



MERCURY MONITORING IN SOIL

September 2019

Development of a Plan for Global Monitoring of Human Exposure to and Environmental Concentration of Mercury (UNEP/GEF Project ID: 5409)

Executive Summary

Soil plays an important role in the global and regional Hg fluxes, which includes:

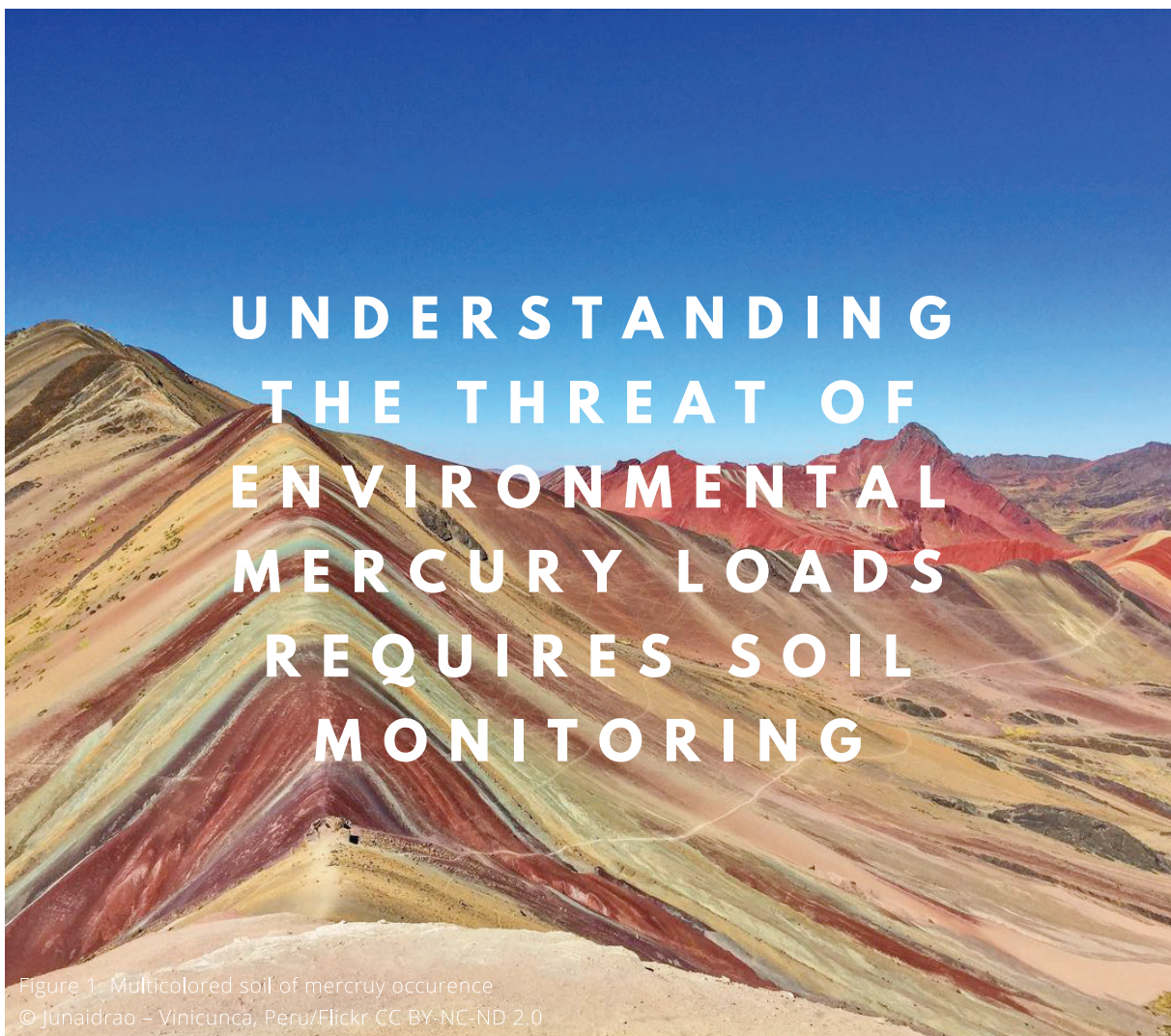
- (i) the mercury which is biologically available or potentially available in the ecosystem (e.g. sorbed to soils or sediments),
- (ii) the mercury which is released from geogenic sources (e.g. ore deposits and geothermal sources) and,
- (iii) the mercury which is released by anthropogenic activity.

A major issue is the importance of anthropogenic mercury relative to the mercury content in pristine environments.

Total Hg monitoring in the environment provides limited data, and speciation/fractionation analysis is mandatory as it provides useful information related to anthropogenic sources, distribution of Hg forms, potential toxicity and health risk.

For example, it used to understand:

- (i) the transportation of Hg is from its sources to the local human environment and wildlife;
- (ii) how Hg is bound in the environment and its availability to cause adverse effects, and
- (iii) the transformation and build-up of monomethyl mercury (MMeHg) in biota in aquatic and terrestrial foods.



Mercury in Soil Systems

Soil plays an important role in global mercury cycling as it can act as its sink and its source. Mercury is present in the soil due to atmospheric wet and dry deposition, litterfall, geogenic (natural) sources, and due to anthropogenic contamination. The main Hg sinks include volatilization to the atmosphere and transport to groundwater or surface water.

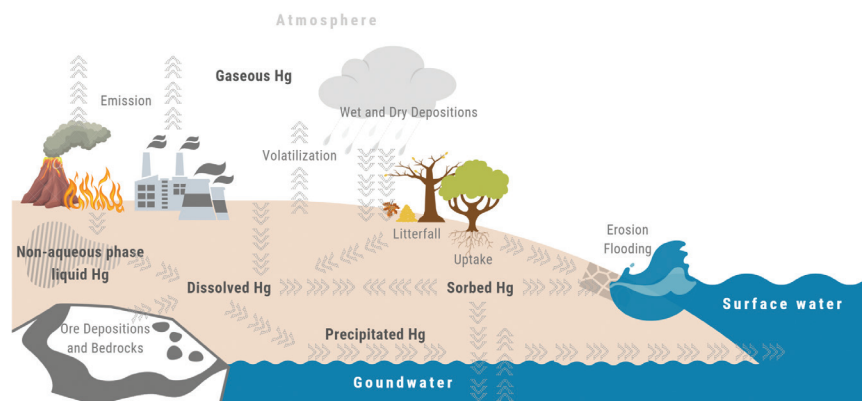


Figure 2. Mercury sources, sinks and phases in soil

Mercury may be present under different phases in soil systems:

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

Mercury transitions that occur in soil systems are: dissolution, precipitation, sorption, adsorption, volatilization. Such complexity of mercury dynamics in different soils need to be well understood before it can be considered as a matrix for effectiveness evaluation.

Figure 3. About 38% of anthropogenic emission of mercury to the environment are associated to Artisanal and Small-scale Gold Mining (ASGM)



Soil plays an important role in global mercury cycling as it can act as a sink and source of atmospheric mercury.

Mercury Sources and Sinks in Soils

Mercury stored in soil is a source of mercury to (i) the atmosphere due to volatilization of elemental mercury, (ii) the plants via root uptake, and (iii) to the ground and surface water due to leaching, dissolution and colloidal transport. In this context global vs local implications of mercury contaminated sites need to be carefully evaluated.

All time anthropogenic mercury releases to land and water at the global scale are estimated to be much higher than into the atmosphere. The anthropogenic mercury contamination may result in much higher Hg concentrations in soil systems than from other sources, particularly at contaminated site. Overall, mercury loading to soil needs better quantification including sources that have not been accounted for in the present inventories (i.e. sewage sludge).

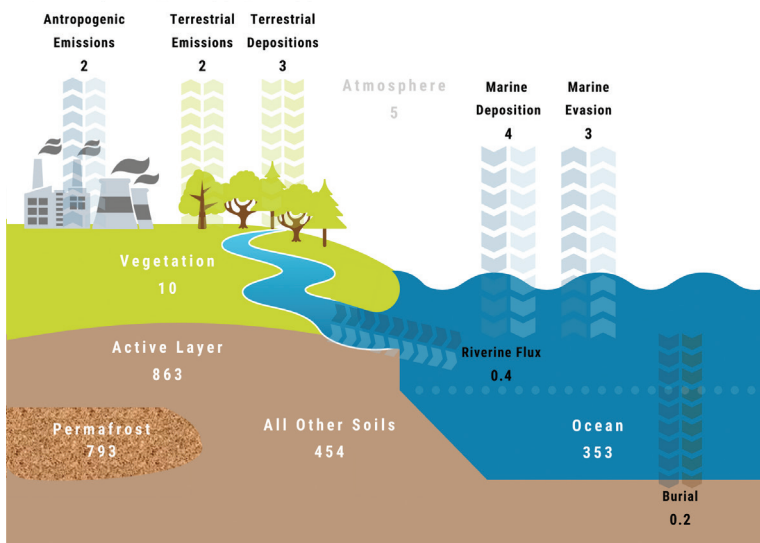
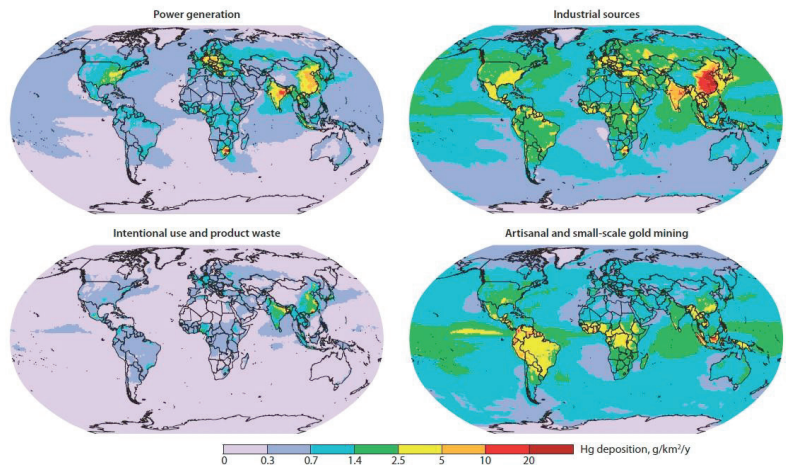


Figure 4. An updated schematic of the current global Hg cycle with major reservoirs in white/light grey (Gg Hg) and fluxes in black (Gg Hg/yr). Adapted from Amos et al. (2013) with the soil reservoir shown as an average of previously published estimates (Schuster et al., 2018)

Figure 5. Model predictions of the global distribution of Hg deposition from four groups of emissions sources in 2015 (GMA, 2018)



Global distribution of Hg deposition from four groups of emissions sources (power generation, industrial sources, intentional use and products waste, and artisanal and small-scale gold mining) identify the importance of atmospheric deposition as a source of Hg in terrestrial environment (Figure 5). Hg deposition through litterfall represents an important input to terrestrial forest ecosystems via cumulative uptake of atmospheric Hg (most Hg⁰) to foliage (Figure 6).

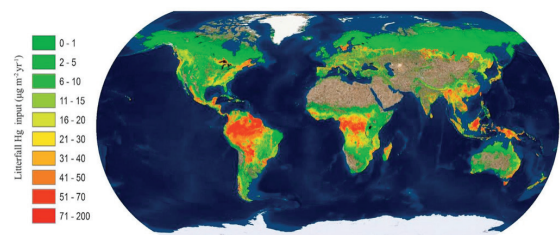


Figure 6. Annual global deposition through litterfall is estimated at 1180 ±710 Mg (Wang et al., 2016)



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Figure 7. Water in this stream has been stained by runoff Cinnabar that was mined to produce mercury

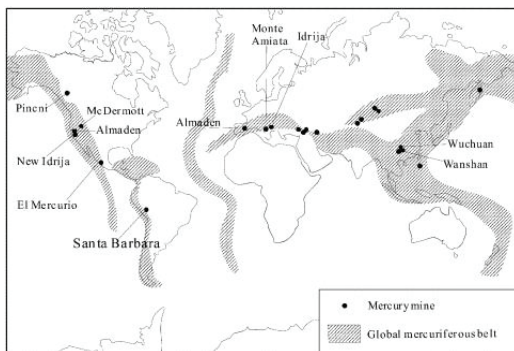


Figure 8. Mercury planetary belts (Wang et al., 2005)

Long-time scales need to be considered for removal of Hg from soil due to complex nature of Hg dynamics in non-homogenous solid, gaseous, aqueous, and biological phases present in soil.

Land management practices and climate change can affect the mobility of mercury in soils at the background sites, and particularly at contaminates sites.

Existing estimates greatly underestimate Hg in permafrost soils, indicating a need to re-evaluate the role of the Arctic regions in the global Hg cycle. Mercury is not evenly distributed throughout the lithosphere but is concentrated in three areas known as Hg planetary belts that lie over tectonic plates boundaries, where almost all of the world's mercury mines are concentrated. Permafrost regions contain twice as much mercury as all other soils, the atmosphere, and the oceans combined. Due to rising temperatures, Hg is vulnerable to release as permafrost thaws over the next century with unknown consequences to the environment.

Figure 9. Landscape showing soil erosion



Mercury mobility in soil is considerably impacted by the land use and climate change induced processes: thawing of the permafrost, erosion, flooding, etc.

Existing Capacities Monitoring Networks

Although several networks exist for soil monitoring at the national and international level, mercury is rarely included in such programmes; nonetheless, several maps exist across wider geographical regions, based on measurement results and modelling.

The main issue when comparing Hg soil monitoring programmes at national or international scales is the comparability of data due to differences in monitoring designs, sampling grid resolution, soil profile depth, and soil fractions analysed. Also, data evaluation and interpretation lack harmonization, particularly the ancillary data that is needed to determine the mobility of mercury in soils.

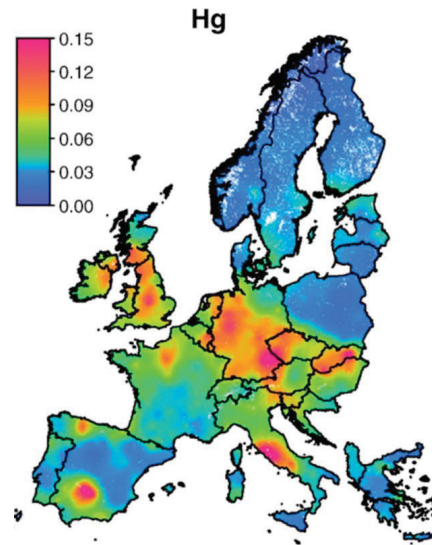


Figure 10. Map of mercury concentrations in topsoils [mg/kg] interpolated using block regression-kriging (support size=5 km). All maps described in this paper are available online via the <http://eusoiils.jrc.it> website. (Lado et al. 2008)

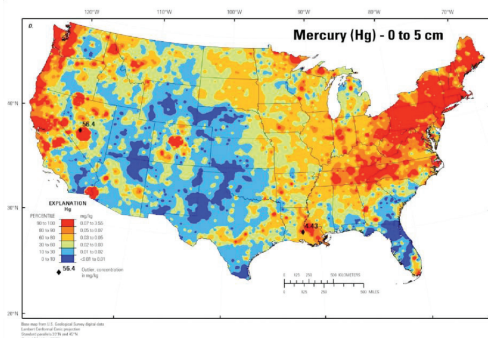


Figure 11. Mercury (mg/kg) in topsoil in the US (USGS, online Aug. 2019)

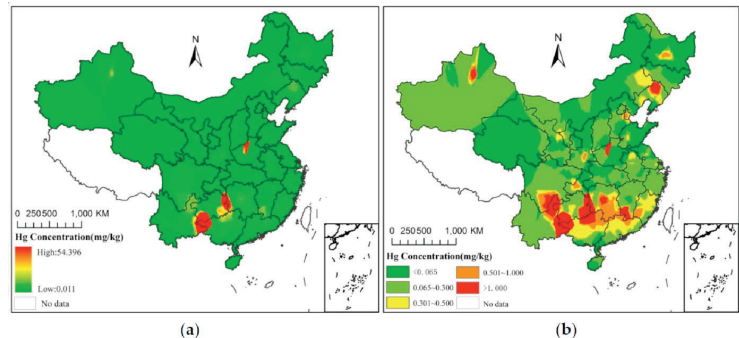


Figure 12. Spatial distribution of estimated Hg concentrations (mg/kg) in agricultural in mainland China illustrated in (a) stretched map and (b) graded map (from Wang et al., 2016)



Figure 13. Soil sampling for the preparation of interlaboratory quality control sample; representative soil sampling is a challenge and requires skills and good understanding of soil properties



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Figure 14. Laboratory analysis requires the provision of trained and skillful personnel.

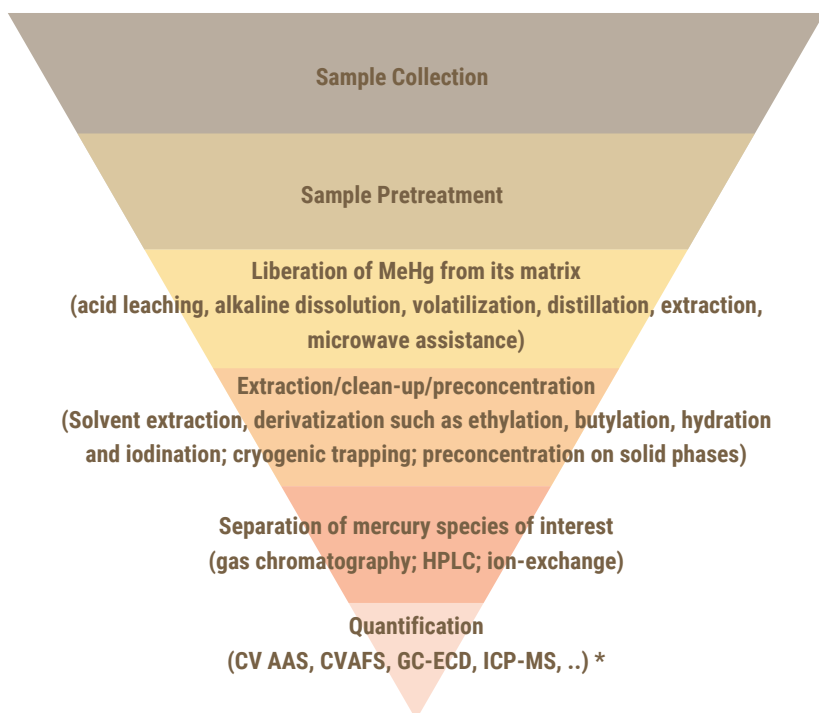
Monitoring total Hg in soil provides limited data to assess Hg bioavailability, potential toxicity and health risk, therefore speciation/fractionation analysis of mercury is needed to understand:

- (i) the transportation of Hg from its sources to the local human environment and wildlife;
- (ii) how Hg is bound in the environment and its availability to cause adverse effects, and
- (iii) the transformation and build-up of monomethyl mercury (MMeHg) in biota in aquatic and terrestrial foods.



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Figure 15. Tropical ecosystems where mercury methylation is elevated



However, methodologies for speciation/fractionation of mercury in soils are not fully harmonized and agreed, consequently such method-specific protocols should be avoided unless they provide biogeochemically meaningful information.

Figure 16. Steps for determination of organomercury compounds (Horvat et al., 2005)

*CV AAS – cold vapour atomic absorption spectrometry; CV AFS – cold vapour atomic fluorescence spectrometry; GC-ECD – gas chromatography – electron capture detector; ICP-MS – inductively coupled mass spectrometry; HPLC – high-performance liquid chromatography

General conclusions

In terms of the regional and global relevance of the mercury present in the terrestrial environment, particularly in soil, the evaporation of elemental mercury is of considerable concern and must be considered for the proper understanding of the elemental mercury oscillations at monitoring sites.

However, measurement of elemental mercury flux from the terrestrial environment and the determination of elemental mercury in the soil are not harmonized/standardized and comparability of such data is questionable. Overall, methodologies for mercury fluxes measurements between environmental compartments (soil/water/atmosphere) require further harmonization and standardization.

Therefore, numerous elements would need to be considered for soil as a monitoring matrix in the frame of the effectiveness evaluation of the Minamata convention. Careful evaluation of the relevance of the matrix, the mercury compounds and fractions to be monitored and the frequency of monitoring. These elements suggest that soil monitoring needs further science-based developments, especially for background sites. However, in the case of terrestrial mercury contaminated sites, mercury determination in soils is needed as part of the characterization and identification methodologies and particularly for the evaluation of the effectiveness of remedial actions.

Evaporation of elemental mercury from soil is of considerable concern.

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Full Report and References:

Technical Information Report on Mercury Monitoring in Soil

Available at: <https://www.unenvironment.org>

