TECHNICAL INFORMATION REPORT ON MERCURY MONITORING IN SOIL

September 2019

© StaryLyss/Shutterstock.com - Multicolored soil of mercruy occurence in Atlai steppe near Kyzl-Chin

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Acronyms

Aqua regia - 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 spectometry

MM - micrometeorogical 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 Hg^0.

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 $Hg^{0,}$ 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 Hg^0 in the soil is of particular importance. Measurements of Hg^0 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.

1.Introduction

In the global fate and transport of mercury, soil is an environmental compartment (pool) often seen as a sink/source of mercury (GMA, 2008, 2018). Soil plays an important role in 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 question is the importance of anthropogenic mercury relative to the levels of mercury in pristine environments. To address this question and the usefulness of soil as an indicator of change and appropriateness of soil as a matrix for the effectiveness evaluation of the Minamata convention it is important to address the complexity of Hg presence and phase transitions in soils. Therefore, this Introduction includes basic information on mercury in a soil system summarized from a reviews (Davies et al., 1997, Diederik (2013), Grigal, 2002, Schlüter, 2000, Schuster, 1991, Aiken et al., 2011; Gabriel and Williamson, 2004, Zhang et al., 2009, Subir et al., 2011, Lin and Pehkonen,1999) and recent papers (Streets et al, 2017; Agnan et al., 2016; Wang et al., 2016; Jiskra et al., 2018), which are needed to justify the conclusion related to the soil as a matrix for effectiveness evaluation.

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Figure 1. **About 38% of anthropogenic emission of mercury to the environment are associated to Artisanal and Small-scale Gold (ASGM).**

1.1. Mercury in soil systems

Hg cycle from the perspective of soil systems is presented in Figure 2.

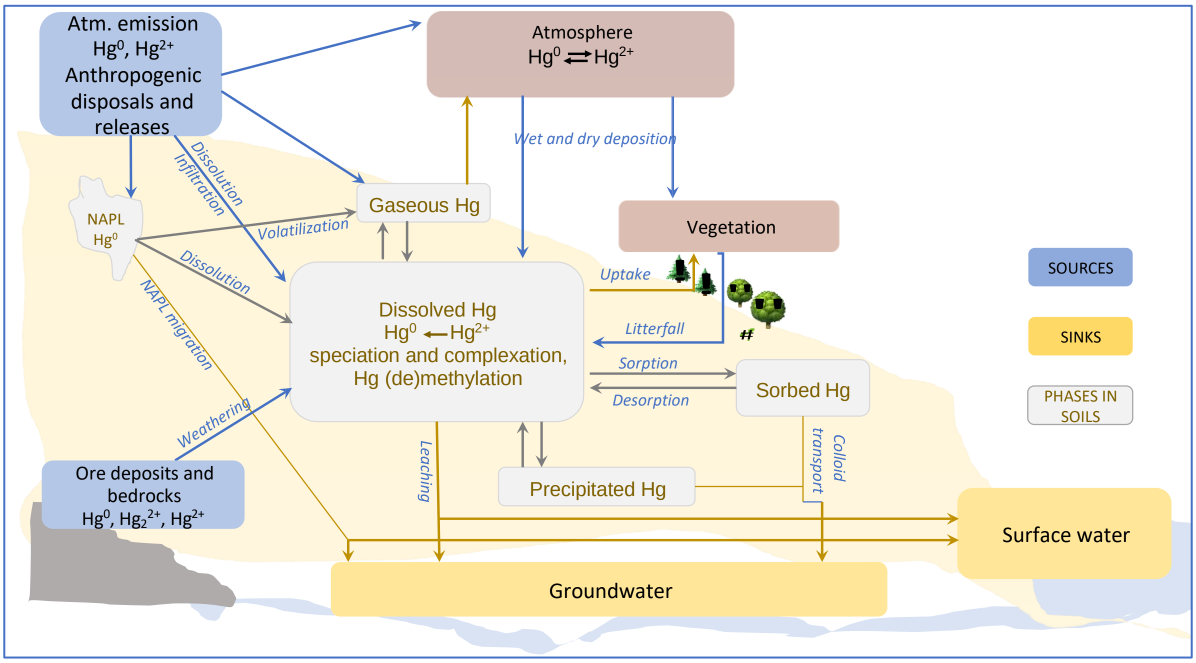

***Figure 2.* Mercury sources, sinks and phases in soil (Adapted from Diederik, 2013).**

Sources of Hg in soil include atmospheric wet and dry deposition, geogenic sources and anthropogenic contamination. The main Hg **sinks** include volatilization to the atmosphere and transport to groundwater or surface water. Hg sources and sinks are discussed in subchapter 1.2.

1.2 Mercury forms and partitioning among soil phases

Mercury may be present under different **phases in soil systems**:

- dissolved in the aqueous phase as a free ion (Hg^{2+}) or complexed with inorganic 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, and
- in solid (precipitated) phase.

Mercury can exist **in the three valence states** in soils: elemental Hg (Hg^0), monovalent (Hg_2^{2+}) and divalent (Hg^{2+}). The presence of monovalent Hg in soils is negligible compared to Hg^0 and Hg^{2+}, of which the latter is the most abundant. The main dissolved Hg species in soil systems are Hg^{2+} complexes with various inorganic and organic ligands. The key factors controlling the aqueous species of Hg are pH, ionic strength and redox potential (Gabriel and Williamson, 2004; Skyllberg, 2012). Concentrations of dissolved organic matter (DOM), dissolved oxygen, sulfide and suspended solids can also play a role (Ravichandran, 2004).

Under oxidized soil conditions, the predominant **inorganic mercury species** are $Hg(OH)_2$, $HgCl_2$, $HgOH^+$, HgS, and Hg^0. The **organic mercury species** in the soil are the methylated forms: (mono)methylmercury (MMeHg) and dimethylmercury (DMeHg), that are synthesized in soil or aqueous systems mostly by microbial activity although abiotic methylation is also possible (Ulrich et al., 2001; Skyllberg, 2012). In soil systems, the concentration of MMeHg is typically < 2% of the total mercury concentration, while DMeHg is almost absent. Few studies report the presence of ethylmercury compounds (EtHg) in environmental samples (Holmes and Lean, 2006; Mao et al., 2010). Holmes and Lean (2006) found that EtHg levels in wetland sediment sometimes exceed MeHg concentrations, while Mao et al. (2010) reported the presence of EtHg in Everglades soil, presumably as a consequence of ethylation occurring in the wetland. Moreover, a recent study of contaminated soil around a former mercury mine in Idrija reported, for the first time, a significant amount of EtHg in soils (Tomiyasu et al., 2017). These studies suggest that Hg ethylation could be a significant part of the Hg cycle in environments, especially in contaminated sites.

Mercury strongly interacts with **soil organic matter** (Haitzer et al., 2002; 2003; Khwaja et al., 2010; Ravichandran, 2004, Diederik, 2013). Mainly the sulfur-containing functional groups (especially thiol groups) are considered important for Hg and MMeHg binding to DOM (Gabriel and Williamson, 2004; Ravichandran, 2004; Skyllberg, 2012). In *non-contaminated soils,* the fraction of mercury bound to organic matter is much higher than the amount of available mercury (Ravichandran, 2004; Haitzer et al., 2002). The complexation of Hg to natural organic matter (NOM), except under extreme conditions of contamination, outcompetes $Hg(OH)_2(aq)$ and $HgCl_2(aq)$ (Skyllberg, 2012). Besides, it is often the case that inorganic Hg species, although soluble, are further complexed with organic ligands (mainly fulvic and humic acids) and mineral colloids (GMA, 2008, 2018; Gabriel and Williamson, 2004). Although mercury has an affinity to sulphur, it also interacts with DOM, possibly reflecting the formation of a DOM-Hg-sulfide complex or the hydrophobic partitioning of neutral Hg-sulfide complexes into higher-molecular-weight DOM (Miller et al., 2007). Migration of Hg to deeper soil layers is often suggested to be most effective if Hg is bound to soluble organic complexes (i.e. colloid-facilitated transport).

1.3 Mercury phase transitions in soils

Different **phase transitions** of mercury occur in soil systems: dissolution, precipitation, sorption, adsorption, volatilization.

Dissolution:

Solid HgS (cinnabar) is the common ore of mercury. In the presence of Cl^- or DOM, HgS(s) **dissolution** occurs, and **precipitatio**n is inhibited (Gabriel and Williamson, 2004; Gerbig et al., 2012, Miller et al., 2007; Skyllberg, 2012; Waples et al., 2005,). The presence of polysulphides also increases the solubility of solid HgS (Skyllberg, 2012).

In the case of anthropogenic contamination, mercury can be present in the form of a (dense) **nonaqueous phase liquid** ((D)NAPL), which can further dissolve or volatilize in soil systems (Mercer and Cohen, 1990; Devasena and Nambi, 2010).

Sorption:

Inorganic Hg^{2+} has high reactivity and high solubility, but in soil solution, it is present as uncharged complexes. Consequently, the dominant mechanism for sorption is via stable insoluble inorganic and organic complex formation rather than ion exchange (Schuster, 1991).

Sorbents can be *mineral or organic surfaces and* categorized as either particulate (>0.45 µm) or colloidal (<0.45 µm and >1 nm) sorbents. Due to their large surface area, the finest particles (i.e. colloidal particles) have the highest adsorption capacities (Aiken et al., 2011; Gabriel and Williamson, 2004).

Sorption capability of Hg^{2+} is highest for organic matter in the particulate and dissolved phases (especially humic and fulvic substances). Under conditions of low Hg/DOM ratios (i.e. low Hg contamination), sorption of Hg to DOM is controlled by a small fraction of DOM molecules containing reactive thiol functional groups (Haitzer et al., 2002; Ravichandran, 2004).

Other potential sorbents are oxides, hydroxides, oxyhydroxides of Fe/Mn/Al (best sorbents MnOOH and FeOOH), amorphous FeS under reducing conditions, and clay minerals (Gabriel and Williamson, 2004). However, except under highly contaminated conditions and low organic matter environments, Hg and MMeHg will not directly bind to oxygen functional groups (Skyllberg, 2012).

Although highly volatile, elemental mercury (Hg^0) can also be adsorbed to soil with a stronger sorption affinity for DOM than for minerals (metal oxides) (Schlüter, 2000). Sorption to colloids is important in understanding the fate of mercury in soils because colloidal-facilitated transport is the primary Hg transport process (Gao et al., 2011; Slowey et al., 2005).

Adsorption rate depends mainly on initial Hg^{2+} concentration, organic matter content and ions in solution. For example, chloride ions interfere with Hg adsorption. In general, an increase in Cl_- concentration reduces the adsorption of Hg^{2+} to inorganic and organic adsorbents (Gabriel and Williamson, 2004). Mercury also forms a covalent bond with OH^-, which also minimizes the bond between the mineral surface (oxide) and OH^-. As a result, the amount of Hg adsorbed onto mineral surfaces decreases (Schuster, 1991).

The formation of mercury-DOC complexes has an impact on Hg adsorption, as is generally the case for toxic metals, but contrasting effects have been reported for mercury (Schuster, 1991). On the one hand, a decrease in Hg adsorption to mineral surfaces could be due to the stability of the DOC-Hg complex that prevents mercury from adsorbing to mineral surfaces. On the other hand, an increase in Hg adsorption results from the high affinity of the dissolved organic ligand for the mineral surface (Gabriel and Williamson, 2004; Schuster, 1991).

Mercury adsorption is also influenced by soil pH (Gabriel and Williamson, 2004). When pH is <4.5-5, organic matter is the most efficient mercury sorbent. In neutral to alkaline soil, mineral components are more efficient sorbents. As with all metals, adsorption generally decreases with decreasing pH; however, it is known that mercury adsorption to humic matter increases at lower pH levels (Jing et al., 2007; Sarkar et al., 2000).

Volatilization

The most widely noted Hg reaction in soils is the *reduction of Hg^{2+} to Hg^0* (Gabriel and Williamson, 2004), which is the first step in the volatilization of mercury from soil to the atmosphere. Although the volatilization of Hg^0 from soils has been studied extensively, it still represents the primary source of uncertainty in the global/regional annual budget of nonpoint source mercury transport (Grigal, 2002; Schlüter, 2000; Gabriel and Williamson, 2004). Volatilization of mercury occurs in soils, and Hg vapor flux to the atmosphere is especially important in the case of anthropogenic contamination (Subchapter 1.2.2.).

The reduction of Hg in soil can be either biotic or abiotic and occurs more readily in lower or saturated horizons, which are generally reducing environments (Schlüter, 2000). **The abiotic reduction** of Hg can be mediated by reductants, such as dissolved organic matter (humic and fulvic acids) or Fe^{2+}. Mercury reduction by humic and fulvic acids was shown to be affected by pH, dissolved oxygen concentration and chloride levels (Gabriel and Williamson, 2004; Schlüter, 2000, Ravichandran, 2004).

Abiotic reduction is influenced by adsorption because free Hg^{2+} in solution has a higher reduction potential than an adsorbed Hg compound (Mishra et al., 2011; Schlüter, 2000; Schuster, 1991). As a consequence, the reduction of Hg^{2+} by reaction with dissolved organic matter (DOM) in the soil upper layers will benefit from the availability of recently deposited atmospheric Hg^{2+}, which has not yet been incorporated into the soil matrix and is still relatively available (Schlüter, 2000). Abiotic reduction of mercury can also result from photochemical reactions in the first few millimeters of soil (Gabriel and Williamson, 2004; Ravichandran, 2004).

Biotic reduction of Hg^{2+} to Hg^0 can be mediated by various microorganisms. Similarly, to abiotic reduction, an increase in DOM inhibits biotic reduction due to the relative unavailability of adsorbed Hg compounds. Biological reduction of mercury is favoured in soils with high Hg^{2+} availability and microbiological activity. In contrast, the abiological reduction of Hg compounds is favoured in soils with a high organic matter content and low oxidation-reduction potential (Eh). Microbiological reactions can cause considerably higher mercury evaporation rates than abiologically mediated evaporation (Gabriel and Williamson, 2004, Schlüter, 2000).

Apart from sunlight and heat, all other factors affecting mercury reduction are also expected to influence volatilization. For instance, mercury volatilization decreases with increasing DOM/Cl^- content and decreasing moisture content (Schlüter, 2000). Soil moisture content is important for determining the volatilization rate (Schlüter, 2000). Generally, volatilization increases with increasing water content up to a certain level (Rinklebe et al., 2010; Song and Van Heyst, 2005). Other factors influencing volatilization are the soil's physical characteristics, e.g., sorption capacity, mercury species and content and pH (Schlüter, 2000).

Meteorological conditions (e.g., wind speed, relative humidity, and turbulent mixing of air layers) can affect Hg volatilization by limiting or stimulating transport and release (Gabriel and Williamson, 2004; Schlüter, 2000). Meteorological factors are especially important in Hg enriched or contaminated areas.

Transport of gaseous mercury can also be significant laterally (horizontal transfer). Walvoord et al. ,2008 observed long-distance (several tens or hundreds of meters) migration of elemental mercury released from a buried landfill and transported through the unsaturated zone.

Further discussion on mercury volatilization and its global implications are discussed in Subchapter 1.2.2.

Methylation/demethylation

Mono methylmercury (MMeHg) and dimethylmercury (DMeHg) are the most common methylated forms synthesized by microbial activity (Davis et al., 1997). DMeHg is practically insoluble in water and is highly volatile, while MMeHg has a much higher water solubility (Gabriel and Williamson, 2004).

Generally, the concentration of MMeHg is less than 2% of the total mercury concentration in soil (Schlüter, 2000), but this percentage can be higher in wetland or riparian zones (EPA, 1997; Skyllberg et al., 2003). The percentage of MMeHg also increases the further away from the source of Hg deposition (Skyllberg et al., 2003; Ullrich et al., 2001). The percentage of MMeHg compared to the total Hg is generally higher in the aqueous phase compared to the solid phase (Skyllberg, 2012).

Factors controlling methylation and demethylation of Hg have often been studied in aqueous systems such as wetlands, rivers and lakes since these are the proximate pools of methylmercury before bioaccumulation in the food chain. Ullrich et al., 2001 provide an extensive review of mercury methylation in aqueous systems. Some points of their review are reported here because the soil solution can be considered as an aqueous system, although most of the literature the authors cite is specific to surface water.

Mercury methylation can occur in both aerobic and anaerobic environments, but in sediments, biotic methylation and MMeHg stability appear to be enhanced under anaerobic conditions (Ullrich et al., 2001). The concentration of bioavailable Hg^{2+} (rather than the total Hg pool) is a primary factor controlling methylation. For example, in a study of arctic soils over one summer period, Oiffer and Siciliano, 2009, found a net loss of MMeHg because most of the mercury was complexed with DOM and unavailable for methylation. Hg^{2+} dissolved in soil solution is more available for methylation processes than adsorbed Hg^{2+} (Gabriel and Williamson, 2004; Skyllberg et al., 2003). Using isotope tracers, Jonsson et al. (2012) confirmed that the methylation rate could vary depending on the Hg^{2+} species present in soil.

The efficiency of microbial Hg methylation also depends on microbial activity, which in turn is influenced by temperature, pH and redox potential. Moderately high temperatures likely stimulate microbial activity, which explains the higher MMeHg production rates observed during summer. Besides this, enhanced rates of MMeHg production (in aqueous systems) are associated with low pH and the presence of decomposable organic matter in reducing environments (Ullrich et al., 2001). For example, Munthe et al. (2001) found more rapid methylation in wetland soils than in dry forest soils.

The influence of organic matter on Hg methylation is not fully elucidated. On the one hand, organic carbon can enhance methylation by stimulating microorganisms or through direct abiotic methylation of Hg by humic or fulvic substances (Ullrich et al., 2001). On the other hand, high DOM concentrations can decrease the bioavailability of Hg to bacteria, particularly in the neutral pH range (Ullrich et al., 2001).

Importantly due to demethylation, MMeHg concentrations reflect net methylation rather than actual rates of MMeHg production (Ullrich et al., 2001). MMeHg is kinetically stable but is degraded by microbial action and photodecomposition. MMeHg degradation by bacteria mainly involves Hg^{2+} reduction to Hg^0 and appears to be favoured under aerobic conditions (Ullrich et al., 2001). Natural demethylation is usually caused either by microbial activity or light photoreduction. There are generally two types of microbial demethylation reactions: reductive and oxidative. Reductive demethylation degrades MeHg to Hg^0 and CH_4 and is mediated by mercury resistance (*mer*) operon systems, dominating in more aerobic settings (e.g. oxic water layers), and can be induced by high Hg concentration (Oremland et al., 1991; Marvin-Di Pasquale et al., 2000; Schaefer et al., 2004). However, oxidative demethylation – up to 8-10 % per day and production of Hg^0 and CO_2 has also been observed and is dominant in anaerobic environments with low levels of Hg, e.g., in sediment or soil (Hines et al., 2000; Marvin-DiPasquale et al., 2000; Schaefer et al., 2004, Ullrich et al., 2001).


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Figure 3. **Tropical ecosystems where mercury methylation is elevated.**

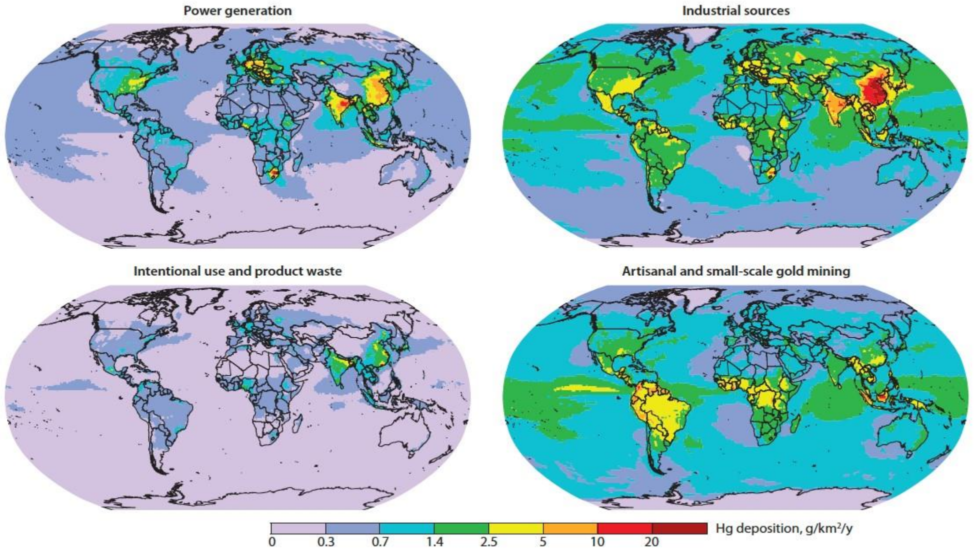
1.2. Mercury sources and sinks in soils

1.2.1 Mercury sources in soils

Atmospheric wet and dry deposition and litterfall

In the atmosphere, mercury in the form of gaseous Hg^0 is dominant (>95%; Zhang et al., 2009). Reviews of atmospheric mercury cycle, chemistry and modelling can be found in Lin and Pehkonen,1999, and Subir et al., 2011. The wet and dry deposition of Hg is mostly in the form of inorganic Hg^{2+} (Zhang et al., 2009), possibly in the form of Hg- halide ions with a large fraction being associated with particles (Schlüter, 2000). Deposition in the form of MMeHg is usually less than 5% of total deposition (Schlüter, 2000).

The latest model predictions for Hg deposition from the atmosphere from the main four groups of emission sectors (GMA, 2018) identify the importance of atmospheric deposition as a source of Hg in the terrestrial environment (Figure 4). Mercury deposition from the power generation group is primarily restricted to industrial regions in East and South Asia, Europe, North America, and South Africa, where the majority of large stationary combustion sources are located. Emissions from the industrial sectors group are widely distributed over the world. Therefore, significant deposition from industrial sources covers broad areas in Asia, Europe, North and South America, and Africa. The impact of the intentional use and product waste group of sectors is also mostly related to major industrial regions, but its contribution is considerably lower. The majority of artisanal and small-scale gold mining emission sources are located in low latitudes of both hemispheres. Mercury emissions from this sector are transported globally, but the most significant deposition occurs closer to emission sources and thus impacts mainly South America, equatorial Africa, and East and Southeast Asia (GMA, 2018).



Power generation

Industrial sources

Intentional use and product waste

Artisanal and small-scale gold mining

Figure 4. **Model predictions of the global distribution of Hg deposition from four groups of emissions sources in 2015: power generation, intentional use and products waste, and artisanal and small-scale gold mining (GMA, 2018).**

Litterfall

From the perspective of soil systems, litterfall can be considered as a source of Hg. Atmospheric Hg is the main source of Hg in aboveground vegetation tissues, and when these fall to the ground, Hg can be released in soils (Obrist et al., 2011). Mercury deposition through litterfall is considered as the low end of Hg dry deposition to the forest ecosystem.

Direct measurements and stable isotope studies have suggested that Hg deposition through litterfall is significantly higher than wet deposition and influences the size of Hg storage in forest soil/peats (Jiskra et al., 2015, 2018; Grigal et al., 2002, 2003; Demers et al., 2013).

A recent study by Wang et al. (2016) confirmed that Hg deposition through litterfall represents an important input to terrestrial forest ecosystems via cumulative uptake of atmospheric Hg (most Hg^0) to foliage. Spatial distribution of Hg deposition through litterfall suggests that deposition flux decreases spatially from tropical to temperate and boreal regions. Approximately 70% of global Hg^0 dry deposition occurs in the tropical and subtropical regions. A major source of uncertainty in this study is the heterogeneous geospatial distribution of available data. More observational data in regions (Southeast Asia, Africa, and South America) where few data sets exist will significantly improve the accuracy of the current estimate. Given that the quantity of global Hg deposition via litterfall is typically 2–6 times higher than Hg^0 evasion from the forest floor, global forest ecosystems represent a significant Hg^0 sink (Figure 5).

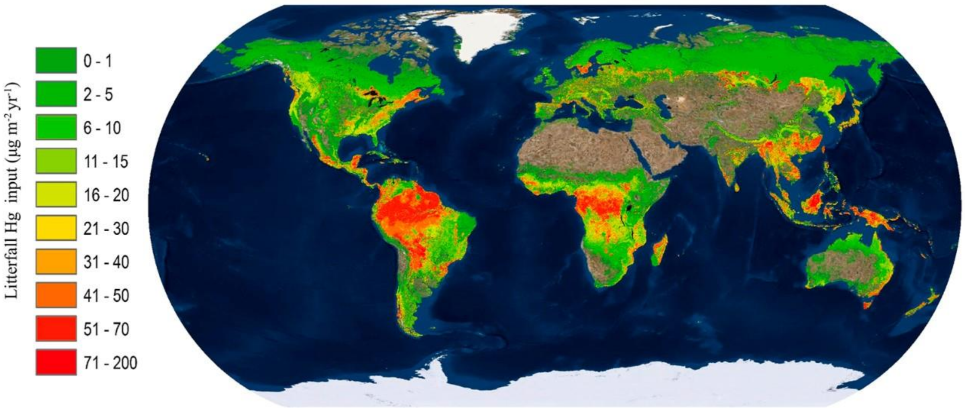


Figure 5. **Annual global deposition through litterfall is estimated at 1180 ±710 Mg (Wang et al., 2016)**

In a study by Obrist et al. (2011), the levels of Hg in soil and litter are shown to be closely linked to the C content, consistent with well-known associations between organic matter and Hg. The consistent link between C and Hg distribution may reflect a long-term legacy whereby old, C-rich soil and litter layers sequester atmospheric Hg depositions over long periods. Based on a multiregression model, Obrist et al. (2011) present a distribution map of Hg concentrations in surface soils of the United States. Such an approach could be applied to other regions.

Moreover, in the work of Jiskra et al. (2018), the role of **Hg^0 uptake by vegetation as an alternative mechanism for driving gaseous elemental mercury in the atmosphere (GEM) seasonality was investigated.** At terrestrial sites in the Northern Hemisphere, GEM co-varies with CO_2, which is known to exhibit a minimum in summer when CO_2 is assimilated by vegetation. The amplitude of seasonal oscillations in the atmospheric GEM concentration increases with latitude and is more significant at inland terrestrial sites than coastal sites. Satellite data revealed that the photosynthetic activity of vegetation correlates with GEM levels at individual sites and across continents. This work has global implications and should be considered in the design of the global monitoring of Hg in the atmosphere as the GEM concentrations measured in the planetary boundary layer at terrestrial background sites reflect both deposition and emission processes. Observed GEM oscillations must be considered as variations in net exchange, namely natural and anthropogenic emissions, vegetation uptake, and soil and vegetation re-emission. Substantial depletion of atmospheric GEM 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 GEM. All 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.

Jiskra et al. 2018 concluded that there is a need to incorporate seasonal and spatial variability in vegetation uptake of GEM into global Hg models. Trends in vegetation activity should be incorporated into models reconstructing past GEM levels and predicting future GEM levels. Also, the importance of vegetation GEM uptake as a Hg deposition pathway, demands revised Hg deposition monitoring strategies by environmental agencies.

Geogenic (or lithogenic) mercury

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. In planetary Hg belts, almost all of the world's mercury mines are concentrated. Geogenic (or lithogenic) sources provide Hg via oxidation and weathering of ore deposits and bedrocks. Mercury is then transported to soils via Hg^0 degassing or in rising groundwater. A distinction is usually made between Hg enriched areas (global "mercuriferous belt") and background areas (Schlüter, 2000). The former show high rates of mercury degassing and weathering. It is also in these areas that most of the mercury mines are found (mainly in the form of HgS(s) ore). See also the cover page of this report. More details on the location of Hg enriched areas and their origin can be found in (Schlüter, 2000). Background areas are zones where the geogenic flux of mercury to soils and atmosphere is either small or negligible, and in the field, methods exist to discriminate between atmospheric and geogenic sources of soil Hg (Gustin et al., 2006; Guedron et al., 2006).

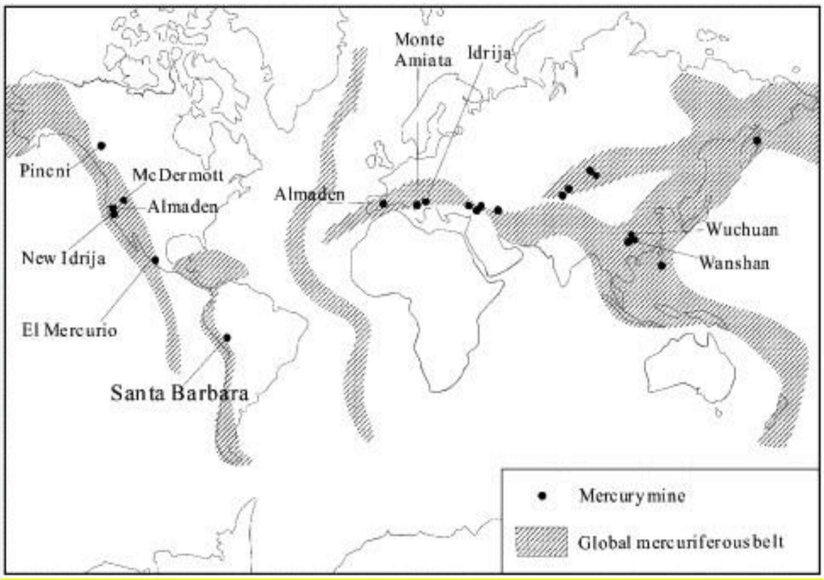


Figure 6. **Mercury planetary belts (Wang et al., 2005)**

Moreover, Schuster et al. (2018) recently estimated the amount of natural mercury stored in **perennially frozen soils** (permafrost) in the Northern Hemisphere. Permafrost regions contain twice as much mercury as all the other soils, the atmosphere, and oceans combined. They estimated that the Northern Hemisphere permafrost regions contain 1,656 ± 962 Gg Hg, of which 793 ± 461 Gg Hg is trapped in the permafrost. This Hg is vulnerable to release as the permafrost thaws over the next century, with unknown consequences to the environment. 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.

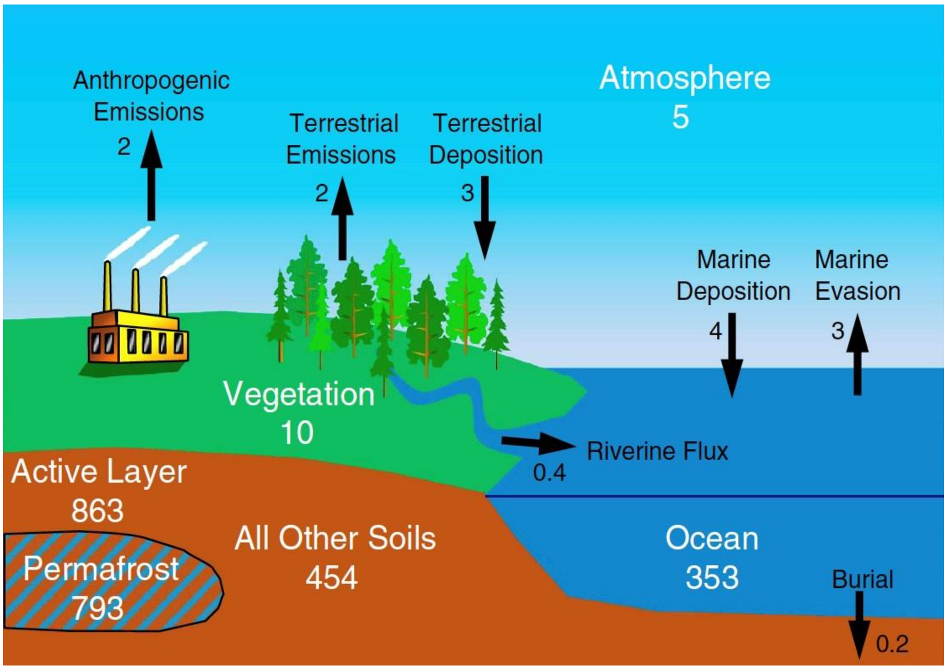


Figure 7. **An updated schematic of the current global Hg cycle with major reservoirs in white (Gg Hg) and fluxes in black (Gg Hg/yr). Adapted from Amos et al. (2013) with the soil reservoir shown as an average of previously published estimates (Schuster et al., 2018)**

Anthropogenic contamination

Anthropogenic soil contamination can result from direct sources (Table 1), but it can also occur indirectly, for example via deposition of prior atmospheric emissions (GMA, 2018; Streets et al., 2017). In the recent work of Streets et al. (2017), the total release of mercury to land and water until 2010 was estimated to be 1070 Gg (Table 1), which significantly exceeds total mercury emissions to the atmosphere (470 Gg). Streets et al. (2017) concluded that the total amount of Hg released to the environment by human activities is 1540 Gg. Based on the primary release estimate for geogenic sources of 90 Mg yr−1 (excluding re-emission of previously deposited Hg), Amos et al., (2013) estimate that the total anthropogenic input since 1850 (1120 Gg) is 78 times that of total geogenic input (14.4 Gg). The presence of such large amounts of anthropogenic Hg in the environment has led to widespread pollution of land and water bodies, and severe contamination of specific sites where Hg was produced or used for metals extraction. Table 1, however, does not include recent studies reporting the contribution from sewage sludge disposed directly on land (Liu et al., 2018), which although significantly contributes to the direct input of Hg in soil has not been well studied.

Anthropogenic mercury contamination may result in much higher Hg concentrations in soil systems than from other sources and has important consequences for assessing the fate and transport of Hg in soils, by affecting, for instance, Hg speciation/fractionation in soils (Table 2).

Table1. **Cumulative anthropogenic remissions and releases of Hg to air, land and water up to 2010 (Streets et al., 2017)**

Process	Emissions to air (Gg)	Fraction of Hg^0 in air emissions	Releases to land and water (Gg)	Ratio of air emissions and releases to land/water	Total emissions and releases
Copper smelting	4.91	0.64	**12.6**	0.39	17.5
Zinc smelting	10.5	0.73	**25.3**	0.42	35.8
Lead smelting	6.04	0.74	**8.57**	0.71	14.6
Ironmaking	1.2	0.40	**1.45**	0.83	2.65
Steelmaking	0.41	0.45	**2.41**	0.17	2.85
Mercury production	91.7	0.80	**321**	0.29	42.3
Gold, large-scale	21.0	0.80	**114**	0.18	135
Gold, artisanal	34.4	1.00	**51.6**	0.67	86.0
Silver production	146	0.80	**219**	0.67	365
Cement production	3.29	0.51	**3.47**	0.95	6.76
Caustic soda	8.80	1.00	**63.6**	0.14	72.4
Coal combustion	26.4	0.53	**11.4**	2.32	37.8
Oil combustion	0.77	0.50	**0**	-	0.77
Municipal waste incineration	34.6	0.22	**0**	-	34.6
Other waste burning	27.8	0.20	**0**	-	27.8
Electrical and measuring equipment	5.52	0.71	**97.7**	0.06	103
Chemical manufacturing	47.5	1.00	**131**	0.36	179
Dental	1.06	0.71	**5.69**	0.19	6.75
total	472	0.74	**1070**	0.44	1540

1 Gg=10^9 grams = 1000 tonnes

Hg preferentially binds to S-containing functional groups on organic ligands. These are always in excess relative to Hg concentration in uncontaminated soils, while contaminated sites may show much lower S/Hg ratios. In soils affected by anthropogenic contamination, the ratio of organomercury species to total mercury is usually lower than in uncontaminated areas (Boszke et al., 2008).

Gray et al. (2006) showed that *methylation and demethylation processes* were significant in mercury mine tailings. Methylmercury concentrations were positively correlated with Hg^{2+}, organic carbon and total sulfur concentrations. Remy et al. (2006), however, drew different conclusions from a study of soils contaminated by a former chlor-alkali plant where methylmercury concentrations in the soil show a negative correlation with total Hg concentrations, organic carbon and total sulfur concentrations. The high methylmercury/Hg$_{tot}$ ratios were mainly related to a combination of low Hg$_{tot}$, low organic C/N ratios and relatively low pH. Frohne et al. (2011) studied methylation in floodplain soils contaminated by the textile and metal industries. They suggested that the dissolved organic carbon (DOC)/Hg$_{tot}$ ratio might be a more important factor for the Hg net methylation (with a positive correlation) than DOC alone. Other important factors influencing methylation were the DOC, the sulfur cycle, and the structure of the microbial community, whereas Eh and pH values, dissolved Fe^{3+}/Fe^{2+} and Cl$^-$ concentrations play a minor role.

***Table 2.* Type of anthropogenic source of mercury and its presence in soil**

Type of contamination	Comment	References
Hg^0 discharged by manometer spills	Even after decades, or as an amalgam for mining, may remain as Hg0 "globules" or NAPL in the soil.	Davis et al., 1997
HgCl$_2$ used for wood preservation	Most Hg in soil was Hg bound to mineral soil compounds (e.g. iron/aluminium oxides and hydroxides or clay minerals), whereas in the aquifer reduction to Hg^0 could be observed	Bollen et al., 2008
Hg^0 industrial spill	The main transformations were volatilization to the atmosphere and oxidation to Hg^{2+} followed by binding to humic matter and 21ulphide. Indeed, even after high contamination events, very few Hg^0 persists in the liquid form: Hg0 is either rapidly volatilized or more slowly oxidized to Hg^{2+}.	Boszke et al., 2008; Biester et al., 2002
Historical gold mine tailing	Hg^0 had been oxidized and transformed into mineral and organic sorption complexes, highly insoluble cinnabar (HgS), Hg oxides and Hg chloride. Moreover, colloidal transport of cinnabar was identified as the dominant leaching mechanism in the mine tailings.	Slowey et al., 2005, Lowry et al., 2004
	Most of the mercury was associated with organic matter and sulfur.	Palmieri et al., 2006
	>99.8% of mobilized Hg was in the form of Hg-CN complexes	Shaw et al., 2006
	Differences in speciation depend on the time of contamination: older incomplete ore roasting gave more cinnabar than younger tailings in which mineral sorbed Hg^0 and unbound Hg^0 predominated.	Biester et al., 1999; Kocman et al., 2006, 2010
	Predominant Hg species in soils and mine wastes were cinnabar (HgS), mainly formed from the weathering of Hg-rich pyrite and elemental Hg^0 in the matrix, whereas in calcines and tailings the dominant species was Hg^0.	Navarro et al., 2006
Mercury mining areas	Almadén (Spain) mercury mining industry, fractionation analyses of soil samples showed predominant Hg 21ulphide21, then associated with Fe-Mn oxyhydroxides and with organic matter, and traces of Hg^0. Land use influence on Hg speciation was also indicated by different speciation results in agricultural and pastoral areas.	Millan et al., 2011
soils polluted by Hg^0 wastes from a chlor-alkali plant.	Cinnabar and metacinnabar (HgS), corderoite ($Hg_3S_2Cl_2$), and small quantities of HgSO$_4$ and HgO.	Bernaus et al., 2006; Terzano et al., 2010; Santoro et al., 2010
	HgO(s) and HgCl$_2$(s) are typically species that are sometimes found in highly contaminated soils but not under background conditions.	Skyllberg, 2010
Sco-contamination by hydrocarbons	Over time Hg has transformed to Hg^{2+} and is mostly sorbed to soil organic and mineral materials. Association of Hg with hydrocarbon is also possible.	Renneberg and Dudas, 2001
Cinder contamination in a site of historical mercury fulminate (Hg(CNO)2)	Mercury 21ulphide21 were detected in soil and cinder while other forms of mercury (i.e. adsorbed Hg) were likely present but not analysed.	Bessinger and Marks, 2010
Soil/sediments from acetaldehyde production in Minamata	Stable β-mercury 21ulphide (HgS) based on transmission electron microscopy inked with energydispersive X-ray spectroscopy (TEM-EDX) and X-ray absorption fine structure (XAFS). MmeHg was less than 1% of the total Hg.	Sakamoto et al., 2019

1.2.2. Mercury sinks from the soil systems

Mercury sinks from the perspective of soil systems are (Figure 1): (i) atmosphere, (ii) plants (via root uptake), (iii) groundwater, and (iv) surface water. Irreversible sorption sites are sometimes considered as a sink in the budget of soil Hg, but are not treated as sinks in this report, since this process does not affect the total Hg budget in the soil.

Atmosphere

Volatilization to the gas phase of soil and eventually to the atmosphere is discussed in Subchapter 1.3.

Plants

Plant root uptake from soils is low and can be neglected (Pant et al., 2010; Schuster, 1991). Roots act as significant adsorption sites and are a barrier for Hg transport to foliage (Grigal, 2003). Therefore, transport through the roots to the above-ground parts the plants is limited although exceptions do exist (e.g. Pérez-Sanz et al., 2012). Also, mercury phytoremediation can benefit from genetic engineering (Ruiz and Daniell, 2009) or association with rhizobacteria (Sorkhoh, 2010). Nonterrestrial plants like mangroves can show significant Hg root uptake (Ding et al., 2011).

© Christiane Fischer – Victor Estellano, Palca Canyon, Bolivia

Figure 8. **Landscape showing soil erosion.**

Groundwater and surface waters

In the unsaturated zone, mercury transport to surface water (i.e. via subsurface flow) and groundwater occur via convection, dispersion, diffusion and colloid-facilitated transport. On sites of heavy contamination, the migration and entrapment of NAPL must be taken into account. In the vadose zone, gaseous diffusion of mercury also determines the fate of Hg in soils.

Irreversible sorption

Retardation of Hg in soils is mainly due to adsorption processes.

1.2.3. Terrestrial surface-atmosphere fluxes

Due to the global relevance of the Hg^0 evaporation from the soil/terrestrial systems, this chapters summarizes some of the recent findings to be considered when interpreting atmospheric mercury data.

Hg^0 surface-atmosphere exchange has been studied at Hg-enriched sites, both naturally enriched and atmospherically influenced (Engle et al., 2001; Ferrara et al., 1998, Nacht and Gustin, 2004; Wang et al., 2005, 2006) and background sites (Kim et al., 1995a,b; Poissant and Casimir, 1998) during the last 30 years. These calculations suggest that background areas also contribute significantly to atmospheric Hg^0 emissions despite low soil Hg concentrations and therefore, low atmospheric emission potential (Gustin et al., 1997; Frescholtz and Gustin, 2004). In a recent study, mercury evaporation from contaminated sites accounts for more than 5 % of the total mercury emission from anthropogenic activities (Kocman et al., 2013; GMA, 2018).

Hg^0 flux studies thus far have revealed several important environmental factors that modulate Hg^0 fluxes from terrestrial surfaces, including the following: (1) **solar radiation** which induces photoreduction (Fu et al., 2012); (2) **air and soil temperatures** with higher temperatures generally stimulating Hg^0 evasion (Almeida et al., 2009; Poisant et al., 1999); (3) **precipitation and soil moisture** that stimulate emissions at some sites but reduce emissions at others (Lindberg et al., 1999; Gustin and Stamenković, 2005), and (4) **atmospheric Hg^0 concentrations** that also have both positive and negative effects on fluxes (Zhu et al., 2015). A summary of factors contributing to Hg^{2+} reduction is addressed in subchapter 1.3.

Effects of these variables have been quantified in many studies, while other potentially important controls have been poorly characterized—including, for example, the roles of **UV–B radiation** (Edwards and Howard, 2013), litter **cover** (Choi and Holsen, 2009; Coolbaugh et al., 2002) or overburden at **geogenic sites** (Edwards et al., 2001, 2013). Their importance, however, appears to vary from site to site and from study to study (Ma et al., 2013; Wang et al., 2006).

A comprehensive comparison and a review were performed by Agnan et al. (2016) with the intent to constrain uncertainties such as the magnitude of reported Hg^0 fluxes and discrepancies in the processes that control Hg^0 exchange among sites and studies, and ultimately to better quantify the magnitude of terrestrial-atmosphere fluxes. A new global database integrating terrestrial Hg^0 flux measurements and controlling processes available in the literature was created to complete this analysis. As part of their work, the authors (1) characterized the spatial and temporal coverage of current global terrestrial surface-atmosphere Hg^0 measurements; (2) evaluated the magnitude of Hg^0 fluxes over terrestrial surfaces with different levels of Hg contamination and land cover types; (3) compared the influences of environmental variables that control Hg^0 fluxes and their consistency across studies and the global data set; (4) determined if the measurement method causes differences in Hg^0 fluxes; and finally (5) constrained the net global-scale terrestrial Hg^0 exchange using statistical frequency distribution and confidence intervals for various ecosystems and soil Hg burdens.

Figure 9 shows that the substrate Hg concentrations exert a dominant control on Hg^0 emission across data from Hg-enriched sites. In contrast to the background sites, high substrate Hg concentrations lead to enhanced surface Hg^0 emissions.

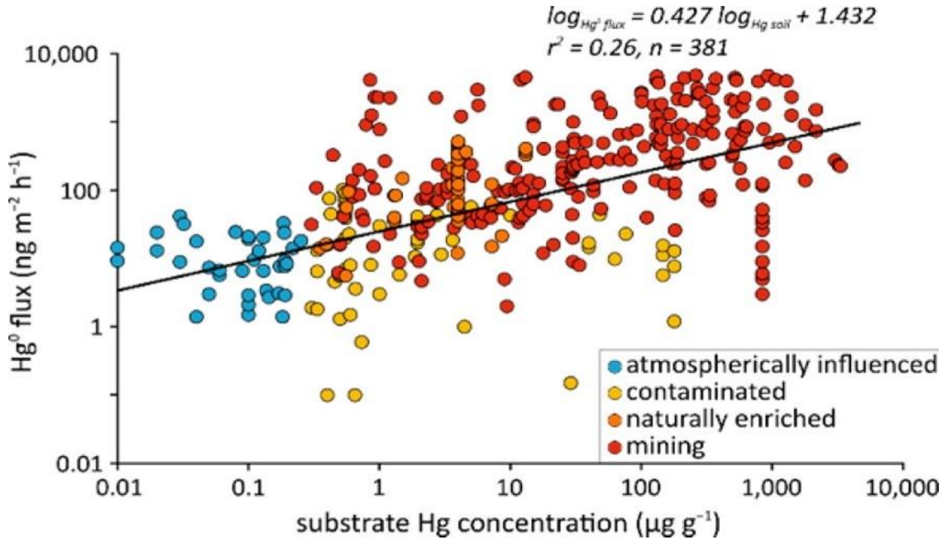


Figure 9. **Hg^0 flux vs substrate Hg concentration relationship for Hg-enriched sites (Agnan et al., 2015).**

Figure 10 below demonstrates Hg0 fluxes for bare soil surfaces and compares these across different sites, different land cover types, and later includes other surfaces (Agnan et al., 2016). Bare soil measurements accounted for the majority of all Hg0 flux measurements both in Hg-enriched (80%) and background (65%) categories, whereas measurements over other surfaces (in particular vegetated surfaces) were underrepresented.

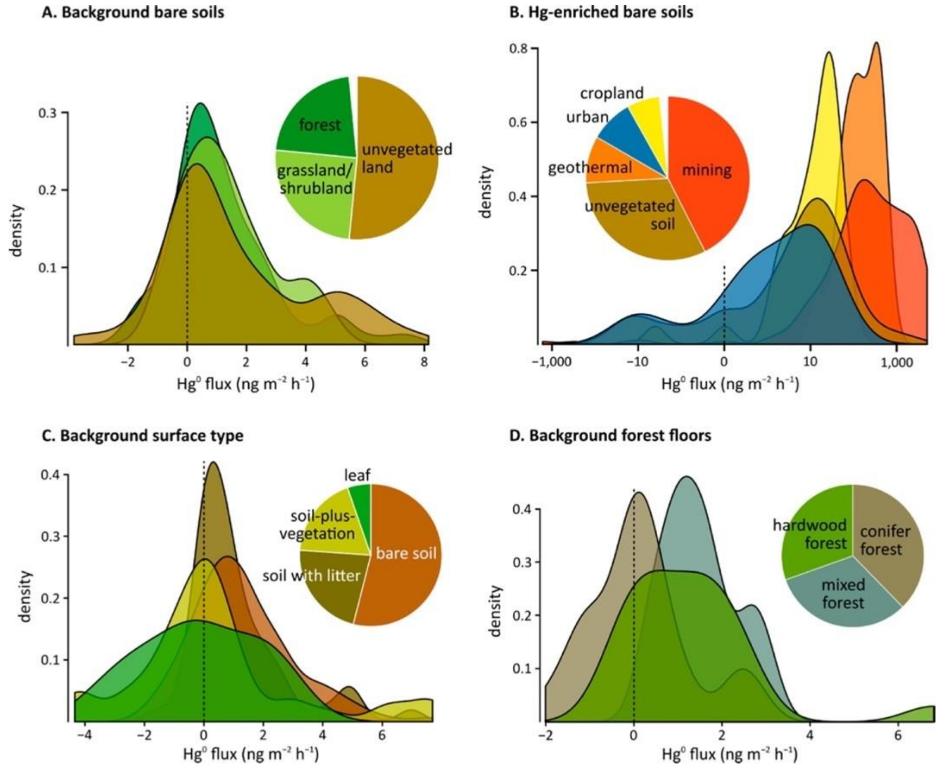


Figure 10. **The distribution density of Hg^0 fluxes from the background (A) and Hg-enriched (B) bare soils by land cover (n > 10), background surfaces by vegetation cover type (C), and background forest floors by forest type (D). Only classes with n >10 are presented (Agnan et al., 2016).**

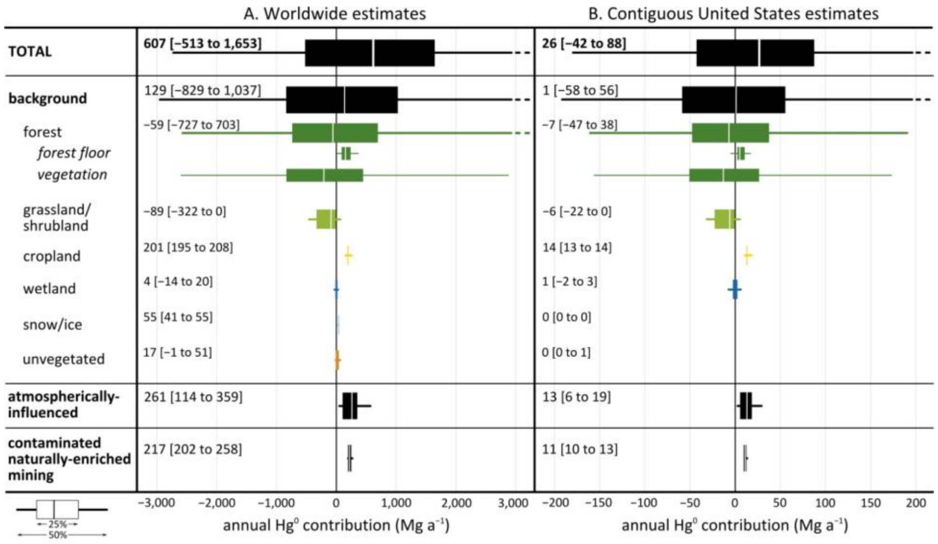


Figure 11. **Global annual estimates of Hg^0 exchange (Mg/year) over terrestrial surfaces across different land covers: worldwide (A) and the contiguous United States (B). Positive values signify emissions, and negative values signify deposition. Numbers indicate medians and uncertainty ranges between 37.5th and 62.5th percentiles. The background represents the sum of six subcategories (forest, grassland/shrubland, cropland, wetland, snow/ice, and unvegetated (i.e., bare soils). Forest fluxes were calculated based on forest floor Hg^0 flux measurements and leaf fluxes multiplied by leaf area indices since whole-ecosystem forest fluxes are mostly missing in the literature (Agnan et al., 2016).**

A global scaling up of Hg^0 fluxes revealed the following patterns (Agnan et al., 2016):

(1) Background areas contribute Hg^0 emissions in the same order of magnitude as Hg-enriched sites (contaminated, naturally enriched, and mining) (Figures 10 and 11).

(2) Hg^0 emissions from atmospherically influenced sites (i.e., sites exposed to air concentrations >3 ng m^{-3}), particularly in East Asia, need to be considered as an important global-scale Hg^0 source and contribute the major fraction of Hg^0 emissions to the atmosphere.

(3) Vegetated areas likely constitute an important Hg^0 sink, although reliable vegetation flux measurements, notably over forests, are lacking (Jiskra et al., 2018).

(4) Uncertainties in the role that vegetation plays are large and likely due to methodological problems in quantifying foliar fluxes; the flux uncertainty of forest foliar measurements could potentially offset any terrestrial Hg0 emissions, or double current Hg^0 emission estimates, and lead to a shift in the role of global terrestrial ecosystems serving as a net source to a net sink of atmospheric Hg^0.

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Figure 12. **Water in this stream has been stained by runoff Cinnabar that was mined to produce mercury.**

2. Existing capacities/networks

Soil monitoring is defined as the continuous or repeated observation, measurement, and evaluation of soil and related environmental or technical data for defined purposes, according to prearranged schedules in space and time, using standardized methods for data collection and analysis (ENVASSO 2007). A soil monitoring network is defined as a spatial arrangement of soil monitoring sites, designed to be representative of soil type, land use and climatic zones; the spatial arrangement may be random or on a regular grid (ENVASSO 2007). A soil monitoring network (SMN) was defined by Morvan et al. (2008) as a set of sites/areas where changes in soil characteristics are documented through periodic assessment of an extended set of soil parameters. Most of these networks are either in the planning stage or have been sampled once, and therefore, can at this point only be used to determine Hg stocks rather than quantify Hg dynamics. Many national and international soil monitoring networks or monitoring activities exist, but information on mercury and its compounds in soil are rare and incomplete. For instance, if monitoring activities for mercury in soil exist, they only look at total Hg, and if a more in-depth distinction is needed, additional parameters are studied. An extensive review of European soil monitoring efforts, including recommendations on the sampling and testing protocols, was carried out in the ENVASSO project (Morvan et al. 2008).

Several international organisations and societies for soil sciences exist, such as the International Union of Soil Sciences, but mercury reviews are rare. The Food and Agriculture Organization of the United Nations (FAO) Global Soil Partnership established the Global Soil Laboratory Network (GLOSOLAN) to monitor soil properties and contamination, but mercury was not included in the monitoring activities. More common are national soil monitoring networks, and national soil surveys that vary among countries and mercury is included only in some, but rather other metallic elements are studied (Šebkova and Kuta, 2019).

Slovenia and Croatia

An example of the most common monitoring design is the national Hg monitoring in topsoil in Slovenia. The Geological Survey of Slovenia recently published the Geological Atlas of Slovenia (Novak and Rman, 2018) where the mercury distribution map was created on the base of soil sampling performed on 5 X 5 km grid between 1990 and 1993. A total of 817 samples of topsoils (0-10 cm) were collected. Air-dried samples were sieved through a 2 mm sieve, then pulverised in an agate mill to a grain size of 0.075 mm. Total mercury was determined by Inductively coupled plasma mass spectrometry (ICP-MS) after aqua regia digestion of sample (Novak and Rman, 2018). The Slovenian Environmental Agency performed similar Hg soil monitoring (Zupan et al., 2008) using a different sampling grids, sampling depths (<20 cm), soil fraction analysed, and data presentation. A similar approach was used by other national monitoring networks. For instance, Croatian national Hg monitoring differs in sampling depths, fraction analysed, sample preparation procedure and sampling grid resolution, and consequently, both sets of national data are hard to compare. The problem with such monitoring designs is that the temporal component is missing, and only total Hg was determined.

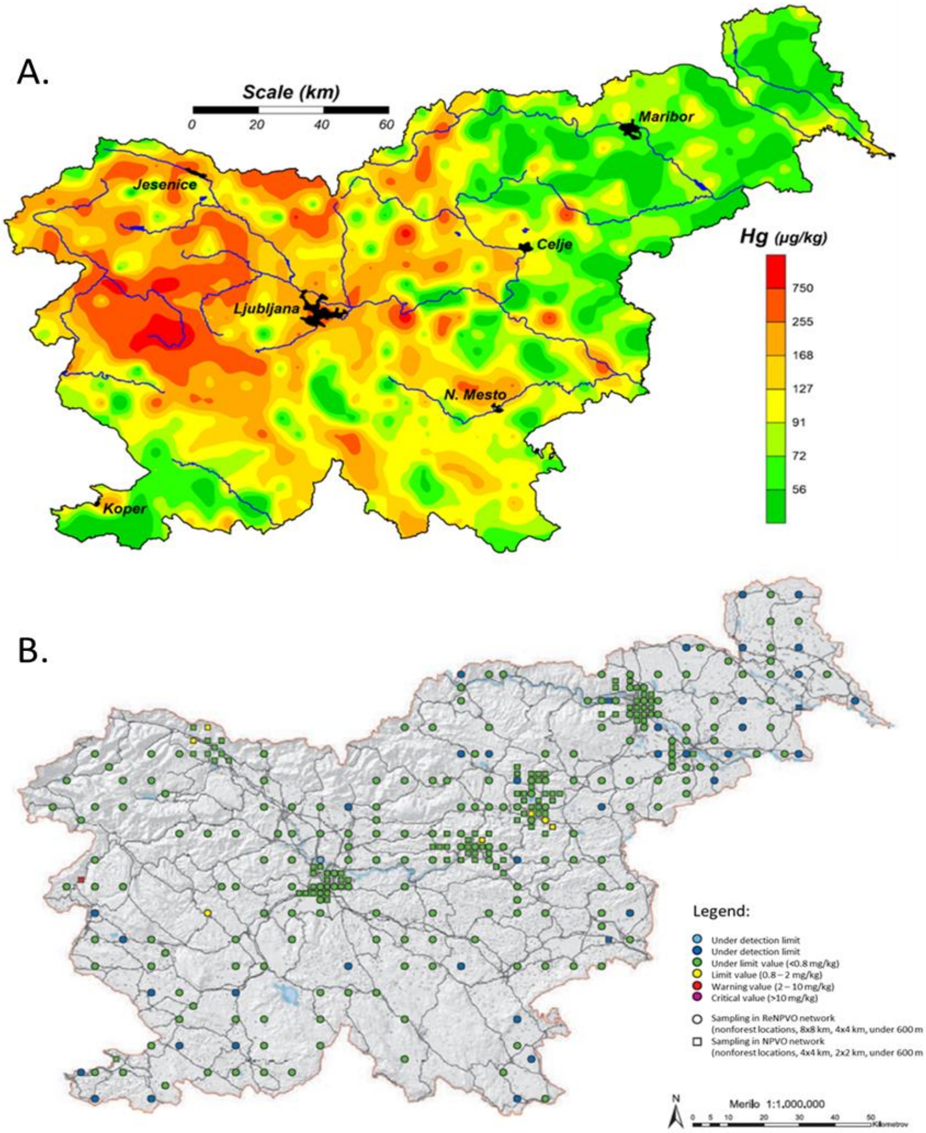

***Figure 13.* An example of Slovenian national soil Hg (µg/kg) monitoring with different sampling and data presentation strategies. A. Hg soil monitoring performed by the Geological Survey of Slovenia (Gosar et al., 2016) and B. monitoring performed by the Slovenian Environmental Agency (Zupan et al., 2008).**

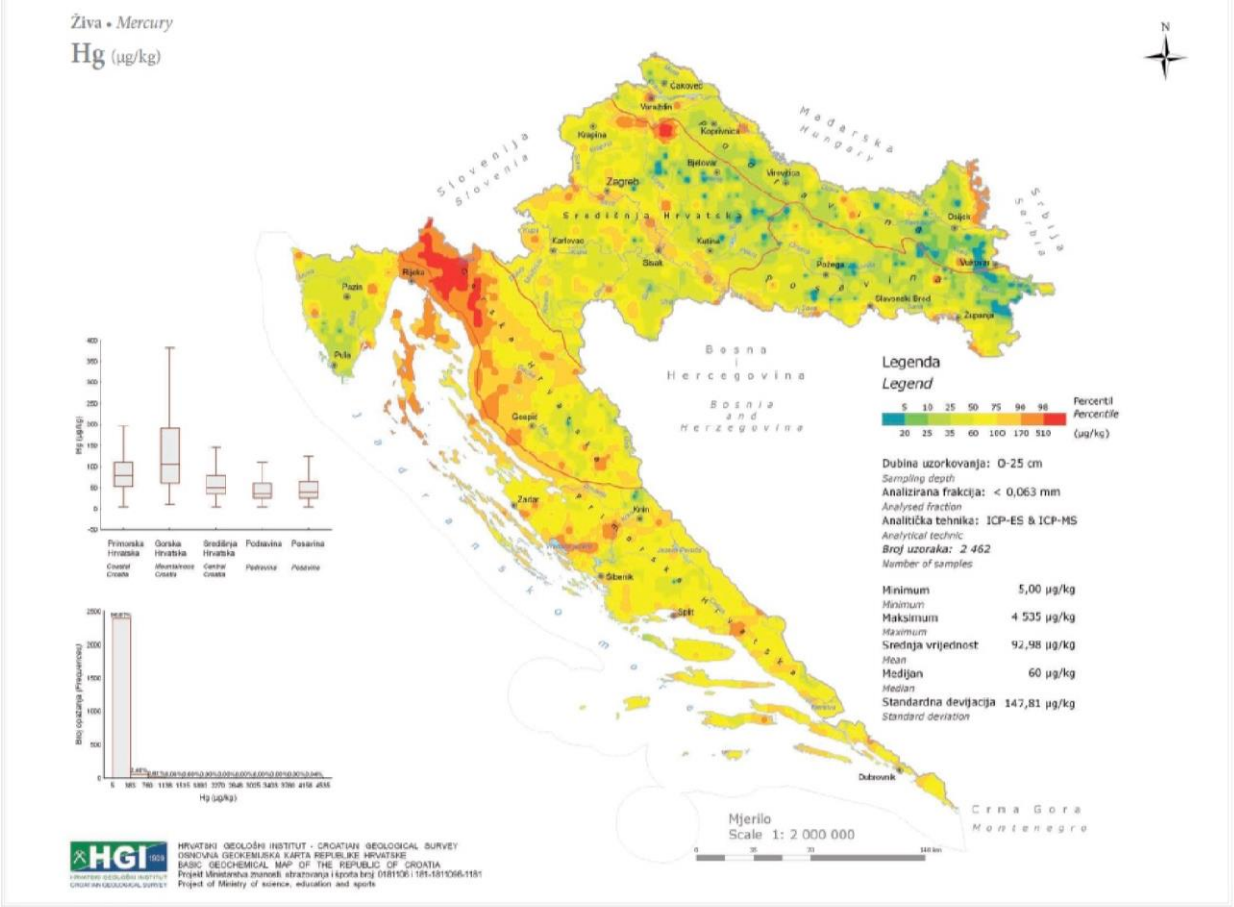

***Figure 14.* An example of Croatian national soil Hg monitoring. Distribution of total Hg (µg/kg) in soils in Croatia (Halamić and Miko, 2009).**

Czech national

A better example is the Czech national soil monitoring programme (Poláková et al., 2017) established in1992. It includes 214 sampling sites characterizing land use and soil type. For specific soil parameters sampling is performed yearly, but Hg measurements are only performed every 6 years. At most sampling locations between 1995 and 2013, a decrease in Hg concentrations in the different types of soil is observed.

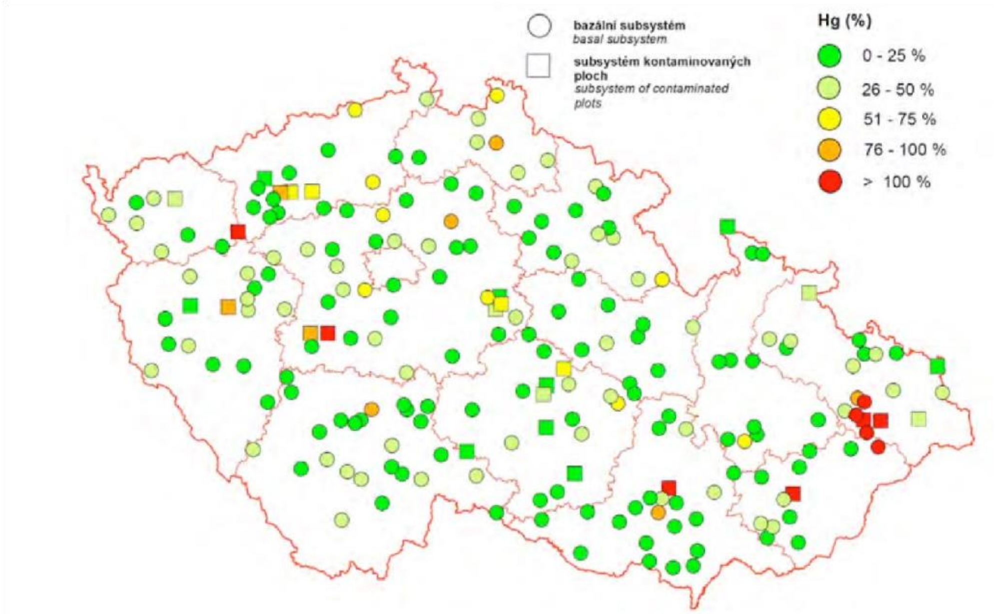

Figure 15. **Mercury (Hg) concentrations in BSMS soils, 2013 (214 monitoring plots); concentrations are expressed as a percentage of the precautionary value (Poláková et al., 2017).**

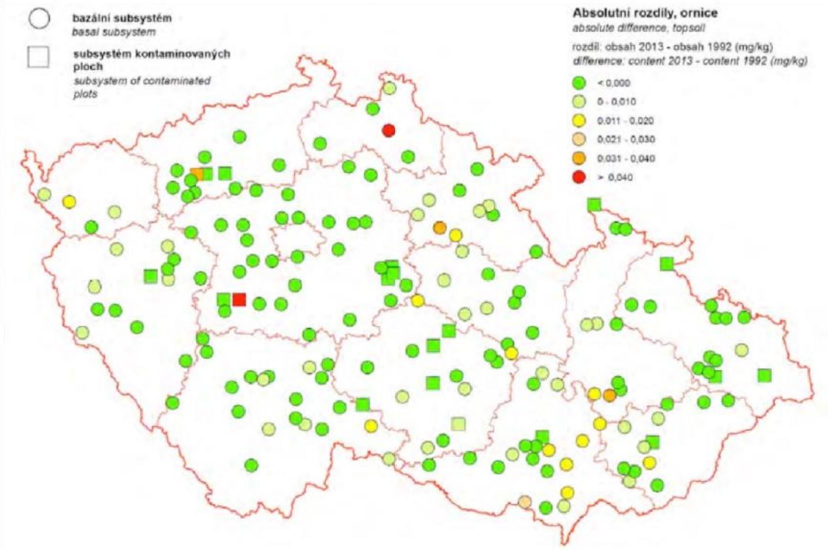

Figure 16. **Changes in mercury (Hg) concentrations (mg/kg) between the periods 2013 and 1992 (mg kg^{-1}, Aqua Regia extraction, 177 monitoring plots) (Poláková et al., 2017).**

European Union

At the European scale, several attempts were made to determine the spatial distribution of heavy metals in European soils. The European Environmental Agency (2006) merged the sampling points from three different soil databases to create a map of the concentration of lead in topsoils across Europe (http://dataservice.eea.europa.eu). In principle, the only official maps of heavy metals in soils of Europe are those presented in the "Geochemical Atlas of Europe". This atlas contains maps for 85 variables for five different media: floodplain sediment, humus, soil, stream sediment and stream water (Lado et al., 2008). The Soil Atlas of Europe is the result of a collective effort by more than 40 National soil surveys and soil science institutions cooperating across Europe within the European Soil Bureau Network (ESBN). This network, established by the Joint Research Council (JRC) in 1989, formalised already existing collaborations among soil surveys already initiated in 1959 by the UN FAO as the first steps towards a common soil map for the European Union.

The main European added value of the ESBN has been the joint effort towards bringing together soil information collected in separate European countries, using very different methodologies, standards and scientific backgrounds, into one single geographic information system (GIS). Lengthy cross-border harmonisation sessions between bordering countries have resulted in a fully harmonised soil geographical database of Europe at a nominal scale of 1:1,000,000. Although this database has allowed the production of elemental maps, Hg is not included in the Atlas.

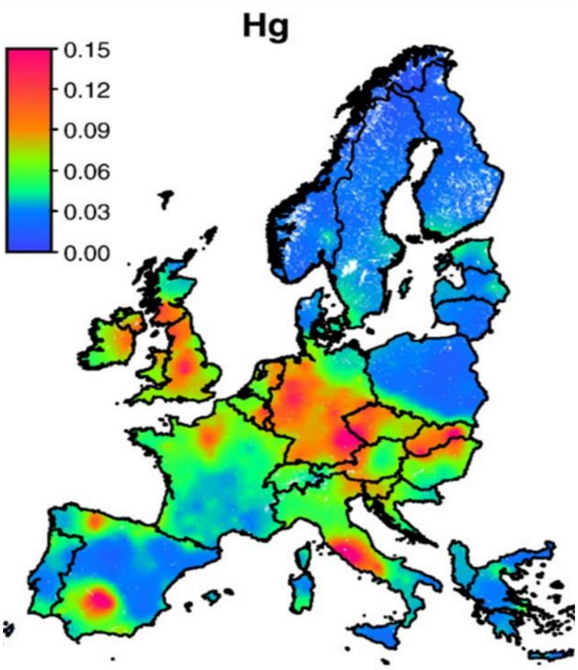

***Figure 17.* Map of mercury concentrations in topsoils [mg/kg] interpolated using block regression-kriging (support size=5 km). All maps described in this paper are available online via the http://eusoils.jrc.it website. (Lado et al. 2008).**

Recently a pan-European soil monitoring effort was undertaken by the statistical office of the European Union (Eurostat). Regular surveys (LUCAS - Land Use and Coverage Area Frame Survey) to monitor the situation of land use, land cover and changes over time across the EU, but no contaminants such as mercury are followed. The 'Land Use/Cover Area frame statistical Survey Soil' (LUCAS Soil) is an extensive and regular topsoil survey that is carried out across the European Union to derive policyrelevant statistics on the effect of land management on soil characteristics. LUCAS Soil represents the largest harmonized open-access dataset of topsoil properties available for the European Union at the global scale. It was developed as an expandable resource, with the possibility to add new properties and sampling locations during successive sampling campaigns. Data are available to the scientific community and decision-makers, thus contributing to both research and the development of the landfocused policy agenda (Orgiazzi et al., 2017). The interval of these surveys was fixed to three years. The sampling is based on a regular grid across the EU (2 × 2 km grid, about 1 000 000 georeferenced points). Each point has been classified according to seven land cover classes using orthophotos or satellite images. Of these points, approximately 270 000 points are visited in the field by surveyors to assess the validity of the remote sensing observations and to collect additional information that cannot be assessed remotely. Physical inspection/analysis accounts for about 10% of sites, but chemicals/risk elements are performed through national networks.

LUCAS Soil was created from the outset as a monitoring and dynamic database. Thus, repetition of measurements, new locations and new properties can be added during subsequent surveys. The geographical extent of the LUCAS project was extended to non-EU countries including Albania, Bosnia and Herzegovina, Macedonia, Montenegro, Serbia and Switzerland. LUCAS Soil is one of the world's largest and most comprehensive, harmonized continental-scale soil databases on account of the range of properties analysed. Furthermore, it is an open-access tool, with data freely available from the European Soil Data Centre (ESDAC) (Panagos et al., 2012). All LUCAS Soil-derived output (e.g. maps of soil properties for the EU) is also available from the ESDAC platform (Orgiazzi et al., 2017).

United State of America

USDA-NRCS Soil Monitoring Network is an example of a US national scale network of sites sampled and analysed periodically to track changes in soil properties. The current concept of monitoring period is 100 years, with 5-10 years return frequency for sites expected to change rapidly. The database is publically available to supply data to improve resource assessment and conservation programs. Mercury and its compounds are not monitored within network.

The US Natural Resources Conservation Service (NRCS) operates comprehensive, nationwide soil moisture and climate information network. The Soil Climate Analysis Network, also known as SCAN, supports natural resource assessments and conservation activities through its network of automated climate monitoring and data collection sites. SCAN focuses primarily on agricultural areas of the U.S., Puerto Rico and the Virgin Islands. The network consists of over 200 stations in almost every state and is growing every year. Mercury and its species are not included in the monitoring program.

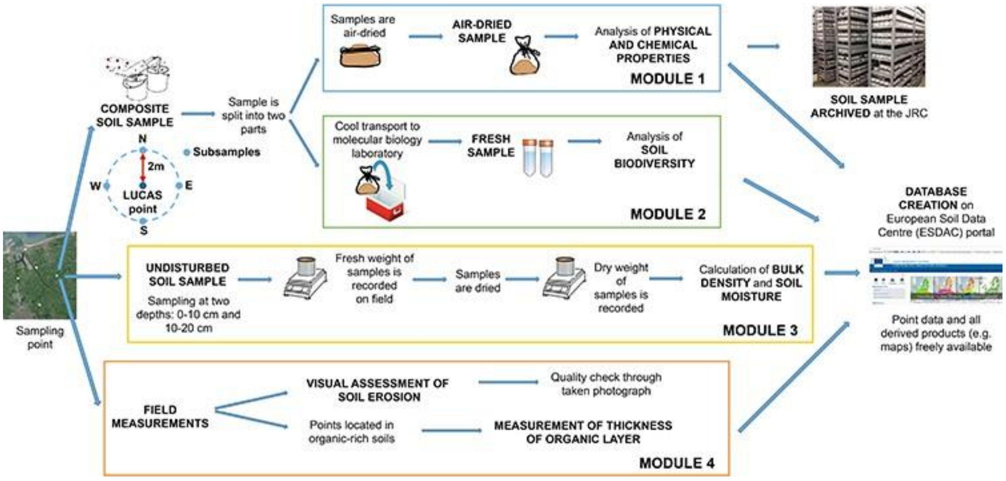

Figure 18. **LUCAS Soil workflow from sampling to database generation (https://esdac.jrc.ec.europa.eu/projects/lucas).**

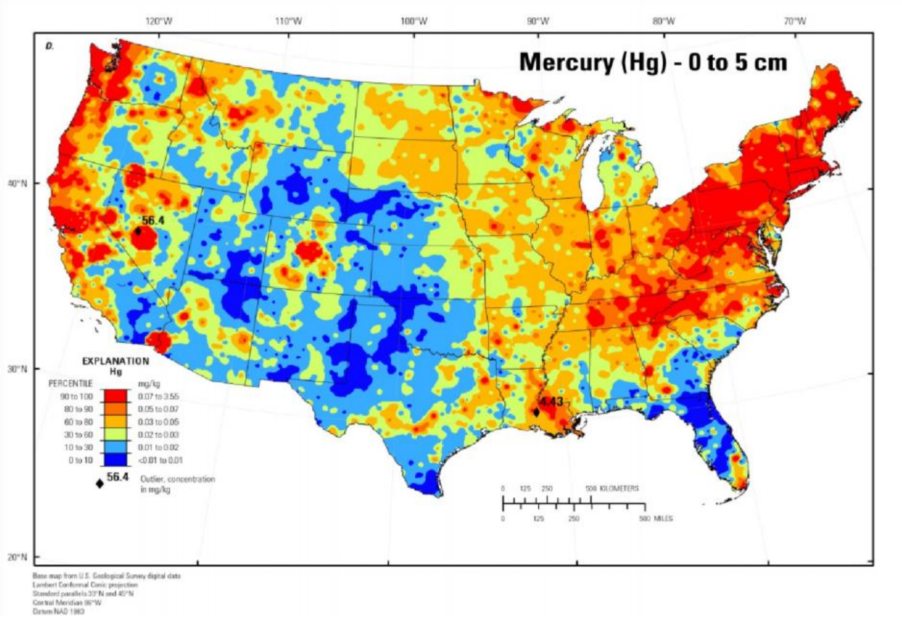

Figure 19. **Mercury (mg/kg) in topsoil in the US (USGS, online Aug. 2019)**

The US Geological Survey (USGS) provides environmental mercury datasets, including atmospheric mercury emissions, National Atmospheric Deposition Program (NADP) monitoring sites, and mercury concentrations in fish-tissue, soils, stream sediments, and coal.

China

On the Asian scale, the Chinese government investigated 6,300,000 km^2 of soils from 2005 to 2013 from across China and reported that 1.6% of the investigated samples exceeded the Hg reference, but it did not give the Hg contaminated locations and areas (MEP & MLR 2014). Wang et al. (2016) obtained the spatial distribution of Hg concentrations in agricultural soil and evaluate the risk of soil Hg contamination on food safety across China, based on the meta-data analysis method. Levels of Hg in

Chinese agricultural soil were collected from the published papers during 2005–2015 and soil-sample weighted averages of Hg concentration in soil under seven land uses were calculated. The spatial distribution of Hg concentration is obtained based on a kriging method. Finally, the risk of Hg on food production is assessed based on the Environment Quality Standard for soils in China.

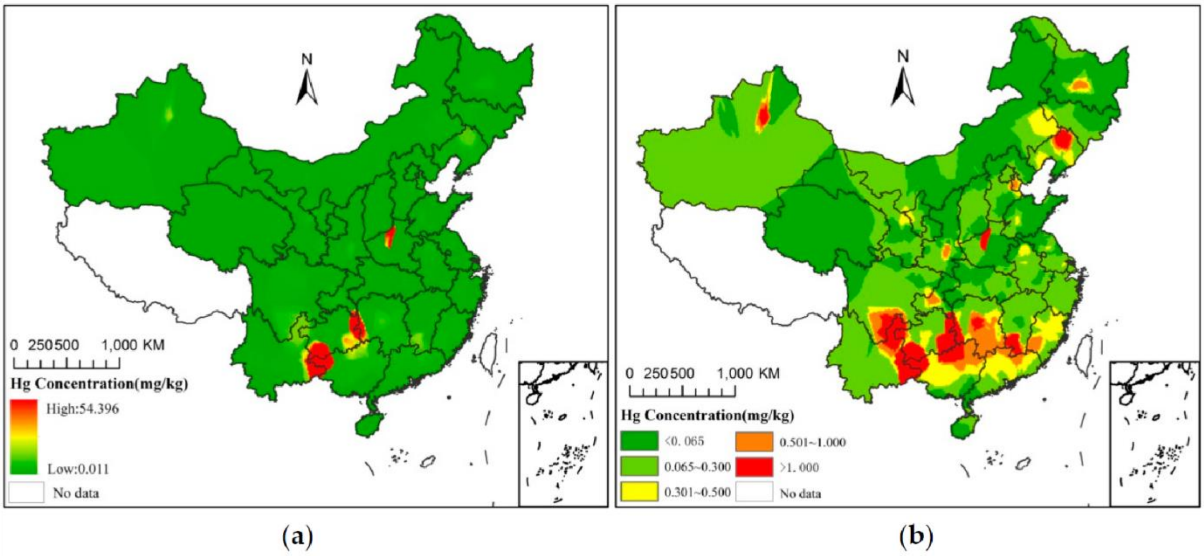

Figure 20. **Spatial distribution of estimated Hg concentrations (mg/kg) in agricultural in mainland China illustrated in (a) stretched map and (b) graded map (from Wang et al., 2016).**

Policy relevance

European Union

At the moment, only a few EU Member States have specific legislation on soil protection. Soil is not subject to a comprehensive and coherent set of rules in the Union. Existing EU policies in areas such as agriculture, water, waste, chemicals, and prevention of industrial pollution do indirectly contribute to the protection of soils; however, these policies have other aims and scope of action and are not sufficient to ensure an adequate level of protection for all soils across Europe.

In order to ensure soil protection, the EC developed a thematic strategy, proposing a series of environmental measures, designed to prevent soil degradation, including legislation relating to mining, waste, sewage sludge and compost and integrating soil-protection concerns in major EU policies. The EU Commission has proposed a way forward towards a Thematic Strategy for Soil Protection based on the distinction of seven soil functions and eight threats (EU Soil Strategy. The continued unsustainable use of soils is compromising the Union's domestic and international biodiversity and climate change objectives. For these reasons, the Commission adopted a Soil Thematic Strategy intending to protect soils across the EU (EU, 2006). While the Commission in May 2014 decided to withdraw the proposal for a Soil Framework Directive, the Seventh Environment Action Programme recognised that soil degradation is a serious challenge. It provides that by 2020 land is managed sustainably in the Union, soil is adequately protected, and the remediation of contaminated sites is well underway and commits the EU and its Member States to increase their efforts to reduce soil erosion and increase soil organic matter and to remediate contaminated sites. EU law does not address all the threats comprehensively and not all Member States have specific legislation on soil protection. The European Commission has launched a global cross-EU strategy to deal with all aspects of soil protection while taking into account the variety of situations in each country. Adopting the soil strategy is the first stage in the development of a proper soil policy in the European Union (European Commission, DG Environment, 2019). Once adopted by the Council and the European Parliament, the soil framework directive will have to be transposed into the national legislation of the Member States. The Commission will facilitate the exchange of information and good practice between Member States and encourage active public participation, especially on the part of regional and local governments, agriculture, industry and civil society. Through the soil strategy, the Commission is establishing a framework based on common EUwide principles and objectives to address the different facets of soil degradation. It will be an obligation for the Member States to identify where the problems occur, but they are free to decide what to do, and to what extent, in order to address these problems (European Commission, DG Environment, 2019). Mercury emissions and releases to air, water and soil in the EU are regulated by the Industrial Emissions Directive (IED) read in combination with the Water Framework Directive and with the Surface Water Directive that establishes maximum concentration levels of mercury into surface water bodies, sediment and biota.

Minamata Convention

The **Minamata Convention on Mercury** is an international treaty designed to protect human health and the environment from anthropogenic emissions and releases of mercury and mercury compounds. The convention was approved and signed on 2013 in Geneva. In May 2017, the EU, together with several Member States, ratified the Minamata Convention on Mercury, reaching the 50 parties which ratified the convention and thereby triggering its entry into force. The Convention covers the whole mercury life-cycle, from primary mining to waste disposal, and contains specific legally binding control measures, not just declarations of intent[1].


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Figure 21. **First meeting of the Conference of the Parties to the Minamata Convention on Mercury.**

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[1] http://www.mercuryconvention.org/

United State of America

Soil mercury regulation in the United States is a set of laws and regulations limiting the maximum concentrations of mercury (Hg) that is permitted in air, water, soil, food and drugs. These laws and regulations are promulgated by US Federal Agencies such as the Environmental Protection Agency (EPA) and the Food and Drug Administration (FDA), as well as a variety of State and local authorities.

National and international standards for the maximum permitted Hg concentration in soil as well as its loading rates differ among countries. For instance, the US EPA's national standards for POTW sludge disposal set the following limits for mercury:

- 57 mg/kg (maximum sludge concentration – no limit values for soil)
- 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 lands, or in landfills.

Contrary, the EU prescribes lower limits for Hg concentrations and loadings:

- Limit concentration in soil: 0,8 mg/kg
- Sewage sludge for agricultural use: 1.5 mg/kg
- Annual Hg loading rate: 0.015 kg/ha

Gaps in Hg soil monitoring programmes and policy-relevant questions

- The main issue when comparing Hg soil monitoring, either on national or international scales, is the comparability of obtained data due to different monitoring designs and data presentation. Monitoring designs vary regarding sampled soil types, land use, sampling depths, sampling (network) grid resolution, soil fraction analysed, sample digestion and analytical methods, Hg species or fraction measured, and obtained data evaluation, interpretation and presentation. Accessibility of obtained data for further scientific analysis, land management and policy is also an important aspect.
- Hg in soil exists in various chemical forms, which are difficult to identify. As a proxy for mercury reactivity, fractionation methodologies exist, but the comparability of the data among these fractions are questionable.
- Topsoil layer consists of different sublayers with different depths, depending on many factors such as type of bedrock, vegetation, climate, and land use. Topsoil sublayers also contain different size fractionated particles. Decisions on sampling depth when preparing monitoring design must be carefully considered.
- Sampling network grid size, soil type, land use, type of vegetation (i.e. forests vs agricultural) also need to be considered when preparing, analysing and interpreting the data.

- Sample preparation, digestion and analytical methods can contribute serious bias to obtained data. It is necessary to consider Hg species (e.g. total Hg and MeHg) or fraction to be analysed, as methods differ for each analysed species, and obtained data cannot be compared. Standardization of analytical methods will also need serious consideration by an international audience.
- Obtained data can be evaluated, interpreted and presented in many different ways that can influence political and management decisions. Therefore, special attention should be addressed to these questions.
- When preparing and designing a soil monitoring programme, international and national authorities must consider such questions, to ensure the comparability of the data obtained and land use management policies.

Figure 22. **New Almaden quicksilver mine in the Capitancillas range in Santa Clara County, California, United States.**

3. What are the main elements to consider for soil as a matrix to be considered in the effectiveness evaluation framework and monitoring under the Convention?

3.1 Relevance of the Matrix

Mercury in soil systems is described in the Introduction and is mostly associated with organic matter. In contaminated sites (particularly mining areas) it is mostly present as HgS. Following methylation, methylmercury does not usually build up in soils to more than about 1 % of the total mercury present, which represents an approximate equilibrium level between formation and removal. Methylation-demethylation reactions are assumed to be widespread in the environment, and each ecosystem attains a steady-state concerning individual mercury species. Dimethylmercury is considered to be unstable in soils but is assumed to be stabilized by a conjunction of factors, such as high sulphide levels, salinity, anoxic conditions and constant inputs of methane into the media (Weber et al., 1998; Horvat et al., 2005; Leermarkers et al., 2005).

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

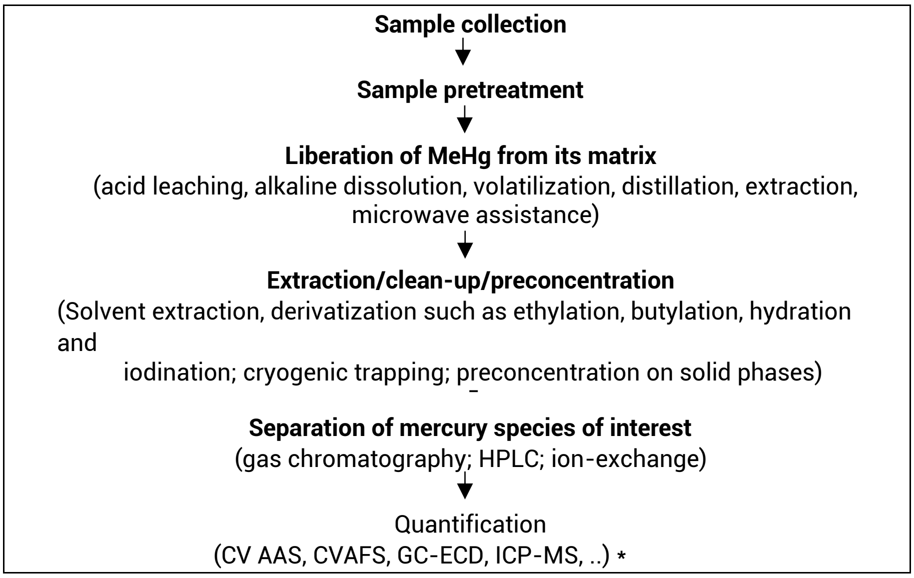
The terms "speciation" and "fractionation" are addressed by the International Union for Pure and Applied Chemistry (IUPAC) which has published guidelines (Templeton et al., 2000) or recommendations for the definition of speciation analysis:

- *"**Speciation analysis** is the analytical activity of identifying and/or measuring the quantities of one or more individual chemical species in a sample.*
- *The **chemical species** are specific forms of an element defined as to isotopic composition, electronic or oxidation state, and/or complex or molecular structure.*
- *The **speciation** of an element is the distribution of an element amongst defined chemical species in a system.*
- *In case that it is not possible to determine the concentration of the different individual chemical species that sum up the total concentration of an element in a given matrix, that means it is impossible to determine the speciation, it is a useful practice to do fractionation instead.*
- ***Fractionation** is the process of classification of an analyte or a group of analytes from a certain sample according to physical (e.g. size, solubility) or chemical (e.g. bonding, reactivity) properties."*

In terms of the regional and global relevance of mercury present in the terrestrial environment, particularly soil, the evaporation of elemental mercury is of concern and measuring the mercury flux from terrestrial environment and determination of Hg^0 in soil is of particular importance. Therefore, a special sub-chapter is dedicated to methodological challenges to measuring Hg^0 in soil and its subsequent evaporation to the atmosphere.

Mercury speciation in soils

In general, methods are classified according to the isolation technique and the detection system (Drasch et al., 2004; Sanchez Uria and Sanz Medel, 1998). Most methods for the isolation/separation of organomercury compounds are based on solvent extraction, differential reduction, difference calculations between "total" and "ionic" mercury, derivatization, or on paper- and thin-layer chromatography. Figure 23 provides a schematic of conventional approaches for the separation and detection of organomercury.



*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

Figure 23. **Steps for determination of organomercury compounds (Horvat et al., 2005)**

When speciation is required for insoluble samples (such as sediments and soils), it is difficult to estimate recovery. In such samples, recovery of spiked methylmercury is not equivalent to the methylmercury initially present. By comparing various isolation techniques for methylmercury compounds in sediment samples and soils, it has been shown that conventional methods based on acid leaching of organomercury compounds before their extraction into an organic solvent are not suitable for releasing methylmercury from sediment samples. Improved recoveries have been achieved by extracting methylmercury with nitric acid at elevated temperatures or assisted by microwave energy (Liang et al., 2004). Some protocols can lead to the formation of artefacts (methylmercury), especially in procedures where methylmercury is isolated at higher temperatures (Falter, 1999). The quality of the results should, therefore, be regularly checked by the use of appropriate reference materials, if available, or by comparison of the results from different laboratories and the use of different analytical approaches. Also, the use of ICP-MS and isotope dilution analysis (IDA) overcomes problems associated with incomplete recoveries of organomercury species, particularly in biological samples, but less with solid samples such as soils. The key stage in the IDA procedure is the equilibration of the isotopically modified spike and the sample MeHg; if this is achieved, the spike material acts as an ideal internal standard. So far, such a protocol has been successfully applied to numerous environmental and biological samples (Clough et al., 2003; Hintelmann, 1999; Falter, 1999; Snell et al., 2000).

There are also a few methods that are based on differential reduction and pre-separation of organomercury by (a) anion exchange (May et al., 1987), (b) volatilization and trapping on cysteine paper (Zelenko and Kosta, 1973) and (c) water vapour distillation (Horvat et al., 1993). Prior to detection by CV AAS, the organomercury compounds must first be destroyed by either UV-irradiation or acid digestion. In most biological samples, the organomercury concentrations usually correspond to methylmercury. In some environmental samples such as sediment, soil, and water samples, the concentrations of organic mercury (particularly if separated by anion-exchange) are much higher than those of methylmercury compounds, which is probably due to presence of unidentified organic mercury compounds.

Among organomercury species currently of interest, ethylmercury (EtHg) is a compound that requires further attention as it is still used in Thiomersal for preservations of vaccines. It is important to analyse ethylmercury in vaccines, in wastewater from waste treatment plants in industries using ethylmercury. In principle, methods developed for methylmercury can also be used for ethylmercury, except in protocols using derivatization by ethylation. In such cases propylation is recommended (Logar et al., 2004). Ethylmercury has been reported in some soils, especially in contaminates substrates (Holmes and Lean, 2006; Mao et al., 2010; Tomiyasu et al., 2017)

Mercury fractionation in soils

The biogeochemical and especially the ecotoxicological significance of Hg input is determined by its specific binding form and coupled reactivity rather than by its accumulation rate in the solid material. Consequently, these are the parameters that have to be determined in order to assess the potential for Hg transformation processes (such as methylation, reduction, demethylation), and to improve data for environmental risk assessment. Hg pyrolysis followed by AAS detection was developed to distinguish among cinnabar bound Hg, metallic Hg and matrix-bound Hg (Biester et al., 2002, Bloom et al., 2003). Alternative approaches for mercury fractionation are based on sequential extractions and leaching to provide information on the solubility and reactivity of Hg. Sequential extraction schemes developed by Bloom (Bloom et al., 2003) consists of six steps, including water-soluble, 'human stomach acid' soluble, organo-chelated, elemental Hg, mercuric sulfide and residual fraction. An additional step was incorporated into this scheme to provide information on the volatilization potential of mercury present in soil (Kocman et al., 2004). It is important to note that these schemes are based on the analytical protocols used, and slight changes may result in a different relative distribution of mercury fractions. Further harmonisation is required for comparability purpose.

Methylation/demethylation/reduction potential using tracers

In order to assess the potential for mercury transformation rates under various environmental conditions and matrices, especially in sediments and topsoils, analytical protocols using stable and radioactive isotopes of mercury have been used by different groups. As mentioned above, enriched stable isotopes in combination with ICP-MS are increasingly used (Monperrus et al., 2004). Multiple stable tracer experiments allow studies of the fate of Hg species in the environment and biological systems. This concept allows the investigation of multiple transformation processes simultaneously (Monperrus et al., 2004; Hintelmann and Ogrinc, 2003; Demuth and Heuman, 2001). The use of radioisotopes to trace different transport and transformation processes is also widespread; in the case of mercury the most frequently used radiotracer is 203Hg (t1/2 = 46 d) (Guimares et al., 1995). However, when adequate facilities are available 197Hg (t1/2 = 64.14 h) can also be employed successfully, as demonstrated in mercury methylation/de-methylation studies in soils and sediments (Guevara et al., 2004). Demethylation was studied by the use of $^{14}CH_3Hg^+$, where the amount of $^{14}CH_4$ produced indicates reductive demethylation, and $^{14}CO_2$ oxidative pathways of detoxification mechanisms (Hines et al., 2000; Oremland et al., 1991).

Methodological bias for flux measurements

Measurements of Hg^0 fluxes from terrestrial environments are primarily based on two measurement methodologies. First, dynamic flux chambers (DFC) have been used for the majority of flux measurements (85%) and are based on comparisons between inlet and outlet air Hg^0 concentration measurements in a chamber placed over a specific surface area. (Schroeder et al., 1989; Kim et al., 1995).

The second type, micrometeorological (MM) approaches, are based on measurements of vertical concentration gradients above the surface, coupled with characterizations of atmospheric turbulence (Eckley et al., 2010; Zhu et al., 2015; Gustin et al., 2000).

Direct comparisons between these two methods at individual sites highlight a potentially large influence of the employed method on Hg^0 flux measurements and each method has benefits and drawbacks related to its application. The DFC method, for example, disturbs the system under measurement (e.g. inside temperature may be quite different from the outside chamber temperature) and the limited footprint of measurements make scaling up fluxes to the ecosystem level difficult. Alternatively, with current MM technologies, background sites are often at or near detection limits, and measurements need to be time-averaged to detect fluxes.

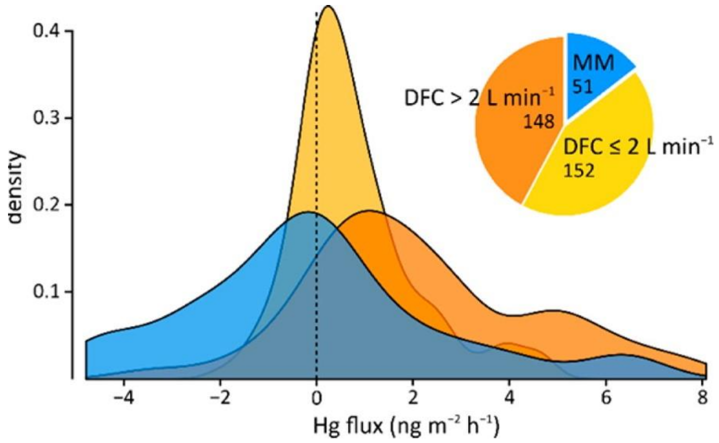


***Figure 24.* Methodological influence on Hg^0 flux measurements in background sites: distributions obtained by MM, DFC with a flushing flow rate ≤2 L min^{-1}, and DFC with a flushing flow rate >2 L/min (Agnan et al., 2016).**

3.2 Mercury and its compounds to be monitored

Soil is considered as one of the most complex matrices for all stages of the measurement procedure: *representative sampling, sample treatment, storage and analysis.*

Representative sampling requires the implementation of procedures that comply with standard protocols to assure representative sampling. The approaches that exist for collecting representative soil samples include judgmental, random, stratified random, systematic grid, systematic random, search, and transect sampling. A strategy for the sampling of soil is best discussed and described in IAEA (2004).

For speciation and fractionation, soil samples should be prepared with caution since the percentage of methylmercury in these samples is very low (e.g. <1% of total mercury), and improper handling and storage may lead to inaccurate results. Moreover, changes in pH, redox potential, and moisture may significantly influence the stability of methylmercury and or other fractions. Due to changes during sampling, conversion of mercury species may also occur (methylation, demethylation, reduction), particularly in the case of soils and sediments taken from oxygen-depleted water bodies (Horvat et al., 2005). These samples are better analysed fresh or, if long-term storage is unavoidable, samples should be frozen and kept in the dark at low temperature in an inert atmosphere.

Analytical methods

During recent years new analytical techniques have become available that have contributed significantly to the understanding of mercury chemistry in natural systems. In particular, these include ultra-sensitive and specific analytical equipment and contamination-free methodologies. These improvements eventually allow for the determination of total and major species/fractions of mercury to be made in the air, water, sediments, and biota. Analytical methods are selected depending on the nature of the sample and, in particular, the concentration levels of mercury. There are several reviews available for detailed information (Horvat, 2005, Leermarkers et al., 2005).

Most of the methods for the determination of total mercury in solid samples require preliminary digestion of the sample. They are classified as *wet (oxidizing digestion*) and *dry (combustion/pyrolysis) decomposition methods*.

In order to quantitatively release mercury from the sample, wet oxidation procedures require one or more oxidizing agents in an acidic medium. Most common reagents that have been used include HNO_3, HCl, BrCl, H_2SO_4, $HClO_4$, H_2O_2, V_2O_5, $KMnO_4$, $K_2Cr_2O_7$. Mixtures of various other reagents have also been used (Horvat, 1989). It is important to note that these reagents should be of proper quality (low in mercury). Samples are usually digested in closed, semi-closed, or sealed containers at elevated temperatures (max. 90-100°C). Particular attention should be paid to preventing mercury loss at elevated digestion temperatures. Therefore, closed or sealed digestion containers should be employed (Horvat et al., 1991). Frequently, incomplete digestion of the matrix has led to erroneous results. In the case of solid samples such as soil and sediments, it is strongly recommended to use acid digestion including hydrofluoric acid (HF) in order to completely remove Hg from the inorganic matrix (Kocman et al., 2004). Combustion or pyrolysis procedures (dry ashing) are often advised in the literature as an alternative decomposition method. They can be performed under reductive or oxidative conditions (Horvat, 2005). Usually, they are combined with a noble metal (amalgamation) or pre-concentration in an oxidizing solution or other absorbent material. The general advantage of these approaches is a rapid quantitative separation by a physicochemical process not requiring any chemical manipulation and the avoidance of chemical interferences that are connected with either the reduction or aeration step. Automated procedures are readily available from instrument producers (Lumex, Nippon, and Milestons) for total Hg determination in solid samples and the US EPA has issued a standard method (EPA Method 7473(SW846).

In practice, inconsistencies are often observed when determining total mercury using wet digestion techniques and combustion techniques. Each time total mercury data get reported the method for sample digestion has must be specified in order to avoid inconsistencies. A learning example is presented for the soil samples on the ASGM sites in Ghana where three different techniques were employed. This example demonstrates that incomplete acid digestion using *aqua regia* (HNO_3/HCl – a standard protocol in most legislative documents) provides lower and inconsistent results. The recommended methods should, therefore, either be based on complete digestion with HF, combustion and or any method that is not matrix biased.

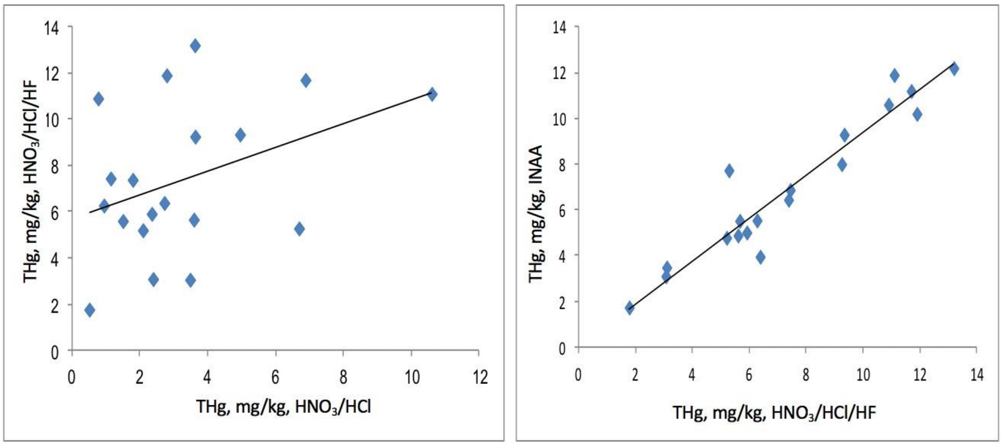


Figure 25. **A comparison of the methods for total Hg determination in soils from ASGM sites in Ghana. Left: Incomplete digestion using (aqua regia) was compared to complete digestion using a combination of HNO_3/HCl/HF. Hg was measured using CV AAS. Right: A complete digestion was compared with the k_0-Instrumental Neutron Activation as a reference method to total mercury in solid samples (Odumah Hood, 2018).**

For the determination of low-level mercury concentrations, several *instrumental analytical methods* can be used. Among the most frequently employed are the following: Cold vapour CV AAS, CV AFS, ICPMS, electrochemical methods, and neutron activation analyses (NAA). During the last two decades, CV AAS and CV AFS have replaced most of the other techniques.

In both methods, *CV AAS and CV AFS*, a reduction/aeration step is used. Apart from spectral interferences, there are several interferences dependent on the composition of the sample. These interferences may cause non-specific absorption (volatile organic compounds), interfere with the reduction (bind ionic mercury in complexes or amalgamate Hg^0), and interfere with the pre-concentration of Hg on the adsorption trap (volatile halides and hydrides). A number of these interferences can be avoided by careful optimization of the analytical procedure. The most severe interferences may occur during the determination of mercury in geological samples (Horvat et al., 1991), due to high concentrations of palladium, platinum, gold, silver, antimony, copper, zinc, or lead. By proper selection of the pH and the reducing agent ($SnCl_2$ or $NaBH_4$), these interferences can be minimised or completely removed, which is particularly important when analysing soil samples from mining and contaminated sites.

ICP-MS has become increasingly used in mercury research studies and has been demonstrated to be a powerful tool (Hintelmann and Ogrinc, 2003). The introduction of mercury in the form of gaseous species into a dry plasma significantly reduces memory effects, which was a problem for the effective use of ICP-MS initially. ICP-MS can achieve absolute detection limits of less than 100 pg of Hg. Moreover, the capability of ICP-MS to take advantage of isotope dilution methods makes this technique suitable for precise and accurate measurements. Also, multiple stable tracer experiments to study the fate of Hg species in the environment and biological systems are available for investigating multiple simultaneous transformation processes (Domuth and Heuman, 2001; Stoichev et al., 2004; Tseng et al., 1998).

Neutron Activation Analysis. Because sample preparation and handling steps are minimal before the irradiation of the sample (almost no contamination problems), NAA is often used as a reference method against which other methods are checked and compared (Jacimovic and Horvat, 2003). However, it requires costly nuclear research facilities, well-trained personnel and lengthy procedures, and it is not suitable for use in the field and routine settings.

Other instrumental techniques that are less frequently used include Atomic Emission Spectrometry, Photo-acoustic spectroscopy. X-ray fluorescence is convenient as the sample preparation is minimal, analysis is quick and non-destructive, and it is indifferent to the chemical or physical state of the analyte. However, it is less sensitive than AAS and NAA, and detection limits are in the µg range when measuring the sample directly. Recently, X-ray absorption spectroscopy (XAS), in particular, extended X-ray absorption fine structure (EXAFS) spectroscopy has been applied for mercury speciation in mercury– bearing mine wastes (Kim et al., 2000; Sakamoto et al., 2019).

Comparability and future needs

Quality assurance Quality Assurance (QA/QC)

Quality assurance refers to those procedures that ensure that analytical results are valid, traceable, reproducible, representative, complete and accurate, i.e., close to the "true value". It also includes measures developed to assess performance. It is generally accepted that mercury analysis and speciation must be done by well-trained staff who, in principle, should be involved in the measurement process from sampling to the production of final results, particularly if speciation of mercury is intended. The use of reference materials certified for mercury and its compounds play an essential role in method validation and demonstration of traceability. At present, there are many reference materials certified for total mercury concentrations in various matrices (sediment, soil, ash, water, plants, and tissues) of different origin. Unfortunately, only a few reference materials are certified for methylmercury compounds.

It is understood that these materials are not sufficient to satisfy the quality assurance requirements in many laboratories performing methylmercury analyses. Therefore, apart from the analysis of CRMs, the accuracy of analytical procedures for determination of methylmercury should be tested by participating in several intercomparison exercises involving biological, soil, and sediment and water samples. A review of these exercises has shown that the determination of total methylmercury compounds in samples such as soil, sediment, and water is complicated and method dependent.

It is generally accepted that the use of Certified Reference Materials (CRMs) represents only one aspect of the QA/QC programme and can only cover a limited number of environmental samples. For example, concentration levels of mercury in air and water are extremely low and even highly sophisticated equipment cannot guarantee accurate measurements. The reliability of the results depends on the overall procedure, including sampling, storage, and laboratory handling. One way to check the accuracy of the results is to participate in field intercomparison exercises or by comparison of the results obtained by various methods. Such exercises are now regularly organized by different international agencies, RM producers, and programmes. The results obtained are encouraging, demonstrating the comparability of the data sets being generated by diverse groups around the world.

Further development and optimisation are needed for mercury analyses and speciation/fractionation in soils and sediments and “dynamic” measurements (transformation and transport measurements). It is suggested that "method-specific" techniques should be avoided unless they provide biogeochemically important information.

In conclusion, chemical metrology in mercury analysis and speciation needs to develop further in order to achieve comparability of results. Currently available matrix CRMs are not sufficient to establish comparability of chemical measurements due to inadequate coverage of concentrations and matrices. 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 (e.g. RGM, and reactive Hg in water) need to be addressed metrologically to demonstrate comparability of results.

In the case of soil, the comparability of the data is even more complicated since, besides analytical bias, sampling strategy and data interpretation play a crucial role. In order to use soil as a matrix for global monitoring these fundamental questions and uncertainties need to be addressed and resolved.

Highlights

- ❖ 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. 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.
- ❖ 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 and species determination in soils is needed as part of the characterization and identification methodologies and particularly for the evaluation of the effectiveness of remedial actions.

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