impacts on biogeochemical Hg reservoirs*
- *The **time scales** for removal of Hg from land and water have been shown to range from decades to millennia*



Source: Streets et al, EST, 2017

New evidence

AGU PUBLICATIONS

Geophysical Research Letters

RESEARCH LETTER
10.1002/2017GL075571

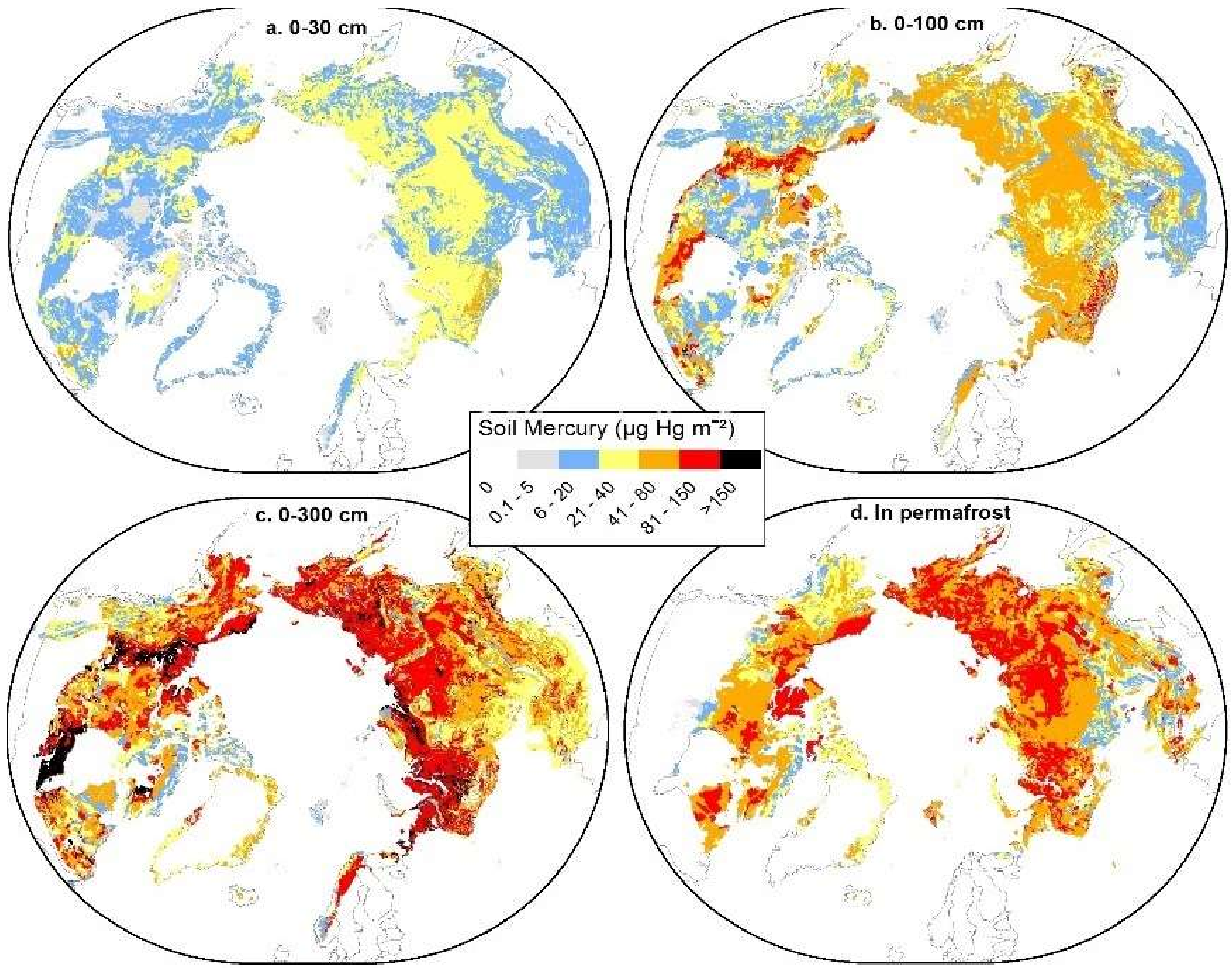
Key Points:
- Permafrost stores a significant amount of mercury
- Permafrost regions store twice as much mercury as all other soils, the ocean, and atmosphere combined

Permafrost Stores a Globally Significant Amount of Mercury

Paul F. Schuster[1], Kevin M. Schaefer[2], George R. Aiken[1,3], Ronald C. Antweiler[1], John F. Dewild[4], Joshua D. Gryziec[5], Alessio Gusmeroli[6], Gustaf Hugelius[7], Elchin Jafarov[8], David P. Krabbenhoft[4], Lin Liu[9], Nicole Herman-Mercer[1], Cuicui Mu[10], David A. Roth[1], Tim Schaefer[11], Robert G. Striegl[1], Kimberly P. Wickland[1], and Tingjun Zhang[10]

Global mercury storage in soils

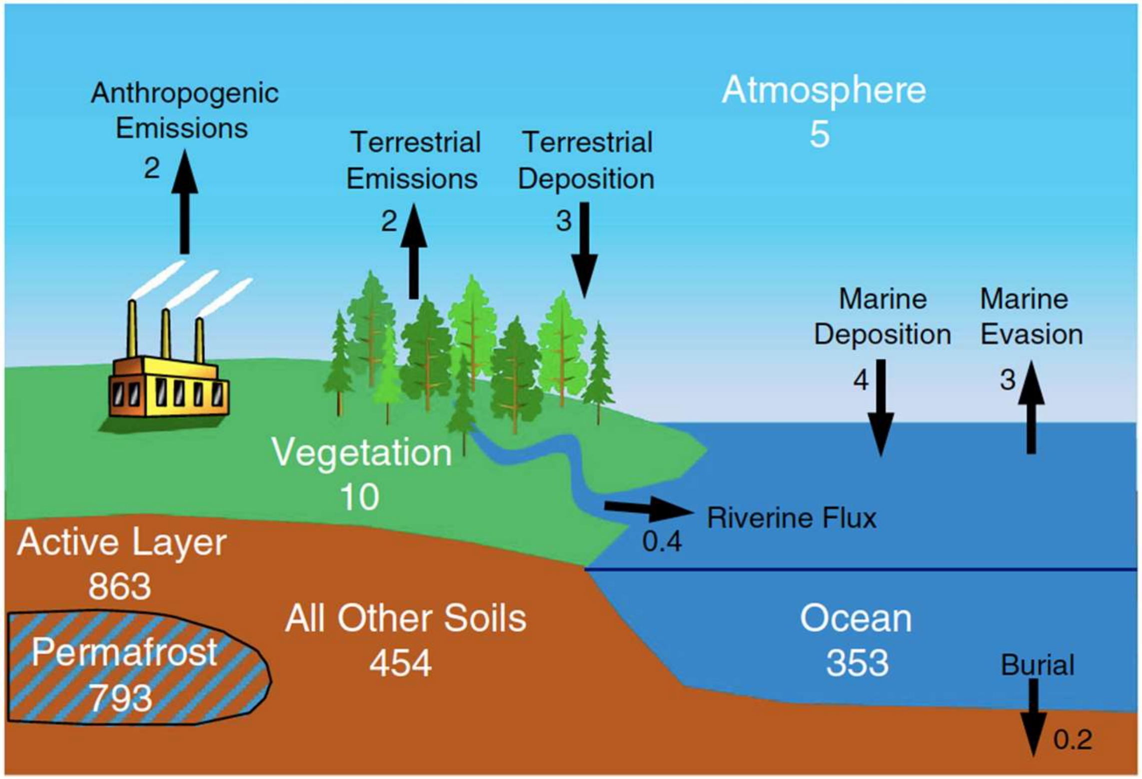
Hg in Northern Hemisphere permafrost zones for four soil layers: 0–30 cm, 0–100 cm, 0–300 cm, and permafrost



The permafrost map represents the Hg bound to frozen organic matter below the active layer depth (ALD) and above 300 cm depth.

Source: Schuster et al., Geo.. Res. Lett., 2018

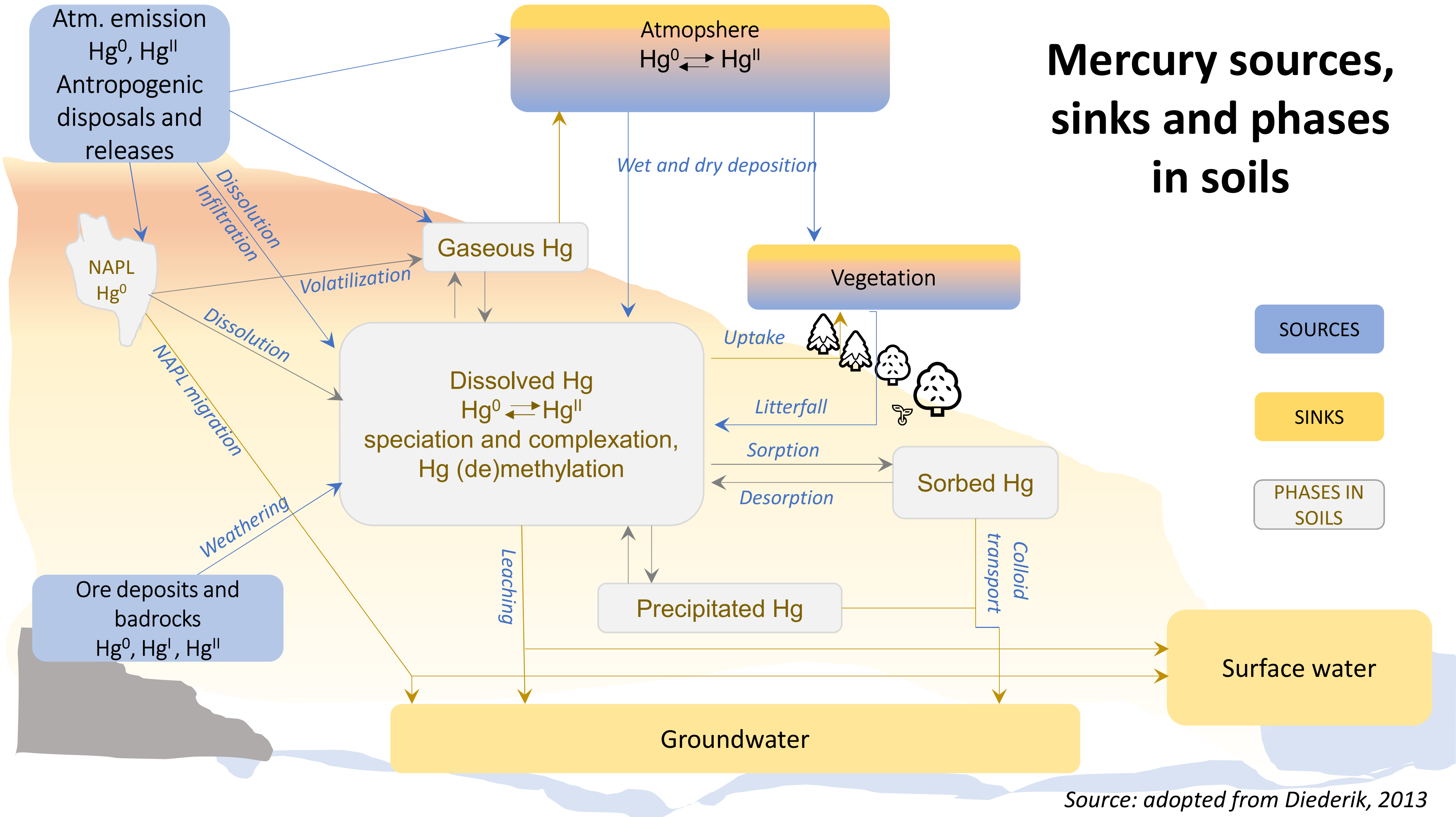
Up-dated global Hg cycle



An updated schematic of the modern global Hg cycle with major reservoirs in white (Gg Hg) and fluxes in black (Gg Hg yr-1). Adapted from Amos et al. (2013) with the soil reservoir shown as an average of previously published.

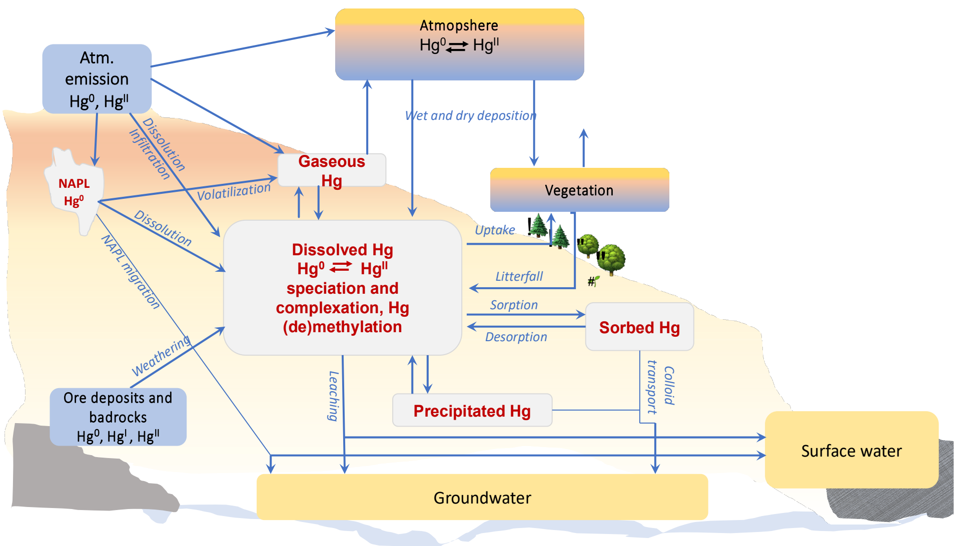
Source: Schuster et al., Geo.. Res. Lett., 2018

Mercury sources, sinks and phases in soils



Source: adopted from Diederik, 2013

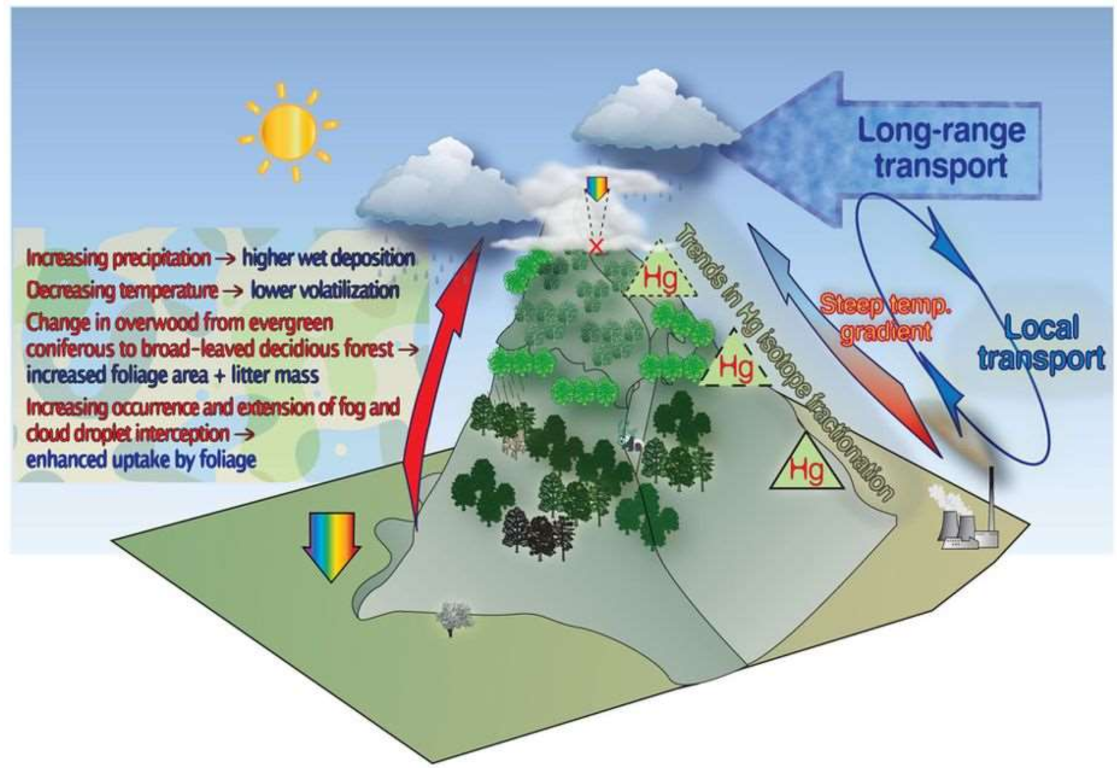
Mercury occurrence in soils



- **dissolved** in the aqueous phase as a free ion (Hg^{2+}) or complexed with inorganic and/or organic ligands
- **metallic** (or elemental) Hg^0 as a non-aqueous liquid phase (NAPL),
- **sorbed** on soil minerals and insoluble organic matter
- in the **gas phase**
- in **solid** (precipitated) phase.

Mercury sources in soils

- atmospheric wet and dry deposition and litterfall
- geogenic (or lithogenic) mercury
- anthropogenic contamination.



Zhang et al., Sci. Rep. Nature,2013

Mercury sources in soils

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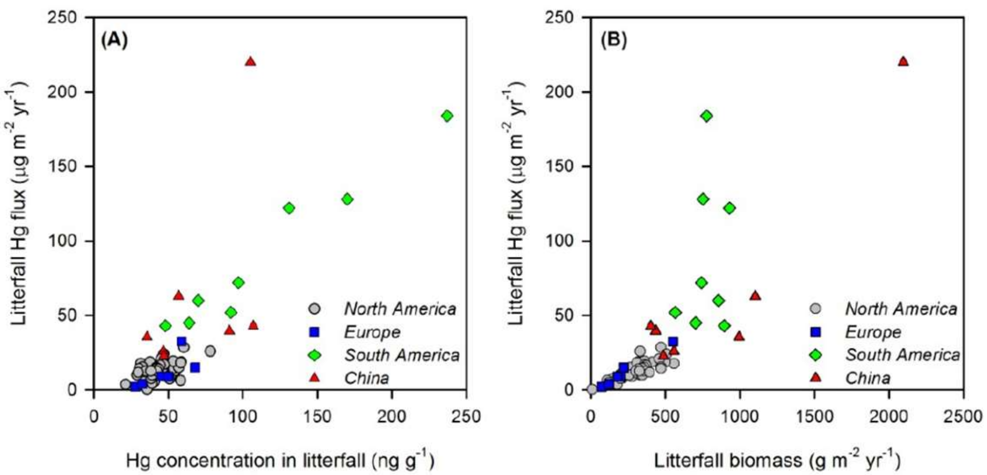
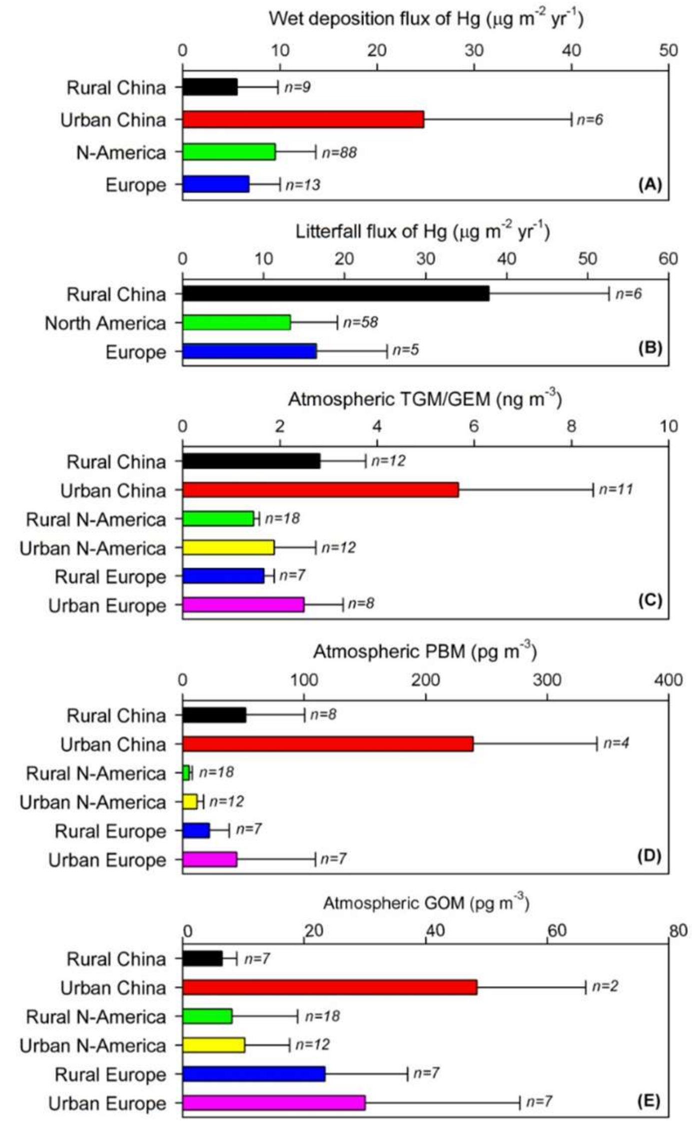
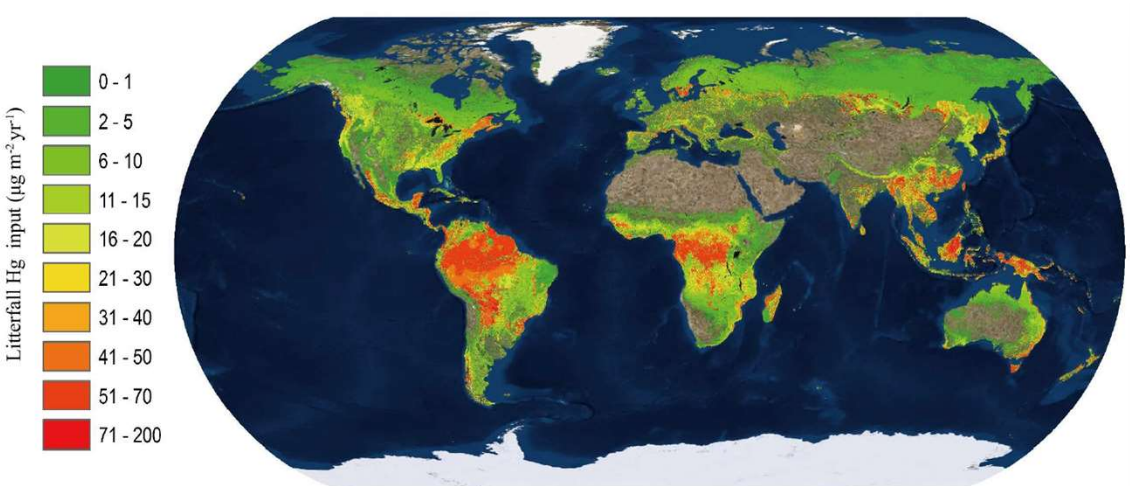


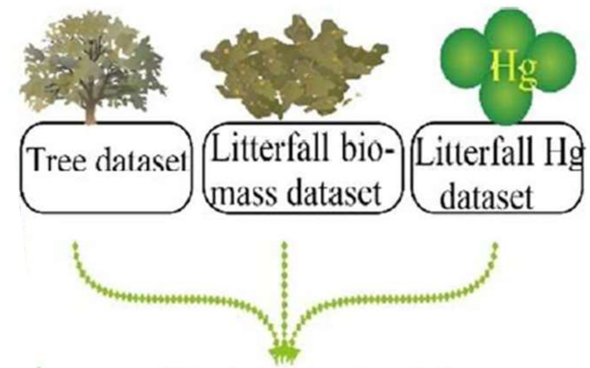


Source: Fu et al, 2016
Atmos. Chem. Phys. Discuss., doi:10.5194/acp-2016-505

Litterfall as a source:

Annual global deposition through litterfall 1180 +/-710 Mg





Monte Carlo simulation

Source: Wang et al., 2016

Mercury sources in soils

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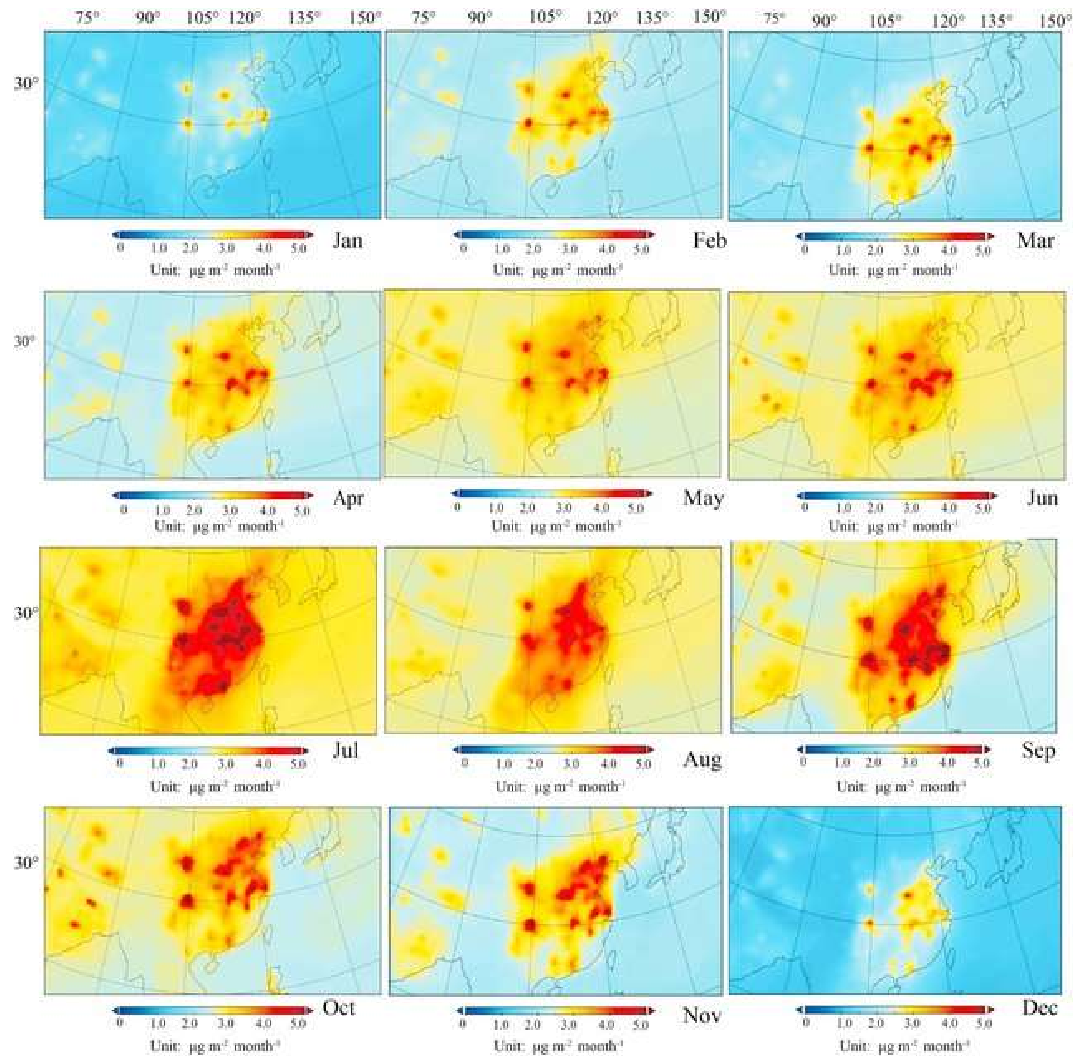
- geogenic (or lithogenic) mercury
- anthropogenic contamination.

Spatial distribution of simulated total deposition for the base-case simulation.



Source: Wang et al, 2018,
J Geophys Res Atmos. DOI: 10.1029/2018JD028350

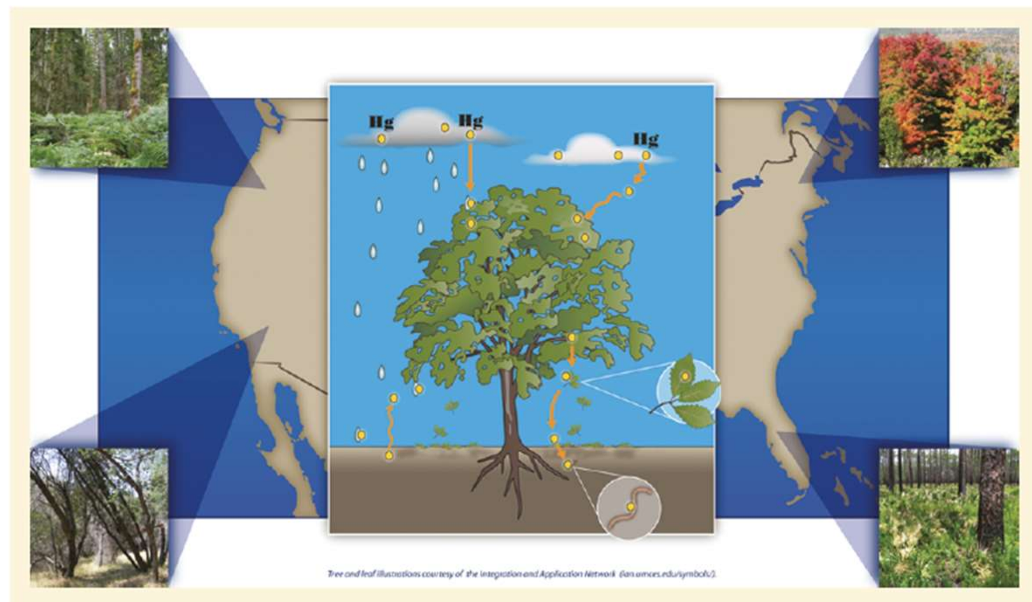
Mercury sources in soils

- **atmospheric wet and dry deposition and litterfall**
- geogenic (or lithogenic) mercury
- anthropogenic contamination.

Environmental Science & Technology
ARTICLE
pubs.acs.org/est

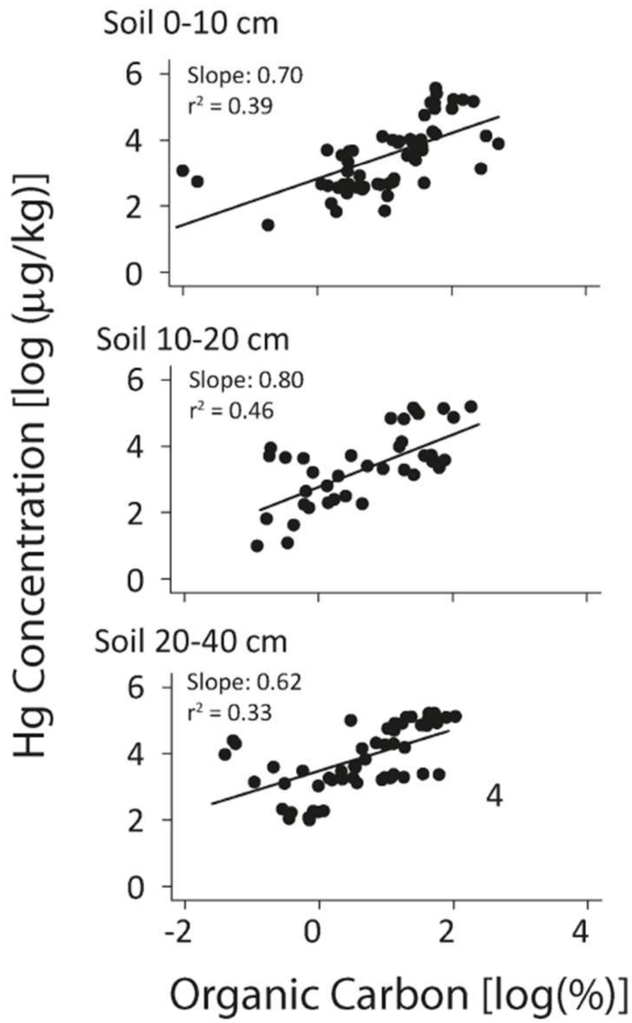
Mercury Distribution Across 14 U.S. Forests. Part I: Spatial Patterns of Concentrations in Biomass, Litter, and Soils

D. Obrist,[†,*] D. W. Johnson,[‡] S. E. Lindberg,[§] Y. Luo,[‖] O. Hararuk,[‖] R. Bracho,[⊥] J. J. Battles,[#] D. B. Dail,[▽] R. L. Edmonds,[○] R. K. Monson,[◆] S. V. Ollinger,[¶] S. G. Pallardy,[▲] K. S. Pregitzer,[‡] and D. E. Todd[□]



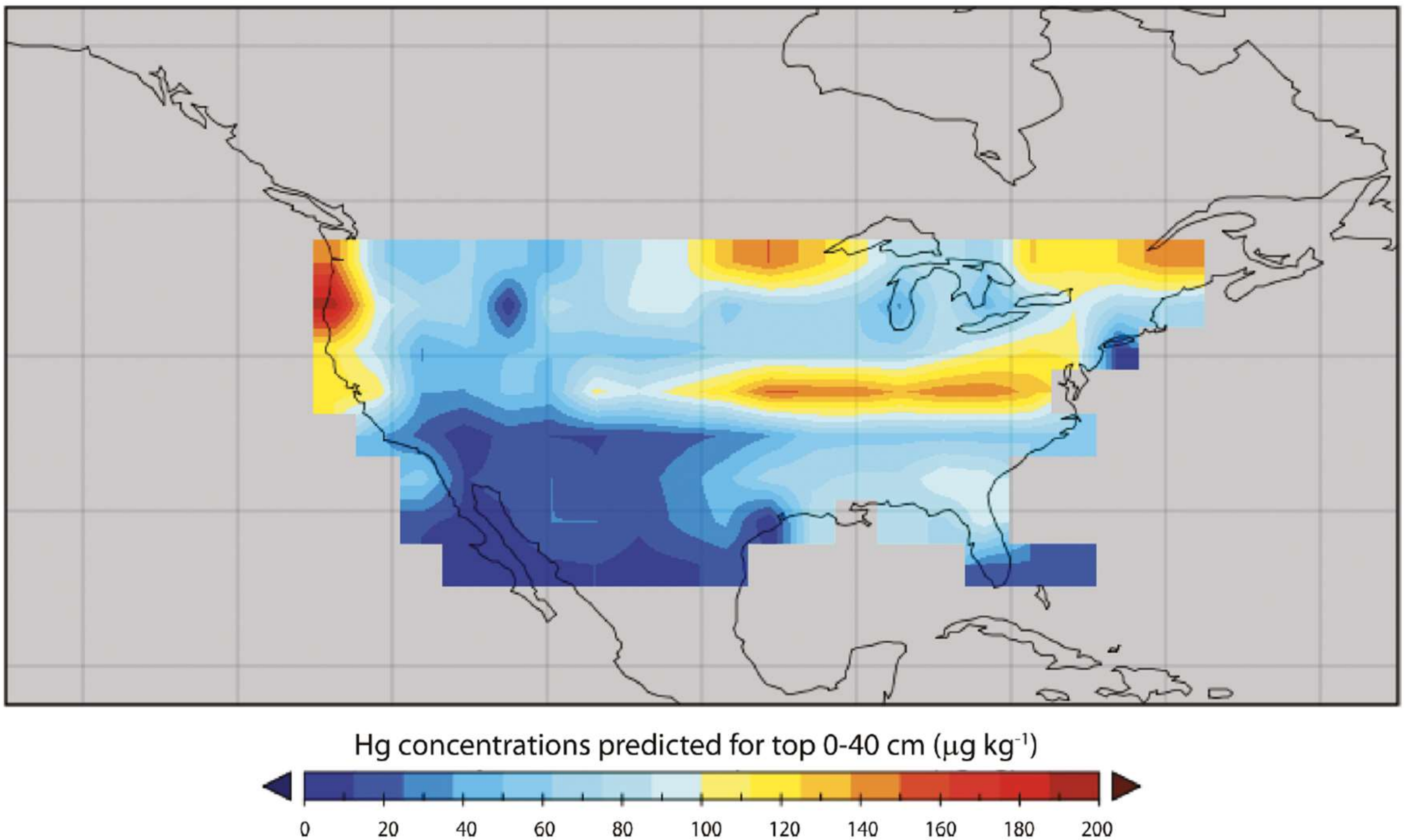
A: Hg to Carbon correlations in soils

B: Hg/C ratio to C/N ratio correlation in litter and soils



Source: Obrist et al., EST, 2018

Spatial extrapolation of top soil (040 cm) Hg concentrations based on multiregression modeling using independent variables latitude, precipitation, soil C content, and clay content



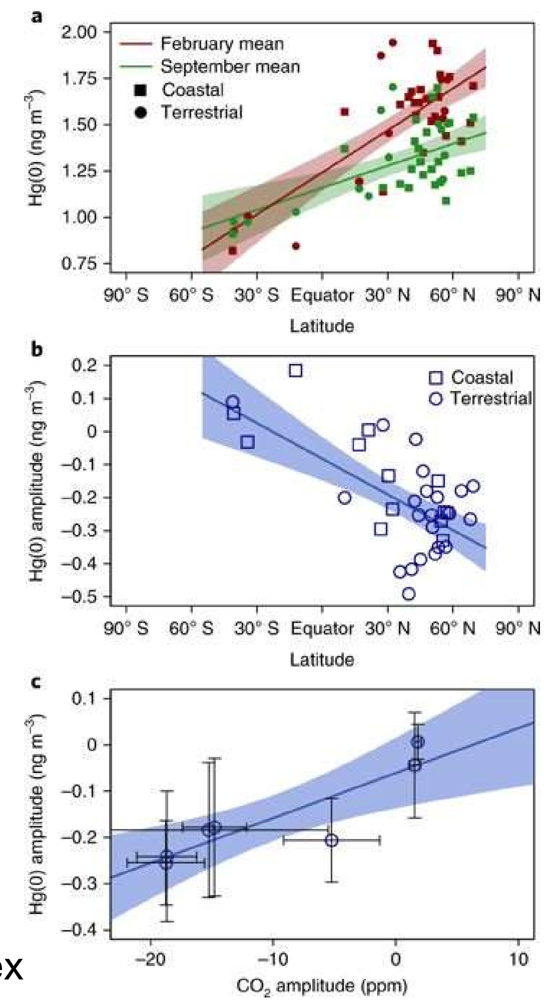
Source: Obrist et al., EST, 2018

ARTICLES
https://doi.org/10.1038/s41561-018-0078-8
nature geoscience

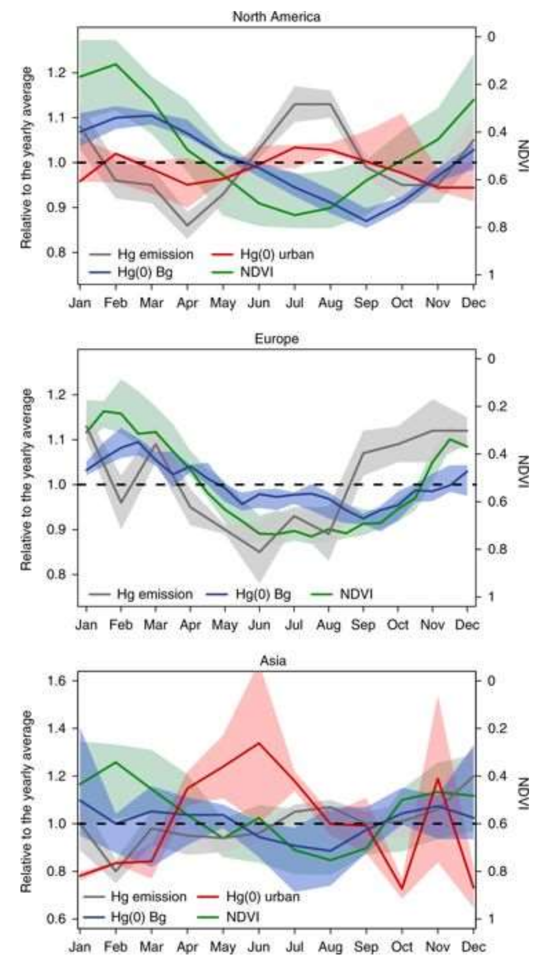
A vegetation control on seasonal variations in global atmospheric mercury concentrations

Martin Jiskra[1,2*], Jeroen E. Sonke[1], Daniel Obrist[3], Johannes Bieser[4], Ralf Ebinghaus[4], Cathrine Lund Myhre[5], Katrine Aspmo Pfaffhuber[5], Ingvar Wängberg[6], Katriina Kyllönen[7], Doug Worthy[8], Lynwill G. Martin[9], Casper Labuschagne[9], Thumeka Mkololo[9], Michel Ramonet[10], Olivier Magand[11] and Aurélien Dommergue[11]

Effect of latitude on Hg(0) seasonality



Seasonal variation of Hg emissions, vegetation activity and atmospheric Hg(0) concentrations.



NDVI - normalized difference vegetation index

Global implications

- TGM concentrations measured in the planetary boundary layer at terrestrial background sites reflect both deposition and emission processes.
- Observed Hg(0) oscillations must be considered as variations in net exchange
  - natural and anthropogenic emissions,
  - vegetation uptake, and
  - **soil** and vegetation re-emission.
- Strong depletion of atmospheric Hg(0) observed at terrestrial background sites in summer, despite highest solar radiation and therefore, potential photo-reductive re-emission, suggests that terrestrial ecosystems serve as net sinks for Hg(0).

Global implications

- This suggests that at least **half of the annual primary anthropogenic emissions are assimilated by terrestrial vegetation**, where it is efficiently retained against re-emission to the atmosphere but susceptible **to transfer via soils** *to continental and coastal aquatic ecosystems*.
- It is suggested that the vegetation pump controls, to a large extent, **diurnal and seasonal cycling of atmospheric Hg(0)** in the terrestrial planetary boundary layer, which has large implications for global Hg cycling and the **interpretation and forecasting of long-term trends.**

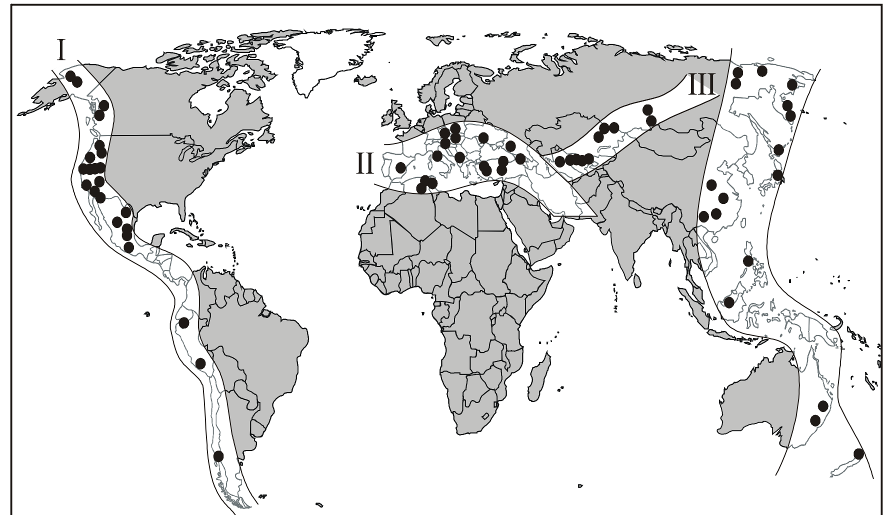
Global implications

- There is a need to incorporate **seasonal and spatial variability** in vegetation uptake of Hg(0) into **global Hg models**.
- Trends in vegetation activity should be incorporated in models reconstructing past Hg(0) levels and predicting future Hg(0) levels.
- The importance of vegetation *Hg(0) uptake as a Hg deposition pathway demands revised Hg deposition monitoring strategies by environmental agencies.*

Mercury sources in soils

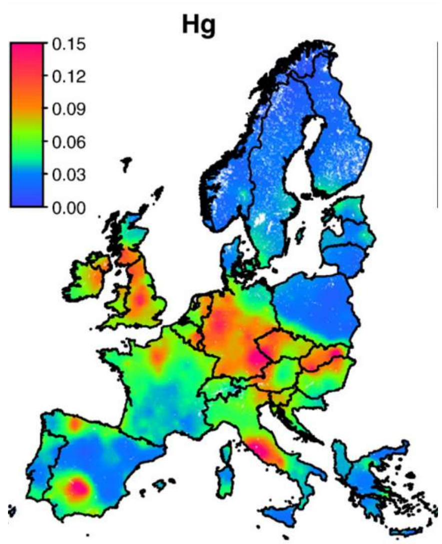
- atmospheric wet and dry deposition and litterfall
- **geogenic (or lithogenic) mercury**
- anthropogenic contamination.

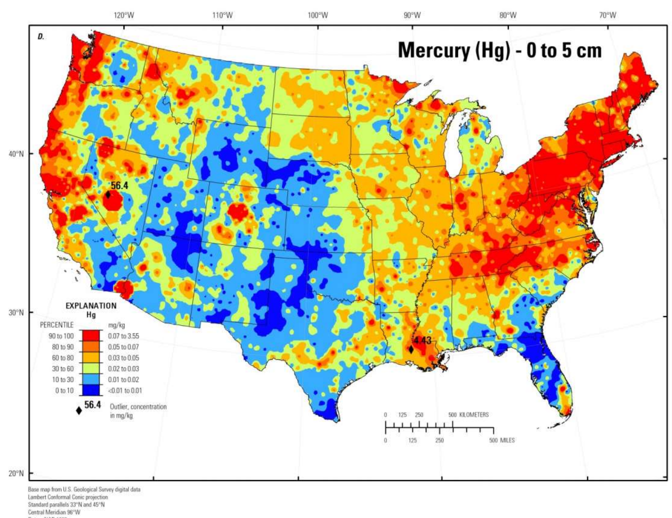
Natural mercury –planetary Hg belts

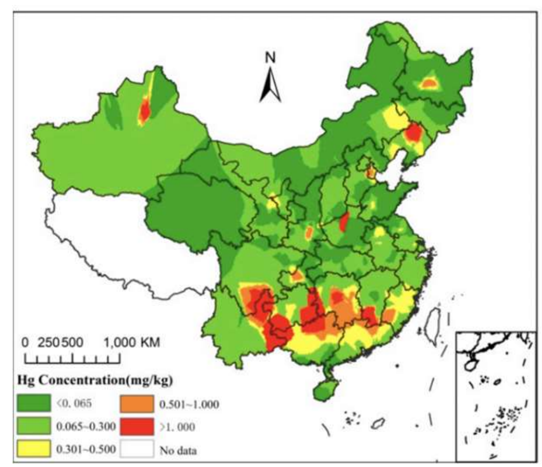


Planetary belts: I - Pacific, II - Mediterranean, III - Central Asian

EU level: FOREGS database (from Lado et al., 2008, pdf attached, concentrations in mg/kg)







Mercury sources in soils

- atmospheric wet and dry deposition and litterfall
- geogenic (or lithogenic) mercury
- **anthropogenic activities**

- *mercury mining*
- *gold and silver mining*
- *manufacturing (chlor-alkali plants, manometer spill)*
- *wood preservation*
- *cemeteries (release of mercury from dental amalgams).*
- *ammunition*
- *polluted sewage sludge applications*
- *………*

GMA 2018: Chapter 6: releases to water: Sectors

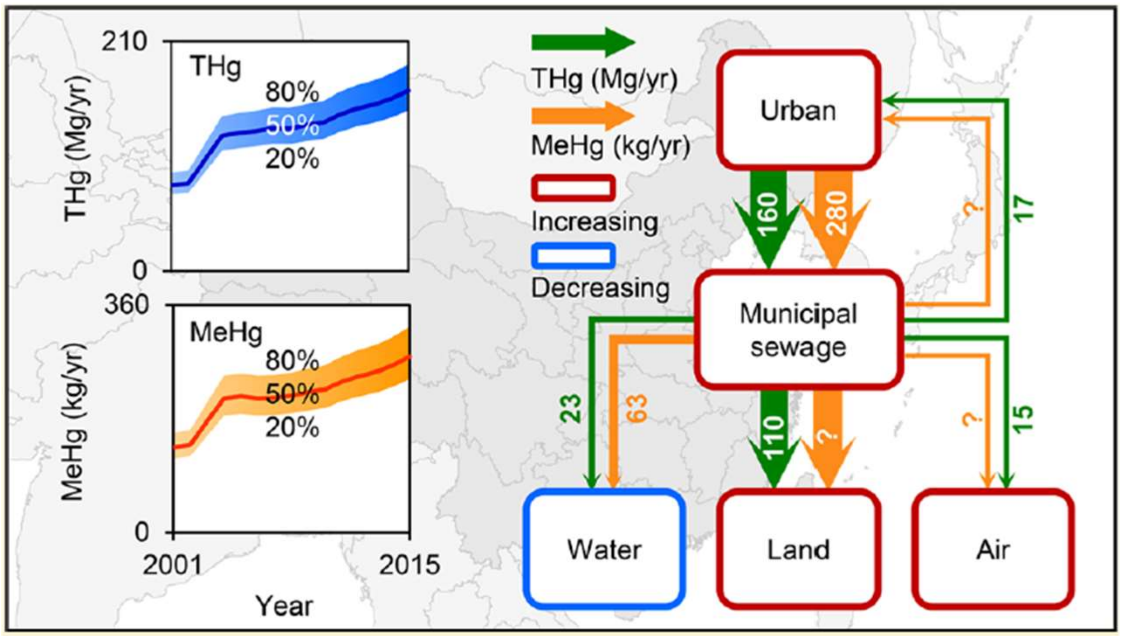
Category	Sectors
Ore mining and processing	• Non-ferrous metal production (primary Al, Cu, Pb,Zn) • Mercury production • Large-scale gold production • Artisanal and small-scale gold mining (ASGM)
Energy	• Coal-fired power plants • Coal washing • Oil refining
Waste treatment and disposal	• Chlor-alkali production (Hg cells) • Municipal waste water (MWW) • Hg-added products use and disposal

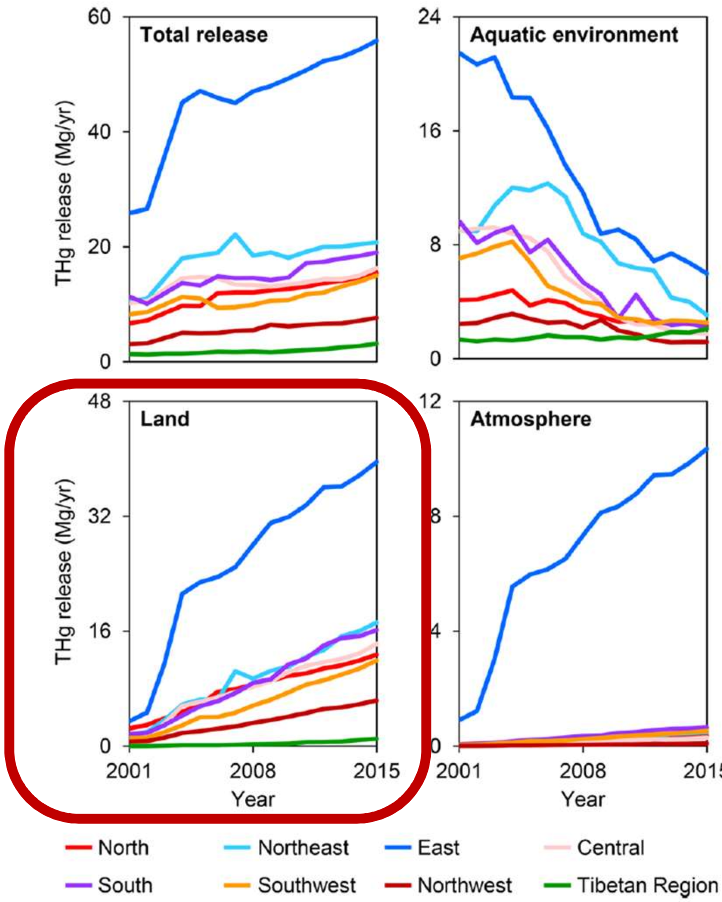
- Additional sources exist not yet possible to quantify - may be of local or regional significance
- Some processes leading to Hg release may not have been considered

Contribution from ASGM – a “special“ sector

- Large uncertainties in how to release mercury and whether emissions are on land or water
- Combined releases from this sector to water and land ~**1220 tonnes**

Sewage sludge as a source – case study China





Source: Liu et al., EST 2018

Sewage sludge disposal on agricultural land

- US EPA regulation:
- A Plain English Guide to the EPA Part 503 Biosolids Rule (PDF)(183 pp, 37 MB, September 1994, EPA 832-R-93-003)

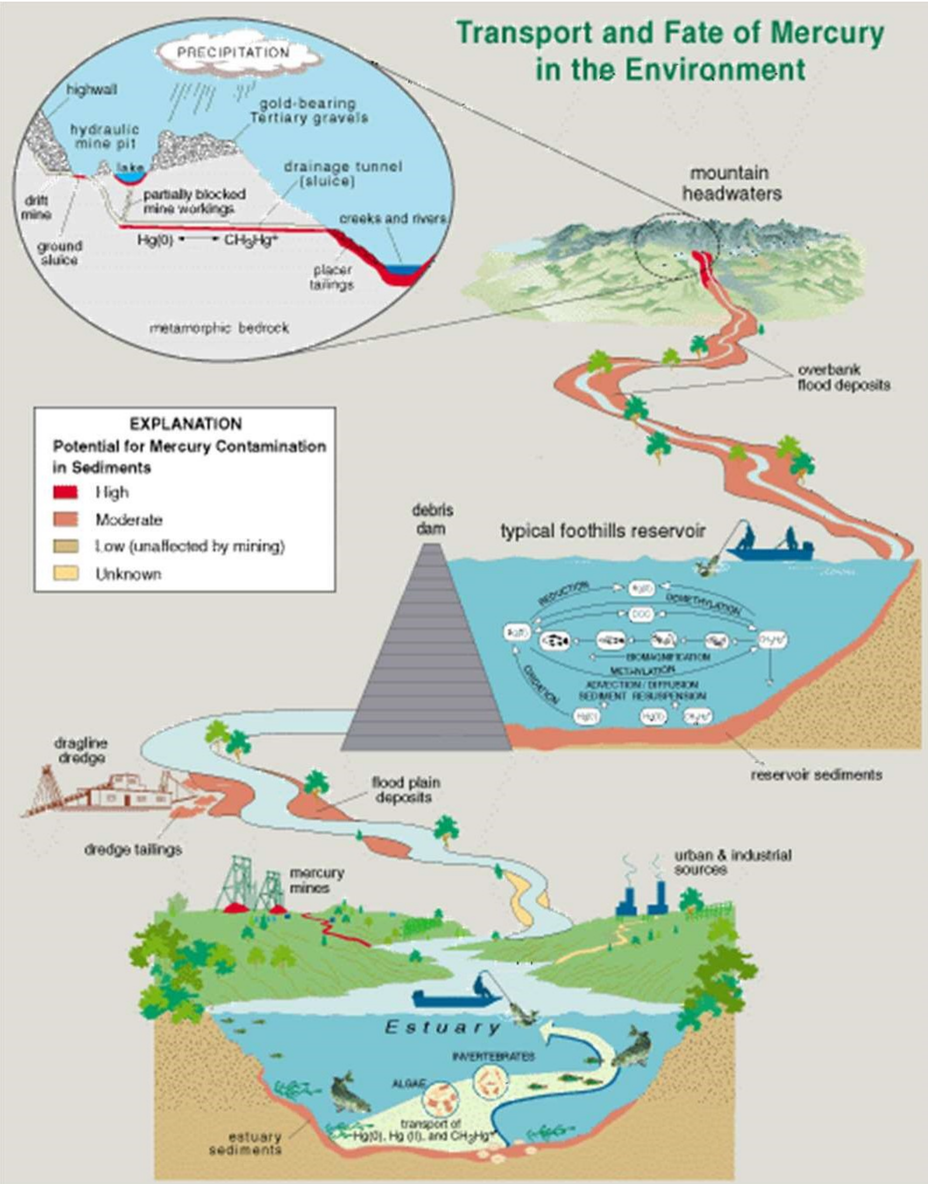
Sewage sludge disposal standards

EPA's national standards for POTW sludge disposal set the following limits for mercury:

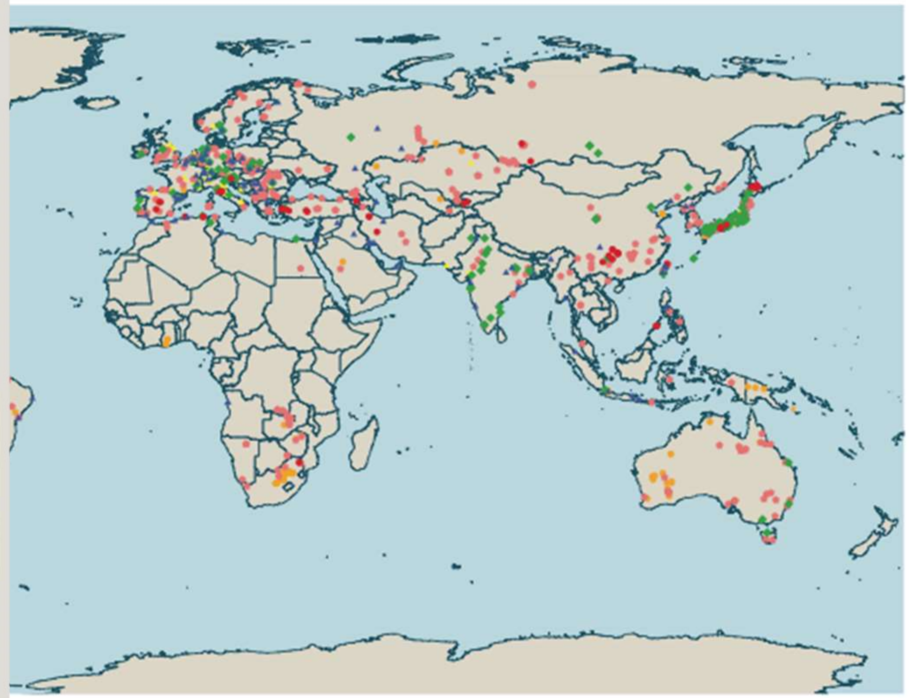
- 57 mg/kg (maximum concentration)
- 17 kg/ha (cumulative pollutant loading rate)
- 0.85 kg/ha per 365-day period (annual pollutant loading rate).

Sludges applied below these levels may be disposed of on farms or other open land, or in landfills.[

- Regulation in Slovenia
  - Limit value in soil: 0.8 mg/kg
  - Sewage sludge for agricultural use: 1.5 mg/kg
  - Annual Hg pollution loading 0.015 kg/ha



f mercury-contaminated sites.



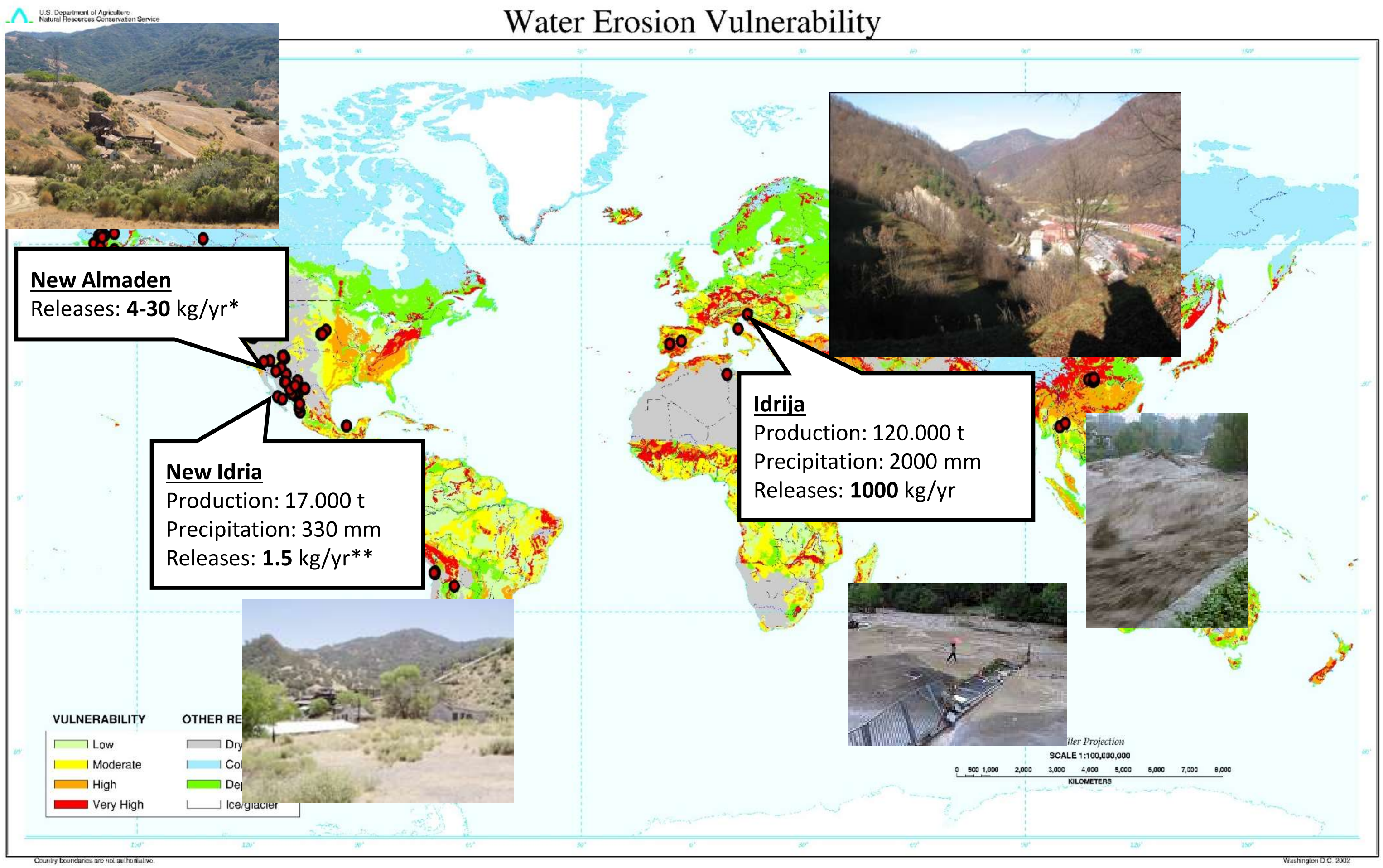
ng/ore processing

etals (gold and silver) mining

s metals ore processed

Source: adapted from Kocman et al. (2013).

CSs vs. meteorological and land cover conditions



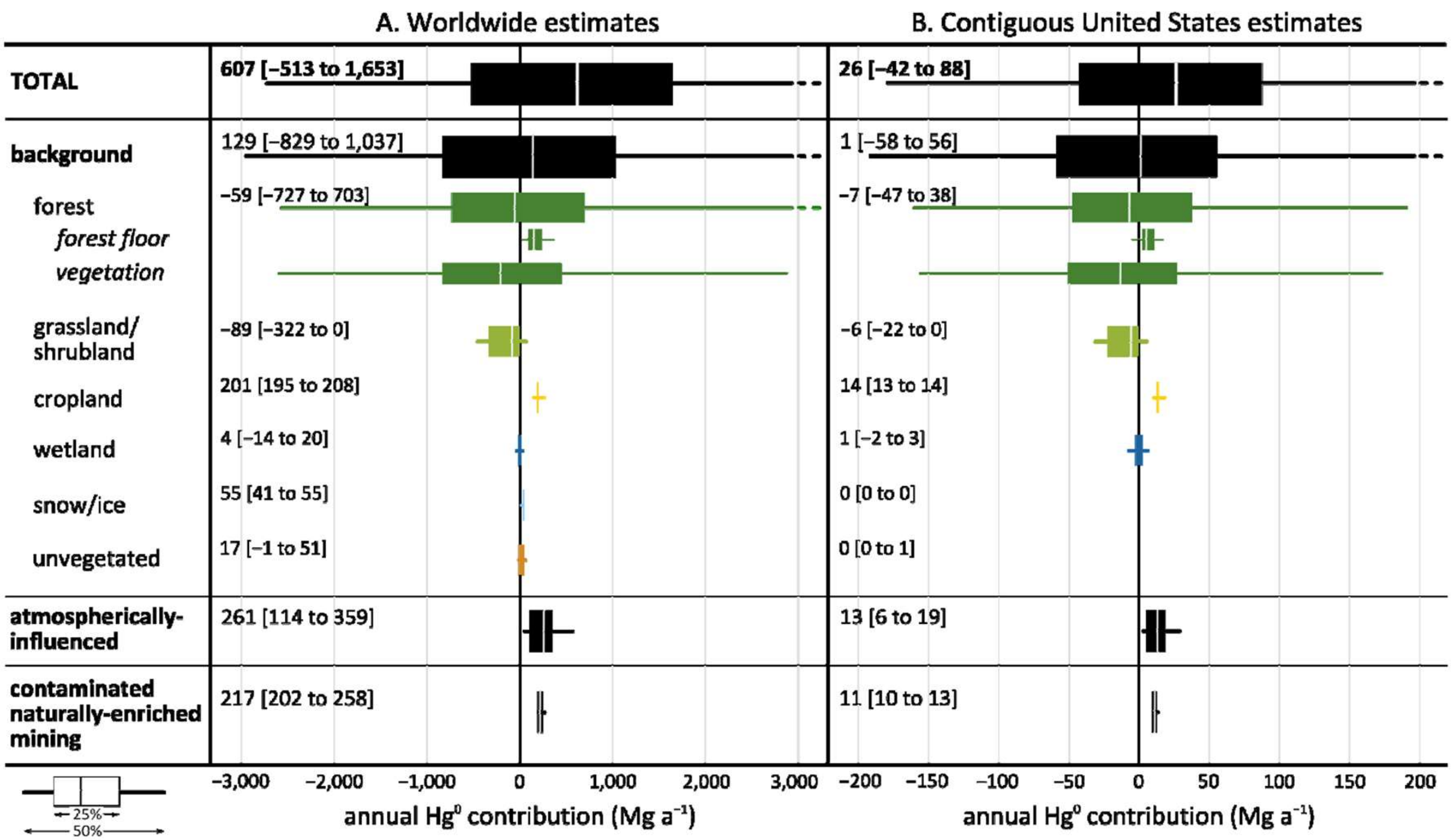
* Thomas et al., *Geochem* (2002), **Ganguli et al., *ES&T* (2000)

Total mercury re-emissions from contaminated sites

	Atmosphere ($t\ yr^{-1}$)	Hydrosphere ($t\ yr^{-1}$)*
Mercury mining	5-20	6.7 – 26.6
Chlor-alkali industry	1-3	0.09 – 0.48
Non-ferrous metal processing	1-5	0.12 – 0.54
Precious metal processing (large scale)	2-10	1.35 – 5.54
Artisanal and small scale gold mining (ASGM)	50	50 - 100
Other industrial and urban sites	10-20	0.06 – 0.33
Total	70-110	58.3 – 133.5
Total (A+H)	**≈ 130 - 245**	

Adopted from Kocman et al. 2013 and AMAP/UNEP, 2013

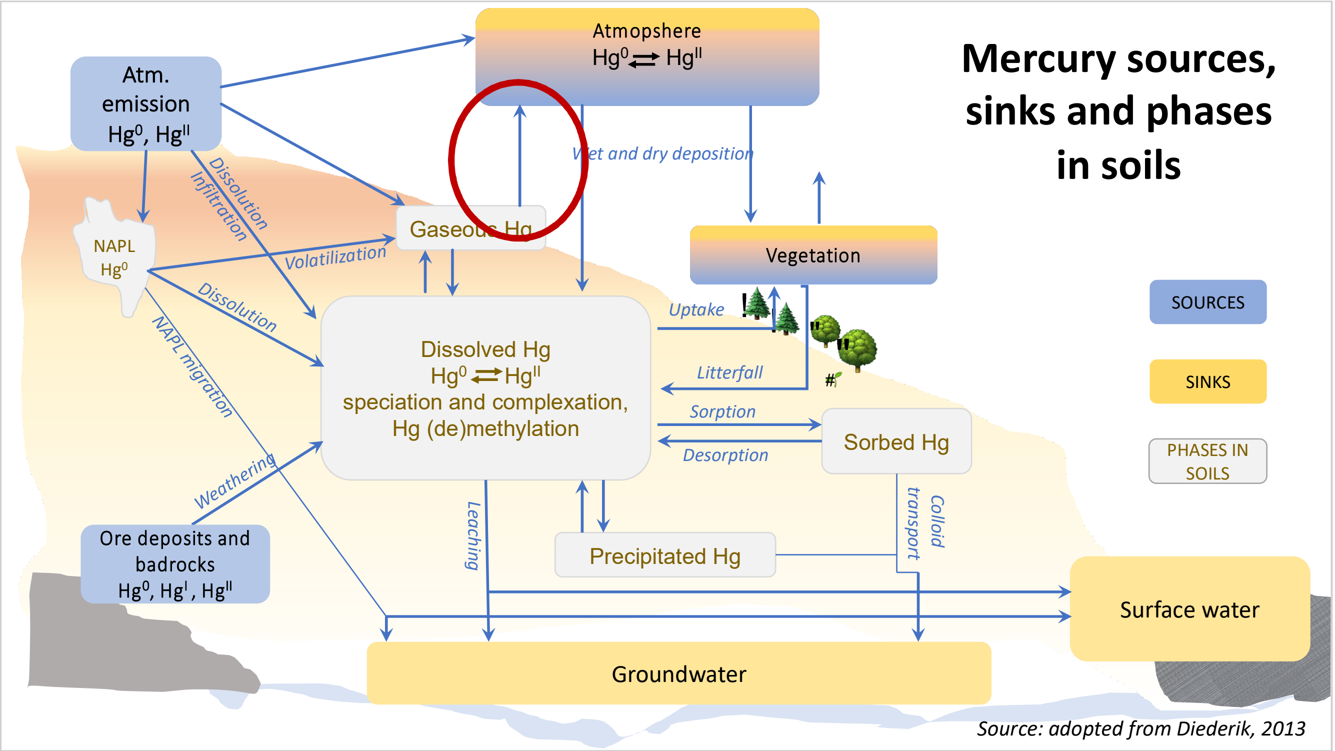
Hg emissions calculated on measured fluxes from soils



Source: Agnan et al., EST, 2016

Mercury sinks from the soil systems

- atmosphere
- plants (via root uptake)
- groundwater
- surface water
- irreversible sorption



Mercury sinks from the soil systems

- **atmosphere**
- plants (via root uptake)
- groundwater
- surface water
- irreversible sorption

Volatilization

- **reduction** of Hg^{2+} to Hg^0
- **diffusion** or mass transport of Hg^0 *to the soil surface* (in gaseous and aqueous phases)
- **diffusion** or mass transport of the Hg^0 *across the soil–air boundary* layer into the atmosphere.

Notes:

- Hg^0 is the main form of Hg evaded from the soil
- DMHg is also volatile and can contribute to mercury volatilization from soils
- MMHg and Hg^{2+} salts are of minor importance. CH_3HgOH and CH_3HgCl are volatile compounds
- MMHg volatility decreases due to the high affinity to solute and solid organic matter

Volatilization – *factors*

- **Sunlight** (UV radiation) and **heat** emitted from sunlight (air and soil temperature) are considered the main factors
  - Emissions from soil follows a multicompartment model (surface <2 cm; subsurface phenomenon)
- **Moisture content**: increasing volatilization rate
- Soil physical characteristics, sorption capacity, mercury species and content and pH
- **Meteorological conditions** (wind speed, relative humidity, turbulent mixing of air layers, etc.), especially important in Hg enriched or contaminated areas

Mercury(II) reduction in soils

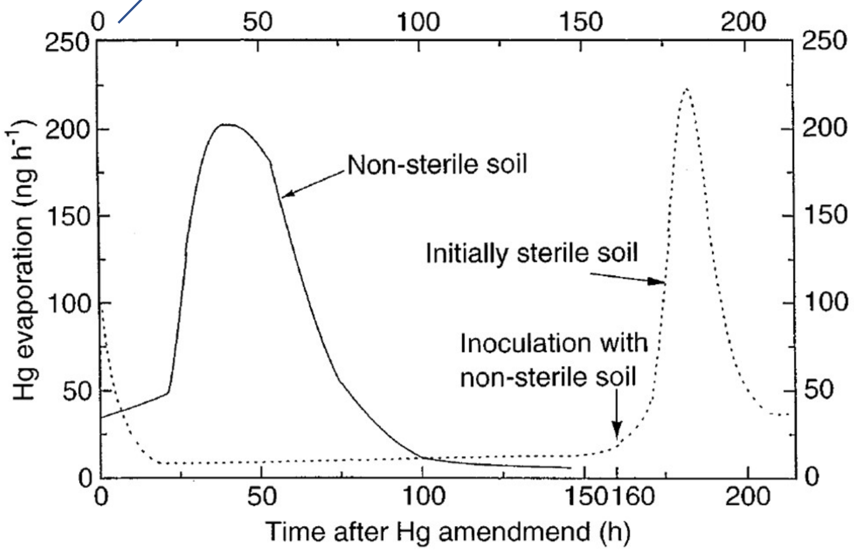
a. Abiotic reduction

- Hg(I) ⇔ Hg(0) + Hg(II)
- Dominated by the presence of DOM (dissolved organic matter)
  - FA have higher reduction potencial than HA
- Presence of other reductants (Fe^{2+})
- *Hg^{2+} reduction by interaction with DOM is more favourable for recent atmospheric Hg deposition:*
  - *Fraction of airborn Hg in the upper layer in soil is dominated*
  - *Interaction of fresh Hg^{2+} with $DOM_{red.}$ is higher than „old“ Hg*

b. Biotic reduction

- Favoured in soils of high Hg^{2+} availability and microbiological activity
- **Direct:** biotic reduction of Hg^{2+}
- **Indirect:** microbiological degradation of organic matter followed by Hg^{2+} abiotic reduction

Mercury evaporation from sandy soil amended to 1 mg $Hg.kg^{-1}$ [as $Hg(NO_3)_2$]

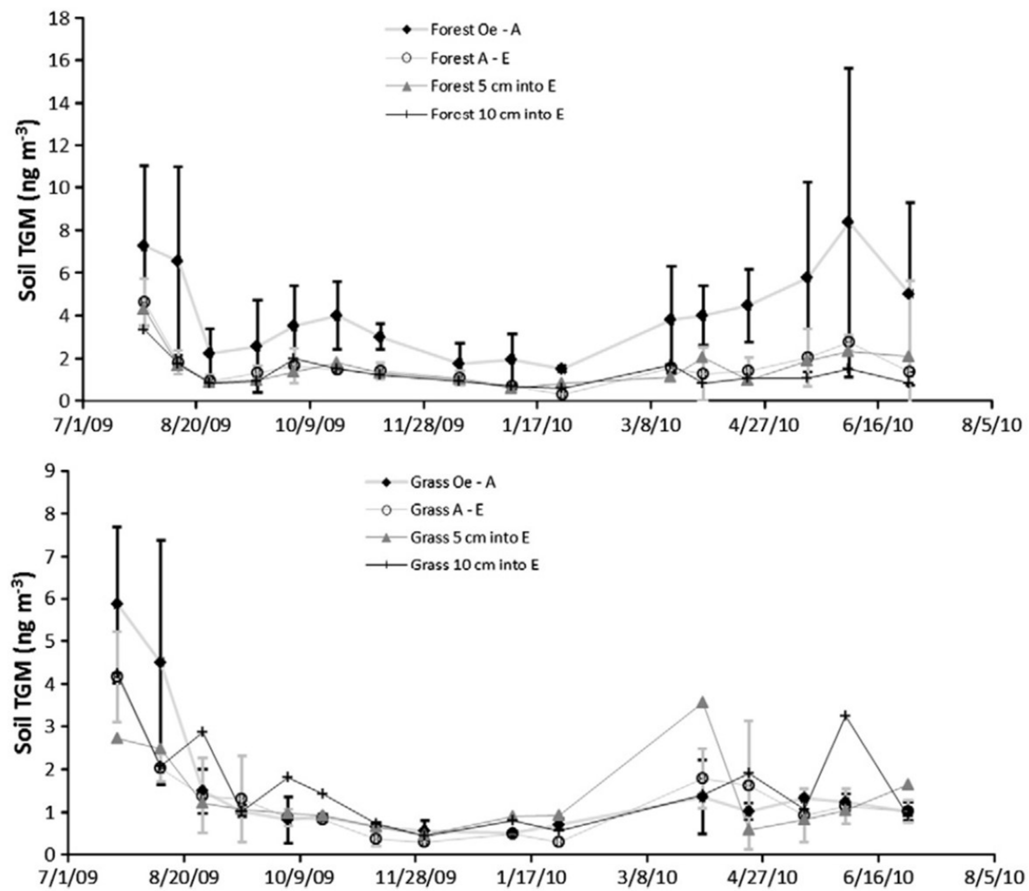


Source: Rogers and McFarlane 1979

Volatilization –
noncontaminated forest soils

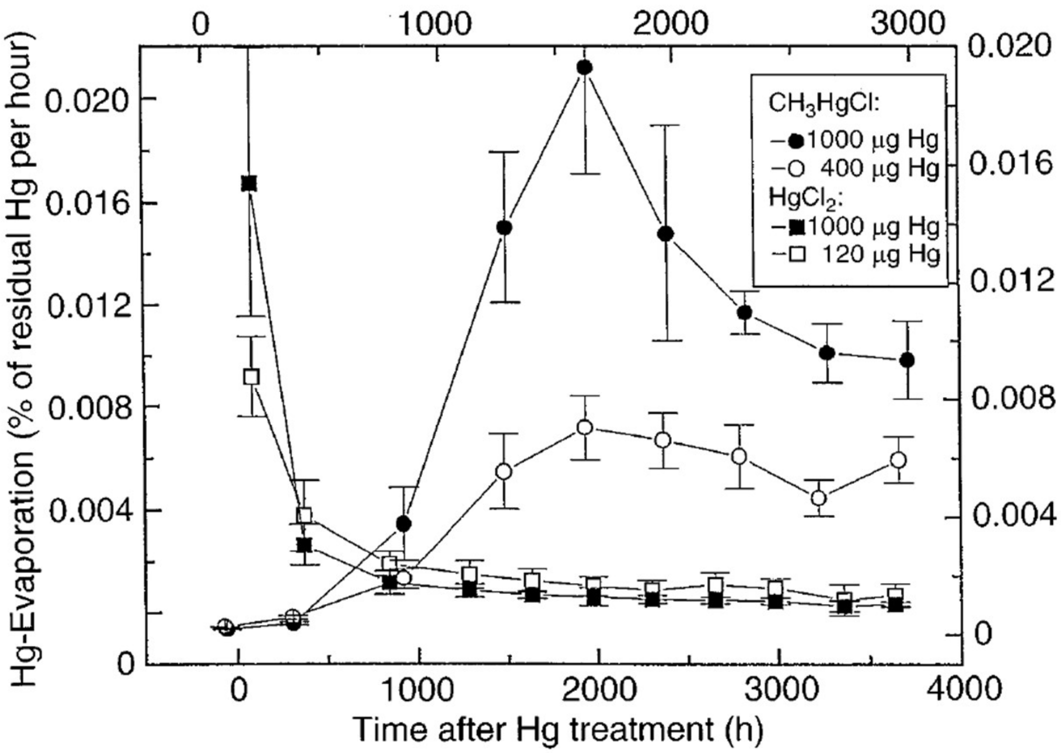
Significant factors affecting gaseous mercury concentrations:

- Hg soil temperature
- redox conditions
- organic matter



Source: Moore and Castro, STOTEN, 2012

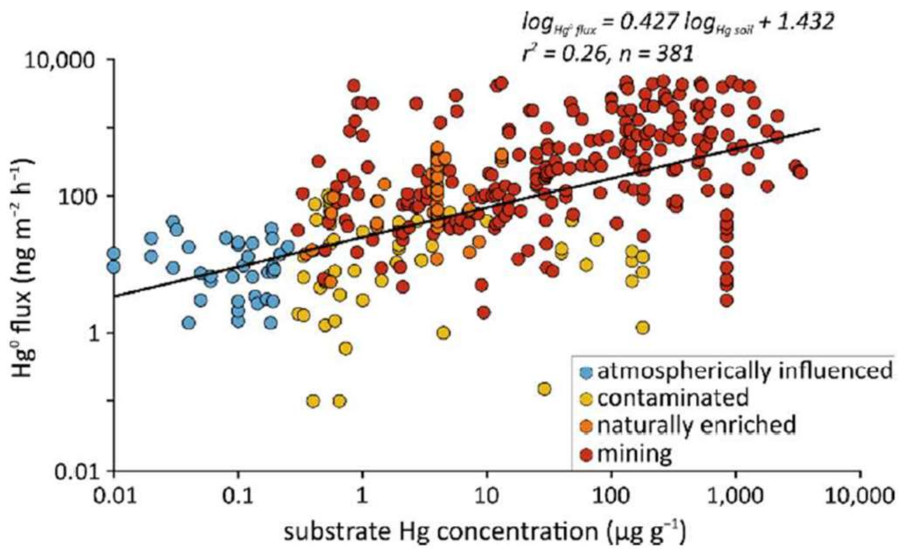
Demethylation processes in soils



- MeHg breaks down to CH_4 and Hg(0) (demethylation prevails; low levels of MeHg in soils)

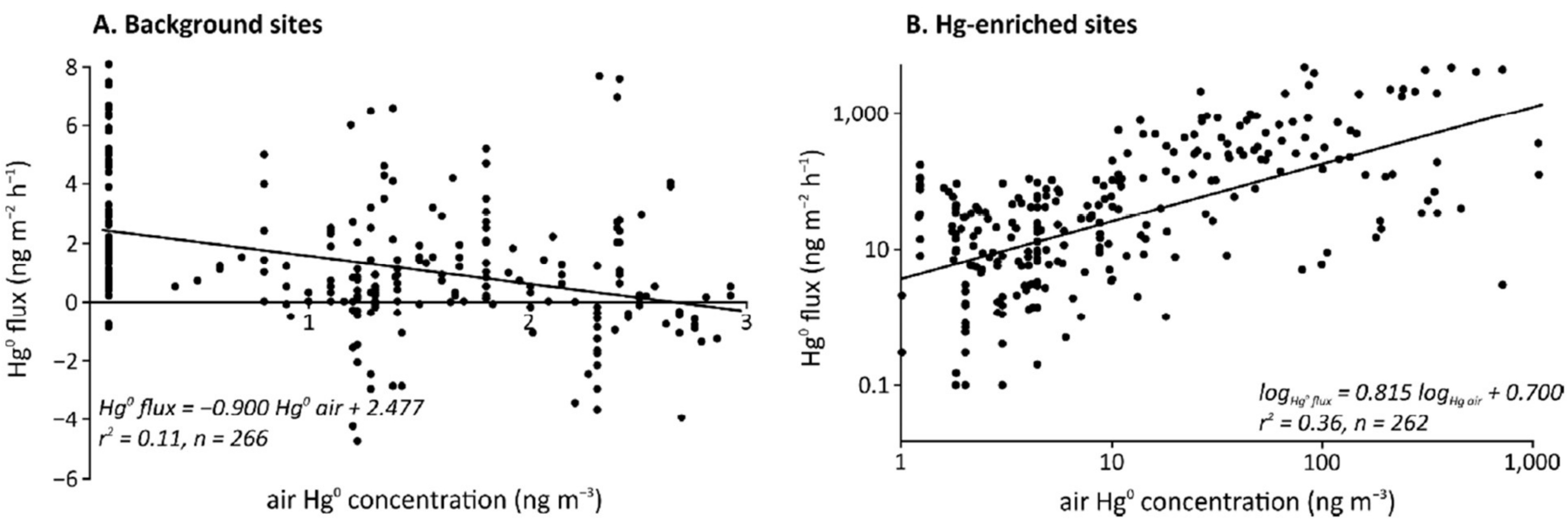
Volatilization – emission rates

- Background areas: **0.001 to 0.2 μg m^{-2} h^{-1}**
- Uncontaminated urban: **8.7×10^{-4} to 4.5×10^{-3} μg m^{-2} h^{-1}**
- Contaminated floodplain: **0.01 to 0.85 μg m^{-2} h^{-1}**
- High volatilization losses in the subsurface from NAPLs
- Significant losses laterally



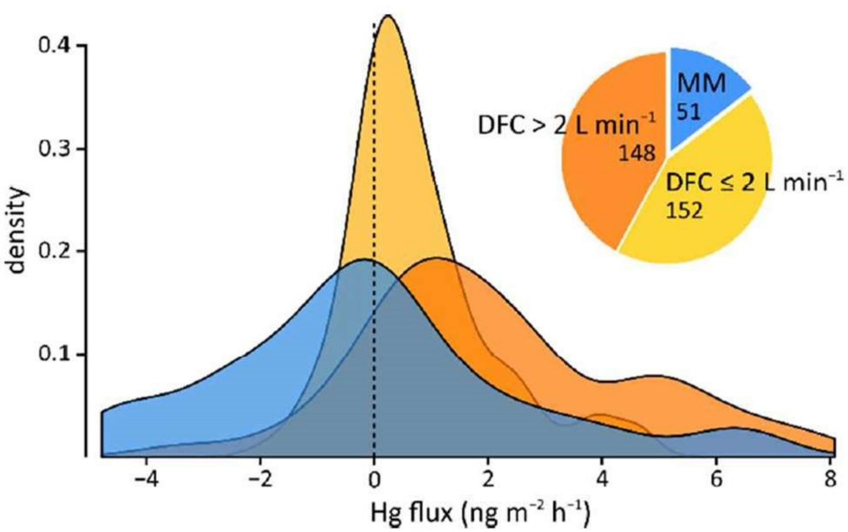
Comparability of the measured fluxes is questionable?

Hg^0 flux vs. air Hg^0 concentration relationship



Source: Agnan et al., EST, 2016

Issues related to flux measurements



	Advantages	Dissadvantages
DFC -dynamic flux chamber		Effects of: - chamber shape, - chamber material, - flushing flow rate. Blank correction needed
MM – micro-meteorological approach	best represent natural conditions	

Background sites:
DFC flushing flow rate: ≤ 2 L min and > 2 L min

Source: Agnan et al., EST, 2016

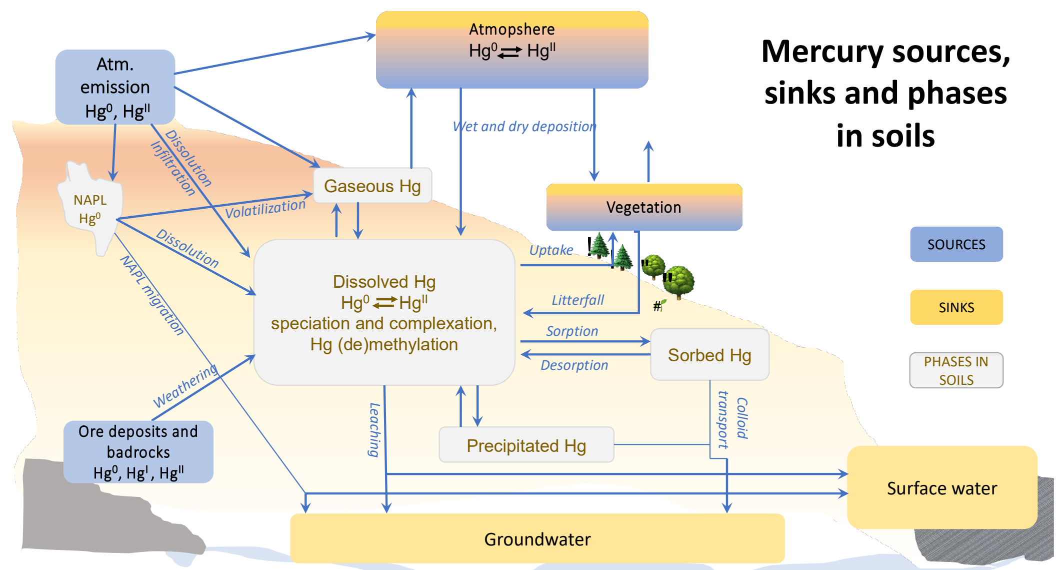
Mercury sinks from the soil systems

- atmosphere
- **plants (via root uptake)**
- groundwater
- surface water
- irreversible sorption

- Hg uptake from plants is low
- Bioavailability monitoring ?
- Genetic engineering for phytoremediation
- Phytostabilization
- Non-terrestrial plants – mangrove with significant uptake
- Rice accumulate Hg and MeHg

Mercury sinks from the soil systems

- atmosphere
- plants (via root uptake)
- **groundwater**
- **surface water**
- **irreversible sorption**



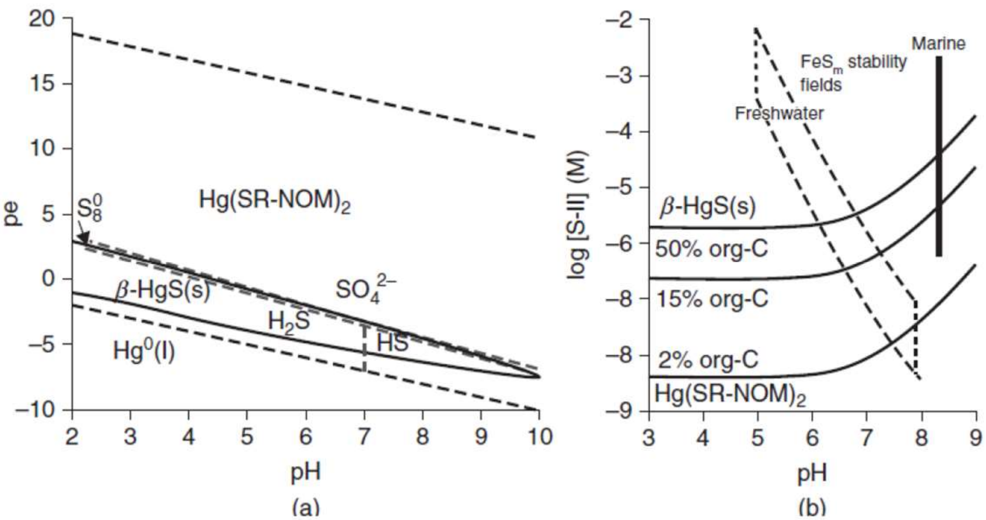
Source: adopted from Diederik, 2013

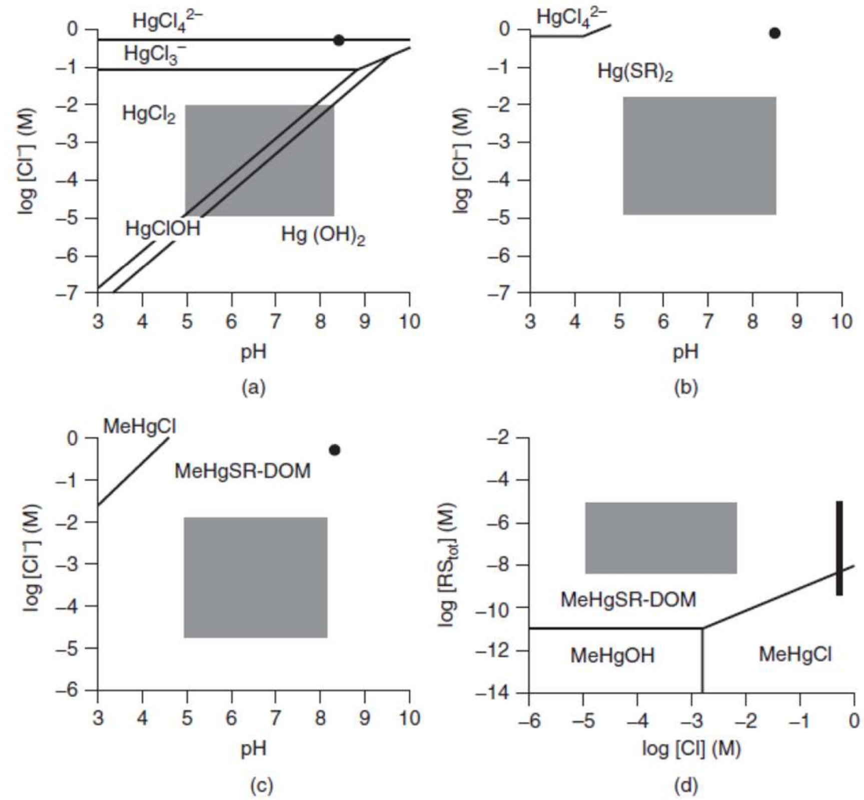
- ***Unsaturated zone:*** *transport occurs via convection, dispersion, diffusion and colloid-facilitated transport.*

Hg in soil aqueous phase

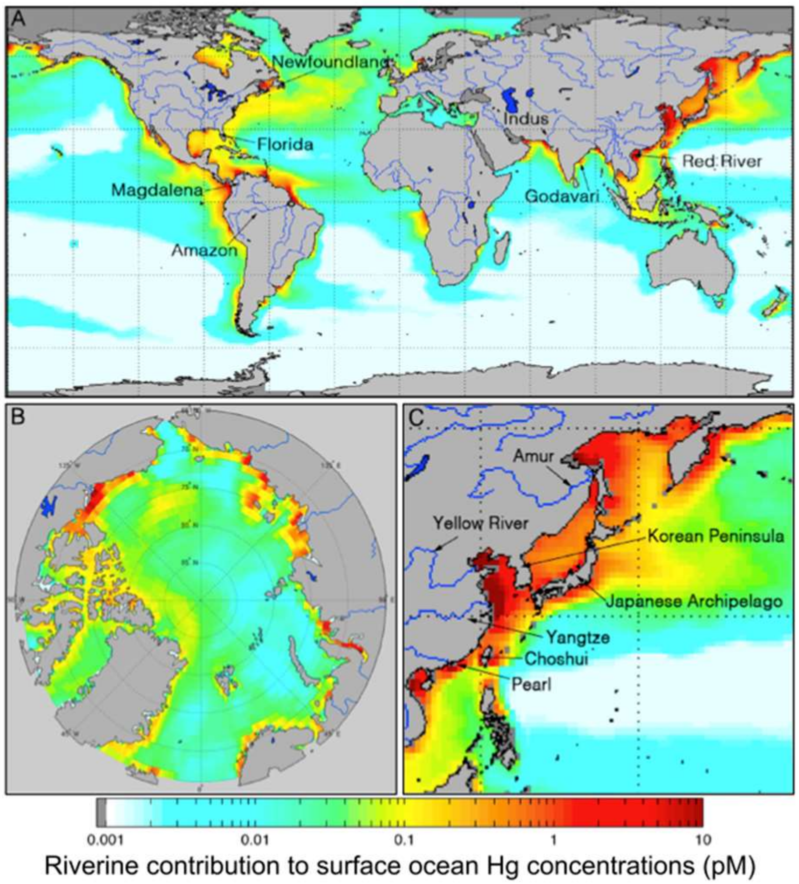
- Dissolved Hg species: **complexes with inorganic and organic ligands**
- Factors influencing Hg speciations are **pH, ionic strength, redox potential, DOM, dissolved O_2, sulphide, suspended solids** in solution
- Under *oxidized* surface soil conditions, Hg and MMHg form almost **exclusively complexes with thiols**. Common inorganic mercury forms are $Hg(OH)_2$, $HgCl_2$, $HgOH^+$, HgS and Hg^0. In *reduced* environments common mercury forms are $HgSH^+$, HgOHSH, and HgClSH. These mercury forms are generally bound to organic and mineral ions/molecules.

Dominant Hg species in soils aqueous phase



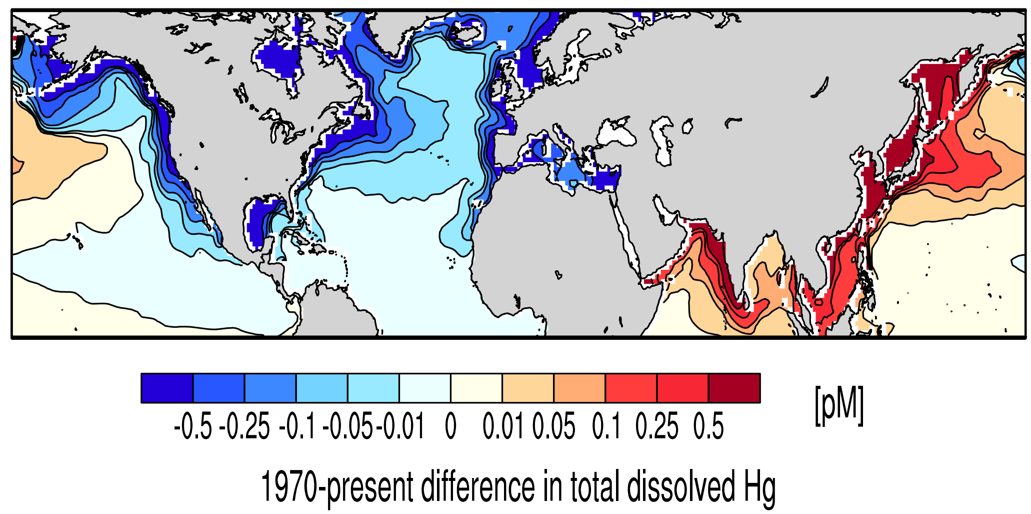


Riverine contribution to surface ocean Hg concentrations (pM)



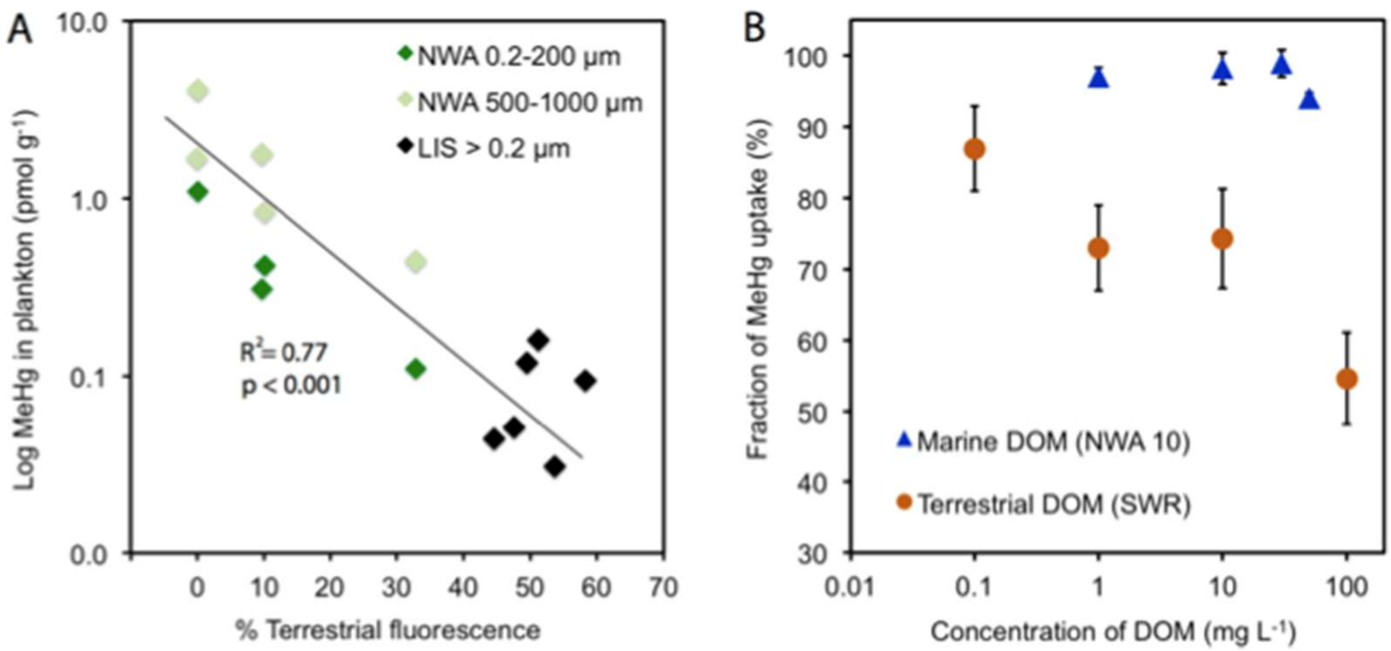
Zhang et al., Global Biogeochemical Cycles, 2015

The simulated change in the riverine contribution to annual mean dissolved Hg concentrations in the surface ocean (0 to 55 m) given 10 years of discharge representative of the 1970s and then present day.



Amos et al. ES&T, 2015

Field (A) and experimental (B) measurements of the effects of DOM composition on MeHg uptake by plankton



Long Island Sound (LIS)
Northwest Atlantic continental margin (NWA)

Suwannee River (SWR)

Schartup et al., ES&T, 2015
Hammerschmidt et al.2006

What to measure in soil?

Are the measurement results comparable?

Determination of total mercury in soils

Sampling +	Processing +	Measurement =	Result
Representative Appropriate Contamination Stability Handling	Dissolution Extraction Dilution	Comparison to SI units or conventional scale	± uncertainty
✓	?	?	?

Measurement principles for THg

CV AAS
Easy to maintain,
field applications;
0,01 ng/mL

Sample

Acid digestion
- Aqua regia
- with HF

Aqueous solution

(Reduction)

Detection
(CV AAS, CV AFS, ICP MS, AES,..)
AES,..)

Manual

Automated

Combustion → amalgamation → cv **AAS**

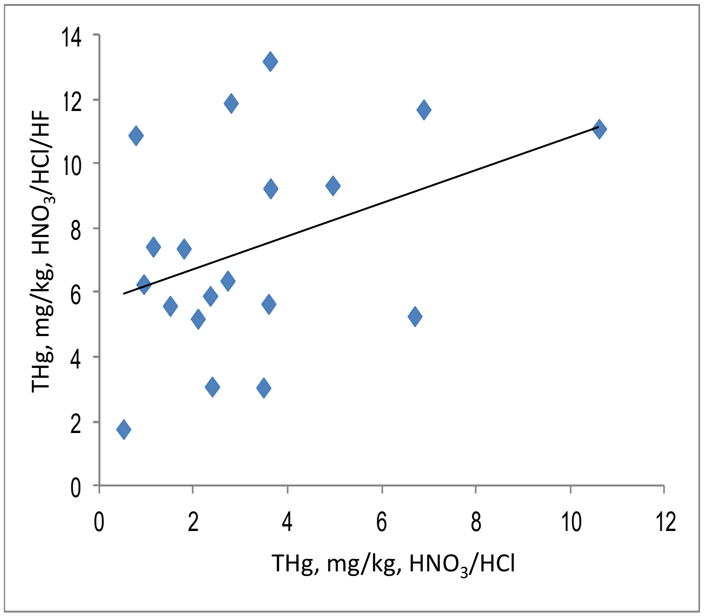
High throughput, reproducible, sensitive

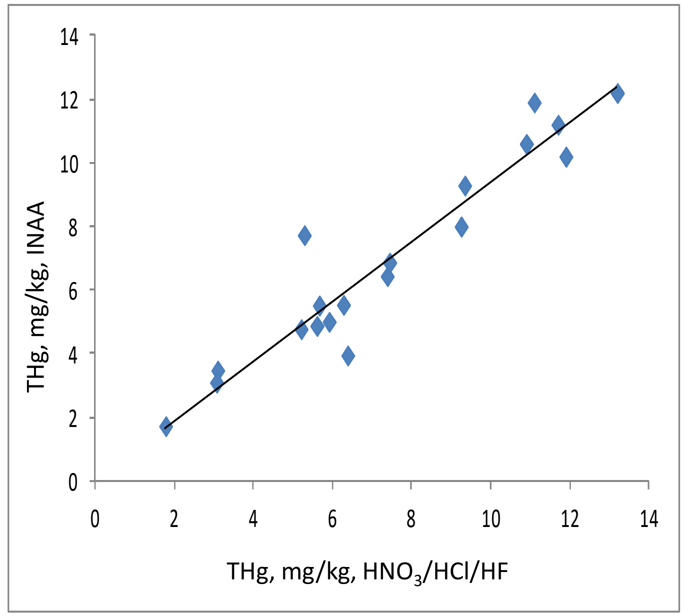
Standard methods used

- **EPA Method 7473 (SW-846): Mercury in Solids and Solutions by Thermal Decomposition, Amalgamation, and Atomic Absorption Spectrophotometry**
- **EPA Method 200.7 USEPA SW-846 Method 3050B, acid extractable fractions**

Total mercury determination in soils from Ghana ASGM sites:

comparison of methods using HNO_3/HCl and HNO_3/HCl/HF by k_0-INAA

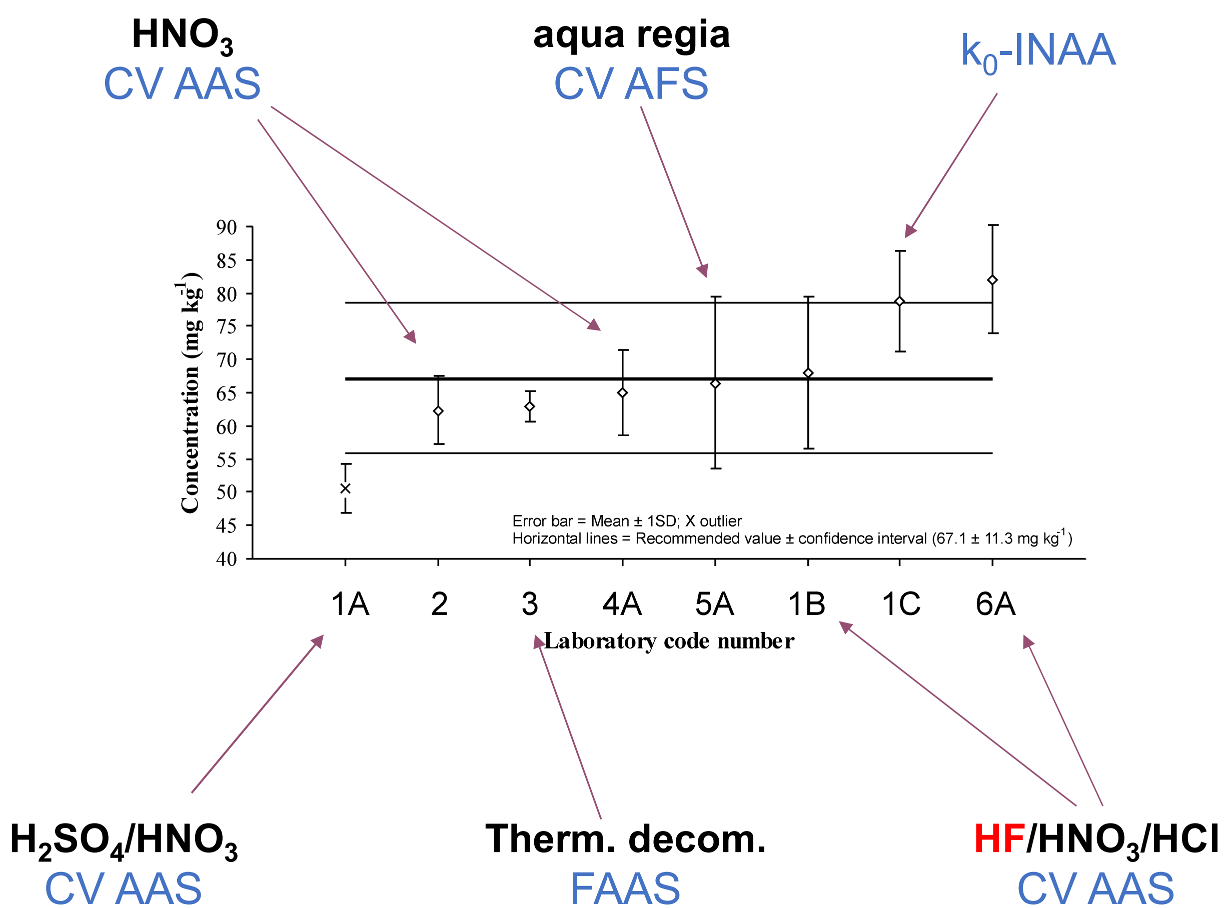




- Acid combination with HF totally digested THg into solution for measurement

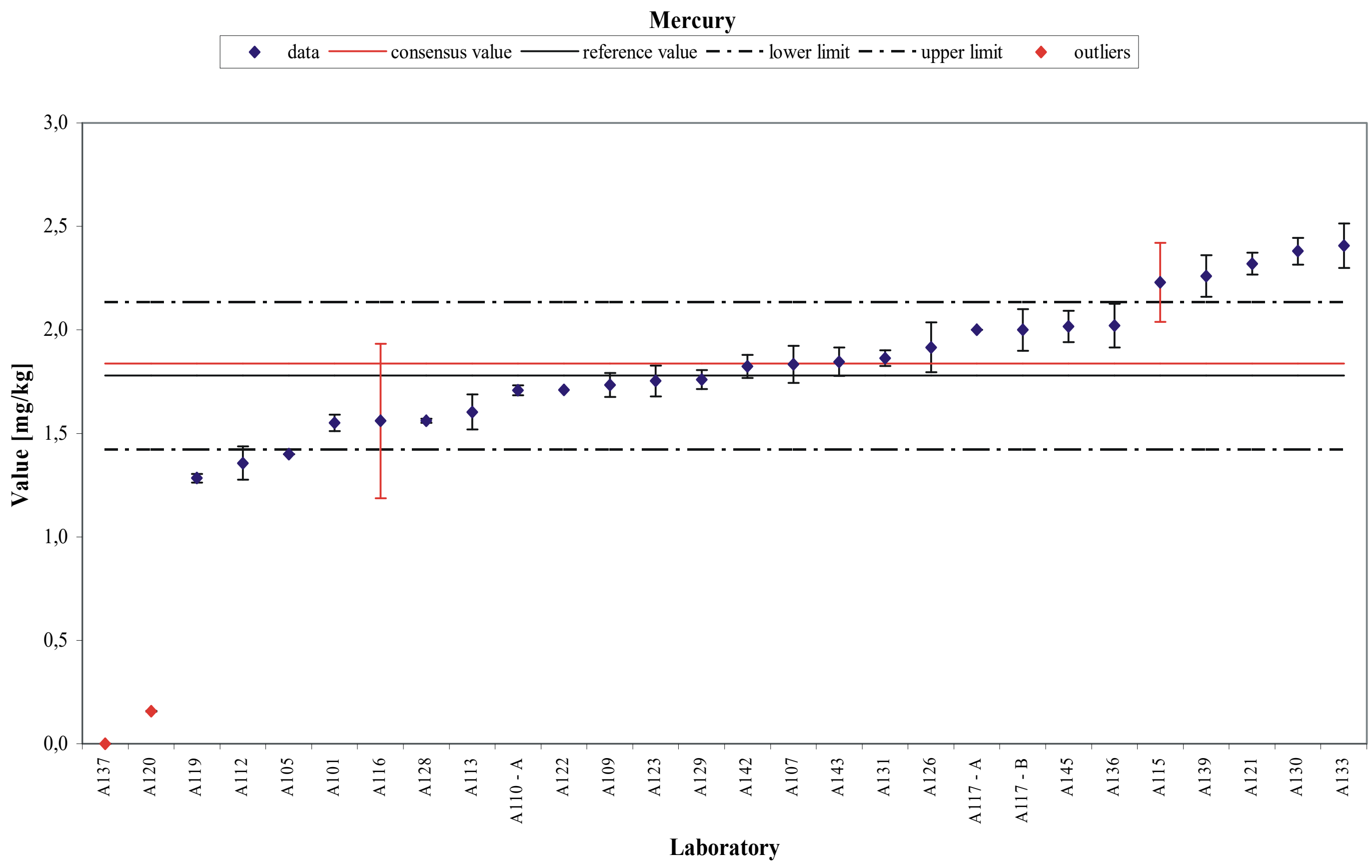
Odumah, PhD, 2019

Interlaboratory comparison exercise for contaminated soils



Kocman et., 2003

Mercury– PT-SL1



RM	Soil/sediment type	Hg species	Certified value (mg/kg)
JRC - BCR-141R	Trace elements in calcareous loam soil	THg Aqua regia (AR)	0.25 ± 0.02 0.24 ± 0.03
JRC - BCR-142R	Light sandy soil	THg	0.067 ± 0.011
JRC - BCR-143R	Sewage sludge amended soil	THg	1.10 ± 0.07
JRC - BCR-277R	Estuarine Sediment	THg (AR)	0.128 ± 0.017
JRC - - BCR-280R	Lake sediment	THg (AR)	69 ± 5
JRC - BCR-320R	Channel Sediment	THg (AR)	0.85 ± 0.09
BAM RM-CC018	Contaminated sandy soil	Hg (AR)	1.38 ± 0.06
BAM - ERM-CC020	Trace elements in contaminated river sediment	Hg (AR)	27.4 ± 0.6
JRC - ERM-CC580	Total and MeHg in estuarine sediment	Total Hg CH_3Hg	132 ± 3 0.075 ± 0.004
NRC/CNRC - HISS-1	Marine Sediment for Trace Metals and other Constituents	THg	± 0.01 (inf. value)

RM	Soil/sediment type	Hg species	Certified value (mg/kg)
IAEA SL-1	Lake sediment	THg	0.13 (0.08-0.18)
IAEA - 456	Marine sediment	THg MeHg	0.077±0.005 0.125±0.019 (ng/g)
IAEA-457	Marine sediment	THg	0.143±0.012
IAEA-458	Marine sediment	THg	0.044±0.003
NRC/CNRC-MESS-3	Marine Sediment	THg	0.098±0.04
NRC/CNRC-PACS-2	Marine Sediment	THg	2.98±0.36
NIST - SRM 2702	Inorganics in Marine Sediment	THg	0.4474±0.0069
NIST - SRM 2703	Sediment for Solid Sampling (Small, Sample) Analytical Techniques	THg	0.474±0.066
SRM 2709a	San Joaquin Soil	THg AR	0.9 ± 0.2 *0.79 – 0.92*
SRM 2710a	Montana I Soil	THg AR	9.88 ± 0.21 *9.3–12*
SRM 2711a	Montana II Soil	THg AR	7.42 ± 0.18 *6.3–8.3*
... and more			

Soils – what to quantify?

- Total Hg, CH_3Hg^+, Hg^0
- Other chemical forms:
  - Sequential extraction
  - Pyrolysis/combustion
- EXAFS, XANES, LA-ICP MS
- Transformation potential: methylation, demethylation, reduction?
- Microbiology, ...

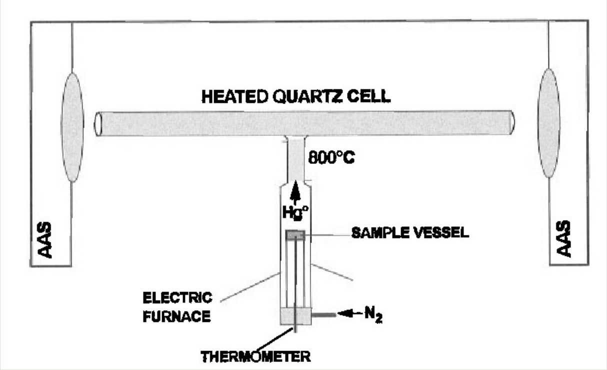
Mercury binding forms (1)

Pyrolysis

(Biester et al. 1997)

Study of thermal release behaviour

Hg^0, $HgCl_2$,
Hg bound to humic acids, HgS

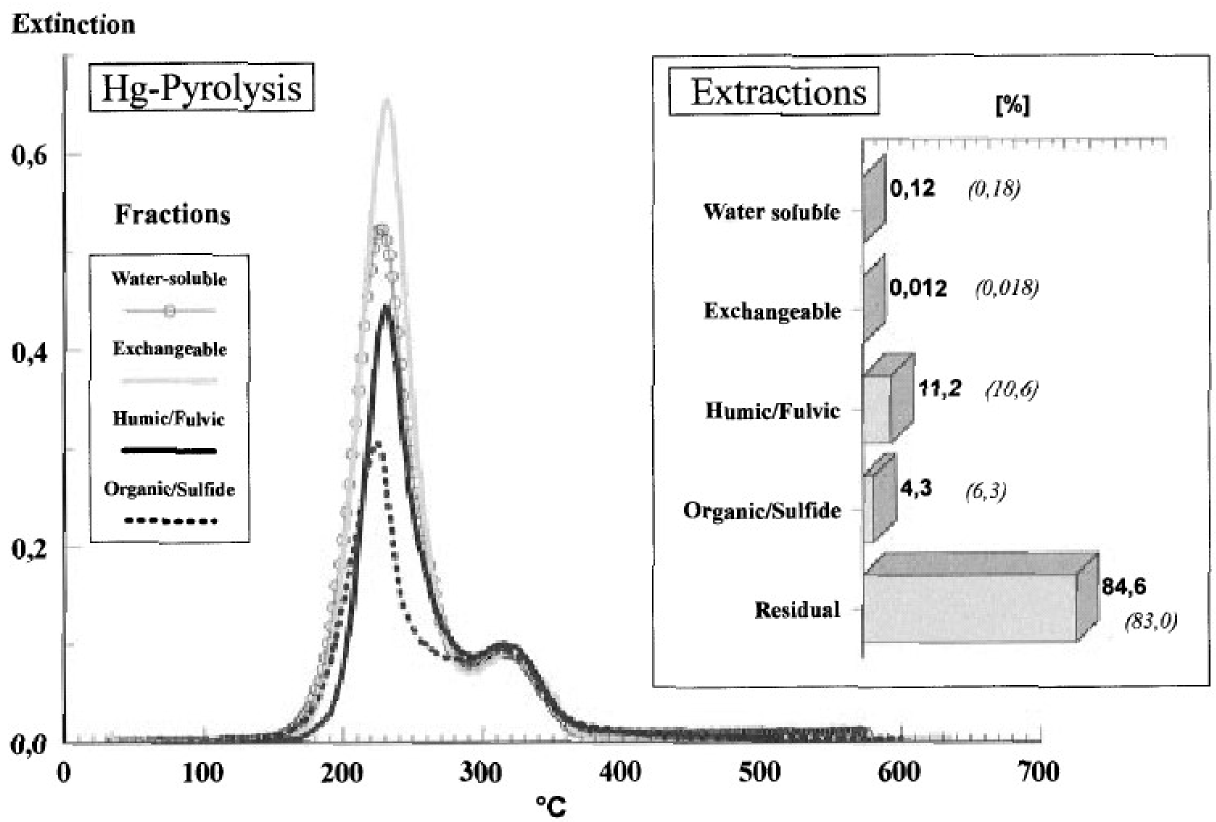


Sequential extraction

(DiGuilioo and Ryan, 1987)

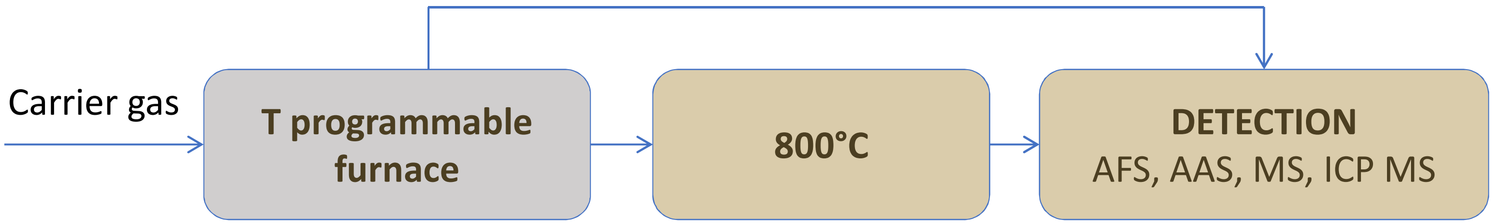
1. (Thermal desorption – Hg(0)), 60⁰C
2. Water soluble
3. Exchangable
4. Humic/fulvic
5. Organic/sulfide
6. Residual

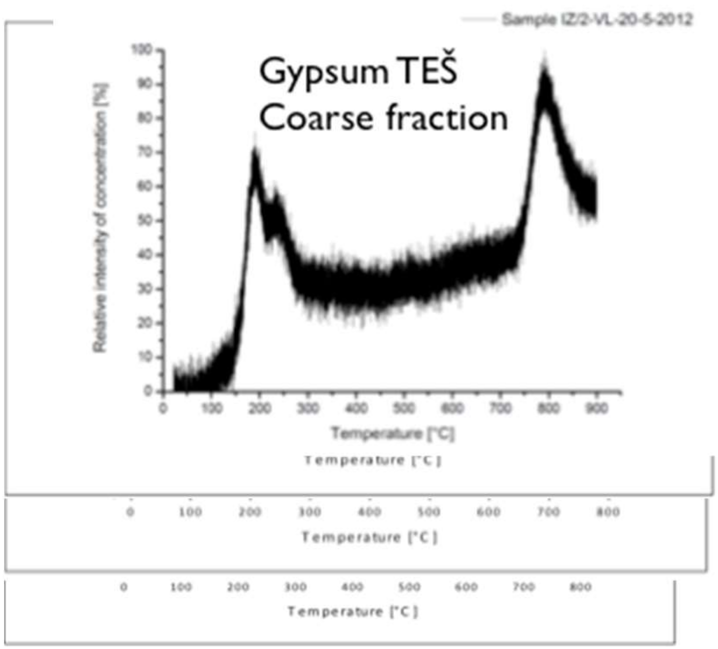
Mercury binding forms (2)
Soil sample distant from cinnabar deposits

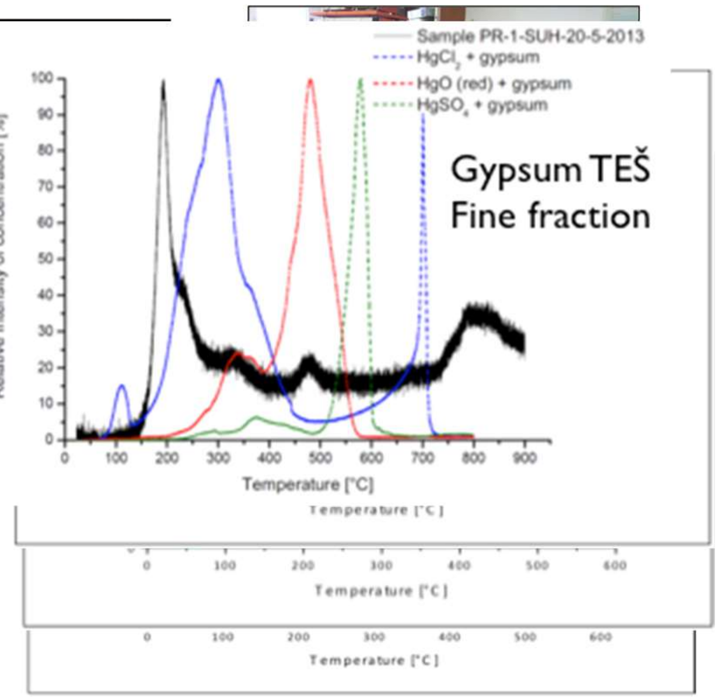


(Biester et al., 1997)

Fractionation of Hg in solids by thermal desorption



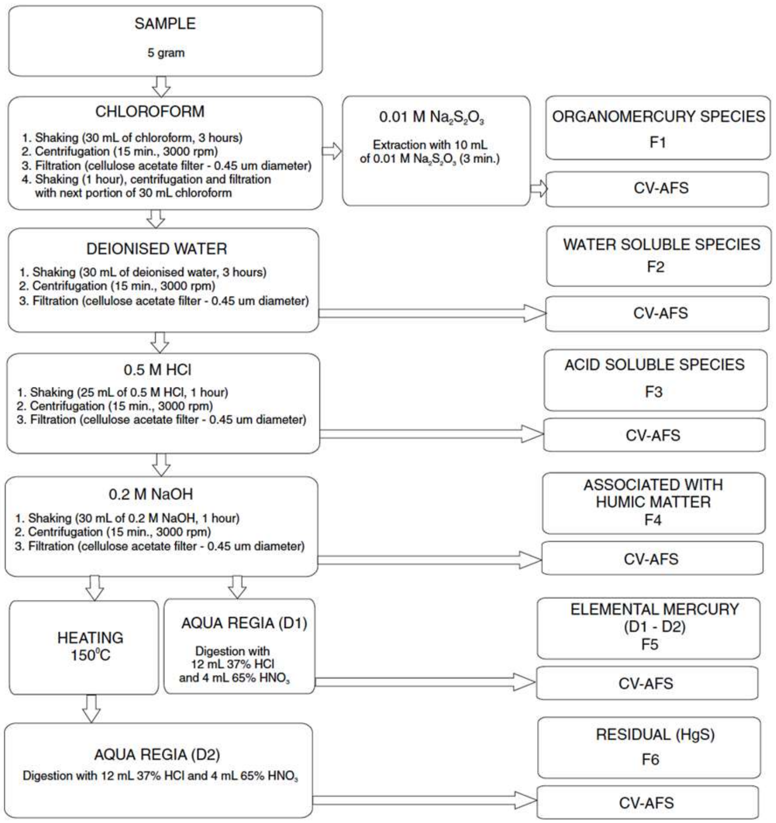




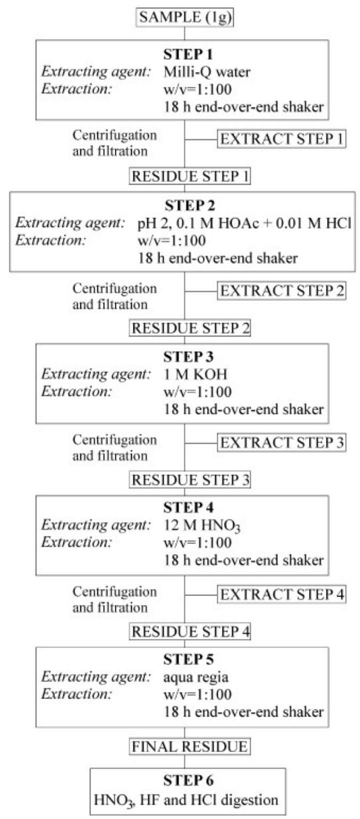
Sources:
Pavlin et al2018
Stergaršek et al2013

How to assess mobility and bioavailability of Hg in soils ?

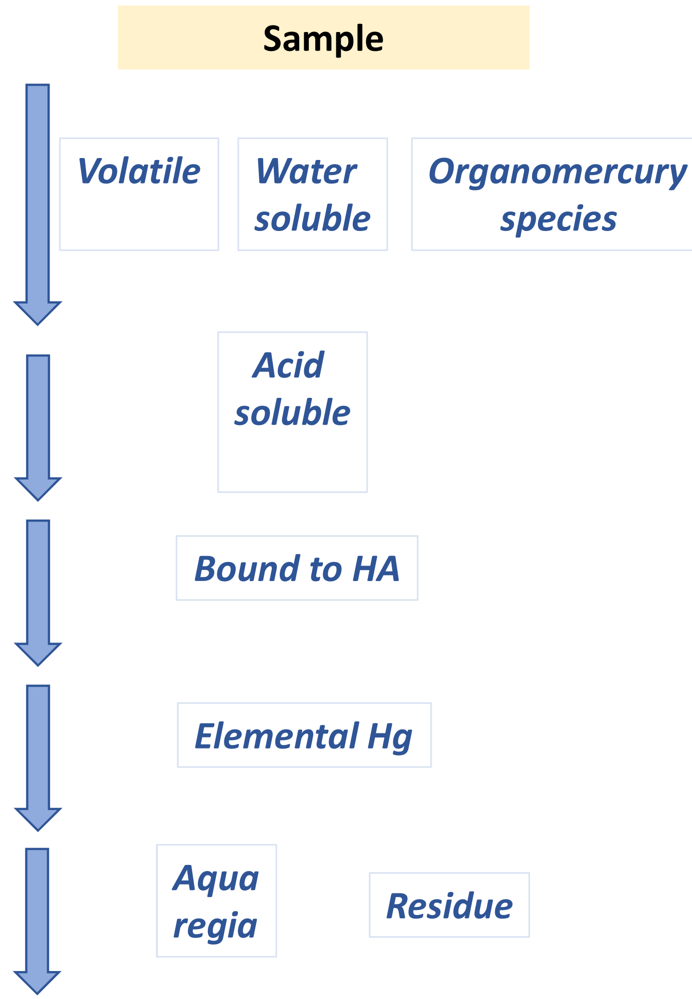
Solvent extraction schemes (SES)



Boscke et al., 2008



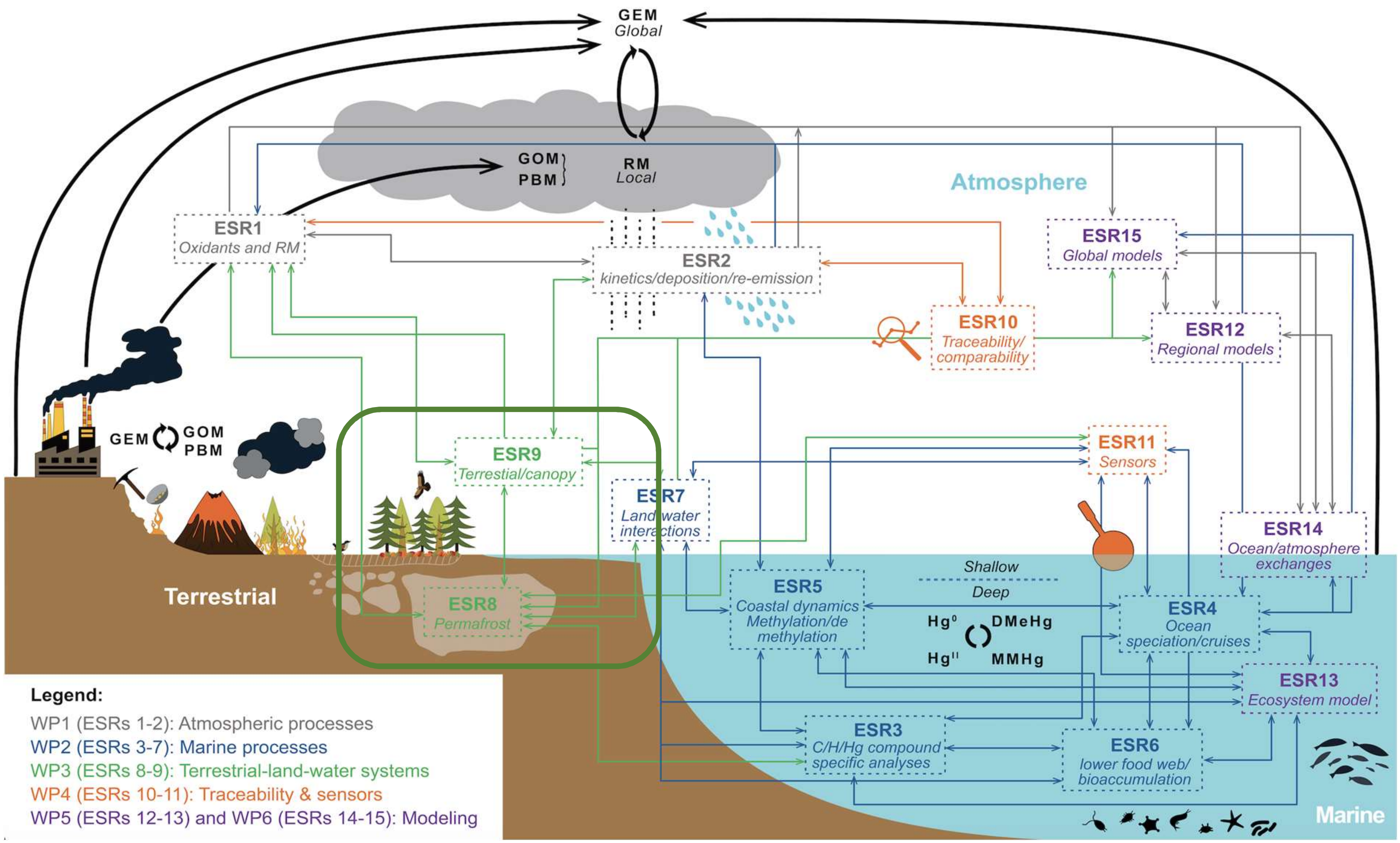
Kocman et al. 2008, ,
Bloom et al.,2003



Conclusions

- **Complexity** of Hg dynamics in soils: nohomogenous solid phase, aqueous, solid and biological phases
- Soil as source: **emissions to air and releases to water** (point vs. diffusive)
  - **Long-time scales** for removal of Hg from land and water (background vs. contaminated sites)
- **Climate change** induced processes (i.e permafrost, errosion, flooding)
- Hg loading to soil needs better **re-quantification** (litterfall, sewage sludge, etc.)
- Global vs. local implications of Hg contamined soils
- **Comparability** of Hg measurements (total/speciation/fractionation) in soils, standardization for flux measurements
- Inventory of local and regional legislations
- ...

Next step: GMOS-Train project EC funded (2020 -2023)



Acknowledgements:

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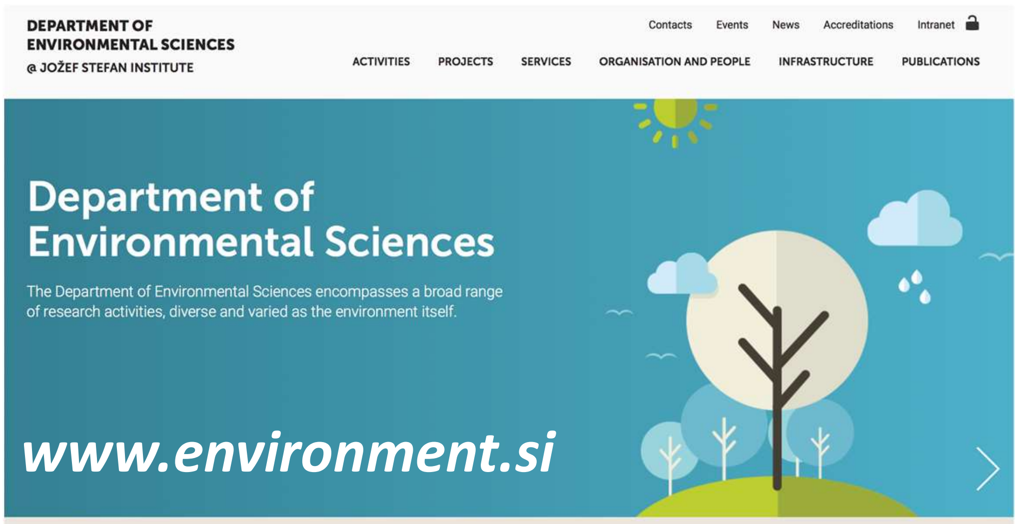

milena.horvat@ijs.si