Mercury in the terrestrial environment: a review

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Review

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Abstract

Environmental contamination by mercury is and will continue to be a serious risk for human health. Pollution of the terrestrial environment is particularly important as it is a place of human life and food production. Publication presents a review of the literature on issues related to Hg pollution of the terrestrial environment: soil and plants and their transformations. Different forms of atmospheric Hg may be deposited on surfaces by way of wet and dry processes. These forms may be sequestered within terrestrial compartments or emitted back into the atmosphere, and the relative importance of these processes is dependent on the form of Hg, the surface chemistry, and the environmental conditions. On the land surface, Hg deposition mainly occurs in the oxidized form (Hg $^{2+}$), and its transformations are associated primarily with the oxidation-reduction potential of the environment and the biological and chemical processes of methylation. The deposition of Hg on ground with low vegetation as 3–5 times lower than that in forests. The estimation of Hg emissions from soil and plants, which occur mainly in the Hg 0 form, is very difficult. Generally, the largest amounts of Hg are emitted from tropical regions, and the lowest levels are from the polar regions.

Background

Mercury is recognized as a toxic, persistent, and mobile contaminant; it does not degrade in the environment and becomes mobile because of the volatility of the element and several of its compounds. Moreover, mercury has the ability to be transported within air masses over very long distances [1].

Over the last few decades, considerable scientific knowledge has been developed on the sources and emissions of mercury, its pathways and cycling through the environment, human exposure, and impacts to the environment and human health [2]. Hg is the only element on the periodic table to have its own environmental convention, i.e., the Minamata Convention on Mercury, thus highlighting the importance of the Hg pollution issue [3].

An improved understanding of the global mercury (Hg) cycle is important for our capacity to predict how regulatory efforts to reduce current emissions to air, water and land will affect Hg concentrations in environmental compartments, biota and humans. Hg is released into the environment through human activities and via natural sources and processes, such as volcanoes and rock weathering. Following its release, Hg is transported and recycled between the major environmental compartments, i.e., air, soil and water, until it is eventually removed from the system through burial in coastal and deep ocean sediments, lake sediments, and subsurface soils [2,4].

Hg is considered to be a peculiar chemical element because it displays particularly strong chemical and biological activity as well as variability in form (liquid and gaseous). Hg compounds with very different chemical and physical properties are included in various cycles of its natural circulation [5-6]. Hg is a globally distributed pollutant due to characteristics such as low melting and boiling points, conversions between chemical forms and participation in biological cycles. As a result of anthropogenic emissions, the global atmospheric Hg deposition rate is approximately three times higher than that in preindustrial times and has increased by a factor of 2-10 in and around the most industrialized regions [7].

Hg-contaminated land environments pose a risk to global public health, with Hg being listed as one of the ‘ten leading chemicals of concern’ [8]. In 2013, the United Nations (UN) introduced the ‘Minamata Convention on Mercury’ [9], which aims for a more global effort for managing the risk presented by Hg to human health and the environment. The convention had 128 signatories, and more countries are expected to join in the future. This concerted action, if successful, will have great implications for public health for decades to come; however, there are many hurdles on the way to achieving this goal [10-11].

Our understanding of the critical processes driving global Hg cycling, particularly those that affect the large-scale exchange of Hg among major environmental compartments, has advanced substantially over the past decade. This progress has been driven by major advances in three interconnected areas: new data, new models, and new analytical tools and techniques [12].
The main task for improving our knowledge of mercury sources, fates, impacts, and emission control options was defined at the 14th ICMGP Conference in 2019 [13] as “Bridging knowledge on global mercury with environmental responsibility, human welfare and policy response”. The main four questions that require urgent answers within this subject are defined as follows:

1. How is mercury biogeochemical cycling changing on global, regional, and local scales in response to perturbations caused by major anthropogenic drivers of environmental change?
2. What is the relative risk of mercury exposure to human health and wildlife in the context of human welfare?
3. How can technological development contribute to the reduction in mercury exposure and improvement of environmental responsibility?
4. How can scientific knowledge contribute to the implementation and effectiveness evaluation of the Minamata Convention and other regulatory agreements, and what is the importance of integrating and implementing emerging and future mercury research into the policy making?

Methods

While developing this paper, the method recommended by Liberati et al. [14] was used to some extent. However, the strict use of this method was not possible due to the specifics of our publication. The problems of pollution and Hg transformation in the environment caused by significant threats to human health represent the subject of research by numerous research teams around the world. However, many publications do not meet the criterion of quality of research results. Therefore, the following criteria were used to eliminate publications:

i. Accurate descriptions of the research methods were lacking;
ii. Methods that did not guarantee the quality of the results were used;
iii. The latest publications were selected, but historical works were not omitted; and
iv. Publications from various countries and regions were cited.

Hg emission

The advances achieved over the last decade for the assessment of Hg emissions from major man-made and natural sources have contributed to improvements in the assessment of the impacts of atmospheric deposition of Hg on the terrestrial environment [15]. The assessment of Hg emissions poses serious methodological problems. In estimating these impacts, state institutions mainly focus on inventories of their sources, while international organizations apply different models and use emission factors and statistical data of industrial production and consumption of Hg-containing materials. It is particularly difficult to distinguish natural and anthropogenic emissions from re-emissions from the land and oceans [16-17]. Hg emission sources include both natural processes unfolding in the biosphere and anthropogenic sources. In 2008, the following classification was adopted in a UNEP report [18], which distinguished three emission sources:

- Current emissions from natural sources;
- Current emissions from anthropogenic sources; and
- Re-emissions from historical deposits from natural and anthropogenic sources.

Environmental archives offer an opportunity to reconstruct temporal trends in atmospheric Hg deposition at various timescales. Lake sediment, peat, ice cores, tree rings, and Hg stable isotope measurements are offering new insights into historical Hg cycling. Preindustrial Hg deposition has been studied over decadal to millennial timescales extending as far back as the Late Pleistocene. Exploitation of mercury deposits (mainly cinnabar) first began during the Mid- to Late Holocene in South America, Europe, and Asia but increased dramatically during the Colonial era (1532-1900) for silver production [19-
Artisanal gold mining is now thought responsible for over half the global stream flux of Hg, followed by the burning of coal [2,21].

Fluxes of Hg to the air occur via the volatilization of Hg\(^0\) as well as through wind entrainment of Hg bound to dust particles (often referred to as fugitive dust emissions). The relative magnitude of these two types of Hg emission sources varies depending on site-specific conditions. However, due to the long atmospheric lifetime of Hg\(^0\), these emissions mostly contribute to the global pool of Hg, whereas the fugitive dust emissions impacts are more local [22].

The update global mercury budget shows the impact of human activities on the mercury cycle and the resulting increase in mercury accumulated in soil and oceans. The updated global mercury budget in 2018 [2] is shown in the Table 1. The annual deposits were 480 tons higher than the emissions, indicating considerable enrichment in the environment. In general [23-24], Hg\(^0\) emissions from undisturbed nongeologically thermally enriched areas are <1 ng m\(^{-2}\) h\(^{-1}\), whereas fluxes from contaminated sites can be several orders of magnitude higher at >5000 ng m\(^{-2}\) h\(^{-1}\). For contaminated sites that cover large spatial areas (such as mining operations), the annual emissions from the entire surface area have been shown to range from 19 to 105 kg yr\(^{-1}\) from active industrial gold mines and 51 kg yr\(^{-1}\) from a large abandoned Hg mining area.

Table 1. The update global mercury budget [2] (Mg/yr).

| Emission:                              |       |
|----------------------------------------|-------|
| i) Natural (geogenic)                  | 500;  |
| ii) Re emission/re-mobilization (natural and legacy): |       |
| - biomass burning                      | 600   |
| - from soil and vegetation             | 1000  |
| iii) Anthropogenic                     | 2500 (2000-3000) |
| iv) Ocean, net evasion (gaseous elemental Hg) | 3400 (2900-4000) |
| total                                  | 7000  |

| Deposition:                            |       |
|----------------------------------------|-------|
| i) to land / freshwater                | 3600  |
| ii) to ocean                           | 3880  |
| total                                  | 7480  |

Various models are applied to estimate Hg emission levels into the atmosphere. However, the emission levels determined by using these models differ substantially. Travnikov et al. [25] compared the global emission levels from natural and anthropogenic sources determined by using four models [26-29]. The models differed significantly in their estimations of global total emissions, with values ranging from 4,000 Mg yr\(^{-1}\) to 9,230 Mg yr\(^{-1}\), of which natural emissions and re-emission ranged from 45% to 66% of the total emissions. A later summary of the four models [30] estimated that global anthropogenic emissions were 1,870 Mg yr\(^{-1}\), although the global natural emissions and re-emissions were already significantly different from each other at 3,995 Mg yr\(^{-1}\) to 8,600 Mg yr\(^{-1}\) [31]. The proportions between the amounts of natural emissions and anthropogenic emissions are not precisely determined. The ratios vary by authors and encompass a relatively wide range from 0.8-1.8 [32-34]. The relatively broad emission ranges presented in various studies are caused by the following factors: volatility of Hg compounds, distribution of sources, low levels of Hg
concentrations in the air, concentrations that are much lower than levels of other basic pollutants and difficulty of determination [35-36].

Annual mercury emissions in selected regions of the world in 2000-2015 are shown in Table 2. Despite the many applicable global, regional and national programs and conventions aimed at reducing Hg emissions, the global THg emissions in the years 2000-2015 increased by 1.8% [11]. Emission reductions only took place in North America and Europe without the former USSR, and the largest increase was in Central America (5.4%) and South Asia (4.0%).

| Table 2. Annual emissions of mercury by selected world region [11] (Mg/yr). |
|-----------------------------|--------|-----------------|-----------------|
|                             | 2000   | 2015            | 2000-2015 growth (%/yr) | 2010-2015 growth (%/yr) |
| USA                         | 127.7  | 42.7            | -66.6            | -10.2            |
| OECD Europe                 | 106.2  | 38.0            | -64.2            | -5.8             |
| Canada                      | 12.7   | 8.3             | -34.6            | -3.2             |
| Eastern Europe              | 49.4   | 33.6            | -32.0            | -1.3             |
| Central America             | 33.5   | 34.3            | 2.4              | 5.4              |
| South Asia                  | 120.8  | 191.6           | 58.6             | 4.6              |
| Eastern Africa              | 19.1   | 72.9            | 281.7            | 4.0              |
| East Asia                   | 532.7  | 1012.3          | 90.0             | 2.6              |
| South America               | 239.0  | 275.8           | 15.4             | 0.7              |
| Southeast Asia              | 224.6  | 187.5           | -16.5            | 2.2              |
| Global Total                | 1964.1 | 2389.8          | 21.7             | 1.8              |

Emission values [11] for the aggregated source categories and their composition are shown in Table 3. Three categories had the highest absolute value in 2015: gold ASMG (775.1 Mg/yr), coal combustion (558.3 Mg/yr) and cement production (206.3 Mg/yr). From 2010-2015, the largest increase in emissions was demonstrated by cement production (6.3%), gold production at a large scale (5.2%) and industrial metal extraction (4.6%). The reductions [37] were in the following fields: dental (-5.6%) and electrical equipment (-5.2%). This finding is consistent with the continued expansion of the global economy but is less than the growth in world GDP over the same period (5.7%/yr), suggesting continuous improvement in pollutant emissions per unit of production.

| Table 3. Annual emissions of mercury by selected source category [11] (Mg/yr). |
| Source category       | 2000  | 2015  | 2000-2015 growth (%/yr) | 2010-2015 growth (%/yr) |
|-----------------------|-------|-------|-------------------------|-------------------------|
| Gold ASMG             | 583.7 | 775.1 | 32.8                    | 1.3                     |
| Coal combustion       | 359.9 | 558.3 | 55.1                    | 0.7                     |
| Cement production     | 74.3  | 206.3 | 177.7                   | 6.3                     |
| Waste burning         | 201.9 | 165.6 | -18.0                   | 2.1                     |
| Municipal waste       | 202.6 | 140.6 | -30.6                   | 2.5                     |
| Gold, large-scale     | 82.7  | 112.1 | 35.6                    | 5.2                     |
| Zinc smelting         | 81.7  | 103.6 | 26.8                    | 1.4                     |
| Copper smelting       | 53.7  | 70.0  | 30.4                    | 3.2                     |
| Dental                | 49.4  | 16.1  | -67.4                   | -5.6                    |
| Electrical equipment  | 118.7 | 62.0  | -94.8                   | -5.2                    |
| Global Total          | 1964.1| 2389.8| 21.7                    | 1.8                     |

**Mercury emissions from natural sources**

The estimate of Hg emissions from natural sources includes contributions from primary natural sources and the re-emission processes of historically deposited Hg over land and sea surfaces. Hg emitted from volcanoes, geothermal sources and topsoil enriched in Hg pertains to primary natural sources, whereas the re-emission of previously deposited Hg on vegetation, land or water surfaces is primarily related to land use changes, biomass burning, meteorological conditions and gaseous Hg exchange mechanisms at the air-water/topsoil/snow-ice pack interfaces [15, 38].

A characteristic feature of natural Hg emissions compared to anthropogenic sources is their distributed nature and wide range of distribution. Hg from natural sources is introduced on a global scale into the atmosphere, and Hg from anthropogenic sources is deposited mainly locally and regionally; therefore, determining emission levels and applying effective control methods are difficult. Natural Hg emission processes also include re-emission of Hg previously deposited from the atmosphere in the process of wet and dry deposition from both natural and anthropogenic sources, which increases the difficulty of estimating Hg emissions from natural sources [34-35, 39].

Annual global Hg emissions from natural sources on land are estimated by various authors and cover a wide value range, e.g., total emissions of 1,600-2,500 Mg yr\(^{-1}\), including re-emissions of 790-2,000 Mg yr\(^{-1}\). According to most authors, re-emissions were higher than primary emissions [40-42].

**Volcanoes**

Volcanoes and geothermal activities are important sources of Hg pollution in terrestrial environments. Hg is emitted from volcanoes primarily as gaseous Hg\(^0\), and the Hg/SO\(_2\) ratio is generally adopted to estimate Hg emissions. The annual average of Hg released to the atmosphere without episodic strong eruptions for volcanoes and geothermal activities is ~75-112 Mg yr\(^{-1}\) of Hg, accounting for approximately < 2% of the contribution from natural sources [15, 43-45]. In volcanic plumes, Hg is present both in the gas phase as elemental Hg\(^0\) and reactive Hg\(^I\) and in the particle phase as Hg\(_0\) forms. The proportions of these species are highly variable. Hg\(^I\) and Hg\(_0\) typically amount to < 5% of THg, with Hg\(^*\) as the most abundant form [46-48]. Hg levels in volcanic ash nanoparticles (36±4 mg kg\(^{-1}\)) are dramatically higher than their bulk
concentrations (0.08 mg kg\(^{-1}\)) [49]. Many areas of geothermal activity have long been associated with elevated levels of Hg in the soil and air in places such as Hawaii, Iceland, western parts of the United States and New Zealand [43, 50].

The average annual global Hg emissions estimate from biomass burning (emissions from wildfires: forests, savannas and grasslands) for 1997-2006 was 675 (±240) Mg yr\(^{-1}\), which accounts for 8% of all current anthropogenic and natural emissions. The largest Hg emissions are from tropical and boreal Asia, followed by Africa and South America [51-52]. The important factor for Hg concentrations in forest soils is the time since stand-replacing fires have occurred, and high soil burn severity has the potential to reduce the concentrations of Hg in burned soils for tens to hundreds of years [53-54]. In a specific emission source in Nisyros Island (Greece), Hg concentrations in fumarolic gases in Nisyros Island (Greece) ranged from 10,500 to 46,300 ng/m\(^3\), while Hg concentrations in the air ranged from high background values in the Lakki Plain caldera (10-36 ng/m\(^3\)) up to 7100 ng/m\(^3\) in the fumarolic areas [55].

### Exchange of mercury between atmospheric and terrestrial ecosystems

Air-, soil- or vegetation-covered exchange fluxes are an important part of global and regional biogeochemical cycles [56]. Much of the Hg\(^{II}\) deposited in precipitation or taken up by plants is reduced to Hg\(^0\) and may be released back to the atmosphere. Recent vegetation and soil Hg studies suggested that vegetation Hg\(^0\) uptake dominates (50-80%) Hg net deposition at terrestrial sites [57-59].

The different forms of atmospheric Hg may be deposited on surfaces by way of wet and dry processes. These forms may be sequestered within terrestrial compartments or emitted back to the atmosphere, with the relative importance of these processes being dependent on the form of Hg, surface chemistry, and environmental conditions. Many models assume that the net GEM (gaseous elemental mercury) exchange with soil surfaces is zero; however, as discussed below, some components are assimilated into foliage over the growing season and accumulate in soils [59]. Smith-Downey et al. [60] estimated that evasion of Hg linked to the decomposition of soil organic carbon pools and subsequent liberation of Hg\(^{II}\) sorbed to soil organic matter is over 700 t/y, thus reflecting the large pool of Hg stored in terrestrial ecosystems globally (over 240 kgt). In total, this study estimated that 56% of Hg deposited to terrestrial ecosystems is reemitted. Similarly, Graydon et al. [61] found that 45–70% of isotopically labeled Hg\(^{II}\) wet-deposited to a forested watershed had been reemitted to the atmosphere after a year.

Litter deposition is the predominant source of Hg in soil. Forest litter horizons show significant increases in mass-dependent fractionation (MDF) during decomposition concurrent with augmented total Hg mass, and this relationship is most significant at high-elevation sites [62-63]. Measurements of mercury in litterfall and throughfall have been increasingly used to provide knowledge of mercury deposition over forest canopies. The majority of mercury in litterfall is considered to be from the stomatal uptake of Hg\(^0\) and can be used as a rough and conservative estimation of atmospheric mercury dry deposition (the portion that is retained in leaves). Mercury in throughfall also includes a portion of previously dry-deposited mercury (the portion that is washed off from the canopy). Concurrent measurements of litterfall, throughfall, and open-space wet deposition measurements can be used to estimate dry deposition on seasonal or longer time scales, whereby dry deposition is approximated as litterfall plus throughfall minus open-space wet deposition [64-65].

On the land surface, Hg deposition is mainly in the oxidized form (Hg\(^{2+}\)), and its transformations are associated primarily with the oxidation-reduction potential of the environment and with the biological and chemical processes of methylation. For soils in which oxidizing conditions predominate, the Hg\(^{2+}\) and Hg\(^{2+}\) forms dominate, and in soils with reducing conditions, Hg and sulfur compounds are mainly present. Methyl-Hg compounds are most commonly found in soils with transient conditions [5].

For GEM (Hg\(^0\)), the residence time is estimated at 6 to 18 months, while GOM (gaseous mercury in oxidized form) and TPM (total particulate mercury) are quickly removed from the air through wet and dry deposition, and their residence times are...
estimated to be hours or days at most [66-67]. Given the long time for removal from the air, GEM can be transported over large distances [16]. The particular Hg species are characterized by different dry deposition rates, which also determine their residence times. The dry residence times of the different Hg species form the following series [68]:

\[ \text{GEM } 0.19 \text{ cm} \text{s}^{-1} < \text{TPM } 2.1 \text{ cm} \text{s}^{-1} < \text{GOM } 7.6 \text{ cm} \text{s}^{-1} \]

According to Marsik et al. [69], the dry deposition rates of GOM and GEM are much higher during daytime than nighttime. As with Lindberg et al. [68], these authors explain this fact by the closure of plant stomata at night. The deposition rates also depend on the type of surface [70]. Caffrey et al. [71] determined that the deposition rates of particulate air pollutants on the ground with low vegetation were 3-5 times lower than those in forests. Deposition is also affected by the weather conditions, air humidity, insolation and atmospheric precipitation. Research by Converse et al. [72] in an uncontaminated high-elevation wetland meadow in Shenandoah National Park, Virginia (USA) showed the highest Hg deposition occurred in spring (4.8 ng m\(^{-2}\) h\(^{-1}\)), with a decrease occurring in summer (2.5 ng m\(^{-2}\) h\(^{-1}\)) to near zero flux in fall (0.3 ng m\(^{-2}\) h\(^{-1}\)), followed by an increase in winter emissions (4.1 ng m\(^{-2}\) h\(^{-1}\)). These studies also suggest that stomatal processes are not the dominant mechanism for ecosystem-level GEM exchange. Table 4 shows a summary of biome-level Hg depositions and soil Hg turnover times [60]. The concentration of Hg in soils is therefore a function of the deposition rate and carbon turnover time. High soil concentrations in desert ecosystems are driven by a combination of higher deposition and extremely slow Hg turnover. Tropical and temperate lifetimes are similar despite the faster carbon turnover in tropical systems due to the relative balance between Hg provided by wet deposition and leaf uptake.

**Table 4. Summary of Biome Level Hg Deposition and Soil Hg Turnover Times [60].**

| Biome      | Mean Hg deposition (g m\(^{-2}\)) | Mean soil Hg turnover time* (years) |
|------------|-----------------------------------|-----------------------------------|
|            | Preindustrial Present day | Preindustrial Present day |
| Tropical forest | 0.9 3.7 | 234 126 |
| Temperate forest | 0.8 2.9 | 250 151 |
| Boreal forest | 0.5 1.5 | 998 560 |
| Grassland | 1.0 3.5 | 522 269 |
| Tundra | 0.3 0.8 | 1108 702 |
| Desert | 0.5 1.4 | 2387 1748 |

*with respect to respiration.

Emissions from soils have the form of GEM and depend on many factors [73-77]:

- The properties of soils, e.g., Hg content, the contents of organic compounds, and saturation;
- The concentrations of oxidants, mainly ozone, in the air; and
- The weather conditions, e.g., solar radiation, temperature, humidity and winds.

Soil Hg fluxes are significantly lower in dark conditions than light conditions for all sites except grassland [64].

It is most difficult to estimate Hg emissions from plants, and these emissions mainly occur in the form of Hg\(^0\) [79-81]. Ericksen et al. [78] suggested the following hierarchy of environmental parameters that influence Hg flux:

soil moisture > light > air concentration > relative humidity > temperature.
Table 5 shows a summary of total Hg (THg) fluxes from terrestrial regions [82], and Table 6 shows the average fluxes (or, in some cases, the range of fluxes) for various ecosystems measured by a number of investigators.

**Table 5. Summary of mercury fluxes from terrestrial regions [82]**

| Region                                      | Evasion (average) (Mg yr\(^{-1}\)) | Ratio \(^1\) (%) |
|---------------------------------------------|-----------------------------------|-----------------|
| Forest                                      | 342                               | 7,5             |
| Tundra/Grassland/Savannah/Prairie/Chaparral | 448                               | 9,9             |
| Desert/Metalliferous/Non-vegetated Zones    | 546                               | 12,0            |
| Agricultural areas                          | 128                               | 2,8             |
| Evasion after mercury Depletion Events\(^2\) | 200                               | 4,4             |
| Total                                       | 1664                              | -               |
| Volcanoes and geothermal areas              | 90                                | -               |
| Biomass burning                             | 675                               | -               |

\(^1\) calculated over the total evasion from natural sources which sum 4532 Mg yr\(^{-1}\)

\(^2\) Friedli [42] and Mason [68] distinguish as a natural source of mercury emission to the atmospheric air of regions where there are episodes of sudden decreases in mercury concentrations in the air by deposition to the ground and then reemission. These phenomena occur mainly in the arctic regions and Antarctica, and the emission from this source is estimated at 200 Mg ye\(^{-1}\)

When analyzing the data in Table 6, the following generalizations can be made [82-83]:

1. i) The largest amounts of Hg are emitted from tropical regions (45%), followed by the temperate zones (41%), with the lowest emissions from the polar regions (8%), and emissions from volcanoes and geothermal areas account for 5%;
2. ii) Areas with vegetation can be ranked according to the size of their emissions as follows: forests > other areas (tundra, savannas, and chaparral) > agricultural areas > grassland ecosystems; and
(iii) Land areas devoid of vegetation emit more Hg than do areas with plants.

Deforestation can increase GEM emissions due to higher solar radiation and increased temperature at the soil surface [84-85].

**Table 6. Average fluxes, or in some cases the range of fluxes, for various ecosystems measured by a number of investigators.**
| Species/ecosystem                  | Flux$^1$ | References                        |
|-----------------------------------|----------|-----------------------------------|
| Ground Level Forest Floor Sweden  | 1.4-1.7  | Hanson et al. [83]                |
|                                   |          | Lindberg et al. [68]              |
| Model Estimates Hard wood forest  | Max 4    | Bash et al. [87]                  |
| Model Estimates Forest Soil       | 4        | Bash et al. [87]                  |
| Agricultural crops                | Max 11   | Bash et al. [87]                  |
| Temperate forest                  | 5.0      | Rea et al. [88]                   |
| Deforested site                   | 50       | Magarelli and Fostier [89]        |
| Desert Soils                      | 3.6-9.8  | Magarelli and Fostier [89]        |
| High Hg regions                   | Max 1500 | Gustin and Lindberg [90]          |
| Maple                             | 20       | Hanson et al. [83]                |
| Oak                               | 16.4     | Hanson et al. [83]                |
| Spruce                            | 6.1      | Hanson et al. [83]                |
| Prairie grass                     | 12.5     | Obrist et. al. [53]               |
| *Typha* sp.                       | 60       | Gustin et al. [91]                |
| Average global soil               | 1.5      | Selin et al. [92]                 |

$^1$Values have all been converted to a common flux unit of nmol m$^{-2}$ month$^{-1}$. Results from the older literature are combined in estimates given in various review papers.

The overall background soil Hg flux in the United States is estimated to be 0.9±0.2 ng/m$^2$/h [79], and in areas with significant Hg pollution, soil emissions are much larger. In the canton of Valais, Switzerland, elemental Hg (Hg$^0$) is undetectable in soil, although substantial Hg$^0$ emissions were found to occur (20-1,392 ng m$^{-2}$ h$^{-1}$) [94].

Urban areas are of particular concern with respect to the global Hg cycle due to the following [95]:

- Frequently high terrestrial Hg concentrations and the physically and chemically diverse nature of urban surface covers;
- Highly variable time series concentrations of ambient atmospheric Hg as a result of regional and local emissions; and
- Urban meteorology (i.e., heat island effect).

In the city of Tuscaloosa, Alabama (USA), Hg fluxes on bare undisturbed soil surfaces were as follows (median) [95]:

- Residential site - 4.45 ng m$^{-2}$ h$^{-1}$;
- Industrial site - 1.40 ng m$^{-2}$ h$^{-1}$;
- Commercial site - 2.14 ng m$^{-2}$ h$^{-1}$; and
- Mixed land use site - 0.87 ng m$^{-2}$ h$^{-1}$.

Areas of land devoid of vegetation emit more Hg than those with plants. The annual averaged fluxes in the subtropical forest zones in China from soil in the forests were
14.2 ng m$^{-2}$h$^{-1}$, and for open-air sites, they were 20.7 ng m$^{-2}$ h$^{-1}$ [96]. Soil Hg fluxes were significantly lower in dark conditions than in light conditions. In grassland sites, the mean soil Hg flux was 0.6±0.9 ng m$^{-2}$ h$^{-1}$ in darkness, 1.0±0.7 ng m$^{-2}$ h$^{-1}$ in light, and 0.9±0.7 ng m$^{-2}$ h$^{-1}$ overall [64].

Cropland is an important component of terrestrial ecosystems. It is estimated that 33% of natural-source atmospheric Hg comes from the emissions at cropland surfaces [97]. The emission of Hg from cropland soil greatly affects the global Hg cycle. Combinations of different crop cultivars and planting densities will result in different light transmittance under canopies, which directly affects the solar and heat radiation flux received by the soil surface below crops. In turn, this might lead to differences in the soil–air total gaseous mercury (TGM) exchange under different cropping patterns. The light transmittance under the canopy was the key control on soil–air TGM exchange fluxes. High light transmittance can enhance soil TGM emission rates and increase the magnitude of diurnal variations in soil–air TGM exchange fluxes. The estimated annual average soil–air TGM exchange flux was 5.46±21.69 ng m$^{-2}$ h$^{-1}$ in corn–wheat rotation cropland with 30 cm row spacing [98-99].

The bidirectional exchange of Hg between the atmosphere and terrestrial surfaces is better understood because of advancements in research that are primarily associated with the interpretation from Hg isotopes, and the latest estimates place land surface Hg re-emission at values lower than previously thought [100].

**Methylmercury**

High doses of organic compounds of Hg, particularly methyl-Hg, can be fatal to humans and wildlife, and even relatively low doses can seriously affect the nervous system of organisms. Hg has also been linked to harmful effects on the cardiovascular, immune and reproductive systems. Methyl-Hg passes through both the placenta and blood-brain barrier; therefore, the exposure of women of child-bearing age and of children to methylmercury is of great concern [1].

Methyl-Hg can be both biotically and abiotically produced in the environment. Methylation of Hg tends to occur in environments with low oxygen levels, low pH, Hg bioavailability, temperature, redox potential and high levels of dissolved organic compounds and in environments favored by sulfate-reducing bacteria, which are largely responsible for methylation. These conditions are found primarily in deep sea environments, coastal marine sediments, and some freshwater lakes as well as soils. These conditions are also characteristic for paddy soil [101-102]. Organic Hg is much more toxic to living organisms than inorganic Hg [4, 103-104]. The content of methyl-Hg in soils and plants is significantly lower than that of THg; however, due to its much higher toxicity, methyl-Hg is particularly dangerous for living organisms. In soils in the coniferous boreal forests of Sweden, the background level of pollution from methyl-Hg accounted for 0.35-0.59% of THg [105]. In the Idrija Hg mining area of Slovenia, a heavily polluted region, methyl-Hg accounted for 0.003% of THg, and its background presence in controls was 0.17% [106]. The content of methyl-Hg relative to THG was 1.9% in the roots of rice under background conditions and 0.55% in the leaves; in areas of Hg mining sites, the concentrations were 0.07% in the roots and 0.01% in the leaves; and in areas with artisanal Hg mining sites, the concentrations were 0.63% in the roots and 0.02% in the leaves [107]. Methyl-Hg in heavily contaminated soil in the Rhône Valley (Switzerland) accounted for < 0.8% of THg [108].

A number of factors that control microbial activity and/or the geochemical speciation of inorganic Hg$^{2+}$ govern MeHg formation in the environment [109]. Microorganisms that live in soil can transform inorganic Hg$^{(II)}$ species into Hg$^0$ by using the enzyme Hg reductase, which is found in various bacteria, such as *Pseudomonas* sp., *Staphylococcus aureus*, *Thiobacillus* and many others [110]. Increases in temperature might lead to increases in biological activity as well as higher Hg$^{2+}$ methylation rates [111].

The direct conversion of insoluble HgS species to MeHg in anaerobic soils is generally believed to be low, although this condition can change when environmental conditions favor HgS complexation [112]. The redox potential also seems to be a
key factor, as suboxic and mildly reducing conditions seem to promote high Hg$^{2+}$ methylation rates, while anoxic and strongly reducing conditions might lead to elevated sulfide concentrations that eventually prevent Hg$^{2+}$ from being available for methylation of some methymethylating bacteria, including SRB (sulphate reducing bacteria, e.g., *Desulfobacter* sp.), and some that control the availability of Hg$^{2+}$ for methylation (e.g., *Deltaproteobacteria* or *Clostridia*) [113-114].

S plays a major role in influencing Hg$^{2+}$ methylation by directly affecting the activity of some methymethylating bacteria, such as SRB, and controlling the availability of Hg$^{2+}$ for methylation [115-116].

The paddy soils in Hg mining areas have a high methylation ability and may eventually result in heavily biological effects on the local residents through the food chains, such as rice containing high methyl-Hg [117]. In the Wuchuan Hg mining areas (Guizhou, China), soil samples present THg values ranging from 0.33 to 320 mg kg$^{-1}$ and methyl-Hg values ranging from 0.69 to 20 ng g$^{-1}$. The soil grain samples contain elevated methyl-Hg concentrations ranging from 4.2 to 18 ng g$^{-1}$, while corn grain contained only 0.5-2.0 ng g$^{-1}$ [118]. Research carried out in areas with coal-fired power plants in Hunan (China) [119] shows that the soil samples, THg varied from 0.068 to 0.220 mg kg$^{-1}$ (mean value of 0.130±0.040 mg kg$^{-1}$), and methyl-Hg ranged from 0.30 to 3.5 μg kg$^{-1}$ (mean 1.6±1.0 μg kg$^{-1}$). In rice samples, the Hg(0) concentrations varied from 0.002 to 0.022 mg kg$^{-1}$ (mean 0.057 mg kg$^{-1}$), and methyl-Hg concentrations varied from 1.7 to 3.8 ng gg$^{-1}$ (mean of 2.4±0.72 ng g$^{-1}$). Meng et al. [107] showed that rice had high affinity for methyl-Hg and that the concentrations in rice seeds may be 2 to 3 orders of magnitude higher in Hg mining sites than in other local edible crop plants. Freshly deposited Hg is more likely to methylate and be incorporated in rice than stored Hg [100].

Forest fires cause a significant reduction in mercury content in soil. Burned soils in northwestern Ontario (Canada) had 82% less methyl-Hg than fresh soils [120]. Current climate change has had a significant impact on Hg transformation processes, especially in the Arctic. The very large mass of mainly natural Hg found in northern permafrost deposits, which is projected to be released with further climate warming, may profoundly affect biotic Hg levels around the Northern Hemisphere, especially because large amounts of organic carbon, which may stimulate Hg methylation rates, will be simultaneously released [121].

**Mercury in soil**

Mercury has a relatively long half-life in surface soils because of its recycling between the surface environment and atmosphere. Permanent removal of anthropogenic Hg from the biologically active part of the environment will only occur once it is buried in mineral soils [4]. Soil plays an important role in biogeochemical Hg circulation because it accumulates this element and is a source for other environmental components. Hg occurs naturally in soils from geologic sources [12] or as the result of natural events such as forest fires and volcanic eruptions [49]. The total amount worldwide of Hg accumulated in the soils of terrestrial environments is estimated at 200-300 Gg [122-124]. Smith-Downey et al. [60] suggested that organically bound Hg in preindustrial soils is 200 Gg and that a 20% increase in organically bound soil Hg (to 240 Gg) has occurred from preindustrial steady state conditions to the present day.

In the 2013 Technical Background Report for the Global Mercury Assessment [4], based on a global model and budget developed by Mason et al. [124], human activities were estimated to cumulatively increase atmospheric Hg concentrations by 300-500% over the past century. Because of the naturally high Hg amount present in soil, the average Hg increase was only 20% in surface organic soil and negligible in mineral soils. The revolatilization of "legacy Hg" (i.e., Hg from historical sources of pollution) from soil and ocean and its long residence time in those compartments contribute to maintaining atmospheric Hg concentrations and deposition rates at higher levels than those supported by current primary emissions [125]. Recent estimates of the anthropogenic and natural Hg contents in global soils (organic layers) (data in kilotons) included 182 natural and 89 anthropogenic sources based on Amos et al. [126] and 130 natural and 20 anthropogenic sources according to the AMAP/UN Environment [4].
All results for Hg soil content, which are presented in the next part of this publication, pertain to the topsoil layer. Generally, the average background concentration of Hg in soil ranges from 0.03 to 0.1 mg kg\(^{-1}\), with an average value of 0.06 mg kg\(^{-1}\), whereas Hg-contaminated sites often have soil concentrations that are 2- to 4-orders of magnitude higher [127-128]. Kabata Pendias and Pendias [5] defined a narrower range of 0.05-0.3 mg kg\(^{-1}\), although some volcanic and organic soils, especially in Canada, may contain higher values, and in the vicinity of industrial emission sources, the values can be extremely high. Obrist et al. [129] showed that a dataset with more than 1,900 randomly selected sampling points across the western USA indicated median Hg concentrations of 0.019 mg kg\(^{-1}\) and an average value of 24 mg kg\(^{-1}\), with only 1% of soil samples exceeding background values (e.g., >0.10 mg kg\(^{-1}\)).

The LUCAS Topsoil Survey of the European Union organization collected over 23,000 topsoil samples (upper 20 cm) from land in all European Union countries (28) except for Croatia [130]. The average for European topsoil Hg concentrations was 0.04 mg kg\(^{-1}\), with a range of 0-159 mg kg\(^{-1}\). Studies have identified highly polluted, isolated sites, and the larger historical and recent industrial and Hg mining areas show elevated concentrations of Hg. Historically, mining for gold and Hg led to high Hg concentrations in these mining areas, which may explain the high Hg concentrations in some samples from Central Italy, Northwest England and Eastern Slovakia. Moreover, the natural/background Hg level was 0.08 mg/kg in Brazil [131], 0.05 mg/kg in India [132], 0.23 mg/kg in New Zealand [133], 0.11 mg/kg in the Norwegian Arctic [134] and 0.4 mg/kg in Paris [136]. Most soil Hg was found as soil matrix-bound divalent Hg (Hg\(^{II}\)), whereas elemental Hg (Hg\(^0\)) was undetectable in soils [94,108].

Table 7 presents examples of the concentrations of Hg in the soils in the vicinity of industrial emission sources according to different authors, The highest Hg contents were found in soils near Hg mines: Almaden in Spain, with 2,000 years of mining and ore processing (<8,889 mg kg\(^{-1}\)) [142]; Idrija in Slovenia, with 500 years of mining activity (<2,759 mg kg\(^{-1}\)) [106, 139]; and in Alaska (5,326 mg kg\(^{-1}\)) [136]. Chlor-alkali plants are also an important source of environmental Hg pollution. Bernaus et al. [155] estimated that Hg levels in the soil around a chlor-alkali plant in the Netherlands were as high as 1,150 mg kg\(^{-1}\).

According to Richardson and Moore [170], in the urban environment, the diversity of Hg content in soils is relatively high because of the diversity of land functions in towns. Urban soils were found to accumulate higher concentrations and pools of Hg than their rural montane counterparts across New York and southern New England, which highlights the importance of soils in urban systems for sequestering Hg and preventing its movement towards riparian and aquatic ecosystems, where it can bioaccumulate. Moreover, soil Hg concentrations were poorly correlated with pH, loss-on-ignition, and clay content, Instead, proximity to local industrial and agricultural sources proved a significant influence on Hg accumulation.

The lowest median results were determined for soils in Changchun, China, at 0.018 mg kg\(^{-1}\), with a range of 0.012-0.036 mg kg\(^{-1}\) [171] and in Oslo, Norway (0.06 mg kg\(^{-1}\), with a range of 0.01-2.3 mg kg\(^{-1}\)) [172], while the highest concentrations were in Palermo, Italy (median value of 1.85 mg kg\(^{-1}\), with a range of 0.004-2.61 mg kg\(^{-1}\)) [173], and Glasgow, Scotland (1.2 mg kg\(^{-1}\), with a range of 0.312-5.2 mg kg\(^{-1}\)) [174]. Of note is the reduction of 270% (median from 0.68 mg kg\(^{-1}\) to 0.37) in Hg pollution from 1987-2009 for soils from Beijing, China [175].

In agricultural soils, pollution by Hg was relatively low, as indicated by the low median and average values at usually below 0.1 mg kg\(^{-1}\) (e.g., Scandinavia – Ottesen et al. [176]; Poland – Loska et al. [177]; Iran – Ahmadi et al. [178]). However, the ranges of the results were relatively wide, and the maximum values often exceeded 1 mg kg\(^{-1}\), which may indicate a threat to food production due to the need to protect human health in some areas with higher Hg soil levels. In Europe, pastures were slightly more polluted with Hg than plowed fields [177]. Soils in forest environments contained low levels of Hg. Average and median values did not exceed 1 mg kg\(^{-1}\), although compared with agricultural soils, the maximum values were also lower than 1 mg kg\(^{-1}\). Mineral forest soils contained less Hg than organic ones (USA – Woodruff and Cannon, [54] Czech Republic – Navrátil et al. [179]; Sweden – Åkerblom et al. [180]. According to Obrist et al. [129], soil Hg concentrations significantly differed among land covers following the order:
Concentrations in forests were an average of 2.5 times higher than those in barren locations.

The global distributions of soil Hg storage and emissions for both preindustrial and present-day simulations in different biomes are shown in Table 4 [60]. The relatively low soil Hg concentrations in boreal and arctic ecosystems are driven by extremely low deposition. The high soil concentrations in desert ecosystems are driven by a combination of higher deposition and extremely slow Hg turnover. The concentration of Hg in soils is therefore a function of the deposition rate and carbon turnover time.

Physical and chemical properties of the soil affect the Hg cycle in the environment. The soil aggregate size fractions have significant effects on the Hg content in soil. The concentrations of Hg and other heavy metals in soils and sediments generally tend to increase with decreasing grain size, which is due to the propensity of metals to bind with finer particles [181]. Generally, higher values of Hg in soil are found in the fraction at <63 μm [182]. In the Amazonian areas without anthropogenic sources, the fine fraction (< 53 μm) of podzolized soils had higher Hg contents than clayey soils [183]. In a temperate forest podzol, Hg mean values increased as the aggregate sizes decrease, as follows:

\[
\text{clay (170 ng g}^{-1}) > \text{fine silt (130 ng g}^{-1}) > \text{coarse silt (80 ng g}^{-1}) > \text{fine sand (32 ng g}^{-1}) > \text{coarse sand (14 ng g}^{-1})
\]

Total Hg enrichment in clay-sized aggregates were 2 to 11 times higher than the values shown by the bulk soil (< 2 mm) [184]. In a heavily polluted area near the Wanshan Hg mine (China), the fine soil aggregate size fractions < 231 μm showed higher total Hg concentrations and higher soil organic matter content than did the larger aggregate size fractions (231 to 2,000 μm) [185].

Humic acid influences Hg transport and transformation in soil-plant systems, especially for soils having low clay content. Humic acid reduces the amount of available Hg in soil and prevents Hg from being transported into plants or leached from the soil. Leaching can result in Hg leaking into natural water systems under normal environmental conditions. In practice, humic acid can be used to control Hg transportation into food chains from soil heavily polluted by Hg [186].

The chemical and mineralogical properties of soil affect oxidation and retention of atmospheric Hg. Abiotic Hg oxidation occurs because organic matter has -SH groups, which have a high affinity for Hg ions, and Hg oxidation is favored in the presence of compounds with high affinities for the Hg ion [131]. A microbial contribution to Hg oxidation was first proposed by Smith et al. [187], who demonstrated that typical soil bacteria (Bacillus and Streptomyces) can oxidize elemental Hg to Hg²⁺ through enzymatic paths. Recent studies have shown that Hg can also be oxidized by anaerobic bacteria [188-189]. The soil microbial community is very sensitive to Hg concentrations, and this sensitivity is influenced not only by soil properties but also by the plant species growing in the soil. A level of 0.36 mg kg⁻¹ of Hg in soils is proposed to be a critical concentration above which plant and soil organisms will be affected [131].

**Mercury in plants**

Vegetation affects environmental factors at the ground surface by reducing solar radiation, temperature, and wind velocity and serves as a surface for Hg uptake [85]. Many studies have recognized the essential role of terrestrial plants in the biogeochemical cycling of Hg (e.g., Gustin et al. [190]; Fantozzi et al. [191]; Mazur et al. [192]).

Approximately 80% of total Hg accumulated in the aboveground biomass is found in the leaves, and approximately 1% of that Hg is methylated. The concentrations of Hg in aspen tissue grown in high-Hg soil increases in the following order [93]:

\[
\text{stems < branches < petioles < roots < leaves}
\]
Research conducted by Leonard et al. [193] in Nevada (USA) in an area with high levels of Hg contamination revealed that for the plant species *Lepidium latifolium*, 70% of the Hg taken up by the roots during the growing season was emitted to the atmosphere.

The main source of Hg in leaves comes from air pollution with Hg\(^0\) and not from soil contamination [190, 194-195]. The studies by Fleck et al. [196] of *Pinus resinosa* have shown that neither woody tissue Hg nor any amount of Hg in the soil or forest floor were closely related to foliar levels, while for some relationships, the opposite was true. The authors interpret these data as indicating that Hg in plant tissues is derived directly from the atmosphere and not from the soil. It is estimated that in highly contaminated soils, generally less than 2% of the Hg present is available for plants [143]. Total leaf concentrations of Hg varied among species and were most closely correlated with the number of stomates per sample, thus supporting the hypothesis that stomatal uptake of atmospheric Hg (most likely Hg\(^0\)) is a potential uptake pathway [197]. Research by Arnold et al. [198] also indicated the importance of the nonstomatal pathway for the uptake of total gaseous Hg (TGM).

Plants growing beyond the influence of high Hg emissions contained less than 100 ng g\(^{-1}\) THg. Plants growing in the vicinity of factories are large emitters of Hg, such as those around Hg mining sites (e.g., Moreno-Imenez et al. [199]; Qian et al. [200]) and chlor-alkali mining sites [201]. Au mining sites [202-203] may also contain extremely high Hg contents. Mushrooms have been identified as organisms that accumulate more Hg than other plants [204]. A synthesis of published vegetation Hg data from the western United States showed that aboveground biomass concentrations followed the order [129]:

leaves (26 μg kg\(^{-1}\)) ~ branches (26 μg kg\(^{-1}\)) > bark (16 μg kg\(^{-1}\)) > bole wood (1 μg kg\(^{-1}\))

Hg concentrations in leaves were monitored from the emergence to senescence and showed a strong positive correlation with leaf age [195, 197, 205].

**Toxic effects on plants**

Hg does not have any beneficial effects on organisms and is thus regarded as the “main threat” since it is very harmful to both plants and animals; pollutes the air, water and soil; and is toxic [206]. Mercury has toxic effects on plants, even at low concentrations, and leads to growth retardation [207] and many other adverse effects [208].

Hg in plants is strongly bound to sulphydryl/thiol groups of proteins and forms SHgS. Hg toxicity in plants occurs via its binding to SH groups of proteins, displacement of essential elements and disruption of the protein structure [209]. This biochemical property probably determines the toxic effects on plants [5, 210-211]. Studies of the toxic effects of Hg on soil organisms and native plants in fields are limited. The effects of Hg are usually examined in sterile and much-simplified laboratory conditions, which may differ from field conditions to varying degrees [212].

The field study of Moreno-Jiménez et al. [199] was conducted in the mining district of Almadén (Spain), which is a cinnabar (HgS) enriched zone, from which one-third of the total Hg produced worldwide is extracted. Mining activity began more than 2,000 years ago, and no other region in the world has been influenced by Hg for such a long period. The region is considered to be one of the regions most polluted by Hg in the world. Hg concentrations in the field plants *Rumex induratus* and *Marrubium vulgare* grown in these soils can be considered phytotoxic, although no symptoms of Hg toxicity have been observed in any of the studied plant species. In most contaminated soils and mine tailings, Hg is not readily available for plant uptake [213].

The absorption of organic and inorganic Hg from soil by plants is low, and there is a barrier to Hg translocation from plant roots to tops. Thus, large increases in soil Hg levels produce only modest increases in plant Hg levels by direct uptake from soil [212]. In terrestrial vegetation, Hg in the aboveground biomass originates primarily from the atmosphere, whereas Hg in the roots comes from the soil [67,214]. The research conducted by Lomonte et al. [215] suggested the existence of Hg stress-
activated defense mechanisms in plants and hypothesized that these mechanisms were likely the reason for the increased production of sulfur compounds in the tested plant species, which stimulated their growth. Hg has very limited solubility in soil, low availability for plant uptake and no known biological function, which may explain why Hg-hyperaccumulating plants have not yet been identified, meaning that a method for Hg phytoremediation in soils contaminated with Hg has not yet been developed [215]. However, studies suggesting the use of transgenic plants for phytoremediation have been published recently [216-217].

The significant toxic effect of Hg on plants is the generation of reactive oxygen species (ROS) [218], e.g., superoxide anion radicals, H$_2$O$_2$, and hydroxyl radicals (OH) [219-220]. Detoxification mechanisms to combat Hg-induced oxidative stress include enzymatic antioxidants and some nonenzymatic antioxidants, such as the following: glutathione [221], phytochelatin [222], salicylic acids [223], ascorbic acid [224], selenium, [225], proline [226] and tocopherols [227]. This process is correlated with the disruption of biomembrane lipids and cellular metabolism, resulting in plant injury [228].

Increasing levels of mercury species in the soil exert a wide range of adverse effects on the growth and metabolism of plants [206, 229-230], such as reduced photosynthesis, transpiration, water uptake, chlorophyll synthesis [228, 231-232] and increased lipid peroxidation (Cho and Park [219]). A high Hg content in plants affects the activity of most enzymes. The total activity of stress indicators such as superoxide dismutase (SOD), peroxidase (POD) and ascorbate peroxides (APX) increased after Hg treatment, but the vast majority of enzymes were inhibited at higher concentrations (e.g., Manikandan et al. [233]; Mahbub et al. [234]; Zhou et al. [235]).

**Conclusions And Commentary**

- Atmospheric contamination by mercury continues to be one of the most important environmental problems in the modern world. The following general conclusions can be drawn from a review of the literature, with authors’ critical commentary:
  - Models differ significantly in their estimations of global total Hg emissions from 4,000 Mg yr$^{-1}$ to 9,230 Mg yr$^{-1}$, of which natural emissions and re-emission ranged from 45% to 66%.
  - Many factors contribute to such large differences in assessing the level of global emissions: (i) methodological difficulties in assessing re-emission from heavily polluted areas under the influence of contemporary and historical emissions and areas with background pollution (ii) the transformation of various forms of Hg depends on many difficult to evaluate processes, which makes estimating emissions difficult, (iii) occurrence of unusual phenomena associated with the transformation of various Hg forms e.g. mercury depletion events (MDEs), consisting of episodes of sudden drops in total gaseous mercury concentrations and the air in the Antarctic and Arctic.
  - Despite the many applicable global, regional and national programs and conventions aimed at reducing Hg emissions, global total Hg emissions in the years 2000-2015 increased by 1.8%. In many countries, including those with high national income, there is a lack of understanding by societies and politicians about the need to reduce emissions.
  - The proportions between the amounts of natural emissions and anthropogenic emissions are not precisely determined. This ratio, depending on the authors, has been estimated to be over a relatively wide range of 0.8-1.8.
  - Annual global Hg emissions from natural sources on land are estimated by various authors to be over a wide range, with total emissions of 1,600-2,500 Mg yr$^{-1}$, including re-emission of 790-2,000 Mg yr$^{-1}$. The low share of Hg taken by plants from soil is beneficial from the point of view of protecting food against contamination, but also limits the possibility of using plants in phytoremediation of contaminated soils.
  - On the land surface, Hg deposition is mainly in the oxidized form (Hg$^{2+}$), and its transformations are associated primarily with the oxidation-reduction potential of the environment and with the biological and chemical processes of methylation.
  - The main source of Hg in plant leaves comes from air pollution with Hg$^0$ and not from soil contamination. It is very difficult to estimate Hg emissions from plants, which mainly occur in the form of Hg$^0$. 
• Methyl-Hg can be produced both biotically and abiotically in the environment. Methylation of Hg tends to occur in environments with low oxygen levels, low pH, Hg bioavailability, temperature, redox potential and high levels of dissolved organic compounds; environments favored by sulfate-reducing bacteria are largely responsible for the methylation.

• Rice growing conditions mean that the Hg methylation process is extremely intensive. Consequently, rice may contain significantly more Hg than other crops. This is particularly dangerous because rice in many regions of the world is the basis for feeding the population.

• Hg has very limited solubility in soil, low availability for plant uptake and does not have any known biological function. This may explain why Hg-hyperaccumulating plants have not yet been identified, meaning that there is a lack of effective phytoremediation methods for soil contaminated with Hg. This may explain why Hg hyperaccumulator plants have not found practical use in phytoremediation of contaminated soils. It seems that this may be more applicable in wetland environments. The possibility of using contaminated soil in phytoremediation by transgenic plants is promising and it’s the future.

• A huge number of scientific publications have been devoted to the problem of Hg environmental pollution. However, these studies are facing many difficulties: (i) analytical difficulties caused by very low Hg contents in all elements of the environment, (ii) the need to determine a specific form of Hg, giving the result i total Hg is in most cases insufficient, (iii) the form in which Hg occurs depends on many environmental factors, they must be accurately recognized and described. Unfortunately, many scientific publications do not meet these requirements.

### Abbreviations

Hg – mercury

UN - United Nations

UNEP - United Nations Environment Programme

GEM - gaseous elemental mercury Hg⁰

GOM - gaseous mercury in oxidized form

TPM - total particulate mercury

TGM - total gaseous Hg

ROS - reactive oxygen species

OH - hydroxyl radicals

SOD - superoxide dismutase

POD - peroxidase

APX - ascorbate peroxides

### Declarations

Ethics approval and consent to participate

Not applicable.

Consent for publication
Not applicable.

Availability of data and materials
Not applicable; presented information is based on previously published data only.

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WD has been responsible for the concept of the manuscript and drafted the manuscript. BG and AH B-D helped to further elaborate the manuscript. All authors improved the final manuscript.

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