Contribution of contaminated sites to the global mercury budget

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ABSTRACT

Global mercury emission inventories include anthropogenic emissions, contributing via current use or presence of mercury in a variety of products and processes, as well as natural source emissions. These inventories neglect the contribution of areas contaminated with mercury from historical accumulation, which surround mines or production plants associated with mercury production or use. Although recent studies have shown that releases of mercury from these historical sites can be significant, a database of the global distribution of mercury contaminated sites does not exist, nor are there means of scaling up such releases to estimate fluxes on a regional and global basis. Therefore, here we estimated for the first time the contribution of mercury releases from contaminated sites to the global mercury budget. A geo-referenced database was built, comprising over 3000 mercury contaminated sites associated with mercury mining, precious metal processing, non-ferrous metal production and various polluted industrial sites. In the assessment, mercury releases from these sites to both the atmosphere as well as the hydrosphere were considered based on data available for selected case studies, their number, the reported extent of contamination and geographical location. Annual average global emissions of mercury from identified contaminated sites amount to 198 (137–260) $Mg\,yr^{-1}$. Of that, 82 (70–95) $Mg\,yr^{-1}$ contribute to atmospheric releases, while 116 (67–165) $Mg\,yr^{-1}$ is estimated to be transported away from these sites by hydrological processes. Although these estimates are associated with large uncertainties, our current understanding of mercury releases from contaminated sites indicates that these releases can also be of paramount importance on the global perspective. This is especially important as it is known that these sites represent a long-term source of releases if not managed properly. Therefore, the information presented here is needed by governments and NGO's in order to re-focus resources in making decisions regarding mitigation and remediation strategies on a global level.

1. Introduction

In the last decade, considerable progress has been made in better understanding the sources, transport routes and behaviour of mercury in the global environment. Much effort including modelling was made to assess global mercury releases from a multitude of anthropogenic and natural sources (Pirrone et al., 2001; Hedgecock et al., 2006; Pacyna et al., 2006; Bullock and Jaegle, 2009; Dastoor and Davignon, 2009; Friedli et al., 2009; Jaegle et al., 2009; Jung et al., 2009; Seigneur et al., 2009; Travnikov and Ilyin, 2009). The most up-to-date assessments on the global scale showed that the contribution from anthropogenic processes in 2005 ranges between 1926 and 2320 $Mg\,yr^{-1}$ (Pacyna et al., 2010; Pirrone et al., 2010), whereas emissions from natural sources may represent the major contribution (up to 5200 $Mg\,yr^{-1}$) to the global atmospheric mercury budget (Pirrone et al., 2010). However, in these assessments,

anthropogenic mercury releases to the atmosphere associated with current human activities are primarily covered, while the contribution of surrounding contaminated areas is usually not taken into account or neglected. Worldwide, in the framework of the United Nation Environment Programme (UNEP), global mercury strategies have been proposed. The UNEP Mercury Programme is guided by several priorities, of which the remediation of existing contaminated sites affecting public and environmental health is one. In reviewing the existing literature and reports on the analysis of information on the extent of contaminated sites, it was realized that environmentally sound mitigation options and their associated costs should be investigated also for contaminated sites contributing to global releases (UNEP, 2009). Despite important gaps in knowledge have been filled in recent years, many unknowns still exist when considering mercury contaminated sites from a global point of view. Therefore, this paper attempts to summarize for the first time the contribution of mercury released from contaminated sites to the global mercury budget and in this way assess their relative importance. In this assessment, two major transport pathways are considered: (i) re-emissions of mercury from these sites to the

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atmosphere, and (ii) remobilisation of mercury to local river systems by hydrological processes as a result of leaching and erosion of mercury contaminated surfaces, and its consequent transport to aquatic systems.

2. Methodology of release estimates

Based on the review of available published literature, including government reports and work done by NGO's, a georeferenced database of global distribution of mercury contaminated sites was built. Among different sources and uses of mercury resulting in the occurrences of mercury contaminated sites, mercury mining, precious metal processing, non-ferrous metal production and various polluted industrial and urban sites were recognized as the most important categories. The chlor-alkali industry is regarded as a separate source category in this inventory.

For the purpose of estimation of mercury released, a contaminated site was defined as a site with elevated mercury content relative to local background. These sites can be a result of either active or historical anthropogenic disturbances associated with the use or presence of mercury in various products and industrial processes. Two types of sources associated with individual contaminated site were considered. Namely, depending on how mercury was released into the environment, contaminated sites can comprise point and/or diffuse sources (Hinton and Veiga, 2001). Here, various mining and industrial wastes were considered as point sources. These sources are relatively small in size (100 s of square meters) but contain extremely high mercury concentrations relative to the local background levels. On the other hand, diffuse sources can be spread over extensive areas (10 s of square kilometres) as a result of mercury initially emitted from various sources and subsequently deposited in the surroundings. In the latter case, the level of contamination is lower, however it affects the ecosystems at a regional scale (Billaud et al., 2004).

Mercury releases to both the atmosphere and the hydrosphere associated with contaminated sites were estimated following the criteria and assumptions made and discussed in Section 5. While emissions to the atmosphere were estimated for point and diffuse sources separately for most of the contaminated sites categories, only a rather rough estimate of mercury releases to hydrosphere from selected categories is given due to the limited data available, including accumulation in coastal environments. Moreover, it should be noted that in the inventory presented here, only re-emissions and remobilisation of mercury from these sites are covered, while direct current emissions to atmosphere from industrial facilities and releases of mercury with industrial water streams are not included. As all the estimates presented here are associated with large uncertainties, the Monte Carlo technique was used for the uncertainty assessment.

3. Inventory of contaminated sites by source category

3.1. Mercury mining and smelting

This category covers contaminated sites that occurred due to past and present primary mercury mining and smelting. Mercury was mined in mercury deposits globally distributed in several mercury mineral belts and areas of altered native rock that contain elevated concentrations of mercury (Rytuba, 2003). Globally, a total production of close to one million Mg of metallic mercury is reported over the last 500 years (Hylander and Meili, 2003). Based on the global mineral resources data system (MRDS) (USGS, 2005) with the addition of known large mercury mining locations in China (Feng and Qiu, 2008) and Slovenia that are missing in the MRDS database, we identified globally 953 production sites where mercury ore was mined and/or processed (Fig. 1a). Of those, 24 sites were categorised as large (including those in China and Slovenia), 46 as medium, and 601 as small, while for the rest their extent is unknown. Globally, three-fourths of the mercury production has come from five mercury mineral belts (Rytuba, 2003) (Fig. 1a): Almaden, Idrija, Amiata, Huancavelica, and the California Coast Range, which contains the New Almaden and New Idria deposits.
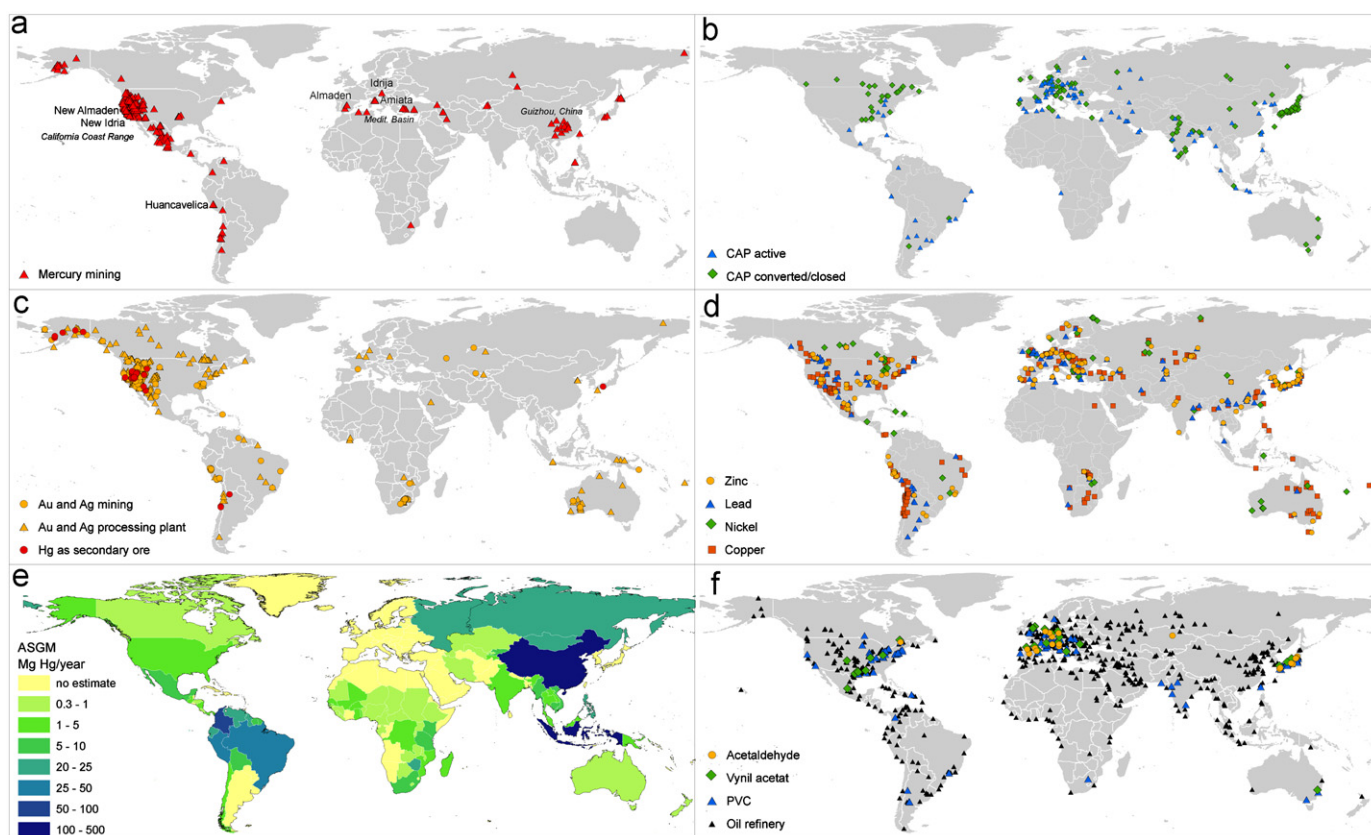
3.2. Chlor-alkali industry

This category covers contaminated sites that occur around chlor-alkali plants (CAPs) where mercury is/was used in the process. In the last decades other cleaner and more energy efficient approaches that do not use mercury have been adopted. However, there are many companies worldwide that still use the old technology, even though it creates large quantities of mercury wastes with associated disposal and clean-up problems (Mahan and Savitz, 2007). Here, we consider both active and converted (or decommissioned) mercury-cell chlor-alkali plants as contaminated sites. Altogether, based on the most recent available information (Mahan and Savitz, 2007; UNEP, 2011) we identified 101 active facilities with industrial mercury cell chlorine capacity and 155 facilities that were either closed or shifted to mercury free technology (Fig. 1b). Most of these facilities are located in Europe where 32% of the chlorine and alkali production is still done with mercury-cells (Euro Chlor, 2011), followed by India, Japan, Canada and USA.

3.3. Precious metal processing: Large scale

Within this category mercury contaminated sites associated with large scale precious metal processing (gold and silver) are considered. Due to the co-occurrence of mercury in many gold and silver ores, mercury is released to the environment during ore processing (Pirrone et al., 1998). Nowadays, precious ore roasting is one of the largest sources of by-product mercury (Jones and Miller, 2005). Countries with intensive large industrial scale precious metal mining operations include South Africa, Australia, the United States, China, Peru and Russia (UNEP, 2008). On the other hand, mercury has been intentionally used in gold and silver mining since Roman times and especially in both Americas during the last 500 years (Lacerda, 1997). Therefore, mercury historically released to the biosphere through these activities still participates in the global mercury cycle through remobilization from abandoned tailings and other contaminated areas (Lacerda, 1997). Based on the dataset on mineral resources obtained from the U.S. Geological Survey (USGS, 2005), we identified 619 locations where gold and 145 locations where silver are/were processed in large scale mining activities. In Fig. 1c, these locations are shown, indicating separately sites of mining activities, ore processing plants, as well as sites where mercury occurs as secondary ore.

3.4. Artisanal and small-scale gold mining

This category covers mercury contaminated sites which are the result of the present use of mercury in artisanal and small-scale gold mining (ASGM). A comprehensive summary of ASGM activities in 70 countries worldwide is provided by Telmer and Veiga (2009). Information regarding this contaminated site category was drawn largely from this source. According to Telmer and Veiga (2009), ASGM activities where mercury is used in amalgamation process are taking place mostly in developing countries and countries with economies in transition (South America, especially

Fig. 1. Global distribution of contaminated sites: primary mercury mining (a), chlor-alkali plants (b), large-scale precious metal mining (c), non-ferrous metals processing (d), ASGM (adopted from Telmer and Veiga (2009)) (e) and other industrial sites (locations of oil refineries based on the Oil and Gas Journal 2006 Worldwide Refining Survey available at http://bbs.keyhole.com/ubb/showthreaded.php/Cat/0/Number/1197575/page/) (f).

the Amazon, China, Southeast Asia and some African countries) and very often miners are unaware of the health risk connected to these activities. As ASGM activities are conducted at hundreds of small sites, they cannot be individually identified. Therefore, in Fig. 1e mercury releases by country in ASGM is shown (Telmer and Veiga, 2009).

3.5. Non-ferrous metal production

In this category contaminated mercury sites resulting from industrial-scale non-ferrous ore processing are included. Contamination occurs because these ores often contain significant amounts of mercury and because thermal methods are used to process them. Within this category we include locations where zinc, copper, lead and nickel ores are processed. Based on the USGS mineral resources dataset (USGS, 2005), we identified 137 zinc, 254 copper, 132 lead and 54 nickel processing plants. These locations are distributed globally, with most of them concentrated in North America and Europe, followed by Asia (especially China and Japan) and South America (Fig. 1d).

3.6. Other industrial sites

In addition to the above categories, there are many other industrial and other human activities where mercury is intentionally or unintentionally used or present in various processes and products, and can result in occurrence of contaminated sites. Use of mercury as a catalyst in production of acetaldehyde, vinyl chloride and vinyl acetate is one such example. Petroleum and natural gas production and processing are also known to release mercury to the environment, primarily via solid waste streams

(Wilhelm, 2001). Moreover, many mercury containing products (e.g., lamps, batteries, thermometers etc.) are disposed to landfills from which mercury is emitted to the atmosphere and leached to local aquatic systems, respectively. In order to give an idea about the global extent of these activities, some of these locations for which information was available are shown in Fig. 1f.

4. Extent of contamination

For each of the above categories point and diffuse source emissions were considered in the assessment. Information available in the literature on the accumulated historic and present releases of mercury from different source categories is given in the following sections and summarised in Table 1.

Primary mercury mining: The extent and magnitude of contamination at a particular mercury mine site depends largely on the amount of mercury that is/was produced at that site. During the operational phase of the mine, especially due to the ore roasting procedures, mercury release to air is the dominant pathway of mercury into the environment. Based on measurements at Almaden, up to 10 Mg of mercury per year was lost to the atmosphere during roasting operations at a production rate of up to 1500 Mg of mercury per year (Ferrara et al., 1998a). Atmospheric emissions of the same order of magnitude were reported for China by Wu et al. (2006). According to the official data of the Idrija mine, the second largest mercury mine in the world, during the operating period of the mine (since 1490) 107,500 Mg of commercial mercury were produced, while an estimated 45,500 Mg of mercury were emitted into the environment (Dizdarevič, 2001). Based on the historical and global mercury primary production data

Table 1
Accumulated historic and present releases of mercury from different source categories.

CS category	Historical/present releases	References	Remarks
Primary Hg mining	20 Mg yr^{-1}	Hylander and Meili (2003)	Losses to air; 10,000 Mg along 500 years
	10 Mg yr^{-1}	Ferrara et al. (1998a)	Almaden, Spain; losses to air
	10–40 Mg yr^{-1}	Wu et al. (2006)	China; losses to air (1995–2003)
	91 Mg yr^{-1}	Dizdarevič (2001)	Idrija, Slovenia; losses to air, soil and water; 45,500 Mg along 500 years
Chlor-alkali industry	163 Mg yr^{-1}	Pirrone et al. (2010)	Globally; losses to air
	144 Mg yr^{-1}	Concorde East-West (2006)	Europe; losses to products, air and water
	1400–2700 Mg	Qi et al. (2000)	China; losses to air, soil and water since 50s
	2000 Mg	Trip and Thorleifson (1998)	Canada; losses to air and water from 16 CAPs (1935–1998)
	3700 Mg	ACAP (2005)	Russia; losses to soils, waste and water from 7 CAPs (1951–1998)
Large scale precious metal production	196,000 Mg	Nriagu (1994)	Latin America; cumulative losses due to production of Au and Ag
	61,380 Mg		North America; cumulative losses due to production of Au and Ag
ASGM	640–1350 Mg yr^{-1}	Telmer and Veiga (2009)	Globally
	350 Mg yr^{-1}		Losses to atmosphere
	650 Mg yr^{-1}		Losses to hydrosphere
Non-ferrous metal production	275–310 Mg yr^{-1}	USGS (2004) Hylander and Herbert (2008)	Losses to air

reported by Hylander and Meili (2003), we estimate accumulated historical global emissions to air, soil, and water at roughly 250,000 Mg.

Chlor-alkali industry: As a consequence of large current and past mercury releases from CAPs within areas adjacent to these production plants, even if shut down, their environments can contain significant amounts of mercury dispersed inside the ground under production buildings, in slurry accumulators, in disposal sites and in water bodies (ACAP, 2005). Due to direct mercury discharges from the process, extremely contaminated soils with concentrations exceeding 10 g kg^{-1} of mercury can be located near the plant (Zagury et al., 2006; Neculita et al., 2005). Although most mercury emitted to the atmosphere from CAPs is subject to atmospheric dispersion and long range transport, elevated mercury levels in soils are usually also seen within a few kilometres of the plant. Contamination factors up to a 50 as the result of atmospheric deposition were reported for these sites (Trip and Thorleifson, 1998; Biester et al., 2002; Remy et al., 2003). For example, Biester et al. (2002) studied the distribution of mercury around three European chlor-alkali plants and calculated that 5–10% of mercury emitted from the plant to the atmosphere was retained in soils around the plant, the rest being attributed to a long range transport. The spatial distribution of contaminated soils depends strongly on the orography of the area and prevailing wind directions (Biester et al., 2002; Hissler and Probst, 2006). Due to high mercury releases from CAPs, the total amount of mercury stored in soils surrounding CAPs can reach several megagrams (ACAP, 2005; Hissler and Probst, 2006). Moreover, in soils contaminated by CAPs, a high proportion of volatile mercury is present (Zagury et al., 2006; Neculita et al., 2005). The level of contamination at active as well as converted CAPs using the mercury cell technology differs from country to country. For example, while contaminated material was sent to hazardous waste disposal facilities during the decommissioning in Canada (Trip and Thorleifson, 1998), in Russia the majority of mercury used ended up in the surroundings of the facilities or waste dumps, with only insignificant amount recycled (ACAP, 2005).

Large scale precious metal production: According to Nriagu (1994), the cumulative losses of mercury to the environment due to the production of precious metals in the Americas totalled 257,400 Mg, with 196,000 Mg dispersed in South and Central America and 61,380 Mg in the United States. Mercury release to the environment due to gold and silver production is also related to the co-occurrence of mercury in many gold and silver ores, with

concentrations ranging from less than 0.1 to over 100 Mg kg^{-1} (Jones and Miller, 2005). Consequently, depending on the type of contamination, reported mercury emissions from these sites range over multiple orders of magnitude and can reach thousands of ng m^{-2} h^{-1} at areas of mining disturbance. For example, Gustin et al. (2003) measured 40 and 220 ng m^{-2} h^{-1} from gold and silver mine waste associated with historic mining, while Zehner and Gustin (2002) estimated mercury emissions from precious metal mines across Nevada in $\sim$5–500 ng m^{-2} h^{-1} range. Due to the mining operations, significant higher mercury emissions at two active industrial gold mines in Nevada were measured recently, which ranged from < 60 ng m^{-2} h^{-1} for waste rock piles to almost 30,000 ng m^{-2} h^{-1} for tailings (Eckley et al., 2011a).

ASGM: During its use in artisanal gold mining significant amounts of mercury are lost in both atmosphere and hydrosphere. When it is used to amalgamate gold, some escapes directly into soils and water bodies as elemental mercury droplets or as coatings of mercury adsorbed onto sediment grains, while mercury that forms the amalgam with gold is emitted to the atmosphere when the amalgam is heated (Telmer and Veiga, 2009). Consequently, mercury atmospheric emissions from areas with polluted soils can be on the order of 400 g h^{-1}, as measured at a Venezuelan gold mining site by Garcia-Sanchez et al. (2006). Moreover, due to the sluicing and dredging of mercury-rich sediments during mining operations, annual riverine flux of mercury from these sites can reach several megagrams (Telmer et al., 2006).

Non-ferrous metal production: Non-ferrous metal production (e.g. zinc, copper, lead and nickel) is a known source of mercury released to the environment, especially in developing countries. As shown in the Global Mercury Assessment report (UNEP, 2002), atmospheric emissions of about 170 Mg yr^{-1} from this sector can be considered as an underestimate. Recent assessments showed that mercury emitted from non-ferrous ore processing are about 275–310 Mg yr^{-1} (USGS, 2004; Hylander and Herbert, 2008) and increasing production, especially in emerging countries, is leading to an increase of mercury releases to the atmosphere (Pirrone et al., 2010). Emissions from the non-ferrous metal industry depend mainly on the content of mercury in these ores, the type of industrial technology employed and the type and efficiency of emission control installations (Pacyna et al., 2006). The influence of non-ferrous metal smelting on elevated mercury concentrations in the vicinity of ore smelters has already been established. For example, Li et al. (2008) found elevated mercury levels in all

environmental compartments in an artisanal zinc smelting area in Guizhou, China. In their study a decreasing trend of soil mercury concentrations with increasing distance from the smelting sites was shown to be a result of mercury emission and subsequent deposition from the Zn smelting process. Most contaminated are soils within 2 km off the smelting site, where elevated atmospheric concentrations were also observed (Li et al., 2008).

5. Mercury releases from contaminated sites

5.1. Mercury re-emissions to the global atmosphere

Due to the number of parameters influencing the emission processes, quantification of mercury emissions from contaminated surfaces can be very data demanding. Usually, area estimates are made based on in situ derived mercury fluxes and adjusted for parameters controlling emission using the advantages of GIS technology (e.g., Engle et al., 2001; Engle and Gustin, 2002; Zehner and Gustin, 2002; Coolbaugh et al., 2002; Gustin, 2003; Gustin et al., 2003, Wang et al., 2005). Scaled mercury re-emissions from contaminated sites as evident from case studies are reported in Table 2. When scaling up emissions from substrates enriched in mercury, the magnitude of emission depends on the proportion of the surface area with high mercury enrichment relative to that of the entire area studied (Gustin and Lindberg, 2005). Therefore, in estimates of mercury releases to the atmosphere from contaminated sites we consider two types of releases: the first is associated with concentrated point sources or so-called "hot spots" containing very high mercury concentrations relative to the background. These sources are various mining and industrial wastes and other anthropogenically disturbed areas. For these point sources, the estimates are backed by up-to-date literature results, based on flux ranges reported for selected case studies and extrapolation to the number/extent of these sites within the individual source category. The second are re-emissions from diffuse sources which are dispersed over extensive areas surrounding those sites where mercury was intentionally or unintentionally used and/or released. Due to the lack of detailed site specific data, especially on substrate mercury content, the use of more sophisticated models for calculating mercury emissions associated with diffuse sources was not possible. Moreover, existing models are site specific and cannot be applied to other locations. Therefore, as atmospheric mercury emission depends strongly on the climatic conditions, a simplified approach was used considering only the temperature dependence of mercury emission flux for these sources as described by an Arrhenius type equation (Eq. (1)):

$$F = A \times \exp(-E_a/R_{univ} \times T_s) \qquad (1)$$

where F is the mercury flux from soil (ng m^{-2} h^{-1}), A is a pre-exponential factor, E_a is the activation energy, R_{univ} is the universal gas constant and T_s the surface temperature (K). Following the approach of Travnikov and Ryaboshapko (2002) that modelled mercury hemispheric transport, a value of 20 kcal mol^{-1} was adopted for activation energy, while pre-exponential factor was adjusted for contaminated soils. According to the model of Travnikov and Ryaboshapko (2002), mean annual emission flux of mercury from background soils is in the $\sim$0.2–1 ng m^{-2} h^{-1} range, considering soil temperatures of $\sim$8–20 °C. Given the fact that reported area averaged mercury emissions from diffused sources at contaminated sites are in the $\sim$10–20 ng m^{-2} h^{-1} range (Table 2), pre-exponential factor for contaminated surfaces was then assumed to be 20–50 times higher (1.3–3.2×10^{16}) than the factor used for background soils by Travnikov and Ryaboshapko (2002). For each of the contaminated sites, surface temperature was then extracted from GIS maps representing the global 30-year mean monthly surface climatology (1961–1990), available from the ORNL DAAC archive (http://webmap.ornl.gov/wcsdown). In this way, resulting mean annual emissions from diffuse sources are in the $\sim$50–200 µg m^{-2} yr^{-1} range for sites at middle latitudes. Emissions from sites located at the high latitudes are considerably lower due to low temperatures ($\sim$10–30 µg m^{-2} yr^{-1}), while they can exceed 300 µg m^{-2} yr^{-1} for sites at the low latitudes. Annual mercury releases associated with diffuse sources were then calculated taking into account the ranges of the extent of contamination that can be expected, as reported in the literature. In some regions these sites are distributed very densely and their areas of influence coincide. Overall, the following

Table 2
Scaled mercury re-emissions from contaminated sites.

Site/Country	Category	Hg re-emission (kg yr^{-1})	Total area (km^2)	References
Almaden (Spain)	Hg mining	1750	–	Ferrara et al. (1998a) [a]
Mt. Amiata (Italy)	Hg mining	~920	–	Ferrara et al. (1998b)[b]
New Idria (USA)	Hg mining	18	229	Coolbaugh et al. (2002)
New Idria (USA)	Hg mining	2.7	0.6	Coolbaugh et al. (2002) [c]
Ivanhoe district (USA)	Hg mining	87	586	Engle et al. (2001)
Ivanhoe district (USA)	Hg mining	8.9	0.1	Engle et al. (2001) [c]
Sulphur Bank (USA)	Hg mining	17	3.8	Nacht et al. (2004)
Knoxville (USA)	Hg and Au mining	37.6	37.6	Gustin et al. (2003)
Knoxville (USA)	Hg and Au mining	19.8	2.7	Gustin et al. (2003)[c]
Langmuchang (China)	Hg and Tl mining	3.5	2.9	Wang et al. (2005)
Wanshan (China)	Hg mining	1–5	0.1	Wang et al. (2007)
Idrija (Slovenia)	Hg mining	17–34	0.25	Grönlund et al. (2005) [d]
Idrija (Slovenia)	Hg mining	51	640	Kocman and Horvat (2011)
Carson R. Super. (USA)	Au mining	12.5	1.4	Gustin et al. (2003) [c]
Flowery Peak (USA)	Au and Ag mining	41	251	Engle and Gustin (2002)
Flowery Peak (USA)	Au and Ag mining	3.3	< 0.1	Engle and Gustin (2002) [c]
Peavine Peak (USA)	Au and Ag mining	10	108	Engle and Gustin (2002)
Cortez-Pipeline (USA)	Au mining	19	14.8	Eckley et al. (2011b) [e]
Twin Creeks (USA)	Au mining	109	26.5	Eckley et al. (2011b) [e]

[a] Emissions from roasted ore, soil and mine structures during operational phase of the mine.
[b] Emissions from abandoned mine structures.
[c] Emissions from various mining disturbed areas.
[d] Emissions from former distillation plant area.
[e] Emissions from disturbed materials at active open-pit Au-mine.

Table 3
Assumption made to estimate mercury emissions from categories of contaminated sites.

	Point source	Surrounding area[b]
Primary mercury		
large	20 kg yr^{-1}	200 km^2
medium	10 kg yr^{-1}	100 km^2
others	2 kg yr^{-1}	50 km^2
CAPs	10–50 µg m^{-2} h^{-1} [a]	2–3 km radius
Non-ferrous metal		2–3 km radius
Precious metal		
mining	5–10 kg yr^{-1}	50–100 km^2
processing	2 kg yr^{-1}	2–3 km radius
ASGM		[c]
Other industries	0.9–9 kg yr^{-1}	

[a] CAPs were assumed to have at least one hectare of mercury-containing wastes and sludges adjacent to the production plant.

[b] Calculated mercury emissions from diffuse sources are ∼10–30 µg m^{-2} yr^{-1} for sites located at high latitudes, 50–200 µg m^{-2} yr^{-1} at middle latitudes and >300 µg m^{-2} yr^{-1} at low latitudes.

[c] Emissions from ASGM were adopted from Telmer and Veiga (2009).

assumptions were made within an individual contaminated site category (Table 3).

For the primary mercury mining category it was assumed that 20 kg yr^{-1} of mercury is emitted from point sources from sites categorised as large, 10 kg yr^{-1} from medium ones and 2 kg yr^{-1} from others. It was then assumed that large production sites result in elevated mercury re-emission from the surrounding 200 km^2, medium ones from 100 km^2 and 50 km^2 was used for other sites.

CAPs were assumed to have at least one hectare of mercury-containing wastes and sludges adjacent to the production plant from which emissions in the 10–50 µg m^{-2} h^{-1} range could be expected (Wangberg et al., 2003; Kotnik et al., 2006). In addition, emissions from contaminated soils within a 2–3 km radius around the CAPs were assumed.

In the assessment of mercury atmospheric releases from non-ferrous metal production sites, only diffuse mercury sources surrounding the smelters (2–3 km radius) were considered.

Mercury releases to the atmosphere from various disturbed areas (wastes, open pits, tailings...) associated with large-scale precious metal (gold and silver) mining and ore processing can vary over several orders of magnitude and cover up to tens of square kilometres (e.g., Zehner and Gustin, 2002 and references therein; Gustin et al., 2003; Eckley et al. 2011a; 2011b). Here we choose a rather conservative 5–10 kg yr^{-1} emitting coefficient from such disturbances at sites where mining activities are/were going on and 2 kg yr^{-1} at sites where ore processing is/was conducted. In addition, emissions from 50 to 100 km^2 diffuse sources in the surroundings of mining sites and within 2–3 km radius for processing plants are expected at these sites.

The estimates for atmospheric re-emission of 50 Mg yr^{-1} of mercury from artisanal and small scale gold mining were taken directly Telmer and Veiga (2009). Their estimates are based on data available on mercury and gold exports and imports by country, and the reported production and technology of extraction from all the countries known to have active ASGM communities.

In addition, under the category other industrial sites, a rather rough estimate of mercury contributions to the atmosphere was made for sites identified, based on the magnitude of the mercury fluxes reported in the literature from such sites. Without information on the surfaces that are polluted and contribute to emission, it is not possible to give a consistent assessment of mercury releases to the atmosphere, nevertheless the importance of this category is confirmed by considering that 10,000 ng m^{-2} h^{-1} result in 0.9 kg ha^{-1} yr^{-1} of mercury, and 100,000 ng m^{-2} h^{-1} emit 9 kg ha^{-1} yr^{-1} (Garcia-Sanchez et al., 2006). In the better case when hundreds of heavily polluted sites can be accounted for, an emission of 10–20 Mg yr^{-1} of mercury can be expected from this category.

5.2. Mercury dissemination through hydrological cycle

5.2.1. Catchment scale

The most important factors controlling terrestrial mercury releases from contaminated surfaces are meteorological conditions. In temperate and humid conditions terrestrial mercury releases can dominate the atmospheric inputs. Riverine transport of mercury from such sites occurs primarily in the particulate form as a result of erosion processes, and most of the mercury flux (75–90%) to downstream environments occurs during peak flow events (Whyte and Kirchner, 2000; Žagar et al., 2006). For instance, out of the 1500 kg of mercury that is annually transported from the contaminated Idrija Hg-mine area in Slovenia, less than 1% is in the dissolved form, the rest being associated with contaminated suspended sediments (Rajar et al., 2000). In arid climates however, riverine transport of mercury from contaminated sites is limited and catchments are usually not impacted at great distances (Gray et al., 2002). In such conditions, release of mercury to the atmosphere dominates. Hence, terrestrial loading of mercury greatly depends on the geographical position of the individual contaminated site as well as on the extent of contamination. Consequently, mercury releases as reported in the literature vary a lot. For example, due to historic gold and mercury mining activities in the Sierra Nevada and Coast Range Mountains (California, USA), David et al. (2009) reported 60–470 kg yr^{-1} of mercury is transported to San Francisco Bay. Schafer et al. (2006) estimated annual mercury fluxes from the Lot River in France, an area affected by coal-fired power plants, mining and metal processing, ranging from 35 to 530 kg yr^{-1} for the past decade. Current use of mercury in small scale gold mining in the Tapajos River basin in the Brazilian Amazon, resulted in an annual export of 1600 kg of mercury (Telmer et al., 2006). Large amounts of particulate mercury in aquatic systems are also released from riverbed and bank erosion and especially during flooding (Wang et al., 2004). For instance, due to the devastating flood that occurred in Nevada in 1997, about 1400 kg of mercury was carried into the Lahontan Reservoir (Carroll and Warwick, 2001). Similarly, during a large flood wave in the course of 8 days the river Soča transported about 4700 kg of mercury into the Gulf of Trieste in the Northern Adriatic (Horvat et al., 1999).

In general, mercury releases to aquatic environments from contaminated sites are poorly documented. Usually annual estimates are based on short observation periods and are not adapted to hydrometeorological conditions. Moreover, mercury is drained into local river systems from the whole catchment, which makes assessment of its relative contribution from contaminated part difficult. Besides, in a single area or a catchment, more mercury sources resulting in the occurrence of contaminated sites can exist, making the identification of relative mercury contribution from different contaminated site categories even harder. Therefore, it was only possible to make a rather rough estimate of mercury releases to hydrosphere from selected contaminated site categories (Table 4). For estimation of mercury releases associated with primary mercury mining, chlor-alkali industry and large-scale precious metal processing the following was considered: (i) ranges as reported in the literature for selected case studies, (ii) ratio of mercury released to hydrosphere to that emitted to the atmosphere, (iii) historic accumulation of mercury within different categories, and (iv) number of contaminated sites in individual climatic zone (e.g., in an arid climate releases to hydrosphere are considered less significant compared to those in a more humid climate and with relief more prone to erosion). For the ASGM category, out of approximately 1000 Mg of

mercury that is annually lost to the environment in these activities, 650 Mg were reported to be released to the terrestrial environment (Telmer and Veiga, 2009). How much of it later enters aquatic environments due to erosion and riverine transport is unknown and hard to establish due to the lack of suitable data. Therefore, mercury release to aquatic environments from the ASGM category was estimated based on the ratio of riverine fluxes reported in case study (Telmer et al., 2006) to reported mercury global consumption in ASGM activities (Telmer and Veiga, 2009). In should be noted, however, that this is a very coarse approach, with large associated uncertainties, as it is known that the dominant source of mercury in such systems is not necessarily the loss of mercury in the gold amalgamation process itself, but the remobilisation of mercury contaminated sediment and floodplain soil during mining operations (Telmer et al., 2006). Anyhow, it is reasonable to expect releases of mercury to aquatic systems from this category to be significant, as many of the countries with high ASGM activity are also countries with very humid climate and consequently high soil erosion rates.

5.2.2. Coastal environments

Mercury released from contaminated sites to the hydrosphere due to leaching and erosion is ultimately delivered to the seas and oceans as a consequence of riverine transport. Moreover, it should be noted that the many of contaminated sites (e.g., > 40% of all chlor-alkali plants) are located at or near the coast and have for decades introduced wastes containing mercury directly into local estuaries. Therefore, due to the historical accumulation, many coastal areas are contaminated with mercury. For example, for more than 30 years mercury-contaminated effluent was

discharged into Minamata Bay from an acetaldehyde producing factory resulting in sediment mercury concentrations as high as 2000 Mg kg^{-1} (Tomiyasu et al., 2006). Furthermore, it was estimated that more than 1800 Mg of mercury was deposited in the sediments of the Gulf of Trieste in the Northern Adriatic during the 500 years of mercury mining in the Idrija mine in Slovenia (Žagar et al., 2006). Due to both mercury and gold mining during the gold rush era (1850–1900) in California, more than 140 Mg of mercury accumulated in San Francisco Bay (MacLeod et al., 2005). Since 1956 mercury has been continuously introduced into northern Haifa Bay in Israel from a nearby chlor-alkali plant. The total influx of mercury from this plant to the bay is estimated at about 22 Mg (Herut et al., 1996). Mercury contaminated estuarine and near-shore systems can also be anthropogenically impacted systems such as the New York/New Jersey harbour estuary, where almost 500 kg yr^{-1} of mercury is released from different sources (Balcom et al., 2007). Recently the mercury mass balance was also calculated for the Mediterranean coastal sites contaminated with mercury. It was estimated that annually 2500 kg becomes subject to the hydrological cycle (Rajar et al., 2007).

Due to the lack of data on releases from different mercury sources to coastal areas, as well as to the extent of contamination, it is not possible to give a consistent estimate of mercury contamination in this category. A rather rough estimate of the amount of mercury accumulated in coastal environments, based on the published data for historical and present mercury releases to estuaries, is 50,000–100,000 Mg.

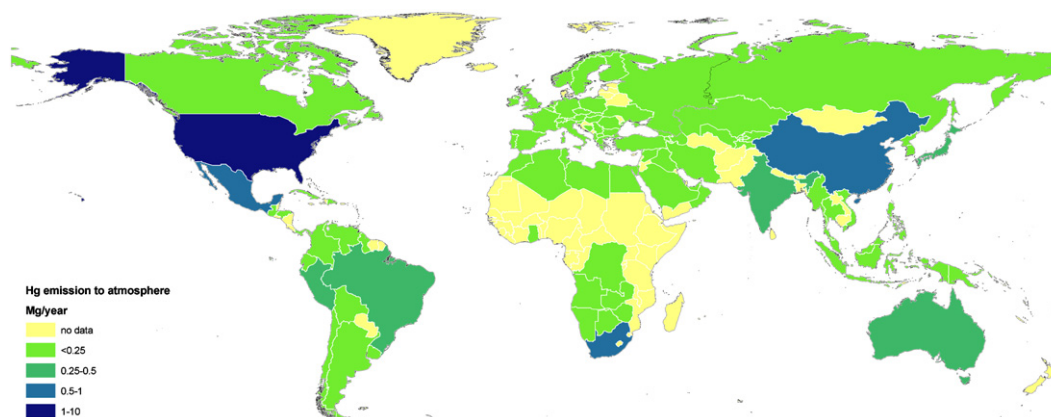## 6. Estimated emission of mercury from contaminated sites and its fate

Summing up the contribution of mercury to both the atmosphere and hydrosphere, about 137–260 Mg of mercury are released annually to the global mercury budget from identified mercury contaminated site categories (Table 4). Based on this, the annual contribution of mercury to the atmosphere from contaminated sites is in the 3–4% range if compared to the global anthropogenic atmospheric emissions reported by Pirrone et al. (2010). On average, majority (68%) of the atmospheric contribution from contaminated sites comes from precious metal processing (both large scale and ASGM), followed by polluted industrial/urban sites including chlor-alkali industry (19%), mercury mining (10%) and non-ferrous metal processing (2%). From a global perspective, the highest cumulative atmospheric mercury emissions from contaminated sites (emissions from ASGM associated with developing countries excluded) occur from industrial regions of North America, South Africa and China (Fig. 2).

Table 4
Mercury releases to the atmosphere (A) and hydrosphere (H) from contaminated sites (Mg yr^{-1}).

	A (point sources)	A (diffuse sources)	A (total)	H*
Mercury mining	3	3–8	6–11	10–50
Chlor-alkali industry	0.2–1	0.2–1	0.4–2	2–5
Non-ferrous metal processing	–	0.5–3	0.5–3	–
Precious metal processing	2–4	1–5	3–9	5–10
ASGM	–	–	50	50–100
Other industrial sites	–	–	10–20	–
Subtotal	*70–95*		*67–165*	
Total (A+H)				***137–260***

* An additional 50–100 Mg yr^{-1} of mercury is expected to be released to the open oceans from contaminated coastal sites.

Fig. 2. Global atmospheric mercury emissions (Mg yr^{-1}) from contaminated sites by country (emissions from ASGM excluded).
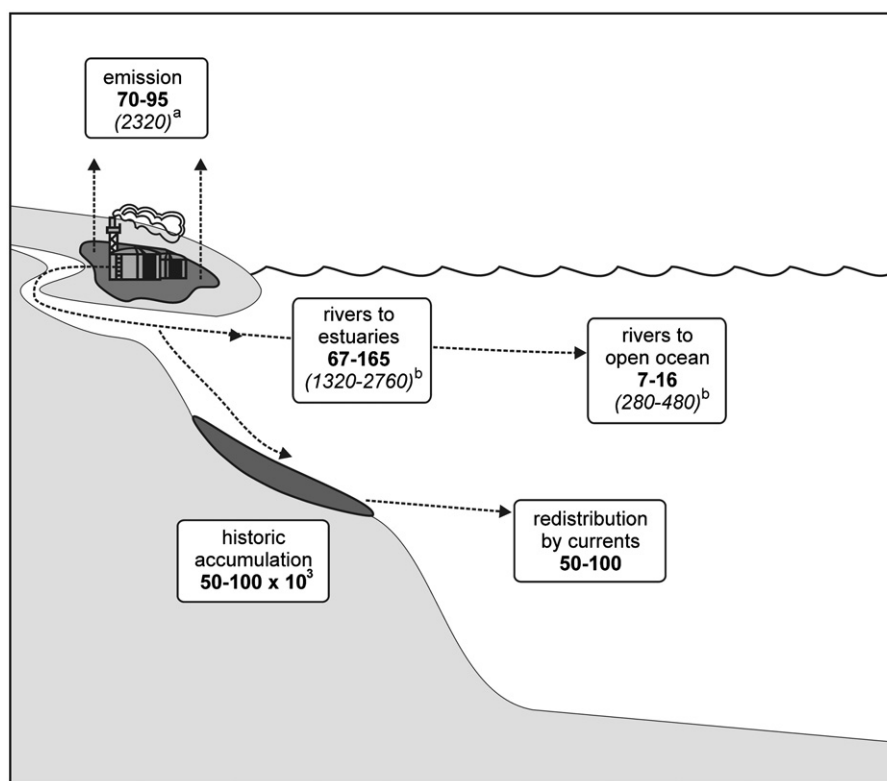
Fig. 3. Summary of the estimated contribution of mercury (Mg yr^{-1}) from contaminated sites (figures in bold) to the current global mercury cycle (figures in italic by (a) Pirrone et al. (2010) and (b) Sunderland and Mason (2007)).

Current estimates of mercury releases via rivers to estuaries due to the erosion of soils and sediments from contaminated sites indicate that these releases can be of paramount importance and are in the same order of magnitude as atmospheric fluxes. In the general global budget for mercury in the environment proposed recently by Sunderland and Mason (2007), some 2000 Mg yr^{-1} are transported via rivers to estuaries. Compared to this figure, the annual contribution of mercury to estuaries from contaminated sites is quite significant and can represent up to 8% of the total riverine flux. Considering that the majority ($\sim$90%) of the mercury load in rivers deposits around the river mouth and on the continental shelf (Cossa et al., 1997; Sunderland and Mason, 2007), it was estimated that up to 16 Mg yr^{-1} of mercury from contaminated sites directly reaches the open ocean. If we assume that only 0.1% of the historic burden is redistributed by currents every year, an additional 50–100 Mg of mercury can be expected to be released to the open oceans from contaminated coastal sites (Fig. 3).

7. Uncertainty simulation

To improve our estimates the uncertainty assessment with the Monte Carlo technique was made. This is a practical way to evaluate uncertainty through a stochastic simulation based on the generation of random values from specified density functions (Buslenko et al., 1966; Hammersley and Handscomb, 1976; Rubinstein, 1981). The simulation randomly generates thousand of data to account for the uncertainty and performance variation associated with a variable. In our case, the uncertainty estimate associated with mercury emissions from contaminated sites was performed by considering the following cumulative probability:

$$Pr\left\{\left|\frac{1}{N}\sum_N \xi - \mu\right| < \frac{3\sigma}{\sqrt{N}}\right\} \approx 0.997 \tag{2}$$

where N is the number of iterations, ξ the variable, μ the average and σ the standard deviation.

Upper and lower bounds have been established on the basis of Table 4. For each category a normal distribution was assumed. The total emission is therefore a normally distributed random variable with a value between the minimum and the maximum. The total error given by $\varepsilon = 3\sigma/\sqrt{N}$ was simulated at 5, 10, 20 and 30%.

Main statistical parameters for each category are reported in Table 5. Calculated without uncertainty, the net evasion into atmosphere averaged 82 Mg yr^{-1}; whereas transport into hydrosphere average 116 Mg yr^{-1}. The stochastic simulation by adopting a 5% confidence interval generated averages of 84.6 and 116.1 for atmosphere and hydrosphere, respectively. The standard deviation was of 12.0 in the former case and 19.0 in the latter; whereas kurtosis and skewness showed a really close overlapping to Gaussian density distribution, despite the resampled mean reflects a small bias (less than 3% in this case) (Fig. 4a and b). Simulations for each source of error (i.e., emissions from different sources) lead to the estimate of true errors. By considering the 5% confidence interval, total errors were between 0.05 and 1.7 for the atmosphere (Fig. 5a) and between 0.13 and 2.63 for the hydrosphere (Fig. 5b). In both cases ASGM were the largest source of error.

8. Conclusions

The contribution of mercury releases from contaminated sites to the global mercury budget was assessed. The inventory of such sites indicates that from a global perspective, most mercury contaminated sites identified ($>$70%) are concentrated in industrial regions of Europe and North America that are adjacent to the Atlantic Ocean and Mediterranean Sea. In contrast to Europe and North America, the number and extent of mercury contaminated sites

Table 5
Key outputs of the Monte Carlo simulation.

	Atmosphere				Hydrosphere			
Error (%)	5	10	20	30	5	10	20	30
Iterations (#)	374	94	23	10	428	107	27	12
Average (Mg yr^{-1})	84.6	84.0	85.3	85.6	116.1	116.7	117.9	118.2
Median (Mg yr^{-1})	84.4	83.3	87.2	87.8	115.7	115.5	119.0	114.6
Standard deviation (Mg yr^{-1})	12.0	11.3	12.6	12.9	19.0	18.1	17.1	15.3
Skewness	0.000	0.102	0.084	0.220	0.099	0.120	−0.183	0.237
Kurtosis	−0.939	−0.826	−1.206	−1.307	−0.635	−0.493	−0.838	0.044
True error (Mg yr^{-1})	1.86	3.49	7.80	12.02	2.75	5.26	9.89	13.31
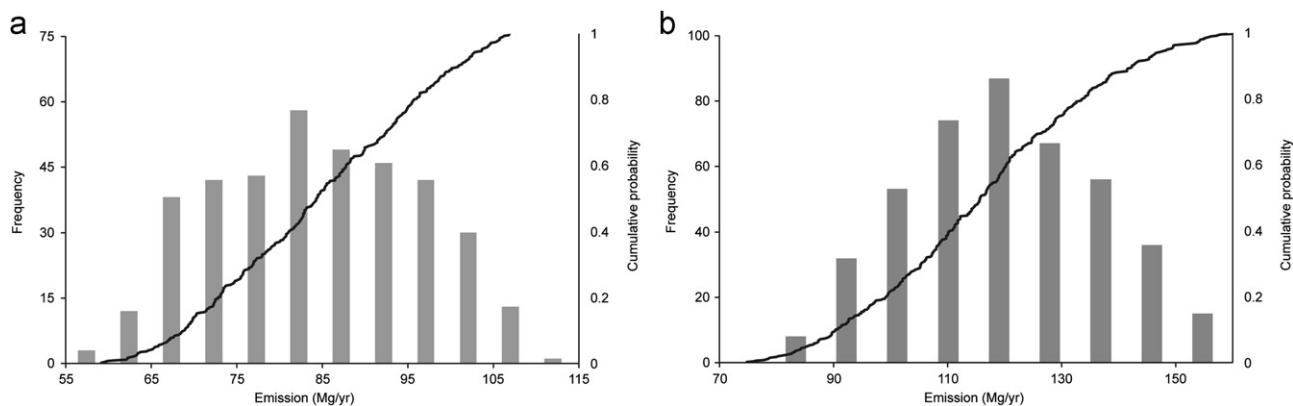
Fig. 4. Distribution frequency (bars) and cumulative probability function (line) for the stochastic simulation of atmosphere (a) and hydrosphere (b).
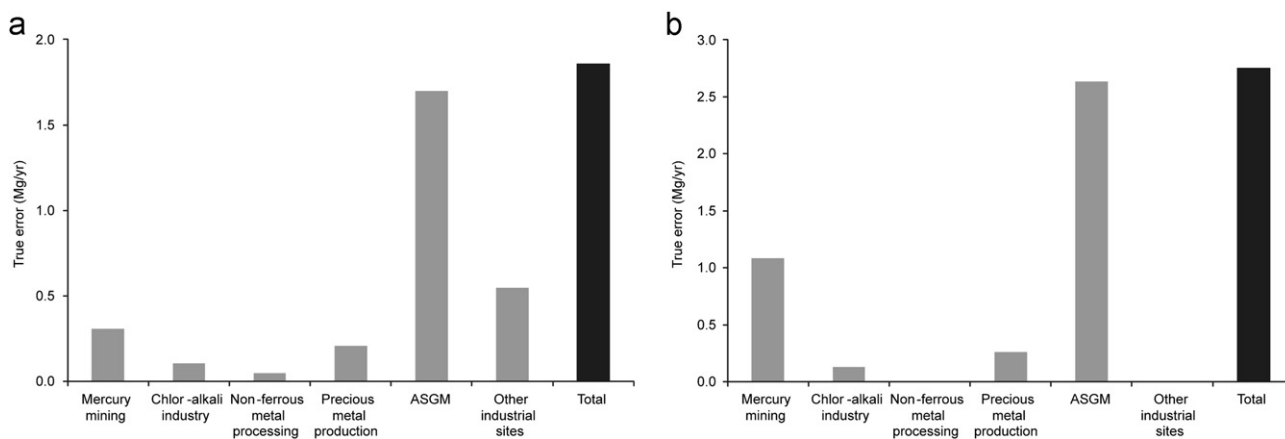
Fig. 5. True error for atmosphere (a) and hydrosphere (b) simulations.

in other parts of the world (especially Asian countries and India) is increasing due to the rising use of mercury in various products and processes. However, the exact location and extent of these sites are unknown and therefore not included in the inventory. Estimated annual releases of mercury from identified contaminated sites to both the atmosphere and hydrosphere are in the 137–260 Mg yr^{-1} range. Although this contribution represents only a few percent to the global mercury budget, these sites should be considered very carefully. Namely, compared to active anthropogenic point sources of mercury emission, mercury contaminated sites represent a long-term source of releases (Gustin et al., 2003). It must be noted, however, that the estimates presented here are associated with large uncertainties, mostly due to the scarcity of data on mercury releases from contaminated sites and our extrapolation of releases from site specific case studies. To discover the true error in our estimate, the Monte Carlo stochastic simulations was performed. It was based on upper

and lower boundaries and the error was found to be rather small. Our assumption does not consider the error associated with the estimates, which is much larger in the case of estimated releases to the hydrosphere, compared to atmospheric emissions and for which more data are needed. Therefore, further systematic and harmonized measurements are required to reduce these uncertainties. Furthermore, as both atmospheric mercury emissions and mercury inputs and distribution into the aquatic environment depend strongly on the climatic conditions and the topography of the site in question, these parameters must be further investigated and taken into account in the inventories. Coordination between the development of a geo-referenced database of mercury contaminated sites and on-site ad-hoc flux measurements can certainly improve future estimates. Moreover, these data would represent a valuable input for global mercury models developed in recent years for assessing the relationship between emission source and receptor regions.

Acknowledgments

References

ACAP, 2005. Assessment of Mercury Releases from the Russian Federation. Arctic Council Action Plan to Eliminate Pollution of the Arctic (ACAP), Russian Federal Service for Environmental, Technological and Atomic Supervision & Danish Environmental Protection Agency, Copenhagen, Denmark, pp. 335.

Balcom, P.H., Hammerschmidt, C.R., Fitzgerald, W.F., Lamborg, C.H., O'Connor, J.S., 2007. Seasonal distributions and cycling of mercury and methylmercury in the waters of New York/New Jersey Harbor Estuary. Mar. Chem. 109 (1-2), 1–17.

Biester, H., Muller, G., Scholer, H.F., 2002. Binding and mobility of mercury in soils contaminated by emissions from chlor-alkali plants. Sci. Total Environ. 284, 191–203.

Billaud, P., Laperche, V., Boudou, A., Maury-Brachet, R., Shoko, D., Kahwai, S., Freyssinet, Ph, 2004. Removal of Barriers to the Introduction of Cleaner Artisanal Gold Mining and Extraction Technologies in the Kadoma–Chakari Area, Zimbabwe. Part A: Environmental Assessment—Final Report. BRGM/RC-53320-FR, pp. 139.

Bullock, O.R., Jaegle, L., 2009. Importance of a global scale approach to using regional models in the assessment of source-receptor relationships for mercury. In: Pirrone, N., Mason, R. (Eds.), Mercury Fate and Transport in the Global Atmosphere: Emissions, Measurements and Models. Springer, New York, pp. 503–517.

Buslenko, N.P., Golenko, D.I., Shreider, Y.A., Sobol', I.M., Sragovich, V.G., 1966. The Monte Carlo Method. Pergamon Press, Oxford.

Concorde East-West, 2006. Status Report: Mercury-cell Chlor-alkali Plants in Europe. Prepared for the European Environmental Bureau. Brussels, Belgium.

Carroll, R.W.H., Warwick, J.J., 2001. Uncertainty analysis of the Carson River mercury transport model. Ecol. Modell. 137, 211–224.

Coolbaugh, M., Gustin, M., Rytuba, J., 2002. Annual emissions of mercury to the atmosphere from natural sources in Nevada and California. Environ. Geol. 42, 338–349.

Cossa, D., Martin, J.M., Takayanagi, K., Sanjuan, J., 1997. The distribution and cycling of mercury species in the western Mediterranean. Deep Sea Res. Part II 44 (3-4), 721–740.

Dastoor, A.P., Davignon, D., 2009. Global mercury modelling at Environment Canada. In: Pirrone, N., Mason, R. (Eds.), Mercury Fate and Transport in the Global Atmosphere: Emissions, Measurements and Models. Springer, New York, pp. 519–532.

David, N., McKee, L.F., Black, F.J., Flegal, A.R., Conaway, C.H., Schoellhamer, D.H., Ganju, N.K., 2009. Mercury concentrations and loads in a large river system tributary to San Francisco Bay, California, USA. Environ. Toxicol. Chem. 28 (10), 2091–2100.

Dizdarevič, T., 2001. The influence of mercury production in Idrija mine on the environment in the Idrija region and over a broad area. RMZ—Mater. Geoenvironmental 48, 56–64.

Euro Chlor, 2011. Chlorine Industry Review 2010–2011, Euro Chlor, Brussels, Belgium.

Eckley, C.S., Gustin, M., Marsik, F., Miller, M.B., 2011a. Measurement of surface mercury fluxes at active industrial gold mines in Nevada (USA). Sci. Total Environ. 409, 514–522.

Eckley, C.S., Gustin, M., Miller, M.B., Marsik, F., 2011b. Scaling non-point-source mercury emissions from two active industrial gold mines: influential variables and annual emission estimates. Environ. Sci. Technol. 45, 392–399.

Engle, M.A., Gustin, M.S., 2002. Scaling of atmospheric mercury emissions from three naturally enriched areas: Flowery Peak, Nevada; Peavine Peak, Nevada; and Long Valley Caldera, California. Sci. Total Environ. 290, 91–104.

Engle, M.A., Gustin, M.S., Zhang, H., 2001. Quantifying natural source mercury emissions from the Ivanhoe Mining District, north-central Nevada, USA. Atmos. Environ. 35, 3987–3997.

Feng, X., Qiu, G., 2008. Mercury pollution in Guizhou, Southwestern China—an overview. Sci. Total Environ. 400 (1-3), 227–237.

Ferrara, R., Maserti, B.E., Anderson, M., Edner, H., Ragnarson, P., Svanberg, S., Hernandez, A., 1998a. Atmospheric mercury concentrations and fluxes in the Almaden district (Spain). Atmos. Environ. 32, 3897–3917.

Ferrara, R., Mazzolai, B., Edner, H., Svanberg, S., Wallinder, E., 1998b. Atmospheric mercury sources in the Mt. Amiata area, Italy. Sci. Total Environ. 213 (1), 13–23.

Friedli, H.R., Arellano Jr., A.F., Cinnirella, S., Pirrone, N., 2009. Initial estimates of mercury emissions to the atmosphere from global biomass burning. Environ. Sci. Technol. 43 (10), 3507–3513.

Garcia-Sanchez, A., Contreras, F., Adams, M., Santos, F., 2006. Atmospheric mercury emissions from polluted gold mining areas (Venezuela). Environ. Geochem. Health 28, 529–540.

Gray, J.E., Crock, J.G., Fey, D.L., 2002. Environmental geochemistry of abandoned mercury mines in West-Central Nevada, USA. Appl. Geochem. 17, 1069–1079.

Grönlund, R., Sjöholm, M., Weibring, P., Edner, H., Svanberg, S., 2005. Mercury emissions from chlor-alkali plants measured by Lidar techniques. Atmos. Environ. 39, 7451–7458.

Gustin, M.S., 2003. Are mercury emissions from geologic sources significant? A status report. Sci. Total Environ. 304, 153–167.

Gustin, M.S., Coolbaugh, M.F., Engle, M.A., Fitzgerald, B.C., Keislar, R.E., Lindberg, S.E., Nacht, D.M., Quashnick, J., Rytuba, J.J., Sladek, C., Zhang, H., Zehner, R.E., 2003. Atmospheric mercury emissions from mine wastes and surrounding geologically enriched terrains. Environ. Geol. 43, 339–351.

Gustin, M.S., Lindberg, S.E., 2005. Terrestrial Hg fluxes: is the net exchange up, down, or neither? In: Pirrone, N, Mahaffey, K.R. (Eds.), Dynamics of Mercury Pollution on Regional and Global Scales. Springer, New York, pp. 241–253.

Hammersley, J.M., Handscomb, D.C., 1976. Monte-Carlo Methods. Methuen & Co Ltd., London 183 p.

Hedgecock, I.M., Pirrone, N., Trunfio, G.A., Sprovieri, F., 2006. Integrated mercury cycling, transport and air–water exchange (MECAWEx) model. J. Geophys. Res. 111, D20302.

Herut, B., Hornung, H., Kress, N., Cohen, Y., 1996. Environmental relaxation in response to reduced contaminant input: the case of mercury pollution in Haifa Bay, Israel. Mar. Pollut. Bull. 32 (4), 366–373.

Hinton, J., Veiga, M., 2001. Mercury contaminated sites: a review of remedial solutions. In: Takizawa, Y. (Ed.), Proceedings of the NIMD (National Institute for Minamata Disease) Forum, Minamata City, Japan, pp. 73–84.

Hissler, C., Probst, J.L., 2006. Impact of mercury atmospheric deposition on soils and streams in a mountainous catchment (Vosges, France) polluted by chlor-alkali industrial activity: the important trapping role of the organic matter. Sci. Total Environ. 361, 163–178.

Horvat, M., Covelli, S., Faganeli, J., Logar, M., Fajon, V., Rajar, R., Širca, A., Žagar, D., 1999. Mercury in contaminated coastal environments; a case study: the Gulf of Trieste. Sci. Total Environ. 237/238, 43–56.

Hylander, L.D., Meili, M., 2003. 500 years of mercury production: global annual inventory by region until 2000 and associated emissions. Sci. Total Environ. 304 (1-3), 13–27.

Hylander, L.D., Herbert, R.B., 2008. Global emission and production of mercury during the pyrometallurgical extraction of nonferrous sulfide ores. Environ. Sci. Technol. 42, 5971–5977.

Jaegle, L., Strode, S.A., Selin, N.E., Jacob, D.J., 2009. The Geos-Chem model. In: Pirrone, N., Mason, R. (Eds.), Mercury Fate and Transport in the Global Atmosphere: Emissions, Measurements and Models. Springer, New York, pp. 533–545.

Jones, G., Miller, G., 2005. Mercury and Modern Gold Mining in Nevada. Final Report to U.S. Environmental Protection Agency Region IX.

Jung, G., Hedgecock, I.H., Pirrone, N., 2009. The ECHMERIT model. In: Pirrone, N., Mason, R. (Eds.), Mercury Fate and Transport in the Global Atmosphere: Emissions, Measurements and Models. Springer, New York, pp. 547–569.

Kocman, D., Horvat, M., 2011. Non-point source mercury emission from the Idrija Hg-mine region: GIS mercury emission model. J. Environ. Manage. 92, 2038–2046.

Kotnik, J., Huremović, J., Kocman, D., Horvat, M., 2006. Mercury Soil–Air Fluxes in Regions Polluted by Different Anthropogenic Activities. In: Proceedings of the Eighth International Conference on Mercury as a Global Pollutant, ICMGP, Madison, Wisconsin, USA.

Lacerda, L.D., 1997. Global mercury emissions from gold and silver mining. Water Air Soil Pollut. 97 (3-4), 209–221.

Li, G., Feng, X., Qiu, G., Xiangyang, B., Li, Y., Zhang, C., Wang, D., Shang, L., Guo, Y., 2008. Environmental mercury contamination of an artisanal zinc smelting area in Weining County, Guizhou, China. Environ. Pollut. 154, 21–31.

MacLeod, M., McKone, T.E., Mackay, D., 2005. A mass balance for mercury in the San Francisco Bay area. Environ. Sci. Technol. 39 (17), 6721–6729.

Mahan, S., Savitz, J., 2007. Cleaning up: Taking Mercury-Free Chlorine Production to the Bank. Oceana, Washington, USA.

Nacht, D.M., Gustin, M.S., Engle, M.A., Zehner, R.E., Giglini, A.D., 2004. Atmospheric mercury emissions and speciation at the Sulphur bank mercury mine superfund site, northern California. Environ. Sci. Technol. 38, 1977–1983.

Neculita, C.M., Zagury, G.J., Deschenes, L., 2005. Mercury speciation in highly contaminated soils from chlor-alkali plants using chemical extractions. J. Environ. Qual. 34, 255–262.

Nriagu, J.O., 1994. Mercury pollution from the past mining of gold and silver in the Americas. Sci. Total Environ. 149, 167–181.

Pacyna, E., Pacyna, J., Sundseth, K., Munthe, J., Kindbom, K., Wilson, S., Steenhuisen, F., Maxson, P., 2010. Global emission of mercury to the atmosphere from anthropogenic sources in 2005 and projections to 2020. Atmos. Environ. 4, 2487–2499.

Pacyna, E.G., Pacyna, J.M., Steenhuisen, F., Wilson, S., 2006. Global anthropogenic mercury emission inventory for 2000. Atmos. Environ. 40, 4048–4063.

Pirrone, N., Allegrini, I., Keeler, G.J., Nriagu, J.O., Rossmann, R., Robbins, J.A., 1998. Historical atmospheric mercury emissions and depositions in North America compared to mercury accumulations in sedimentary records. Atmos. Environ. 32, 929–940.

Pirrone, N., Cinnirella, S., Feng, X., Finkelman, R.B., Friedli, H.R., Leaner, J., Mason, R., Mukherjee, A.B., Stracher, G., Streets, D.G., Telmer, K., 2010. Global mercury

emissions to the atmosphere from anthropogenic and natural sources. Atmos. Chem. Phys. 10, 5951–5964.

Pirrone, N., Costa, P., Pacyna, J.M., Ferrara, R., 2001. Mercury emissions to the atmosphere from natural and anthropogenic sources in the Mediterranean region. Atmos. Environ. 35, 2997–3006.

Qi, X.F., Lin, Y.H., Chen, J.H., 2000. An evaluation of mercury emissions from the chlor-alkali industry in China. J. Environ. Sci. (China) 12, 24–30.

Rajar, R., Četina, M., Horvat, M., Žagar, D., 2007. Mass balance of mercury in the Mediterranean sea. Mar. Chem. 107 (1), 89–102.

Rajar, R., Žagar, D., Širca, A., Horvat, M., 2000. Three-dimensional modelling of mercury cycling in the Gulf of Trieste. Sci. Total Environ. 260, 109–123.

Remy, S., Prudent, P., Hissler, C., Probst, J.L., Krempp, G., 2003. Total mercury concentrations in an industrialized catchment, the Thur River basin (north-eastern France): geochemical background level and contamination factors. Chemosphere 52, 635–644.

Rubinstein, B.Y., 1981. Simulation and the Monte Carlo Method. Wiley & Sons, New York.

Rytuba, J.J., 2003. Mercury from mineral deposits and potential environmental impact. Environ. Geol. 43, 326–338.

Schafer, J., Blanc, G., Audry, S., Cossa, D., Bossy, C., 2006. Mercury in the Lot-Garonne River system (France): sources, fluxes and anthropogenic component. Appl. Geochem. 21 (3), 515–527.

Seigneur, C., Vijayaraghavan, K., Lohman, K., Levin, L., 2009. The AER/EPRI global chemical transport model for mercury (CTM-Hg). In: Pirrone, N., Mason, R. (Eds.), Mercury Fate and Transport in the Global Atmosphere: Emissions, Measurements and Models. Springer, New York, pp. 589–602.

Sunderland, E.M., Mason, R.P., 2007. Human impacts on open ocean mercury concentrations. Global Biogeochem. Cycles 21, GB4022.

Telmer, K., Costa, M., Angélica, R.S., Araujo, E.S., Maurice, Y., 2006. The source and fate of sediment and mercury in the Tapajós River, Pará, Brazilian Amazon: ground and space based evidence. J. Environ. Manage. 81, 101–113.

Telmer, K., Veiga, M., 2009. World emissions of mercury from artisanal and small scale gold mining. In: Pirrone, N., Mason, R. (Eds.), Mercury Fate and Transport in the Global Atmosphere: Emissions, Measurements and Models. Springer, New York, pp. 131–172.

Tomiyasu, T., Matsuyama, A., Eguchi, T., Fuchigami, Y., Oki, K., Horvat, M., Rajar, R., Akagi, H., 2006. Spatial variations of mercury in sediment of Minamata Bay, Japan. Sci. Total Environ. 368, 283–290.

Travnikov, O., Ilyin, I., 2009. The EMEP/MSC-E mercury modelling system. In: Pirrone, N., Mason, R. (Eds.), Mercury Fate and Transport in the Global Atmosphere: Emissions, Measurements and Models. Springer, New York, pp. 571–587.

Travnikov, O., Ryaboshapko, A., 2002. Modelling of Mercury Hemispheric Transport and Depositions. EMEP/MSC-E Technical Report 6/2002, Meteorological Synthesizing Centre—East, Moscow, Russia.

Trip, L., Thorleifson, M., 1998. The Canadian Mercury Cell Chlor-alkali Industry: Mercury Emissions and Status of Facilities 1935–1996. Report to Transboundary Air Issues Branch Hull, Environment Canada, Québec, Canada.

UNEP, 2002. Global Mercury Assessment, UNEP, Geneva, Switzerland.

UNEP, 2008. Expanding the Number and Scope of Partnership Areas Within the United Nations Environment Programme Global Mercury Partnership, Geneva, Switzerland.

UNEP, 2009. Overarching framework UNEP Global Mercury Partnership, Geneva, Switzerland.

UNEP, 2011. Global Estimate of Global Mercury Cell Chlorine Capacity, UNEP, Geneva, Switzerland.

USGS, 2004. Minerals Yearbook, Technical Report, US Geological Survey, Washington, USA.

USGS, 2005. Mineral Resources Data System, US Geological Survey, Reston, Virginia, USA.

Wang, Q., Kim, D., Dionysiou, D.D., Sorial, G.A., Timberlake, D., 2004. Sources and remediation for mercury contamination in aquatic systems—a literature review. Environ. Pollut. 131 (2), 323–336.

Wang, S., Feng, X., Qiu, G., Fu, X., Wei, Z., 2007. Characteristics of mercury exchange flux between soil and air in the heavily air-polluted area, eastern Guizhou, China. Atmos. Environ. 41, 5584–5594.

Wang, S., Feng, X., Qiu, G., Fu, X., Wei, Z., Xiao, T., 2005. Mercury emission to atmosphere from Lanmuchang Hg–Tl mining area, Southwestern Guizhou, China. Atmos. Environ. 39, 7459–7473.

Wangberg, I., Hans, E., Ferrara, R., Lanzillotta, E., Munthe, J., Sommar, J., Sjoholm, M., Svanberg, S., Weibring, P., 2003. Atmospheric mercury near a chlor-alkali plant in Sweden. Sci. Total Environ. 304, 29–41.

Whyte, D.C., Kirchner, J.W., 2000. Assessing water quality impacts and cleanup effectiveness in streams dominated by episodic mercury discharges. Sci. Total Environ. 260 (1-3), 1–9.

Wilhelm, S.M., 2001. Mercury in Petroleum and Natural Gas: Estimation of Emissions from Production, Processing, and Combustion. (EPA/600/R-01/066). Research Triangle Park, NC: National Risk Management Research Laboratory, USEPA.

Wu, Y., Wang, S., Streets, D.G., Hao, J., Chan, M., Jiang, J., 2006. Trends in anthropogenic mercury emissions in China from 1995 to 2003. Environ. Sci. Technol. 40, 5312–5318.

Zagury, G., Neculita, C.M., Bastien, C., Deschênes, L., 2006. Mercury fractionation, bioavailability, and ecotoxicity in highly contaminated soils from chlor-alkali plants. Environ. Toxicol. Chem. 25 (4), 1138–1147.

Zehner, R., Gustin, M., 2002. Estimation of mercury vapor flux from natural substrate in Nevada. Environ. Sci. Technol. 36, 4039–4045.

Žagar, D., Knap, A., Warwick, J.J., Rajar, R., Horvat, M., Četina, M., 2006. Modelling of mercury transport and transformation processes in the Idrijca and Soča river system. Sci. Total Environ. 368, 149–163.