

CHAPTER-2. MERCURY EMISSIONS FROM NATURAL AND ANTHROPOGENIC SOURCES

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2.1 OVERVIEW

Processing of mineral resources at high temperatures, such as combustion of fossil fuels, roasting and smelting of ores, kilns operations in cement industry, as well as incineration of wastes and production of certain chemicals result in the release of several volatile trace elements to the environment. Mercury is one of the most important trace elements emitted to the environment due to its toxic effects on the environmental and human health, as well as its role in the chemistry of the atmosphere and other environmental compartments.

Our knowledge of mercury emissions on a global and regional scale is still incomplete. Recent estimates of global emission estimates by Pacyna and Pacyna (2000) indicate that Europe and North America seem to contribute less than 25 % to the global anthropogenic emissions of the element to the atmosphere. The majority of the emissions originate from combustion of fossil fuels, particularly in the Asian countries including China, India, and South and North Korea. Combustion of coal is and will remain in the near future as the main source of energy in these countries. An increase of energy demands in this region is clearly foreseen. It is therefore of utmost importance that the combustion of fuels in the Asian countries will be carried out in installation with efficient emission control, also for mercury. These installations are expensive (e.g. Pacyna, 1997) but the expenses on the purchase and maintenance are fully justified taking into account large emissions of mercury with its adverse effects on the environment. The expenses on emission control of mercury in the Asian countries are so large that international community would need to be called for finding proper solutions to the problem.

It is difficult to compare the emission estimates in this work with the estimates of Hg emissions from natural sources, mostly due to a lack of reliable data on the natural emissions. Assuming that annual emissions from natural sources are about 3000 tonnes, it can be concluded that the anthropogenic emissions contributed about 40 % to the total emissions of mercury from all sources worldwide in 1995.

Information on chemical and physical species of mercury emitted from various sources is needed for the development of models of transport and transformations of the element in the environment and the assessment environmental and human health risks. First approaches to assess emissions of various chemical forms of mercury to the atmosphere have recently been made (e.g. Pacyna and Pacyna, 2000). More than half of mercury is emitted as gaseous elemental mercury, while only 10 % emissions occur on particles. The rest of mercury is emitted as gaseous bivalent mercury.

Various international and national organizations and programs have been involved in assessing the current status of environmental contamination by mercury and in developing strategies and policies to reduce emissions of this pollutant. Major international activity to assess source - receptor relationships for mercury in the environment has been carried out within the UN Economic Commission for Europe (ECE) Convention on Long-range Transboundary Air Pollution Transmission (LRTAP). The aim of this activity is to assess major sources of mercury emissions in Europe, the environmental impact of these emissions, and eventually the emission reductions. There are also at least three other conventions in Europe working on the basis of international agreements which aim at the reduction of environmental fluxes of various pollutants to the marine environment, including mercury. These three conventions include: Oslo and Paris Commissions (OSPAR) program on reduction of land-based pollutants transported to the North Sea and the sister programs for the

Baltic Sea (Helsinki Commission - HELCOM) and for the Mediterranean Sea (Barcelona Convention). There are also national programs in the European countries aiming at the assessment of emissions of mercury and elaboration of emission reduction strategies for this pollutant.

2.2 NATURAL SOURCES

Natural sources can be very important contributors to the total budgets of atmospheric mercury. However, they are very difficult to assess and even to define. Two major source categories would include the sources related to the geological presence of mercury in various minerals and evasion of mercury from aquatic and terrestrial ecosystems. The latter source category is very much related to the historical atmospheric deposition of mercury to these ecosystems, emitted originally also from anthropogenic activities. It is extremely difficult with the current status of our knowledge to differentiate between the re-emission of mercury originally from anthropogenic and natural sources. However, some assumptions need to be made in this respect.

Emissions from volcanoes seem to be one of the major geological sources of mercury globally and in Europe together with evasion of the element from land containing Hg minerals. Southern Europe is the most affected region in Europe in this respect. A number of studies have been carried out in the Mediterranean Sea area to assess emission rates from these sources and eventually to estimate a contribution of natural emissions of Hg to the total emissions of the element in Europe. One of the major studies was recently completed within the EU project on the Mediterranean Atmospheric Mercury Cycle System - MAMCS (Pirrone *et al.*, 2000). The emission rates estimated within this project are presented in Table 2.1 (also discussed in Chapter-4).

Estimates of Hg emission rates within MAMCS can be used to calculate natural source emissions of the element in Europe. An amount of 200 tonnes per year can be proposed as an average value, which corresponds quite well with the earlier estimates of 265 tonnes per year carried out by Axenfeld *et al.* (1991) for the beginning of the 1980's. It should be admitted that both estimates include the total re-emission of Hg from aquatic and terrestrial surfaces.

2.3 ANTHROPOGENIC SOURCES

Processing of mineral resources at high temperatures, such as combustion of fossil fuels, roasting and smelting of ores, kilns operations in cement industry, as well as incineration of wastes and production of certain chemicals result in the release of several volatile trace elements into the atmosphere. Although substantial information has been collected on environmental effects of mercury and its behavior in the environment much less data is available on atmospheric emissions of the element. There are four major groups of parameters affecting emission of mercury to the atmosphere:

- contamination of raw materials by mercury,
- physico-chemical properties of mercury affecting its behavior during the industrial processes,

- the technology of industrial processes, and
- the type and efficiency of control equipment.

2.3.1. Contamination of Raw Materials

Concentrations of mercury in coals and fuel oils vary substantially depending on the type of the fuel and its origin, as well as the affinity of the element for pure coal and mineral matter. The sulfide-forming elements, with mercury included, are consistently found in the inorganic fraction of coal.

Although it is very difficult to generalize on the impurities in coal, the literature data (Gluskoter et al., 1977; Smith, 1987; Pacyna, 1987) seem to indicate that the mercury concentrations in coals vary between 0.01 and 1.5 ppm and that the lignites are somewhat less contaminated than bituminous and subbituminous coals. It should be noted, moreover, that concentrations of mercury within the same mining field might vary by one order of magnitude or more.

There is only limited information on the content of mercury in oils. In general, mercury concentrations in crude oils are about 0.01 ppm. However, on some sporadic occasions these concentrations were as high as 30.0 ppm (Pacyna, 1987). It is expected that mercury concentrations in residual oil are higher than those in distillate oils being produced at an earlier stage in an oil refinery. Heavier refinery fractions, including residual oil, contain higher quantities of ash containing mercury.

Natural gas may contain small amounts of mercury but the element should be removed from the raw gas during the recovery of liquid constituents, as well as during the removal of hydrogen sulfide. Therefore, it is believed that mercury emissions during the natural gas combustion are insignificant.

The most frequently measured concentrations of mercury in coals from various countries, crude oil and natural gas are presented in Table 2.2 after several studies summarized for this document.

Wood and wood wastes are used as fuel in both the industrial and residential sectors. In the industrial sector, wood waste is fired in industrial boilers to provide process heat, while wood is used in fireplaces and wood stoves in the residential sectors. As indicated in the Hg assessment in the United States (US EPA, 1995), wood and wood wastes may contain mercury. Insufficient data are available, however, to estimate the typical mercury content of wood and wood wastes.

Mercury appears as an impurity of copper, zinc, lead, and nickel ores. Obviously, there are also mercury minerals, particularly cinnabar. The element is also present in the gold ores. It is very difficult to discuss the average content of mercury in the copper, zinc, lead, nickel and gold ores as very little information is available in the literature on this subject. On the basis of the review by Pacyna (1983) it can be suggested that on average zinc ores contain larger amounts of the element compared to copper and lead ores.

Chemical composition of input material for incineration is one of the most important factors affecting the quantity of atmospheric emissions of various pollutants from waste incineration.

Very limited information exists on mercury concentrations in various types of wastes. Another difficulty is that it is almost impossible to calculate an average value for these concentrations due to the high variability in the content and origin of wastes to be incinerated, even in the same incinerator. Therefore, it is rather difficult to extend the information on the mercury content measured in one incinerator for another one.

2.3.2 Physico-Chemical Properties of Mercury Affecting its Behavior during the Industrial Processes

Most of the processes generating atmospheric emissions of mercury employ high temperature. During these processes, including combustion of fossil fuels, incineration of wastes, roasting and smelting operations in non-ferrous and ferrous metallurgy, and cement production, mercury introduced with input material volatilizes and is converted to the elemental form. It has been confirmed in various investigations that almost 100 % of the element is found in exhaust gases in a gaseous form (Smith, 1987; Pacyna, 1980). However, mercury in the exhaust gases may be oxidized by HCl and oxygen in the presence of soot or other surfaces as the temperature drops (Hall et al., 1991). Methods capable of determining the exact speciation in exhaust gases from various industrial processes are not readily available, however, a number of reasonable assessments have been made.

2.3.3 Technology of Industrial Processes

Various technologies within the same industry may generate different amounts of atmospheric emissions of mercury. It can be generalized for conventional thermal power plants that the plant design, particularly the burner configuration has an impact on the emission quantities. Wet bottom boilers produce the highest emissions among the coal-fired utility boilers, as they need to operate at the temperature above the ash -melting temperature (Pacyna, 1989).

The load of the burner affects the emissions of trace elements including mercury in such a way that for low load and full load the emissions are the largest (Bakkum and Veldt, 1986). For a 50 % load the emission rates can be lower by a factor of two.

The influence of plant design or its size on atmospheric emissions of mercury from oil-fired boilers is not as clear as for the coal-fired boilers. Under similar conditions the emission rates for the two major types of oil-fired boilers: tangential and horizontal units are comparable (Pacyna, 1982).

Non-conventional methods of combustion, such as fluidized bed combustion (FBC) were found to generate comparable or slightly lower emissions of mercury and other trace elements than the conventional power plants (Carpenter, 1979; Abel et al., 1981). However, a long residence time of the bed material may result in increased fine particle production and thus more efficient condensation of gaseous mercury. Tests carried out in the former Federal Republic of Germany have shown that the residence time of the bed material can be regulated by changing the operating conditions of a given plant, the reduction of combustion temperature, coal size, moisture content, and bed flow rates (Munzner and Schilling, 1985). A literature review of information on the influence of various FBC techniques on emissions of trace elements has been presented by Sloss and Smith (2000).

Among various steel making technologies the electric arc (EA) process produces the largest amounts of trace elements and their emission factors are about one order of magnitude higher than those for other techniques, e.g., basic oxygen (BO) and open hearth (OH) processes. The EA furnaces are used primarily to produce special alloy steels or to melt large amounts of scrap for the reuse. The scrap which often contains trace elements, and on some occasions mercury, is processed in electric furnaces at very high temperatures resulting in volatilization of trace elements. This process is similar from the point of view of emission generation to the combustion of coal in power plants. Much less scrap is used in other furnaces, where mostly pig iron (molten blast-furnace metal) is charged. It should be noted, however, that the major source of atmospheric mercury related to the iron and steel industry is the production of metallurgical coke.

Quantities of atmospheric emissions from waste incineration depend greatly on the type of combustor and its operating characteristics. The mass burn/waterwall (MB/WW) type of combustor is often used. In this design the waste bed is exposed to fairly uniform high combustion temperatures resulting in high emissions of gaseous mercury and its compounds. Other types of combustors seem to emit lesser amounts of mercury as indicated by the comparison of the best typical mercury emission factors for municipal waste combustors (MRI, 1993). It is also suggested that fluidized-bed combustors (FB) emit smaller amounts of mercury to the atmosphere compared to other sewage sludge incineration techniques, and particularly multiple hearth (MH) techniques.

2.3.3 Type and Efficiency of Control Equipment

The type and efficiency of control equipment is the major parameter affecting the amount of trace elements released to the atmosphere. Unlike other trace elements, mercury enters the atmosphere from various industrial processes in a gas form. This section discusses the latest progress in developing the techniques to remove gaseous pollutants from exhaust gases with focus on the removal of mercury and its compounds. Major emphasis is placed on the removal of mercury and its compounds by the application of flue gas desulfurisation (FGD).

The distribution of trace elements in coal-fired boilers with wet and dry FGD was reviewed by Moberg et al. (1982) within the Swedish KHM project. Halogens, mercuric chloride and selenium dioxide, were removed with SO₂ absorption. Large variations of mercury removal were found, probably due to differences in the behavior of specific mercury compounds. Formation of particles of chloride and sulfate salts was considered to be an important removal mechanism for mercury in the FGD process. This would be promoted by high Cl content in the coal and for mercury sulfate, by low temperatures combined with the catalytic effect of activated carbon.

Two major types of FGD systems can be distinguished: wet and dry FGDs.

Wet FGD Systems

Distribution of mercury within various streams of the wet FGD system was studied in various countries (1984). As much as 70 % of mercury in exhaust gases has remained in the gas stream after passing through the FGD. In general, the trace element content of the gypsum and sludge is influenced by the solubility of the elements upstream, the settling behavior of solids

in the thickener, and the waste water volume. In the waste water cleaning plant, the solubility of the trace elements is decreased by increasing the pH to the range of 8.0 to 9.5 so the waste water contains only very small amounts of the elements. Their concentrations in the waste sludge are at low levels (e.g. 6 ppm for Hg).

Wet FGD systems improve retention of trace elements from coal combustion where the elements have not already been retained by particulate control (e.g. mercury). The concentrations of trace elements in scrubber waste products depend largely on the amount of fly ash collected with the FGD wastes. The waste from dual collection FGD systems will resemble fly ash very closely, but for systems with efficient particulate removal, gypsum will contain very low or undetectable amounts of trace elements.

Removal of trace elements from exhaust gases by the wet FGD systems has also been studied in the Netherlands (Meij, 1989; 1992), where only pulverized coal-fired dry-bottom boilers are used, equipped with high-efficiency electrostatic precipitators (ESP) and FGD using a wet lime/limestone-gypsum process with prescrubber. Mostly bituminous coals imported mainly from US and Australia are burnt. In one study (Meij, 1992) the Hg concentration upstream of FGD was $3.4 \mu\text{g}/\text{m}^3$ and downstream was $1.0 \mu\text{g}/\text{m}^3$. The relative distribution of mercury between bottom ash, collected pulverised-fuel ash and fly-ash in the flue gases and in the vapor phase was about 10% on fine particles and about 90% in vapor phase. Flue gases contained 87% of the mercury concentration found in coal, and up to 70% of that was removed by the wet FGD. About 60% of mercury removal takes place in the prescrubber and about 40% in the main scrubber.

In summary, the relatively low temperatures found in wet scrubber systems allow many of the more volatile trace elements to condense from the vapor phase and thus to be removed from the flue gases. In general, removal efficiency for mercury ranges from 30 to 50%.

Dry FGD Systems

Retention of vapor phase mercury by spray dryers has been investigated in Europe and the United States for coal combustors and for incinerators (e.g. a review by Sloss and Smith, 2000). The following conclusions have been reached:

Brosset (1983): Water soluble mercury (40 to 80%) was partly bound in lime slurry and so mostly retained by the lime.

Bergstrom (1983): 50–70% of the mercury from coal was retained in the ESP ash preceding the FGD spray dryer; 75% of the mercury from coal was retained overall, so the major portion of removal was by the ESP.

Nilsson (1981): 30–40% of gas phase mercury was retained.

Karlsson (1986): 52–63% of mercury was removed, with 15–33% retained in the FGD unit (including baghouse).

Moller and Christiansen (1985): inlet gas phase mercury concentrations of $0.2\text{--}0.7 \text{ mg}/\text{m}^3$ reduced to $0.1\text{--}0.01 \text{ mg}/\text{m}^3$ through the FGD unit.

An excellent retention of trace elements by spray dryer systems implies that fly ash or dry end product might contain high concentrations of mercury. Karlsson (1986) showed that precollection was beneficial for some elements. The pattern for carry over of trace elements from the ESP to the dry end product is complicated by condensation of some constituents and varying degrees of enrichment, and interactions among the elements. For example, a high Ca concentration led to high As, Cr and Hg concentrations but low concentrations of other elements.

In summary, the overall removal of mercury in various spray dry systems varies from about 35 to 85%. The highest removal efficiencies are achieved from spray dry systems fitted with downstream fabric filters.

Low NO_x Technologies

Low NO_x technologies are also likely to reduce mercury emission in the exhaust gases due to the lower operating temperatures. Very limited information on this subject is inconclusive. While some sources indicate that the reduction can be achieved, preliminary results of staged combustion in atmospheric fluidized bed combustion (AFBC) units indicated that low NO_x had only little effect on trace element emissions (Sloss and Smith, 2000). It should be noted, however, that low NO_x technologies are far less used compared to the FGD systems.

Technologies to Control Emissions of Mercury on Particles

Coal-fired power plants and municipal incinerators are mostly equipped with either electrostatic precipitators (ESPs) or fabric filters. The ESPs are particularly efficient in removing all types of particles with diameter larger than 0.01 μm, including those bearing mercury after condensation within exhaust gases. The ESPs can tolerate operating temperatures as high as 720 K (Pacyna, 1987). The applicability of conventional precipitators is, however, limited by the electric resistivity of the particles. For example, low sulfur coals produce high-resistivity fly ash, and in such case the control efficiency of the ESPs drops off. The problem can be overcome by applying wet-type ESPs, which have the advantage of treating the exhaust gases under relatively cool saturated conditions.

Concerning the particle size distribution from the ESPs in coal-fired power plants, it has been concluded that the particle mass containing trace elements is concentrated mostly in two size ranges: 1) at ca. 0.15 μm dia., and 2) between 2 and 8 μm dia. Mercury can be found on particles in both size ranges.

Fabric filters are also used in coal-fired power plants. The particle collection efficiency is always very high, and even for particles of 0.01 μm dia. exceeds 99%. However, the life time of fabric filters is very dependent upon the working temperature and their resistance to the chemical attack by corrosive elements in exhaust gases. The temperature of exhaust gases often exceeds the temperature tolerance for fabric filter material and therefore limits the fabric filter application. A bimodal particle size distribution has been measured at the outlet of fabric filters, similarly to the size distribution of particles at the outlet of ESPs.

Summarizing the information on removal of mercury from exhaust gases generated during the combustion processes in power plants and incinerators, it can be concluded that between 30% and 60% of mercury is retained by high efficiency ESPs or fabric filters and FGD systems capture further 10 to 20 %. If coal cleaning is applied prior to combustion, preliminary data from the U.S. Department of Energy indicate 10% to 25% removal of mercury from coal in the case of commercial cleaning (MRI, 1993).

Mercury Removal from Exhaust Gases Generated in Industries other than Electricity and Heat Production and Waste Incineration

Various techniques to remove mercury from exhaust gases generated by industries other than the production of electricity and heat, as well as during waste incineration have been developed, particularly for metallurgical processes. A selenium filter has been applied at both steel and non-ferrous plants. In this dry media process, the volatilized mercury is reacting with red amorphous selenium forming mercury selenide. Mercury removal of 90 % has been achieved through this technique reducing the mercury concentrations to below 10 $\mu\text{g}/\text{m}^3$. Carbon filter is also used showing the removal effects similar to those reached with the selenium filter (SNV, 1991).

Lead sulfide process is another dry media technique used to remove mercury from flue gases generated in non-ferrous metal smelters. The gases containing volatile mercury are passed through a tower packed with lead sulfide coated balls. One study at a Japanese smelter in Naoshima indicates reduction of mercury concentrations from 1–5 mg/m^3 in the feed to the absorption tower to 0.01-0.05 mg/m^3 at the outlet (SNV, 1991).

The two major wet media processes to remove mercury from flue gases include selenium scrubber and so-called Odda chloride process. The selenium scrubber method is in principle similar to the selenium filter technique except for that activated amorphous selenium is circulating in a scrubber with 20–40 % sulfuric acid. The mercury reduction is about 90–95 %.

In the Odda chloride process mercury vapors are oxidized to form mercuric chloride which then precipitates. Mercury is recovered and mercury chloride is regenerated. The mercury concentrations of the treated gases are 0.05-0.1 mg/m^3 .

2.4 PAST AND CURRENT MERCURY EMISSIONS IN EUROPE

The first European-wide emission survey for atmospheric mercury has been elaborated in the mid 1980s (e.g. Pacyna et al., 1990). The reference year of this survey was 1982. The emission of total Hg from anthropogenic sources was estimated about 390 tonnes with 69 % contribution from the combustion of fossil fuels and 18 % from caustic soda production. The latest source was considered as underestimated, mostly due to the underestimation of Hg emission factor for this source.

The first update of the 1982 emissions was made for the reference year 1987 (Axenfeld et al., 1991). The emission of total mercury in 1987 was estimated about 726 tonnes, thus almost

double of that in 1982. Emissions from combustion of fossil fuels have increased by 30 % in the period from 1982 through 1987, mostly due to increase of coal consumption to produce electricity and heat. The largest increase, however, was estimated for the production of inorganic chemicals (chlor-alkali production), mainly caustic soda from about 71 tonnes of Hg in 1982 to more than 235 tonnes in 1987. The reasons for this increase are twofold: 1) increased production of these chemicals, and 2) improvement in estimation of emission factors of Hg, taking account emissions from ventilation and stacks.

The 1987 update was also important because for the first time emissions from natural sources in Europe were assessed, as well as first attempt to present chemical speciation of Hg in emissions from major source categories was made. Natural emissions were estimated concluding that their total amount is about 265 tonnes per year contributing about 27 % to the total emissions in 1987 (Axenfeld et al., 1991). Volcanic eruptions and venting, as well as re-emission from terrestrial and aquatic surfaces were found to be the most important natural sources of Hg in Europe.

It was also concluded that as much as 60 % of the anthropogenic emissions in Europe were in gaseous elemental form, 30 % as gaseous bivalent mercury and 10 % as elemental mercury on particles.

The second update of European emissions of Hg was prepared for the reference year 1990 (Pacyna, 1997). While preparing the 1990 update, special emphasis was placed on:

- improvement of information on mercury emissions during the coal and waste combustion through application of data on the reduction of mercury concentrations in the exhaust gases passing through various kinds of control equipment removing particles and gaseous pollutants (mostly sulfur dioxide),
- review of information on mercury removal with fly and bottom ashes in the European power plants,
- review of information on possible changes in the production quantities of chlorine and caustic soda, as well as in coal consumption, particularly in Eastern Europe after a switch to the free-market economies, and
- revision of information on mercury emissions from major "large point sources" in Europe.

An assessment of atmospheric emissions of mercury from anthropogenic sources in Europe in 1990, including the European part of Russia, concluded that the total atmospheric emission of mercury from anthropogenic sources in Europe was estimated to 627 tonnes. Large portion of the European emissions of mercury in the late 1980's was estimated for the VEB Chemische Werke Buna in Schkopau and for the chemical plants in Bitterfeld in the former German Democratic Republic. These large emissions were related mostly to the production of chlorine and caustic soda using so-called mercury method. The year 1990 was the beginning of the economical decline in these factories. During the last few years mercury emission from these sources has decreased drastically and is nowadays about 2 orders of magnitude lower than in the late 1980's.

Combustion of fuels, particularly coal, was still an important source category for atmospheric mercury in Europe. In some countries where combustion of coal is the predominant

technology to produce heat and electricity, the contribution of mercury emission from fuel combustion to the total national emission of the element is more than half of the total emissions. For example, the fuel combustion in Poland has generated more than 75% of the atmospheric mercury in the country.

Emissions from waste incineration were still underestimated in the 1990 survey. They represent emission data collected from 8 European countries only.

Anthropogenic emissions of mercury in Europe in 1990 were then spatially distributed using the 150 km by 150 km grid system. Emissions from more than 900 point sources were allocated according to their geographical location. Emissions from area sources were allocated using population density data. The highest emissions were estimated in Central and Eastern Europe, particularly in the Black Triangle area of south-western Poland, south-eastern Germany and north western Czech Republic, as well as in the Upper Silesia in Poland and in the region of Bitterfeld in Germany. High emissions were also estimated for Central United Kingdom and certain regions of Western Europe.

Concerning emission trends, an anthropogenic emission decrease of 14 % has been estimated between 1987 and 1990 in Europe, mostly due to the decrease of emissions during fuel combustion. The fuel combustion emissions have decreased by 30 % in this period. Further reduction of mercury emissions has occurred in the period from 1990 to 1993, particularly in Eastern Europe due to further decline of the production of industrial goods. This conclusion can be confirmed by 16 % decrease of average concentrations of total gaseous mercury measured over Scandinavia (Iverfeldt et al., 1995) in the period 1985-1989 as compared to the period 1990-1992.

The latest update and improvement of the mercury emissions from anthropogenic sources in Europe was made for the reference year 1995 (Pacyna et al., 2000). The estimates of total atmospheric mercury from anthropogenic sources in Europe in 1995 are presented in Table 2.3. Three sets of emission data are presented in this table: national estimates with their authors listed in Annex 1, estimates presented to the UN ECE European Monitoring and Evaluation Programme (EMEP) by national authorities (EMEP, 1999), and the estimates by Pacyna et al. (2001). The total amount of Hg emissions was estimated to 342 tonnes. The largest emissions were estimated for Russia (the European part of the country), contributing with about 25 % to the European emissions, followed by Ukraine, Poland, Germany, Romania, and the United Kingdom. All of these countries use coal as a major source of energy in order to meet the electricity and heat demands. In general, countries in the Central and Eastern Europe generated the main part of the European emissions in 1995. Annex-2 reports additional information provided by the European Cement Association (CEMBUREAU) which differ from the official estimates reported above.

Contributions from various source categories to the total emissions in Europe are presented in Figure 2.1. Combustion of coal in power plants and residential heat furnaces generates more than half of the European emissions, followed by the production of caustic soda with the use of the Hg cell process (12 %). Major points of mercury emission generation in the mercury cell process include: byproduct hydrogen stream, end box ventilation air, and cell room ventilation air. This technology is now being changed to other caustic soda production technologies and further reduction of Hg emissions is expected in this connection. A category called "Other Sources" in Figure 2.1 contributes about 15 % of Hg to its total emission in Europe. This category includes various uses of mercury, and particularly: primary battery

production, production of measuring and control instruments, and production of electrical lighting, wiring devices, and electrical switches. All of these uses of mercury decrease and lower emissions of Hg are expected from these sources in the future.

Changes of the Hg emissions from anthropogenic sources in Europe between 1980 and 1995 are presented in Table 2.4. A continuous decrease of emissions can be explained by the installation of efficient abatement technologies, particularly in Western Europe and a change in the production pattern of various industrial goods in Eastern Europe following the switch of their economies from centrally planned to market oriented at the beginning of the 1990's.

2.5 SPECIATION OF MERCURY EMISSIONS

Accurate information on emissions of various chemical forms of Hg is needed by the modelers simulating long-range transport and atmospheric deposition of the element to the marine and terrestrial surfaces. Studies carried out at the end of the 1980's on the chemical speciation of Hg emissions have continued within the EU projects, including the MAMCS project and the Mercury species over Europe: relative importance of depositional methylmercury fluxes to various ecosystems (MOE). Emission profiles of Hg for major anthropogenic source categories in Europe in 1995 have been elaborated and are presented in Table 2.5. These profiles were used to estimate emissions of various Hg species to the atmosphere in 1995.

The major chemical form of mercury emitted from the anthropogenic sources in Europe to the atmosphere is gaseous elemental mercury, contributing with about 205 tonnes in 1995 (about 61 %) to about 342 tonnes of the total Hg. Gaseous bivalent mercury contributed about 108 tonnes (about 32 % of the total), and the emissions of Hg on particles were about 25 tonnes (7 % of the total). Gaseous elemental mercury contributes the most to the total emissions of Hg from all source categories presented in Table 2.5 except for waste disposal. In the latter case, contribution of gaseous bivalent mercury is the highest. It is probably due to the high content of chlorine in wastes resulting in the formation of chlorides of mercury.

Contributions of emissions from various source categories to the total gaseous elemental mercury, gaseous bivalent mercury and emissions on particles are presented in Figures 2.2-2.4, respectively. Combustion emissions contributed the most to the emissions of various Hg species. However, while this contribution was about 45 % in the case of gaseous elemental mercury, it is between 66 and 68 % in the case of the two remaining species.

It should be admitted that more studies are needed to better understand the emission of various chemical and physical forms of Hg to the atmosphere. This information is needed for the assessment of environmental chemistry of the element, its transport pathways with air masses and water currents, cycling through the environmental compartments, and environmental and human health effects.

2.6 MAPS OF POINT AND DIFFUSE SOURCES IN EUROPE

Lists of major point sources and emissions of Hg from these sources in 1995 were prepared for individual countries in Europe. These lists are available from the emission data base at the Norwegian Institute for Air Research (NILU), Kjeller, Norway.

The basis for the lists was a set of similar lists prepared by Pacyna and Pacyna (1996) in an earlier work for the year 1990. These 1990 lists of emission sources were checked for the completeness of sources and their location (new countries in 1995 after the political division of the former Soviet Union, Yugoslavia and Czechoslovakia, as well re-unification of Germany). Then, the estimates of 1995 emissions within major categories were adjusted into major point sources within these categories, using the 1990 emission split as a basis.

The following information is presented within the lists of major point sources:

- name of the source,
- geographical position of the source, including latitude and longitude,
- codes, indicating the type of industry and industrial technology (installation code), and
- emission of total mercury.

Information on emission from "Other sources" is also included in the lists. These sources include major area sources (or diffuse sources) related to the combustion of fuels to produce heat in small residential and commercial furnaces.

The top ten point sources of anthropogenic mercury emissions in Europe in 1995 are presented in Table 2.6.

Information on the geographical location and Hg emissions for point sources was used to prepare spatial distribution of Hg emissions in Europe within the EMEP grid system of 50 km x 50 km. Diffuse emissions were distributed within this system using the information on population density within the grid system. The map of total emissions of Hg in Europe in 1995 within the EMEP grid system of 50 km x 50 km is presented in Figure 2.5. This map was prepared as a joint activity between the EU projects MAMCS (at NILU) and MOE (at the GKSS in Germany).

2.7 GLOBAL VS. EUROPEAN MERCURY EMISSIONS

The 1995 global emissions of total mercury from anthropogenic sources are presented in Table 2.7. It should be added that information of Hg emissions from caustic soda production and "other sources" is not included in Table 2.7. About 1900 tonnes of total Hg was emitted in 1995, which is in the upper part of the range between 1270 (minimum estimate) and 2140 tonnes (maximum) estimated earlier by Pacyna and Pacyna (1996) for the year 1990. The authors of the 1990 emission inventory concluded that the maximum emission estimate is close to the reality (close to the best estimate) rather than the minimum estimate. It should be admitted that the 1995 do not contain emissions from the use of mercury for the gold

production. These data are highly speculative and therefore it was decided not to include them in this paper. They can be, however, high as it was speculated that as much as 325 tonnes of Hg can be emitted from this process annually. More than half of these emissions were assumed to occur in Africa.

A summary of the 1990 maximum emission data is also included in Table 2.7 for comparison with the 1995 data. It can be concluded that no major changes were observed between 1990 and 1995 estimates of global Hg emissions from anthropogenic sources worldwide. Somewhat bigger is, however, contribution of stationary combustion of fuels to the total emissions in 1995. This contribution is as high as 77 % in 1995, compared to 60 % in 1990. Larger Hg emissions from combustion of fossil fuels, particularly coal in 1995 compared to 1990 are due to their increased combustion for the production of electricity and heat in the compared period of time.

There have been major changes in emissions in 1995 compared to 1990, with respect to the location of major emission regions contributing the most to the global emission survey of the element. Whereas the Hg emissions in Europe and North America have decreased quite substantially during the period from 1990 through 1995, emissions in Asia, particularly in China and India, have increased significantly. The Asian sources contributed about 30 % to the total emissions of mercury in 1990, compared to 56 % in 1995. An increase of more than 250 tonnes was estimated for China between the years 1990 and 1995. The increase of Hg emissions in China from 1990 through 1995 is clearly related to the increased of coal combustion in the country. The Hg emission increase due to the increased combustion of coal has overcome a slight reduction of emission of air pollutants in the country due to the installation of high efficient emission control devices starting in the mid 1990's.

Decrease of Hg emissions in Western Europe, the United States, and Canada can be explained by further installation of emission control equipment, particularly various flue gas desulfurisation (FGD) technologies, as already mentioned. Relatively low temperatures found in wet scrubber systems allow many of the more volatile trace elements to condense from the vapor phase and thus to be removed from the flue gases.

Decrease of Hg emissions from combustion sources, as well as other industrial sources in Central and Eastern Europe from 1990 to 1995 was also caused by a general decrease of industrial activities and resulting decrease of the consumption of raw materials. These decreases are related to the switch of economies from centrally planned to market oriented in this part of Europe. It is very difficult to assess to what extent the emission decrease can be accounted for the change of economies and what is the contribution of more efficient control equipment. Informal discussions of the authors with emission expert in Poland seem to indicate that as much as three quarters of emission reductions can be accounted for the decrease of industrial activities in the countries. However, this statement needs to be verified.

The national emission estimates for the incineration of wastes have been available from only a few countries in Western Europe and the United States. These estimates were used directly in this work. Then, statistics on the amount of wastes incinerated were available for another small group of countries. These statistics were used together with emission factor information to assess Hg emissions from waste incineration. These emission data are very much incomplete and therefore largely underestimated. The incompleteness of data has been caused by a lack of information from most countries on emissions of mercury during waste incineration and/or on the amount of wastes incinerated.

Emissions of Hg from pig iron and steel production, as well as the production of cement are very much related to the amount of the production of these industrial goods and the efficiency of emission control installations employed in these plants. No major changes in the Hg emissions have been observed between for these industries between the 1990 and 1995.

2.8 QA/QC AND UNCERTAINTY IN MERCURY EMISSION ESTIMATES

It is very difficult to assess the accuracy of currently available emission data for mercury mostly due to limited information on the accuracy of emission factor estimates, and specific statistical data in various countries. Ideally, emissions from at least major sources, such as large power plants, waste incinerators, smelter, steel and iron plants and cement kilns should be measured. Emission measurements would generate the most accurate data on emissions assuming that the proper sampling methods and analytical techniques are applied and the samples are collected at representative sites along the path of flue gases in the stack. However, to measure emissions at so many point sources is for many reasons impossible to accomplish in many countries. Therefore, less accurate methods, based on emission factors and material balances are applied to assess the emissions.

Anthropogenic mercury has been a subject of a few emission estimates, mentioned earlier in this work. Major sources of Hg emissions are fairly well defined and emission factors established. An emission estimation accuracy of less than 50 % can be assigned for this element in Europe, as proved by the comparison of air concentrations calculated by models using emission data and those measured. Very recent study carried out at the Meteorological Synthesizing Centre-East (MSC-E) of EMEP (EMEP MSC-E) concluded that an agreement between the model estimates of Hg concentrations in the air based on the emission data for Europe, used in this paper and air measurements at various EMEP stations in Europe was as good as within 6 % (Ryaboshapko et al., 1999).

Only single numbers of emissions are often presented instead of emission ranges. In the case that emissions were estimated using emission factors, these factors were the ones selected as the most relevant for a given industrial technology, an industrial development in a given country or region, a progress and improvements in application of advanced emission control equipment, the content of mercury in raw materials, etc. However, emission estimates for one category can be more accurate and complete than the estimates for another source category. It can be concluded that the following accuracy of emission estimates can be assigned to the estimates for individual source categories in Europe:

- stationary fossil fuel combustion: ± 25 %,
- non-ferrous metal production: ± 30 %,
- iron and steel production: ± 30 %,
- cement production: ± 30 %, and
- waste disposal: a factor of up to 5

2.9 CONCLUSIONS AND RECOMMENDATIONS

In recent years our knowledge on the contribution of major anthropogenic and natural sources and source regions in Europe to the regional mercury budget has improved. Various factors affecting the amount of emissions from these sources are also well defined. However, quantitative assessment of the emissions is not always complete and accurate to the extent requested by major users of emission inventories, such as policy makers preparing emission reduction strategies at local, regional, and even global scale, and modelers providing input to these strategies.

Estimates of current emissions of mercury from anthropogenic sources indicate that as much as 340 tonnes of this element can be emitted annually, with more than half of these emissions generated during the combustion of coal in utility, industrial, and residential boilers. A continuous decreasing trend of these emissions in the period from 1980 to 1995 as a result of the introduction of emission control installations (mainly in Western Europe) and the decrease of consumption and production of energy and industrial goods at the beginning of the 1990's (mainly in eastern Europe). Another 200 tonnes of mercury annually is emitted to the European atmosphere from natural sources, including the re-emission of mercury emitted previously from the anthropogenic sources and deposited to the aquatic and terrestrial surfaces. The accuracy of emission estimates for anthropogenic sources is within 30 % except for waste incineration (it could be as high as a factor of 5). No assessment of natural source emissions has been made so far but it is believed that emission estimates for natural sources are much less accurate than the emission estimates for anthropogenic sources.

Information on chemical speciation of mercury in the element emissions is crucial for modelers simulating the fate, behavior, and transport of mercury in the environment and policy makers using the information on environmental human health effects of this element. As much as 60 % of anthropogenic emissions of mercury in Europe is estimated to be in a gaseous elemental form, 30 % as gaseous bivalent mercury and 10 % as elemental mercury on particles. A majority of emissions from natural sources is believed to be in a gaseous elemental form.

At present, the European anthropogenic sources are estimated to contribute below 15 % of the mercury emissions to the total anthropogenic emissions of the element in the world.

It is important to point out that the mercury emission estimates reported in this chapter are based on the official emission data provided by national authorities to the UN-ECE in the framework of EMEP. However, in the review process of this chapter by the member of the Air Quality Steering Group (AQSG) an external contribution was received from the European Cement Association concerning mercury emissions from cement production. Although this data do not represent the official estimates reported by the national authorities, the WG decided to acknowledge this contribution which can be found in Annex-1.

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ANNEX-1

Source of information on Hg emissions from national experts.

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Winiwarter, W. Emission of Cd, Hg and Pb in Austria in 1985, 1990 and 1995. Austrian Research Centers, Seibersdorf, December 10, 1998.

2. Belarus

Belarusian Contribution to EMEP, Annual Report, 1996. Belarusian National Academy of Sciences, Meteorological Synthesizing Center – East, Minsk – Moscow, January 1997.

3. Bulgaria

Syrakov, D. 1997 Annual Report on Bulgarian Contribution to EMEP. National Institute of Meteorology and Hydrology, Sofia, January 30, 1998.

4. The Czech Republic:

Data reported to the UN ECE Task Force on Heavy Metals,

Machalek, P. Emissions estimates data –HMs in Czech Republic (1990-1995). Czech Hydrometeorological Institute, Emission Inventory Section, Division of Air Quality Protection, Prague, January 28, 1999, and

CHI: Air Pollution in the Czech Republic in 1997. The Czech Hydrometeorological Institute (CHI), Air Quality Protection Department, Prague, 1998.

5. Denmark:

Data reported to the UN ECE Task Force on Heavy Metals, and to the PARCOM/ATMOS program,

6. Finland:

Data reported to the UN ECE Task Force on Heavy Metals

7. France:

Fontelle, J.P. Heavy Metals emissions based on the 11 CORINAIR/MNECE/EMEP groups (take care of version SNAP 1997). CITEPA (Centere Interprofessionnel Technique D'Etudes De La Pollution Atmospherique), Paris, February 02, 1999.

8. Germany:

Schwermetallemissionen in die Atmosphäre, TUV Rheinland, Köln, EP 10/93, 1993, and

Jockel, W., Hartje, J. Report on the Development of the Emissions of Heavy Metals in Germany 1985-1995. Umweltforschungsplan Des Bundesministers für UMWELT, Naturschutz und Reaktorsicherheit, Köln, July 1997, letter of Jockel, W. Environmental Protection/Air Pollution Control, Köln, December 02, 1998.

9. The Netherlands:

Emission inventory in the Netherlands. Emissions to air and water in 1992. The Ministry of Housing, Spatial Planning and the Environment, Directorate-General for the Environment, Gravenhage, Publ. No. 22, December 1994, and

Berdowski, J.J.M. et al. Emissions to air for the Inventories of CORINAIR, EMEP and OSPARCOM 1990-1996. Ministry of Housing, Spatial Planning and the Environment, January 1998.

10. Norway:

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11. Poland:

Report on Heavy Metals Emissions in Poland for 1990. The Institute for Ecology of Industrial Areas, Katowice, November 1993,

Mitosek, G. National annual total anthropogenic emissions of heavy metals 1990-1995. Institute of Environmental Protection, Air Protection Division, Warsaw, October 1997, and

Hlawiczka, S. Report on heavy metals emission in Poland for the year 1996. Institute for Ecology of Industrial Areas, Katowice, March 1998.

12. Slovenia:

Rode, B. Heavy Metals emission estimations of Cd, Hg and Pb based on Technical Paper to the OSPARCOM-HELCOM UNECE Emission Inventory, 1990-1996. Ministry of the Environment and Physical Planning Hydrometeorological Institute of Slovenia, Ljubljane, December 29, 1998.

13. Slovakia:

Heavy Metals in Slovakia. Ministerstvo Zivotneho Prostredia Slovenskej Republiky, Bratislava, December 1994.

14. Sweden:

Heavy Metal Emissions to Air in Sweden in 1992. Swedish Environmental Protection Agency, Industrial Department, Stockholm, December 1993.

15. Switzerland:

Vom Menschen Verursachte Schadstoff-Emissionen in der Schweiz 1950-2010. Bundesamt für Umweltschutz, Schriftenreihe Umweltschutz No. 76, Bern, and

16. The United Kingdom:

The UK Atmospheric Emissions of Metals and Halides 1970-1991. National Atmospheric Emissions Inventory. Department of Environment, London, September 1993.

ANNEX-2

Contribution by the European Cement Association

Comment on Table 2.3 “Hg Emissions from Anthropogenic Sources in Europe”

CEMBUREAU has strong indications that the total Hg emissions from the cement industry in the EU15 countries are estimated far too high. This conclusion is based on measured emission data from Austria, Germany, the United Kingdom and Spain as shown below.

A. Austrian Hackl-Study “Emissionen aus Anlagen der österreichischen Zementindustrie (Emissions from the Austrian Cement Plants) II+III - Jahresreihen 1994-1996 +1997-1999 ”

Year	Total Emissions [t/a]	Average Exhaust Gas Volume [Nm ³ /kg Clinker]	Average Emissions [µg/Nm ³]
1994	0.123	2.309	14.0
1995	0.077	2.408	10.9
1996	0.070	2.376	10.2
1997	0.090	2.254	12.8
1998	0.072	2.200	11.5
1999	0.077	2.133	12.7

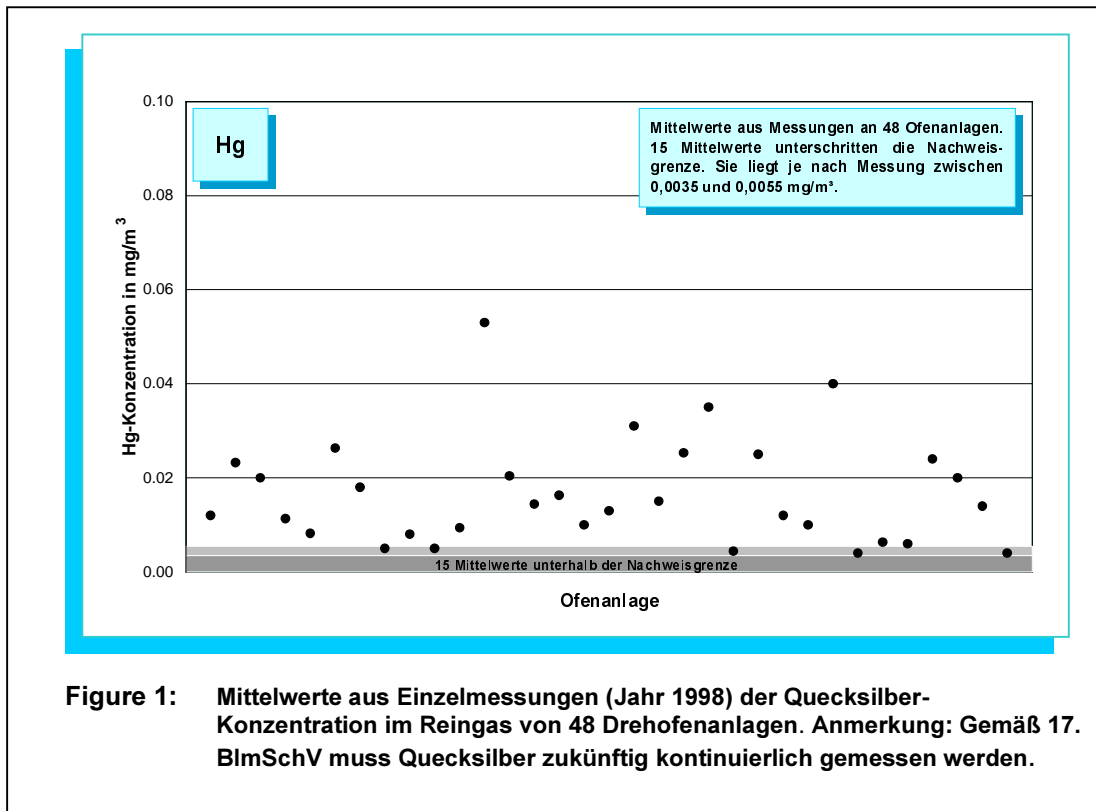
The given data confirm a range of total Hg emissions of 0.07 to 0.08 t/a corresponding to an average Hg emission of about 12 µg/Nm³

B. Umweltdaten der deutschen Zementindustrie 1998” (“Environmental data of the German Cement Industry 1998”) published by the Verein deutscher Zementwerke (VDZ), September 2000.

This survey provides an extensive overview of relevant environmental data and is covering 90% of the German cement industry and can therefore be regarded as representative. The following graph is presenting the average values of Hg measurements.

With respect to the mercury concentration in the stack of cement kilns the available data result in an average mercury concentration of about 13 µg/Nm³. (Values below the detection limit were very conservatively counted as the detection limit).

Taking into account the German clinker production of about 28 million tons over the last years and the conservative approach for the exhaust gas volume in German cement kilns of 2 000 Nm³ per ton clinker, our calculation is leading to a value for the mercury emissions of 0.72 tons per year.



C. Current Data from the United Kingdom

Recent data provided by 2 plants of Castle cement in the UK (wet kiln and a dry kiln with wet slurry induction to the kiln; each of them burning waste) show emission levels in the range of 1.1 to 6 $\mu\text{g}/\text{Nm}^3$ with a weighted average of 3.7 $\mu\text{g}/\text{Nm}^3$ for mercury. These very low figures lead to a specific emission of about 12.8 mg Hg/t Clinker being even lower than the corresponding values of Austria and Germany.

The British Cement Association has collected recent data from 1999 for the all 21 plants operating 34 kilns in the UK. These data provide the most reliable and comprehensive update for the mercury emissions in the UK and has been submitted to the Environmental Agency by each plant. All figures summed up lead to the total mercury emission in the UK by the British cement industry for 1999 of 0.154 t/a. The data are publicly available on the website of the Environmental Agency under <http://www.environment-agency.gov.uk>.

D. Current Data from Spain

A recent internal study performed by the Spanish Cement Association OFICEMEN produced results of mercury emissions from 13 different cement kilns (representing more than 20 % of the total Clinker production of Spain). The weighted average emission level is given as 6.7 $\mu\text{g}/\text{Nm}^3$.

Using the figure of $6.7 \mu\text{g}/\text{Nm}^3$ for the total clinker production of 28 106 kt for the year 2000 and the very conservative figure for the exhaust gas volume of $2.400 \text{ Nm}^3/\text{t}$ Clinker, the annual load of mercury in Spain can be calculated to 0.452 t for the year 2000.

Based on the examples of Austria and Germany, the United Kingdom and Spain CEMBUREAU is of the opinion that there is a big discrepancy between the measurement data and the data provided by Table 2.3 of Chapter 2 of the “Position Paper on Mercury”. The following table compares the results based on measurements with the results based on the data provided in the current Draft of the “Mercury Position Paper”.

Country	Current Clinker Production [kt]	Position Paper values [t/a]	Measurement based data [t/a]
Austria 1996	2 916	0.20	0.08
Germany 1998	27 520	5.60	0.72
United Kingdom 1999	11 410	0.60	0.154
Spain 2000	28 106	2.70	0.452

It may be worthwhile noting that the Hg emission for the EU15 countries given in the “Position Paper” correlate much better to a worst case scenario (emission level of $50 \mu\text{g}/\text{Nm}^3$ = current national emission limit value + Exhaust Gas Volume of $2\,300 \text{ Nm}^3$ per tonne Clinker). This observation raises the question whether national data provided for international inventories could be based on similar estimations as mentioned above rather than on real measurements. CEMBUREAU would like to emphasize that these figures and examples may indicate a general error in the level of emissions in the “Position Paper”. This needs to be checked also for the other EU15 countries.