Contribution of Spanish–American silver mines (1570–1820) to the present high mercury concentrations in the global environment: a review

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Abstract

In this review I evaluate the contribution of Spanish–American silver mines during the period 1570–1820 (a Spanish colonial period of 250 years) to the present high mercury concentrations in the global environment. The evaluation is based upon the following bibliographic information: (1) total amount of mercury consumed in Spanish–American silver mines between 1570 and 1820; (2) percentage of the total amount of mercury consumed in Spanish–American silver mines that may have been emitted to the atmosphere; (3) global natural input of mercury to the atmosphere; (4) worldwide anthropogenic emissions of mercury to the atmosphere; (5) residence time of mercury in the atmosphere; and (6) capacity of mercury to be deposited in the sediments of aquatic systems. From all this information, and owing to the relatively long time that has passed since Spanish–American silver mines were operational, I conclude that most of the mercury lost during the refining of silver via the patio amalgamation process is now sequestered into the sediments of aquatic systems, mainly in marine sediments. The high mercury concentrations now being reported in the global environment essentially are a consequence of the huge pollution caused by human activities during the past 20th century. © 2002 Elsevier Science Ltd. All rights reserved.

Keywords: Spanish–American silver mines; Mercury pollution; Global environment

1. Introduction

Mercury (Hg) is a metal that occurs naturally in the Earth’s crust principally as cinnabar (HgS). Mercury can also be present in the global environment in various physical and chemical forms, depending upon the predominant environmental conditions. The most important Hg forms are (Lindqvist et al., 1991; Baeyens et al., 1996): elemental or reduced mercury (Hg⁰), divalent inorganic or oxidised mercury (Hg²⁺), methylmercury (CH₃Hg⁺), and particulate mercury (Hgₚ). Hg⁰ is relatively unreactive and volatile at ambient temperatures; Hg²⁺ is soluble in water and reactive with anions (e.g., Cl⁻, OH⁻, CO₃²⁻, SO₄²⁻) and inorganic/organic matter; CH₃Hg⁺ is the dominant form in higher organisms, being bioaccumulated and biomagnified through the food chain (e.g., the Minamata tragedy in Japan); and Hgₚ is relatively insoluble and tends to settle to the bottom of aquatic systems. Conversion between these distinct forms provides the basis for the complex pattern of mercury in the global environment. Within that complex pattern, the atmosphere is the main pathway for the distribution of mercury in the global environment. Within that complex pattern, the atmosphere is the main pathway for the distribution of mercury in the global environment. Within that complex pattern, the atmosphere is the main pathway for the distribution of mercury in the global environment. Within that complex pattern, the atmosphere is the main pathway for the distribution of mercury in the global environment. Within that complex pattern, the atmosphere is the main pathway for the distribution of mercury in the global environment. Within that complex pattern, the atmosphere is the main pathway for the distribution of mercury in the global environment. Within that complex pattern, the atmosphere is the main pathway for the distribution of mercury in the global environment. Within that complex pattern, the atmosphere is the main pathway for the distribution of mercury in the global environment. Within that complex pattern, the atmosphere is the main pathway for the distribution of mercury in the global environment.
Nowadays, as a consequence of human activities, mercury has become one of the most hazardous environmental pollutants because its concentration in the global environment is significantly increasing and reaching levels of potential (lethal and sublethal) toxicity for many living organisms (Nriagu, 1990; Lindqvist et al., 1991; Sloss, 1995; Wagemann et al., 2000). Current human activities introducing great amounts of mercury into the global environment are: fossil fuel (coal and oil) combustion, metal mining and metal smelting, chemical production, chlor-alkali factories, cement manufacturing, industrial, municipal and medical waste incineration, emissions from landfill sites, agriculture and forestry practices, and mercury amalgamation for gold mining (Nriagu and Pacyna, 1988; Nriagu, 1990; D’Itri, 1991; Lindqvist et al., 1991; Velga et al., 1994; Sloss, 1995; Carpi, 1997; Lacerda, 1997; Sang and Lourie, 1997; Innanen, 1998; Bullock, 2000; Hladiková et al., 2001). Nevertheless, the impact of past human activities on the present high mercury concentrations in the global environment has been little evaluated. This is the case of silver production by mercury amalgamation (or patio process) in Spanish–American silver mines.

The industrial application of the patio amalgamation process in Spanish–American silver mines was first made at Pachuca mines, New Spain (now Mexico), in 1554 by the Spaniard Bartolome de Medina (Brading and Cross, 1972; Bethell, 1984; Puche et al., 1996), being later introduced in the silver mines of Peru and Bolivia. By the beginning of the 17th century most American silver was produced through the patio amalgamation process. Virtually, all mercury used in Spanish–American silver mines came from three sources (Brading and Cross, 1972; Bethell, 1984; Puche et al., 1996): Almaden in southern Spain, Huancavelica in central Peru, and Idrija in modern Slovenia. In general, Almaden supplied the silver mines of Central America (e.g., Zacatecas, Guanajuato, Santa Barbara, Sombrerete), Huancavelica supplied the silver mines of South America (e.g., Potosi, Oruro, Castrovirreina, San Antonio del Nuevo Mundo), and Idrija only sporadically entered the American market.

The main purpose of this study is to evaluate the contribution of Spanish–American silver mines during the period 1570–1820 (a Spanish colonial period of 250 years) to the present high mercury concentrations in the global environment. Although, at present, the global mercury cycle is not well understood (different models have been proposed; see Lindqvist et al., 1991; Baeyens et al., 1996; Rajar et al., 2000) and the available data are not sufficient to permit a clear conclusion, I consider that these facts should not be an obstacle to try to evaluate the impact of Spanish–American silver mines on the present high mercury concentrations in the global environment. Indeed, Nriagu (1993, 1994a), in a previous evaluation, concluded that the huge cumulative loss of mercury to the atmosphere from the refining of silver in Spanish–American mines is partly responsible for the high background concentrations of mercury now being reported in the global environment. It however seems to me (Camargo, 1993) that other evaluations are necessary and must be taken into account before reaching a scientific consensus on the subject.

2. Materials and methods

Owing to the relatively long time that has passed since Spanish–American silver mines were operational (1570–1820), my initial hypothesis is that most of the mercury lost during the refining of silver via the patio amalgamation process is now sequestered into the sediments of aquatic systems, mainly in marine sediments. The high mercury concentrations now being reported in the global environment would essentially be a consequence of the huge pollution caused by human activities during the 20th century.

In order to test my hypothesis, I have performed the present evaluation on the basis of the following bibliographic information: (1) total amount of mercury consumed in Spanish–American silver mines between 1570 and 1820; (2) percentage of the total amount of mercury consumed in Spanish–American silver mines that may have been emitted to the atmosphere; (3) global natural input of mercury to the atmosphere; (4) world-wide anthropogenic emissions of mercury to the atmosphere; (5) residence time of mercury in the atmosphere; and (6) capacity of mercury to be deposited in the sediments of aquatic systems.

3. Results and discussion

Quinquennial mercury contributions from Almaden, Huancavelica and Idrija to the total amount of mercury consumed in Spanish–American silver mines are shown in Fig. 1. The total amount of mercury consumed in Spanish–American silver mines between 1570 and 1820 may thus be estimated as about 117 000 tonnes (Table 1): Almaden contributed with 65 220 tonnes (55.7%), Huancavelica contributed with 49 030 tonnes (41.9%), and Idrija contributed with 2750 tonnes (2.4%). The mercury from Idrija was primarily consumed in the silver mines of Central America between 1620 and 1645. Nriagu (1993, 1994a) had previously estimated a total Hg amount of 126 000 tonnes (9000 tonnes more than my own estimation) for the same period.

In accordance with several authors (Brading and Cross, 1972; Fisher, 1977; Lang, 1977; Bethell, 1984; Puche et al., 1996), I can assume that 5–10% of the total mercury supply was lost during transport, storage and
handling, and 15–20% was lost in waste waters and other residues. Most mercury was however lost and emitted to the atmosphere through volatilisation (as Hg\textsuperscript{0} vapour) during the process of mercury amalgamation, on the open patio floor, and during the burning of the silver amalgam to free the silver. Therefore, the average percentage of the total amount of mercury consumed in Spanish–American silver mines between 1570 and 1820 that may have been emitted to the atmosphere would be 75%. This percentage is equivalent to a total mercury amount of 87 750 Hg tonnes (average rate of 351 tonnes/year; Table 1), and is comparable to the average percentage for current emissions of mercury to the atmosphere from gold mining in Africa, Asia and South America (Lacerda, 1997; van Straaten, 2000). Although some fraction of the total amount of mercury emitted to the atmosphere (87 750 Hg tonnes) could have been locally deposited by rapid condensation when fumes were mixed with the cold surrounding air, in this evaluation I have assumed the worst scenario for the global environment (i.e., the total amount of mercury emitted to the atmosphere ended up the troposphere and spread globally).

The most important natural sources and processes by which mercury is emitted to the atmosphere are (Nriagu, 1989, 1994b; Lindqvist et al., 1991; Sadiq, 1992; Baeyens et al., 1996; Ferrara et al., 2000a,b; Gustin et al., 2000): degassing of geological mineral deposits in the Earth’s crust (e.g., mineralised areas in South America, Siberia and the Mediterranean basin), emissions by volcanic activities (e.g., Vulcano, Etna and Stromboli volcanoes), photoreduction of Hg\textsuperscript{2+} and biogenic formation of Hg\textsuperscript{0} in soils and waters, and forest fires. Average global estimates of natural mercury emissions to the atmosphere range from 1500 to 2500 tonnes/year (Nriagu, 1989, 1990; Lindqvist et al., 1991; Baeyens et al., 1996; Baeyens et al., 1996; Gustin et al., 2000). I consider the mean value of 2000 tonnes/year as an acceptable estimation of the global natural input of mercury to the atmosphere. Then, the global natural input of mercury to the atmosphere between 1570 and 1820 can be estimated as (2000 × 250 =) 500 000 tonnes (Table 1). This input represents more

Table 1

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<tr>
<th>Total amount (Hg tonnes)</th>
<th>Mean amount (Hg tonnes/year)</th>
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<tr>
<td>Consumption of mercury in Spanish–American silver mines between 1570 and 1820</td>
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<tr>
<td>Emission of mercury to the atmosphere from Spanish–American silver mines between 1570 and 1820</td>
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<td>World-wide natural input of mercury to the atmosphere between 1570 and 1820</td>
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<tr>
<td>World-wide anthropogenic input of mercury to the atmosphere during the 20th century</td>
<td>405 000</td>
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than five times the total amount of mercury (87,750 tonnes; 351 tonnes/year) emitted to the atmosphere from Spanish–American silver mines during the same period.

Average world-wide estimates of anthropogenic mercury emissions to the atmosphere range from 3600 to 4500 tonnes/year (Nriagu and Pacyna, 1988; Nriagu, 1990; Lindqvist et al., 1991; Baeyens et al., 1996; Boll-ock, 2000). It is currently assumed that anthropogenic mercury emissions are, at least, two times larger than natural mercury emissions. Consequently, I consider the mean value of 4050 tonnes/year as an acceptable estimation of the world-wide anthropogenic input of mercury to the atmosphere. Then, the total anthropogenic input of mercury to the atmosphere during the 20th century can be estimated as (4050 × 100 =) 405,000 tonnes (Table 1). This input represents more than four times the total amount of mercury (87,750 tonnes; 351 tonnes/year) emitted to the atmosphere from Spanish–American silver mines between 1570 and 1820.

The major form of mercury in the atmosphere (troposphere) is elemental mercury vapour (Hg0) (Horvat, 1996; Slemr, 1996; Hladíková et al., 2001). From the latitudinal distribution of total gaseous mercury and the lack of significant vertical gradient of mercury concentration, the tropospheric mercury burden has been estimated as about 6000 tonnes, and the mean residence time of mercury in the atmosphere as about 1 year (Slemr and Langer, 1992; Slemr, 1996). This implies an annual (natural + anthropogenic) mercury flux into and out of the atmosphere of about 6000 tonnes/year (Fitzgerald, 1986; Slemr, 1996), which is in agreement with the above estimations of natural (2000 tonnes/year) and anthropogenic inputs (4050 tonnes/year).

But, if annually a mercury flux of 6000 tonnes/year goes out of the atmosphere, which is the fate of this mercury flux?

The Hg0 in the atmosphere must be oxidised (normally by ozone) to Hg2+ to be deposited (Lindqvist et al., 1991; Baeyens et al., 1996; Xu et al., 2000). If we assume that mercury deposits evenly around the globe, it should be evident that a major part of the tropospheric mercury may directly be deposited in the oceans. At present there is no scientific evidence to think the opposite (that mercury deposits more in terrestrial systems than in the oceans). The concentration of mercury in unpolluted sea waters (open sea) exhibits an average value as low as 0.5 ng/l (Sadiq, 1992; Horvat, 1996), and because the entire volume of the world’s oceans is 1340 × 106 Km3 (Gleick, 1993), the total natural (unpolluted) amount of mercury in the world’s oceans would exhibit a conservative value of 670,000 Hg tonnes. On the other hand, a significant fraction of the mercury deposited in terrestrial systems can go to freshwater and marine systems through runoff and fluvial transport (Mason et al., 1994; Cossa et al., 1996; Leermakers et al., 1996; Fostier et al., 2000; Lockhart et al., 2000; Schetagne et al., 2000; Schwesig and Matzner, 2000; Fadini and Jardim, 2001). Moreover, field studies and controlled experiments indicate that significant Hg emissions from soil surfaces and terrestrial vegetation to the atmosphere occur every year (Schroeder et al., 1989; Lindqvist et al., 1991; Johnson and Lindberg, 1995; Kim and Lindberg, 1995; Lindberg, 1996; Carpi and Lindberg, 1998; Poissant and Casimir, 1998; Gillis and Miller, 2000).

Fitzgerald and Mason (1996) have however hypothesised that most (between 90% and 95%) of the annual mercury flux from the atmosphere could be ultimately accumulated in terrestrial systems as a consequence of the conversion of Hg2+ to Hg0 (and, to a lesser extent, dimethylmercury) in aquatic systems, mainly in marine systems, and the subsequent evasion of Hg0 (and (CH3)2Hg) to the atmosphere. Although there is no doubt that, thermodynamically, Hg2+ may be reduced to Hg0 in aquatic systems, kinetically the conversion of Hg2+ to Hg0 is a very slow reaction (Sadiq, 1992). Even if this Hg2+ reduction is induced by the sun light in natural surface waters (photoreduction; Nriagu, 1994b; Costa and Liss, 2000; Ferrara et al., 2000b) and/or catalysed by enzymes (e.g., mercuric reductase) present in aquatic microorganisms (bioreduction; Sadiq, 1992; Mason et al., 1995), it should be evident that the conversion of Hg2+ to Hg0 (and (CH3)2Hg) in aquatic systems must be limited. Indeed, mercury occurs mainly as positively charged ion in waters of most aquatic systems and may thus be adsorbed on the negatively charged surfaces of oxides, hydroxides, carbonates, clay and organic matter (Sadiq, 1992; Horvat, 1996), being subsequently deposited as particulate mercury (Hg0) in the sediments. Furthermore, Yamamoto (1996), carrying out laboratory studies, demonstrated that the oxidation of Hg0 to Hg2+ can actually occur in natural aquatic environments. This oxidation was significantly stimulated by the presence of chloride ions (i.e., the oxidation of Hg0 to Hg2+ would be much higher in sea waters than in fresh waters). In addition, there is no scientific evidence demonstrating that the concentration of mercury in terrestrial systems is increasing, year by year, as a consequence of the conversion of Hg2+ to Hg0 (and (CH3)2Hg) in aquatic systems.

The capacity of mercury to be deposited in the sediments of aquatic systems is well known (see Lindqvist et al., 1991; Sadiq, 1992; Baeyens et al., 1996). Because mercury binds tightly to many organic and inorganic materials, it is reasonable to assume that a significant fraction of the total amount of mercury in fresh and sea waters settles to the bottom of aquatic systems (marine systems, mainly) every year to compensate the annual Hg entry from natural and anthropogenic sources. In fact, lacustrine, estuarine and marine sediments serve as the principal depository for Hg (and other heavy metals) in aquatic systems (Young et al., 1973; Verta et al., 1989; Lindqvist et al., 1991; Sadiq, 1992; Swain et al., 1992;
Rognerud and Fjeld, 1993; Hudson et al., 1995; Landers et al., 1995; Lockhart et al., 1995, 2000; Lucotte et al., 1995; Rood et al., 1995; Cossa et al., 1996; Horvat, 1996; Leermakers et al., 1996; Fabbris et al., 1998; Louchouarn and Lucotte, 1998; Pempkowiak et al., 1998; Gobeil et al., 1999; Pilgrim et al., 2000; Dauvalter and Rognerud, 2001). Concentrations of mercury in sediments of aquatic systems range between 0.01 and 500 mg Hg/kg (dry weight); values lower than 0.10 mg Hg/kg may be related to natural (unpolluted) areas; values higher than 1 mg Hg/kg may be related to contaminated areas. In general, HgCl₂ (calomel) is the most insoluble Hg mineral in oxic and moderately oxic sediments, whereas HgS (cinnabar) is the most insoluble Hg mineral in anoxic sediments. Although desorption of mercury from sediments occurs, this process is limited and depends largely upon redox conditions. Kinetically speaking, adsorption of mercury on sediments is considered to be a faster process than desorption of mercury from sediments (Lindqvist et al., 1991; Sadiq, 1992; Baeyens et al., 1996).

It is interesting to mention, on the other hand, that several data on Hg accumulation in sediments of lakes and wetlands in different regions of the world (e.g., Sweden, Finland, Norway, western Russia, Wisconsin, Minnesota, Florida, Canada, The Arctic) indicate a significant and rapid increase in Hg atmospheric deposition rates during industrial times (starting about 1860) (Verta et al., 1989; Lindqvist et al., 1991; Swain et al., 1992; Rognerud and Fjeld, 1993; Hudson et al., 1995; Landers et al., 1995; Lockhart et al., 1995, 2000; Lucotte et al., 1995; Rood et al., 1995; Louchouarn and Lucotte, 1998; Pilgrim et al., 2000; Dauvalter and Rognerud, 2001), with a Hg enrichment factor between 2.0 and 2.5 for those lacustrine sediments. Moreover, though it has been pointed out that sedimentary diagenetic processes have the potential to reshape mercury profiles in aquatic (marine) sediments (Young et al., 1973; Gobeil et al., 1999), recent studies in three Canadian lakes (Clay lake, Giauque lake and Stuart lake) present compelling evidence that the histories of mercury deposition derived from lake sediment cores agree well with the known histories of mercury contamination for a period of at least half a century (Lockhart et al., 2000). Regarding estuarine and marine sediments, the available data (Young et al., 1973; Sadiq, 1992; Cossa et al., 1996; Horvat, 1996; Gobeil et al., 1999) are unfortunately insufficient to support a valid conclusion on historical trends in Hg atmospheric deposition rates during preindustrial and industrial times.

4. Conclusions

Overall it is concluded that, owing to the relatively long time that has passed since Spanish–American silver mines were operational, most of the mercury lost during the refining of silver via the patio amalgamation process is now sequestered into the sediments of aquatic systems, mainly in marine sediments. The high mercury concentrations now being reported in the global environment essentially are a consequence of the huge pollution caused by human activities during the past 20th century (Table 1). In this respect it should be evident that there is a real need to analyse the sediments of aquatic systems (marine systems, primarily) in order to improve our understanding of the historical trends in Hg atmospheric deposition rates during preindustrial and industrial times.

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References


