

TECHNICAL INFORMATION REPORT ON MERCURY MONITORING IN SOIL



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© StaryLyss/Shutterstock.com - Multicolored soil of mercury occurrence in Atlatay steppe near Kyzyl-Chin

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Acronyms

<i>Aqua regia</i>	- a mixture of nitric acid and hydrochloric acid, optimally in a molar ratio of 1:3.
ASGM	- Artisanal and small-scale gold mining
CV AAS	- cold vapour atomic absorption spectrophotometry
CV AFS	- cold vapour atomic fluorescence spectrophotometry
DFC	- diffusive flux chamber
DIM	- dissolved inorganic matter
DMeHg	- dimethylmercury
(D)NAPL	- (dense) non-aqueous phase liquid
DOM	- dissolved organic matter
E_h	- redox potential (known as oxidation / reduction potential) expressed in millivolts (mV)
EtHg	- ethylmercury compounds
FeO(OH)	- iron(III) oxide-hydroxide or ferric oxyhydroxide
GC-ECD	- gas chromatography – electron capture detector
GEM	- gaseous elemental mercury in air
GOM	- gaseous oxidized mercury compounds in air
GPM	- gaseous particulate mercury in air
HF	- hydrofluoric acid
Hg^0	- elemental mercury
Hg^{2+}	- divalent mercury
Hg_2^{2+}	- monovalent mercury
$HgCl_2$	- mercury (II) chloride
$Hg(OH)_2$	- mercury (II) hydroxyde
HPLC	- high-performance liquid chromatography
HgS	- mercury(II) sulfide
$SnCl_2$	- stannous (II) chloride
$NaBH_4$	- sodium tetrahydroborate
ICP MS	- inductively coupled plasma mass spectrometry
MM	- micrometeorological measurements
MMeHg	- monomethylmercury compounds
MnOOH	- manganese(III) oxyhydroxide
NOM	- natural organic matter

Executive Summary

Soil plays an important role in the global and regional mercury 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.

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. Different phase transitions of mercury occur in soil systems: 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.

Considering the Hg cycle from the perspective of soil systems, sources of Hg include atmospheric wet and dry deposition and litterfall, geogenic (natural) sources and anthropogenic activities. The main Hg releases (sinks from the soil systems) include volatilization to the atmosphere, and transport to groundwater or surface water, while plant root uptake from soils is negligible at the regional and global scale.

Soil plays an important role in global mercury cycling as it can act as a sink and source of atmospheric mercury (global mercury cycling). A re-evaluation of anthropogenic mercury emissions and releases to the environment found that estimates of releases to land and water were much higher than into the atmosphere. The anthropogenic mercury contamination may result in much higher Hg concentrations in soil systems than from other sources.

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

A global scaling up of Hg^0 fluxes revealed that the background areas contribute Hg^0 emissions in the same order of magnitude as Hg-enriched sites (contaminated, naturally enriched, and mining). Vegetated areas seem to constitute an important Hg^0 sink, although reliable vegetation flux measurements, particularly over forests, are lacking. The latest findings indicate that Hg^0 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, including natural and anthropogenic emissions, vegetation uptake, and soil and vegetation re-emission. Strong depletion of atmospheric Hg^0 is observed at terrestrial background sites in

summer, despite the high amounts of solar radiation and the potential for photo-reductive re-emission, suggests that terrestrial ecosystems serve as net sinks for Hg⁰.

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 is susceptible to transfer *via* soils to continental and coastal aquatic ecosystems. Recent findings reveal the important role of vegetation in the uptake of Hg⁰ and therefore Hg deposition pathways in soil and the terrestrial ecosystem require revised Hg deposition monitoring strategies by environmental agencies, particularly when evaluating the effectiveness of the Minamata Convention.

In terms of soil monitoring at the national and international level, several networks exist, and data on soil type, pedological and soil quality parameters are available. Mercury, however, is rarely included in such programmes; nonetheless, several maps exist across wider geographical regions, based on measurement results and also modelling. Moreover, some attempts have been made to model Hg concentrations in soil based on deposition and evaporation fluxes. 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 analyzed. Also, data evaluation and interpretation lack harmonization, particularly the ancillary data that is needed to determine the mobility of mercury in soils.

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.

Comparability of data for total mercury also needs to be evaluated carefully as some data are based on the *aqua regia* extractable fraction of mercury, which provides only the leachable acid fraction of mercury. Total mercury is typically obtained by either total acid digestion or combustion techniques or other matrix independent methods such as neutron activation analysis. Such methodological biases may provide scattered data in particular in the characterisation and identification of contaminates sites, and a strict distinction between acid leachable and total Hg needs to be documented when data are reported and evaluated. Further development and optimization are needed for mercury analyses and speciation/fractionation in soils and "dynamic" measurements (transformation and transport measurements). Also, "method-specific" techniques should be avoided unless they provide biogeochemically important information.

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; therefore, measurement of mercury flux from the terrestrial environment and the determination of Hg⁰ in the soil is of particular importance. Measurements of Hg⁰ fluxes from terrestrial environments are based on

two measurement methodologies: the dynamic flux chambers (DFC) and the micrometeorological (MM) methods. Each method has benefits and drawbacks. Consequently, the comparability of the results is questionable.

In conclusion, chemical metrology in mercury analysis and speciation needs to develop further to achieve comparability of results. Currently available matrix certified reference materials (CRMs) are not sufficient to establish comparability of chemical measurements due to the inadequate coverage of concentrations and matrix matching. In order to demonstrate traceability to international standards calibration standards for Hg speciation with small uncertainties are urgently needed. Questions related to operationally defined parameters (reactive gaseous mercury - RGM, reactive Hg in water, bioavailable fraction of mercury, etc.) need to be addressed from the metrological point of view in order to demonstrate the comparability of results.

In summary, numerous elements need to be considered for soil as a matrix to be used in the effectiveness evaluation framework and monitoring under the Minamata Convention. Careful evaluation of the relevance of the matrix, mercury compounds and fractions to be monitored and the frequency of monitoring suggest that soil monitoring needs further science-based developments, especially for background sites. It is obvious that 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 the remedial actions.

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