Chapter 4
Mercury Emissions from Industrial Sources in India and its Effects in the Environment

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Summary This study describes the atmospheric mercury (Hg) emissions from industrial sources in India for the years 2000 to 2004. In India emission inventories of Hg and other trace elements from anthropogenic sources have been largely neglected, although the GDP (Gross Domestic Products growth) has touched 9.6% at the beginning of the 21st century. In coal production India is the third largest in the world, whereas Indian cement and brick production have reached second place in the world. With increased industrial development, acute pollution problems have been identified in the subcontinent. There is no consistent earlier information for Hg emissions to the environment for any sectors of industry. This paper may be the first road map in which we have tried to find out the total emission of Hg from a wide range of sources, e.g. from coal combustion to clinical thermometers broken during production or packing. There is a lack of basic data and in an attempt to correct this, emission factors suitable for Asian countries have been selected to complete this study. Before this document, there were some efforts in Europe to develop emission inventories for Hg from coal combustion or chlor-alkali plants for India. In this study it was found that total atmospheric emission from industrial sources has decreased from 321 Mg in 2000 to 253 Mg in 2004 due to a switch for the membrane cell process in the chlor-alkali industry. In 2004 the largest part of the Hg emissions stemmed from coal combustion in thermal power plants. Hg-cell technology had been used earlier in chlorine and sodium hydroxide production, as a result of which Hg concentration in terrestrial and aquatic species are nowadays quite high in coastal areas. India can thus be referred to as a mercury "hot spot". We have received limited information on emissions of Hg from industrial sources in India. Estimates are based on emission factors and the values taken from the literature. Against a background of limited data and information, this paper gives an overview of Hg emissions in India and of the recent steps undertaken by authorities to curb the emissions of Hg and its subsequent trans-boundary movement in the global environment.

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4.1 Introduction

Economic advancement of any country whether developed or developing depends on capital to provide the rapid growth of manufacturing industries, infrastructure, and for the modernization of economies and societies. For the past three decades, India has achieved increased production of metals, cement, fertilizers, chlorine, pulp and paper as well as heat and electricity, through burning of coal, natural gases and oil (Table 4.1). Hence the country became one of the most rapidly growing economies with an average annual growth of 9.6 percent and it has later crossed the ten percent level (Choi, 2003). During the course of development, industrial management and the government authorities did not pay adequate attention at the regional or central levels, to pollution problems due to mining operations, metal smelting, electroplating, energy and fuel consumption, sludge dumping and many others operations causing pollution problems in the terrestrial and aquatic environments. Examples of soil pollution as well as other pollution problems in the aquatic and terrestrial environment are well documented in India (Kumar et al., 1995; Choi, 2003). In the industrial area of Chhattisgarh state, water discharged from different industries such as thermal power plants, the steel industry, the cement industry, sulfuric acid plants, rice mills, coal washing etc, was cited to contain total Hg between 6.7 – 678 ng mL^{-1} with mean and median values of 118 and 49.3 ng mL^{-1}, respectively. High concentrations of Hg in human hair have also been reported in Chhattisgarh state. Human activities redistribute Hg in a manner that causes elevated concentrations of pollutants in the human food chain (Nriagu and Pacyna, 1988).

Table 4.1 Production of metals, coal, residue fuel oil and cement in India, 2000-2004 (*Tg*)

Element	2000	2001	2002	2003	2004
Copper, Cu[1]	0.256	0.293	0.385	0.391	0.401
Sec. Copper[4]					0.007
Lead, Pb[1]	0.057	0.074	0.064	0.078	0.042
Sec. Pb[4]					0.040-0.050
Zinc, Zn[1]	0.176	0.207	0.232	0.254	0.238
Sec. Zn[4]					*0.065*
Pig Iron, Fe[1]	21	22	24	24	25
Raw Steel[1]	27	27	29	32	32
Hard coal[2]	310	312.5	333.7	340e	373
Residue fuel oil production[3]	7.965	8.308	7.855	6.905	7.267
Cement[1]	100	100	100	110	111e

In italic = estimated value

[1] http://minerals.usgs.gov/minerals/pubs/commudity

[2] USGS, 2005; www.worldcoal.org accessed on 11.29.2007

[3] IEA (2007);

[4] Secondary metal production for 2004.

Information received from Indian Copper Development Center, Kolkata (2007) and Indian Lead and Zinc dev Association, New Delhi (2007). Note: The authority mentioned that production of secondary lead varies between 40000 to 50000 Mg in a year

Among the several trace elements in the periodic table, Hg is considered as a toxic trace element to humans, animals, and the ecosystem because of its unique geochemical characteristics. It is a natural element that cannot be created or destroyed and the same amount has existed on Earth since the planet was formed. It exists in several states: Hg-metallic liquid, Hg vapour, inorganic $\text{Hg}^{(I)}$ (mercurous salts) inorganic $\text{Hg}^{(II)}$ (mercuric salts) and gaseous Me-Hg (Drasch et al., 2004). There is global concern regarding the recycling of this element, especially in the Indian subcontinent and China where less attention has been paid to the environmental consequences of increased production of chlorine, metals, waste incineration and coal combustion as well as brick manufacturing in India. It has been suggested that the overall amount of Hg mobilized and released in the Indian atmosphere has decreased slightly in recent years, although there is no emission inventory of Hg from these facilities and the data availability is scarce. This is further complicated by the fact that the decision makers still pay minimal attention to the issues concerning Hg emission and related environmental hazards. Even in the international journals little attention has been paid to the atmospheric Hg emission into the techno sphere in India. In general, the state of Hg and other trace metal research is not well established as compared to the western world.

In India, there are no cinnabar ore resources for the production of Hg and neither is there information that indicates whether Hg is recovered as a by-product from certain processes. There is controversy regarding the amount of Hg imported from the European Union (EU) and other countries, but the total import amount has decreased from 253.7 Mg in 1996 to 123.4 Mg in 2004 (Pandey, 2006). This imported Hg is generally used in chlor-alkali plants and the leading Hg users are shown in Table 4.2.

Table 4.2 Leading mercury users in India (1998 – 2001)

Sector	Hg content per unit	Units produced	Total Hg (*Mg*)
Chlor-alkali	~ 200 g Hg used per Mg of Cl_2 produced	450,000 [a]	70
Thermometers	0.6 – 1.0 g	8957,000 [b]	7.2
Batteries	Alkaline not more than 25 mg	NA	
Hg-Zinc	Total 33 to 50% by wt of the battery	1,650 million [c]	25
Zn-Carbon	Total 1% Hg by wt of the battery	NA	
Fluorescent lamps	0.0252 – 0.080 g per lamp [f]	150 million [c]	7.89
Thermostat switches	3 – 6 g	4051,000 [d]	18.23
Alarm clocks	Average 0.6 – 0.7 g unit^{-1}	1481,000P [b]	0.96
Hearing aids	0.4 g unit^{-1}	95,500 [c]	0.04
Sum			129.32

[a] Environmental rating of Indian Caustic-Chlorine Sector, Green Rating Project (2002), Center for Science and Environment.

[b] Industrial Handbook, Centre for Industrial & Economic Research /Delhi), 1998

[c] Industrial Handbook, Centre for Industrial & Economic Research /Delhi), 2000–2001

[d] http://www.Indianfoline.com/auto/db01.html

[e] Telephone conversion with Battery Industrial Official

[f] Draft Wisconsin Mercury Sourcebook, Wisconsin Department of Natural Resources (USEPA, May 1997)

There is no information of cross-boundary flow of Hg vapour from India to other parts of the world except for the Himalayas (covering an area of roughly 6 × 10^5 km^2). The study by Banic et al. (2003) suggests that Hg has the capacity to move to high altitudes. During snow deposition, $Hg^{(II)}$ can be photo-reduced to elemental Hg and remitted back into the atmosphere. It is still unknown how Hg species at the Himalayan region precipitates in the terrestrial and aquatic environment in mountain areas (Loewen et al., 2005).

A recent emission inventory of Hg by Jaffe et al. (2005) indicated that Asian Hg accounts for more than 50% of the global anthropogenic release of Hg. These authors confirmed that the ratio of Hg/CO is a good indicator of Asian industrial flow, including India. These authors suggested that it is possible to calculate Hg emission based on the Hg/CO ratio and the inventory of CO emissions. Lindberg et al. (2007) pointed out that biogeochemical cycling of Hg is similar to that of carbon (C), sulphur (S) and nitrogen (N). However, levels of Hg emissions in the form of aqueous and atmospheric Hg on the Indian subcontinent are alarming. Recently, Srivastava (2003) outlined the sources of Hg and its risks to the Indian environment. Studies by Weiss-Penzias et al. (2003) indicated that industrial emissions of Hg from Asia can be transported across the Pacific within five days.

Mercury in the air consists of two main chemical forms, being elemental Hg (Hg^0) and divalent Hg compounds which are in gaseous forms or are bound to particles in the atmosphere. Mercury can also exist in the environment in the form of organo-metallic compounds e.g. methyl mercury (MeHg). But, the speciation of Hg in the aquatic environment determines its chemical reactivity, mobility and biological activity. Mercury is deposited over land, water, and forest regions either by wet (Figure 4.1) or dry deposition. But the enhanced wet deposition rates close to major Hg sources through cloud-droplet activation and precipitation scavenging

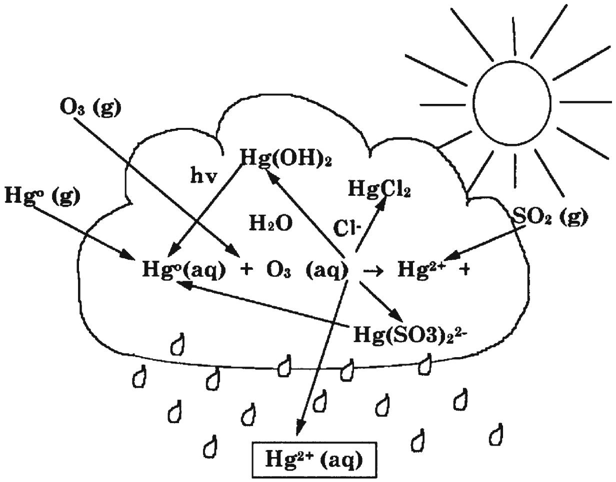

Figure 4.1 Chemistry of wet deposition of mercury (reproduced from Lindqvist et al., 1991)

have been confirmed (Dvonch et al., 1998; Munthe et al., 2001). However, the deposition rate is highest in regions where elevated rain fall or snow fall occurs. The humidity in India is quite high especially in the south, middle and eastern parts, where deposition of Hg is expected to be highest. In northern Europe in the 1990s, an ~ 40% decrease of wet deposition in southern Sweden was a result of a decrease in air concentrations, and thus in the wet deposition rate of Hg (Munthe et al., 2001).

International transport of Hg in the Indian subcontinent has not been studied sufficiently, as a result of which it is impossible to predict its effects in terrestrial, aquatic and freshwater ecosystems. Atmospheric Hg can be deposited to aquatic systems in the Himalayas region, which may be the source of Hg in river water, sediments and head water systems. Subraminium et al. (2003) measured Hg in fish species (0.069 – 3.920 mg kg^{-1} wet wt), sediment (0.16 – 5.71 mg kg^{-1}) and water (0.17 – 2.351 mg L^{-1}) from the Indus River. These authors did not mention Me-Hg in Indian fish. It should be remembered, however, that many variables must be considered, such as atmospheric processes mixed with aquatic variables, which will dictate the overall levels of Me-Hg in fish tissue (Downs et al., 1998).

After the first international conference on "Hg as a Global Pollutant" in 1990 at Gävle, Sweden, understanding of Hg chemistry in the ecosystem has increased among the scientific community. Still our scientific understanding of Hg in ecosystems is not absolute and is rarely complete (Lindberg et al., 2007). Weiss-Penzias et al. (2003) measured gas-phase elemental Hg (Hg^0), inorganic reactive gaseous mercury (RGM) and particulate Hg (Hg(p)) in the marine boundary layer of Washington state, USA in 2001 – 2002. It has also been observed that in the Polar regions, Hg^0 can be converted to RGM by chemical reaction with halogen species (Ebinghaus et al., 2002).

One rather difficult question is whether emission inventories are consistent with observations. Emission factors can be used to estimate the emission of an element, but this approach is far from perfect (Pacyna et al., 2006a). In the view of those authors, the accuracy of emission estimations is based on the accuracy of emission factors available in the Emission Inventory Guidebook (UN ECE, 2000, (http://www.epa.gov/ttn/chief/ap42/ndex.html). However, emission factors will give a useful guideline to the emission of an element or species from industrial or natural sources.

Many authors have identified natural sources of Hg emissions (not in India), for example, from forest fires, sands, oceanic mist, volcanic activities, photo reduction of divalent Hg in natural waters. The weathering of bed rocks may contribute to high concentrations of Hg (100 ng g^{-1}). Wide ranges of Hg in rocks (Table 4.3) determine equally wide ranges of natural background levels in soils and sediments, impacting on Hg bioaccumulation in aquatic and terrestrial species. In addition, laboratory studies have quantified the Hg emissions from soils where solar radiation has enhanced Hg emissions (Gustin et al., 2002). We must understand the natural background levels of Hg species before any conclusions on anthropogenic Hg input may be drawn. The Hg in the freshwater food chain may be due to the global increase in the background level of total Hg (Rohde, 1996).

This study (November 2007 – May 2008) is based on a literature survey with a final goal to estimate Hg emission from industrial sources in India. Stack emission measurements are not mandatory in Indian industry. Hence no emissions data are

Table 4.3 Mercury concentration in different rock samples (from different sources)

Source	Hg (*ng* g^{-1})	Range (*ng* g^{-1})	Location
Ocean ridge basalt	10*		
Granite porphyry	117	5 – 468	Maine
Gabbro, Granite	10	-	Minnesota
Granite, (Granodiorit)	30*		-
Granite,(Rhyolite)	3.5	1.4 – 281	Sweden
Limestone	6	0.8 – 31.2	Sweden
Limestone	-	40 – 50*	-
Sandstone	110	-	-
Sandstone	-	40 – 100*	
Black shale	234	31.9 – 340	Sweden
Shale	5.9	0.9 – 33.5	Sweden
Shale	-	180 – 400*	
Mafic (Basalt)	3.9	0.2 – 17.7	-
Mafic	-	4 – 10*	-

*Source: Kabata-Pendias and Pendias (2001)

available in the literature for trace metals, including Hg. In addition information on atmospheric Hg emissions is very limited or non-existent in sources presented by the government. Several Indian organizations and companies were contacted for information during this study but the response was very poor or nil.

In the present study, the estimated atmospheric Hg emissions are based on emission factors for the European Union (EU), for the U.S., from the literature and from the limited information received from India. An emission factor is a representative value that attempts to relate the quantity of a pollutant released to the atmosphere with an activity associated with the release of that pollutant. The general equation for emissions estimation is:

$$E = A \text{ x } EF \text{ x } (1\text{-}ER/100) \qquad (1)$$

where:
E = emission;
A = activity rate;
EF = emission factor, and
ER =overall emission reduction efficiency, %

Here we did not deal with emissions from secondary metal production as there are no emission data available. This document is by no means complete, but gives a first road map on how to deal with emission patterns of Hg in India.

4.2 Results

There is no doubt that industrial development has contributed to momentous economic growth in India over the last few decades, which has not, however, spread uniformly in society. Industrialization, population growth, urbanization, and unbalanced uses of raw materials have created enormous air pollution, causing acute environmental problems (Garg et al., 2006). Never before in the history of mankind have such vast environmental risk factors from Hg, or natural danger to humans, terrestrial and aquatic species been reported. Hence, education and awareness programs must be launched across the Indian subcontinent to educate the population on the risks from Hg and other trace element exposure, addressing especially the most vulnerable sectors of the population e.g. pregnant women and children (Srivastava, 2003). It is well recognized that Hg is widely spread in India and in this study we have dealt with industrial emissions of Hg from the following sources:

- Coal combustion
- Iron & Steel Industry
- Non-ferrous metallurgical plants
- Chlor-alkali plants
- Cement industry
- Wastes
- Biomass burning
- Others (e.g. brick manufacturing, instruments, clinical thermometers)

In this study, no information was available from the pulp & paper industry or from the oil and petrochemical industry in India.

4.2.1 Coal Combustion

Coal reserves are distributed widely across the planet, but recoverable reserves are reported for only seventy countries. It has been estimated that world coal reserves may be sufficient for at least another 2-3 centuries whereas the figures for oil and gas are 41 and 65 years, respectively, at current production levels. In India, the coal mining area covers some 855 km^2 and the total number of coal mines is 572 (March 2004), of which 170 are opencast, 359 underground and 33 mixed (Mine Closure, 2005), Figure 4.2. India is the third largest hard coal producer in the world after the PR China and the USA. Coal production has increased from 310 Tg in 2000 to 373 Tg in 2004. About 70% of the heat and electricity production in India depends on indigenous coal. From time to time, steam coal (11 Tg in 2001) and coking coal (9.8 Tg in 2001) have been imported, which in 2005 had increased to 41 Tg of steam and coking (19 Tg) coals (GOI, 2006). Coking coals are primarily consumed in the iron and steel industry. There are 81 thermal power plants in India, three of which are not operating currently.

The occurrence and distribution of Hg in different compartments of ecosystems has been studied by many authors. Mercury is a chalcophile element, having great affinity for sulphur-containing compounds. This element (which in pure form and at ambient conditions is a liquid) is generally incorporated in pyrite (iron sulphide) and the concentrations of Hg vary with mineral paragenesis (Kolker et al., 2006). Due to its high vapour pressure and physicochemical properties, the element

Figure 4.2 Coal reserves in India, 2004

vaporizes easily during processing and thereby is released into the atmosphere. In India, gas cleaning equipment is not modern (involving almost exclusively only fly ash (FA) emissions control) and there are no flue gas desulphurisation (FGD) plants.

For estimation of Hg emission from coal and other products, emission factors have been selected and occasionally estimated in the current study (Table 4.4). Mercury in coal has been measured by the Pollution Control Research Institute of Bharat Heavy Electricals Ltd, India (Table 4.5) whereas the Centre for Science and Environment (CSE, 2005) pointed out that the concentration of Hg in Indian coal varies between 0.01 and 1.1 mg kg^{-1} (= ppm-wt). For estimation of Hg emission

Table 4.4 Emission factors of mercury from industrial sources used for India

Source Category	Unit	EF	Reference
Coal fired power plants	$g\ Mg^{-1}$Coal	0.3, 0.324*	1, 2
Residential and commercial boiler	$g\ Mg^{-1}$ Coal	0.5	1
Crude steel production	$g\ Mg^{-1}$ Steel	0.08*	2
Residual fuel oil combustion	$g\ Mg^{-1}$oil	0.065	10, 11
Non-ferrous metal production			
- Copper	$g\ Mg^{-1}$ Cu production	15	3, 4
- Zinc	$g\ Mg^{-1}$ Zn production	8	1
- Lead	$g\ Mg^{-1}$ Pb production	43.6	5, 6
Caustic soda production	$g\ Mg^{-1}$ NaOH production	20.4	7
Cement production	$g\ Mg^{-1}$ Cement	0.042*	2
Wastes			
- Municipal solid waste (MSW)	$g\ Mg^{-1}$ MSW	1.0	1, 3
- Medical waste	$g\ Mg^{-1}$ Medical waste	20	3
- Electronic waste**			8
Miscellaneous			
- Bricks	$g\ Mg^{-1}$ brick	0.0214	9
Chlor-alkali plants	$g\ Mg^{-1}$ of NaOH	20.4	7
Forest burning	$g\ Mg^{-1}$ of fuel	0.242	12
Non-forest burning	$g\ Mg^{-1}$ of fuel	0.041	13

References: (1) Pacyna et al. (2006b); (2) This study; (3) Pirrone et al. (1996); (4) Nriagu and Pacyna (1988); (5) Li (2007); (6) Feng et al. (2004); (7) Qi et al. (2000); (8) Sarkar (2007); (9) USEPA (1997a); (10) Mukherjee et al. (2000); (11) Sunderland and Chmura (2000); (12) Veiga and Meech (1994); (13 Friedli et al. (2008).

*Estimated in this study

**Sarkar (2007): Hg in each computer is 0.0022%, weight of Hg in each computer is 0.00059 kg (assuming average weight of a computer is 27 kg), recycling efficiency is 0%, estimated obsolete computer is 1.38 million. Total annual production of Hg releasing to the environment is (0.00059 kg x 1380000)/1000 = 0.82 Mg.

Table 4.5 Samples collected from eight coal based power plants in India (BHEL, 2004vide Pandey, 2006)

Names of power plants	Hg in coal ($mg\ kg^{-1}$)
GHTTP, Lehra, Mohabatt	0.26
Anpara, UP (BTPS)	0.26
North Chennai	0.33
NLC-TPS II	0.18
Chandrapura STPS	0.325
Kolaghat TPS (West Bengal)	0.61
Talchar TPS	0.33
Gandhinagar TPS	042
Mean (Range)	0.376 (0.18 – 0.61)

Note: Number of samples analyzed are unknown.

from coal it is assumed that Indian coal contains on average 0.376 mg Hg/kg. The emission of Hg to the atmosphere will be more if we use the emission factor 0.5 g Hg Mg^{-1} calculated by Pacyna and Pacyna (2000), and also the efficiency of

Table 4.6 Atmospheric mercury emissions from industrial sources in India for 2000 and 2004, respectively (this study)

Source category	Consumption/ Prod. 2000 (*Tg*)	Hg emissions 2000 (*Mg*)	Consumption/ Prod. 2004 (*Tg*)	Hg emissions 2004 (*Mg*)
Coal fired power plants	310	100.44	373	120.85
Residential & Commercial boiler	7.3	3.65	7.4	3.7
Pig iron & steel production	48	3.84	57	4.56
Cu-production	0.256	3.84	0.401	11.78
Pb-production	0.057	2.49	0.042	1.83
Zn-production	0.176	1.41	0.238	1.90
Residual fuel oil Consumption	7.96	0.52	7.27	0.47
Cement production	100	4.2	111	4.66
Municipal solid waste	50	50	70	70
Medical waste	0.33	6.6	0.33	6.6
E-waste	-	-	0.146	0.82
Biomass burning	32 (16 – 61)	7.74	32 (16 – 61)	7.74
- Forest	116 (58 – 289)	4.76	116 (58 – 289)	4.76
- Crop				
Chlor-alkali plants	0.476	132[a]	0.304[b]	6.2
Brick manufacturing	-	-	350 (140 × 10^9 pieces) [c]	7.49
Sum		321.49		253.36

[a] We have assumed that in 2000, average Hg emissions from Chlor-alkali plants were (185 + 79 = 264/2 = 132 Mg (see section 3.4);

[b] In 2004, the data for 2006 has been used to estimate Hg emissions form Hg-cell plants. The abnormal reduction of Hg emission in 2004 was due to conversion of Hg-cell process to Membrane cell process where no Hg is used.

[c] We have assumed that weight of a Indian brick is 2.5 kg. Based on this information, the total weight of bricks in this study: 140 × 10^9 pieces × 2.5 kg wt of a brick i.e. 350 Tg of bricks.Weight of a brick is obtained by personal communication with TERI, New Delhi on 11.01.2008.

Regarding biomass burning, Venkataraman et al. (2006) mentioned unit: Tg yr^{-1}. For this reason, we have assumed that the same amount of biomass was burnt in 2000 and 2004, respectively.

gas cleaning equipment in power plants is in question. The emissions of Hg from coal fired power plants in Indian in the years 2000 and 2004 are shown in Table 4.6. The emission of Hg from power plants has increased by 17% since 2000 and the amount of Hg discharged into the environment may still be increasing as many plants have no gas cleaning equipment, similar to the situation in China. It is necessary to add, however, that at lower temperatures (350 – 400°C) in the flue gas duct, in the presence of chlorine, sulphur and calcium part of the Hg^0 vapour is oxidized to $Hg^{(II)}$, and/or reacts with carbonaceous ash particles and is deposited as Hg(p). Indian coal typically contains over 35%-wt fly ash (FA), and this particle surface offers an important site for Hg absorption (Mukherjee et al., 2008). In a recent study by USGS on 102 selected coal samples from different basins of India concentrations of Hg were found to be in the range between 0.02.to 0.16 mg kg^{-1}. Further details will be available at the project website of the USGS (http//energy. er.usgs.gov/coal quality/wocqi/collaborators.html) (A. Kolker, USGS, and S. Dunkee USEPA, personal communication, 5, May, 2008).

Currently, the energy sector contributes over 120 Tg of fly ash (FA) across the country. Several recent studies have identified heat, humidity, solar radiation and the presence of water as important factors in the release of Hg from FA, FGD solids or a mixture of these. The current estimation of Hg in FA is about 41 Mg (Mukherjee et al., 2008), although there is a lack of information on Hg in Indian coals and coal FA (Mukherjee and Zevenhoven, 2006).

4.3 Iron and Steel industry

In the 21st century, iron and crude steel production in India has increased from 21.3 Tg in 2000 to 25.0 Tg in 2004, and from 26.9 Tg in 2000 to 32.0 Tg in 2004, respectively. Steel is manufactured mainly by integrated steel manufacturing processes using the chemical reduction of iron ore, and conversion of iron from the blast furnace in a basic oxygen furnace (BOF). Steel can also be produced by melting steel scrap (e.g. from shredded cars) in an electric arc furnace (EAF). Coke, necessary in the iron and steel industry, is obtained by coking in ovens at 1000 °C or more. Here, Hg from coal is passed into the gas and other products of solid, liquid and gaseous by-product phases of the coking process. Coal consumption for the production of iron and steel in India accounts for about 13% of the total consumption i.e. 48.5 Tg in 2004. The emission factor calculated for Hg emission is 0.08 g Mg^{-1} crude steel which is quite realistic (see Table 4.4). It should be stated here that coke still contains a small amount of Hg. Hence some Hg will pass into the atmosphere also from the sintering plant, blast furnace and steel production. Our emission factors are higher than the emission factors calculated by other authors. The simple reason for this is that the quality of coal in India is quite poor due to a high ash content (30-40%-wt). For this reason, more coal is needed per Mg of steel production than in the USA or in Europe. Residual fuel oil was also used in this sector, although the consumption of this decreased from 672 Gg in 2001 to 620 Gg in 2004.

In the electric arc furnace process metal from shredded cars is generally used as a raw material for conversion into steel. It has been reported that Hg-lamps are often removed when scrap cars are processed into crude steel (Personal communication with Dr. Pandey, TERI, New Delhi, April 2008). Otherwise, more Hg will be emitted from the iron and steel industry.

The atmospheric deposition of Hg in the vicinity of iron and steel works was cited as being in the range of 60 to 836 g/km^2/month whereas Hg concentration measured in dust was 56 mg kg^{-1}. In surface soil it varied between 40 and 72 mg kg^{-1} (Srivastava, 2003).

4.3.1 Non-ferrous Metallurgical Iindustry in India

4.3.1.1 Production of Metals by Different Processes and Emissions of Mercury

The primary non-ferrous metal industries are based on copper (Cu), lead (Pb) and zinc (Zn). There are four copper smelters in which the Flash Smelting Process, the Ausmelt process and the Imperial Smelting are practiced. In addition, there is one zinc production plant where Zn is produced by the hydrometallurgical process. The Cu-smelters are situated at Khetri, (Rajasthan), Ghatsila, (Jharkhand), Dahej (Gujarat), Tuticoran, (Tamil Nadu) where the Copper Flash Smelting Process and the Ausmelt Process are used, respectively, besides the later process at Tuticoran, where Australian Cu-concentrate containing 5.0 mg Hg kg^{-1} was reported to be used (Personal communication with Manger of Tuticoran Cu-smelter, December 13, 2007). The Outokumpu Flash Smelting Process was originally developed for Cu-concentrate in Finland. In this, dried concentrate is smelted in the Flash Smelting Furnace in the presence of pre-heated air and oxygen to produce high grade Cu-matte which is then converted into blister copper in the converter.

On the other hand, in the Ausmelt process, feed materials are fed through a port located in the roof of the furnace and fall into the molten bath, which favors material transfer and handling systems. Air and oxygen are necessary for combustion, and molten metal and slag are removed and off-gases from the Ausmelt furnace are cooled and cleaned in gas clean-up systems before discharge.

In Udaipur (Rajasthan), zinc is produced by the hydrometallurgical process which comprises the following steps: roasting, leaching, solution purification, zinc electro-winning, melting, casting, and alloying.

In Tundoo (Jharkhand) lead is produced by the Blast Furnace Process whereas at Chhattisgarh the Imperial Smelting Process has been erected for the co-production of zinc and lead. The total production amounts of copper, zinc and lead for 2000 – 2004 are shown in Table 4.1. For Cu production, the major part of the concentrates is imported from Australia. Emissions of Hg from the Cu, Zn and Pb - industries are shown also in Table 4.6.

Except for the hydrometallurgical process, Hg is evaporated at the high process temperatures that occur during the production of Cu, Zn, and Pb. When Hg is released from ores, concentrates or from fossil fuels and enters into the biosphere, it can be highly mobile, cycling between the Earth's surface and the atmosphere. Speciation of Hg is very important. Mercury as $HgCl_2$ may be captured by some gas clean-up devices (e.g. wet scrubbers), but elemental Hg (Hg^0) is not captured effectively. Once Hg is released from a process, it cycles between soils, the aqueous environment and the atmosphere. It has been confirmed that the common forms of Hg in the environment are: metallic Hg^0, $HgCl_2$ and MeHg (UNEP, 2002).

In India, secondary Cu is produced by Boliden's KALDO process (a Swedish process) where roasting, smelting and converting occur in the same converter, charged with Cu-scrap. Production data is shown in Table 4.1. Beside primary production, Pb and Zn metals are also produced through secondary routes from scrap, dross and residues. Secondary Pb production occurs in less organized sectors (Personal communication with the Director of Indian Lead and Zinc Development Association, New Delhi, December 6, 2007). The emissions of Hg from such secondary metals production are not known.

4.4 Chlor-alkali Industry in India

4.4.1 Chlorine and Caustic Soda Production

The basic raw materials for chlorine chemistry are sodium chloride, water and energy. There are three main electrolytic production technologies utilized in the chlor-alkali industry, being the diaphragm process, the mercury process and the membrane cell processes. Generally, chlorine and caustic soda are co-produced in a fixed ratio (1:1) by chlor-alkali plants and hydrogen is also produced. The primary product is chlorine. In each process, the electrolysed salt solution is directly converted from chloride ions to elemental chlorine by direct application of electric current, and the overall chemical reaction is as follows:

$$2NaCl + 2H_2O \rightarrow Cl_2 + H_2 + 2NaOH \qquad (2)$$

According to the Alkali Manufacturers Association (AMA) in India, forty-two chlor-alkali plants in India have the capacity to produce a total of about 2.2 Tg of chlorine per year, whereas the world production was cited at 55 Tg per year. On the global market, the Middle East played an important role in the production and exporting of caustic soda in 2007. The western region of India is the largest manufacturer of chlorine (1.04 Tg) in twelve chlor-alkali plants, followed by the Southern region (0.44 Tg), the Northern region (0.28 Tg) and the Eastern region (0.24 Tg). Pandey (2006) indicated thirty-five plants in India of which twenty-five have been converted to the Membrane process. These plants are vital for the chemical industry and this industry sector has been in operation in India since 1941. The number of world chlor-alkali industry plants (Hg electrolysis units) has been reduced from eighty-six in 2002 to seventy-four in 2006 (Figure 4.3). In India 86% of the plants have been recently converted to membrane cell technology and the rest, 8 or 10 units, are in the process of conversion to membrane cell technology, which does not use Hg in the process (Pandey 2006, AMA, 2007). The present list of chlor-alkali plants operating in India is given in Appendix 1 and Figures 4.4 & 4.5 indicate Hg-Cell and converted Membrane Cell plants in India, respectively.

A non-governmental organization (NGO) in New Delhi has estimated that in 1999 – 2000, the loss of Hg from the Hg-cell process to be 394 g Hg per Mg of Cl_2 production. during the same period, chlorine production was 0.48 Tg. This correspond to an annual Hg emission of about 185 Mg. (http://www. toxicslink.org/docs/06035_publications-1-33-2.pdf). In another study, Srivastava (2003) estimated that the Hg loss from Hg-cell plants in India is about 142 g Mg^{-1} NaOH produced. From his estimate, Hg loss to the atmosphere between the years 1997-2000 was about 79 Mg yr^{-1}.

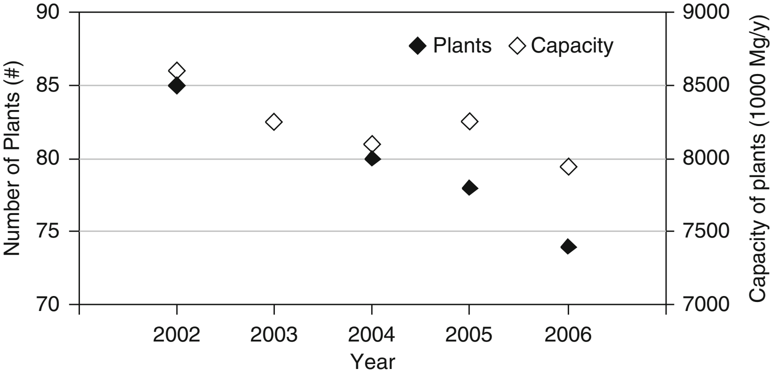

Figure 4.3 The scenario of world's chlorine plants and production capacity, 2006 (WCC, 2007; Reproduced with permission , Veronique Garny, 2007)

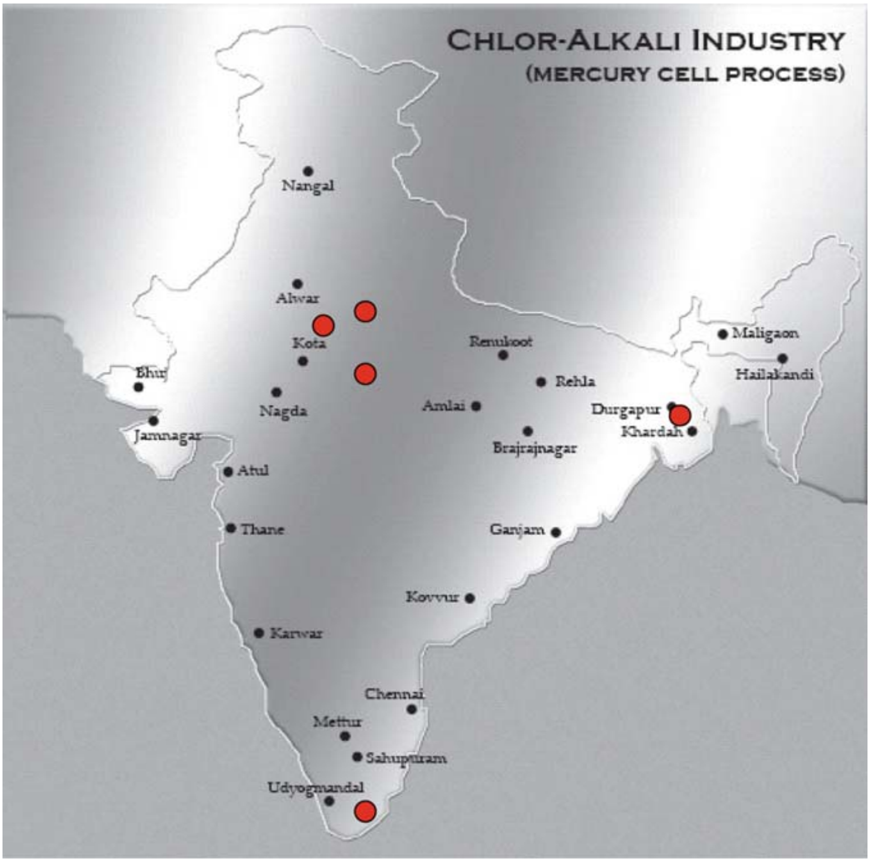

Figure 4.4 Mercury cell chlor-alkali industry in India. Big circles indicate Hg-based thermometer industry. Adapted from Toxicslink, New Delhi. See Appendix I which indicates conversion of major number of chlor-alkali plants from Hg-cell to Membrane cell process where no mercury is used (from http://www.toxicslink.org/docs/06035_publications-1-33-2.pdf)

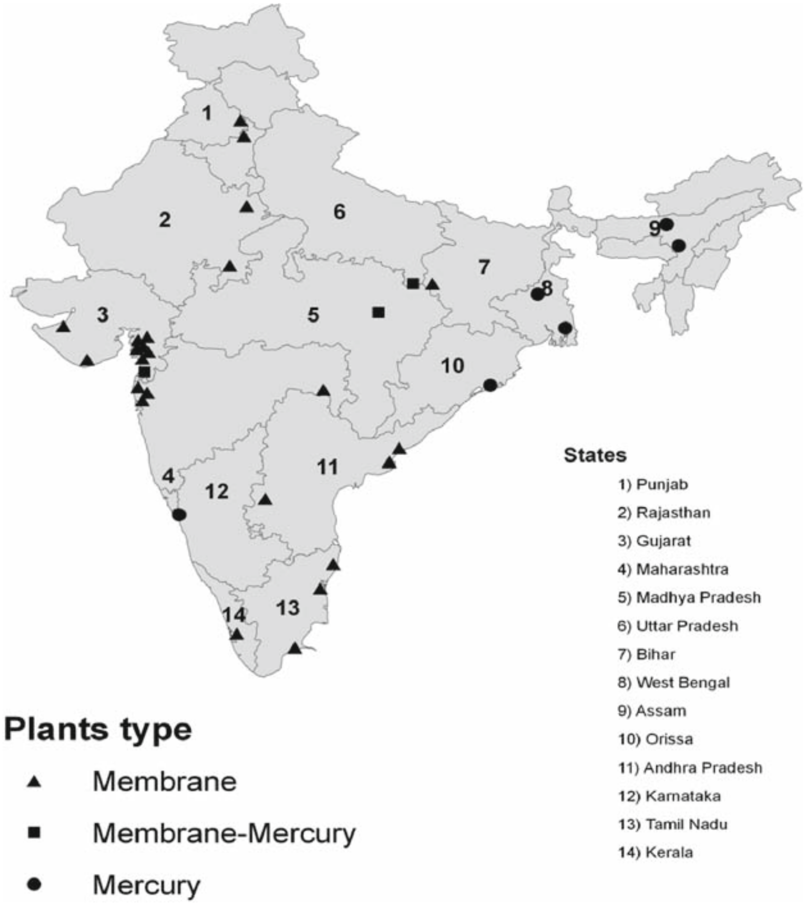

Figure 4.5 Locations of chlorine industries in India, 2008 (Information received from S. Sinha, Toxicslink, New Delhi, 2008: plotted in the map of India); See Appendix 1 for details of plants

Clearly, the information on Hg emissions from this particular chemical sector in the past is highly unreliable. However, more recent information from AMA (2007) indicates that NaOH production by the Hg-cell process was at 0.3 Tg for 2006-07 whereas for the same period the production by the Membrane Process it was 1.7 Tg NaOH. Considering the emission factor for Hg emissions from Chlor-alkali plants to be 20.4 g Hg Mg^{-1}, total Hg passed into the atmosphere from this chemical industry was 6.2 Mg yr^{-1}. (Table 4.6). In the 1990s, chlor-alkali plants were the single largest Hg consuming industry in India, consuming about 70 – 80 Mg of Hg each year (CSE, 2005). Mercury has been detected in groundwater and surface water in the vicinity of Hg-cell chlor-alkali plants. In addition, Hg occurred also in the vicinity of dyes, paints and pigment manufacturing units which use Hg-based catalysts in the manufacturing processes (CSE, 2005). According to the Ministry of Environment and Forest (New Delhi), Indian chlor-alkali plants will be Hg-free in 2012 . In the near future, chlor-alkali plants may be free from Hg-cells, but this does not mean that at the same time Hg will disappear from the vicinity of chlor-alkali plants. The metal will not disappear from the environment, but will convert into MeHg, Hg^0 or mercuric chloride which will then pass into the atmosphere, to again fall on forest soils or the water shed. Speciation of Hg plays an important role in toxicity and the exposure to living organisms.

However, it has also been reported that about 170 Mg of Hg has been imported and consumed in the years 2004–2005 (http://www.dgft.delhi.nic.in/). Chlorine and sodium hydroxide use also provide a range of benefits, such as PVC manufacture which is an important material. It has a long life e.g. it lasts for more than 35 years. It emits about 50% less carbon dioxide and needs less oil for production. Beside these, in many energy saving buildings, foam insulation and PVC windows are based on chlorine chemistry.

4.5 Cement Industry

The Indian cement industry is the second largest cement producer in the world with an installed capacity of 144 Tg annually. Due to technological development some Portland cement production plants are well advanced. In cement production, energy consumption is quite high. In the Indian cement industry, the capacity of kilns varies between 10 Mg day^{-1} and 7,500 Mg day^{-1}. Most cement, 94%, is produced in large (capacity 600 Mg day^{-1}) plants. At present there are 124 large rotary kiln plants. In India, in general Ordinary Portland Cement (OPC) (56%) and blended cement (43%) are manufactured. The dry process (93%) route besides some (much more energy intensive) wet and semi-dry processes (7%) are practiced.

In the cement industry, Hg was found to be emitted from the wide range raw materials and other resources used. There are more than thirty raw different materials used in the manufacture of Portland cements. These materials can be classified as: (a) calcareous, (b) siliceous, (c) argillaceous, and (4) ferriferous. A variety of calcareous raw materials are used in Portland cement including: limestone, chalk, marl, sea shells etc. The thermal treatment of raw materials for the manufacturing of Portland cement is carried out in kilns. It is not known if any plants in India use waste as an alternate fuel in a cement kiln.

However, there are four steps in production:

- Evaporation of uncombined water;
- Dehydration e.g. at temperature 430 ºC, formation of oxides of Si, Al and Fe occurs;
- Formation of calcium oxide at 980 ºC;
- In the burning zone of the rotary kiln, the cement clinker is formed at 1510 ºC

In determining the emission factor, we followed the material balance used by Smith (1999), the input data being as follows:

- 0.40 mg kg^{-1} (Hg / coal)
- 0.1 Mg coal / cement

- 1.2 Mg limestone / cement
- 0.03 mg kg^{-1} (Hg /limestone) (UNEP, 2005)
- Emission factor of coal fired kiln 1.5×10^{-6} kg /Mg cement (UNEP, 2005)

Based on the above information, the emission factor for Hg per Mg of cement production is 45.6 mg Hg Mg^{-1} cement (the EPA's value is 65 mg Hg Mg^{-1} cement, USEPA (1997)). In a dry process, Hg will leave the kiln in gaseous form, but in the pre-heater tower, it may be adsorbed both on the kiln feed and cement kiln dust (CKD). The speciation of Hg is again very important as retention of Hg in gas cleaning equipment depends upon: a) the gas cleaning equipment; b) the form of Hg; c) the temperature and retention time (Senior et al., 2003; Mukherjee and Zevenhoven, 2006).

4.6 Wastes Disposal

4.6.1 Municipal Solid Waste (MSW)

People in India live on 3.28 million km^2 of land. Due to population growth, there is also an increase in municipal solid waste (MSW) in India. The growth rate of MSW is reported to be 1.33% per capita per annum (EPTRI, 1995). The collection efficiency of MSW is about 72.5%, but still waste transport capacity is lacking in 70% of the cities (TERI, 1998 vide Singhal and Pandey, 2001). MSW consists mainly of household garbage, and other commercial, institutional and industrial solid wastes. In household wastes, broken thermometers, instruments, Hg-vapor lamps, toys, electric switches, fluorescent tube lights, Hg-batteries etc. are the expected to be the Hg containing products. In addition, most MSW contains large amounts of organic species.

MSW Rules 2000 indicate that the municipal solid waste should be disposed of in a environment-friendly manner such as: pelletisation, combustion/incineration, land filling, bio-methanation and composting from which power could be produced for local industry (timesofIndia_Indiatimes.Com/articleshow/ 134243.cms). However, MSW generally disposed of by the following ways:

1. Landfill practice
2. Open dumping
3. Open burning

The generation figures for MSW in India are based on the recent study conducted by Singhal and Pandey (2001) (see Figure 4.6). Between the years 2001 and 2004, 50 to 70 Tg per year MSW was generated in India, with most waste generated in Uttar Pradesh where 166 million people live. It has been estimated by those authors that in the year 2047 the amount of MSW might reach 260 Tg. An estimated emission factor for Hg in MSW is 1.0 g Mg^{-1}, without emission control. In India garbage and mixed waste are often burnt near the road side. 94% of MSW is dumped in landfills

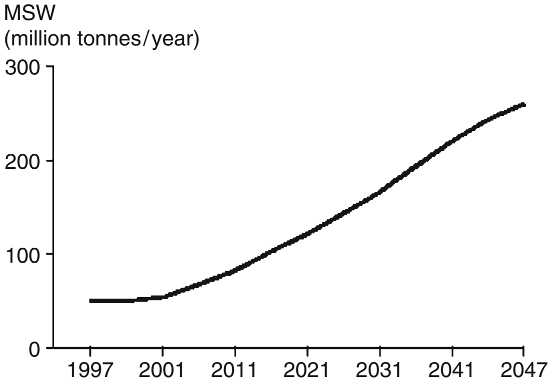

Figure 4.6 Solid waste generation in India (Reproduced from Singhal and Pandey, 2001)

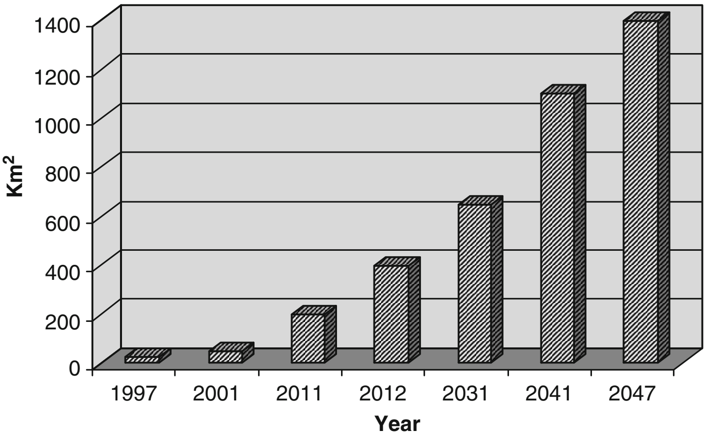

Figure 4.7 Land requirement (*km*^{2}) for disposal of municipal solid waste (reproduced from Singhal and Pandey 2001)

without any proper systems and 5 % of wastes are used for composting (CPCB, 2000). Due to the humid climate and rainy seasons, leaching of Hg can be expected.

The huge amount of MSW produced is a serious problem in India. Unfortunately, little attention is being paid to proper management of MSW. Problems with wastes are not particular to India but occur in most Asian countries. Asian countries face serious problems in the solving of disposal problems for wastes. It is not only a technical problem, but many political, legal and environmental factors are also involved. In addition, land requirements for the disposal of MSW will increase and it has been estimated that by the middle of the 21st century 1400 km^2 of land many be needed for MSW (Figure 4.7). Sharholy et al. (2007) determined the constituents of MSW for Allahabad where 1.1 million people live (2006) and these are shown in Table 4.7. This may represent a rough picture on MSW for whole India.

Table 4.7 Estimation of the essential parts of MSW in India based on the study for Allahabadcity (After Sharholy et al. 2007)

Elements in MSW	Weight %	% weight based on 21 class 1stcities*
Paper	3.6	5.7
Cardboard	1.09	-
Metal, tin cans	2.54	2.1
Glass	0.73	2.1
Food wastes	45.3	41.80
Textile rags	2.22	3.5
Plastic (Poly bag)	2.86	3.9
Miscellaneous (bricks, ash, fine dust, rubber, wood, leather, wastewater etc.	41.66	41.1
Total	100	100
Moisture	25 %	

*(CPCB, 1999)

4.6.2 Medical Wastes

There is limited information available regarding medical wastes in India. It is generally expected that medical wastes contain more Hg than MSW does. In this sector, there are many instruments in hospitals which contain large amounts of Hg. There are basic regulations related to health care in India, but unfortunately these regulations are not followed properly. Visvanathan (2006) estimated medical waste generation in Asia, the figure for India being 0.33 Tg yr^{-1}. Based on 20 g Hg emission per Mg of medical waste (USEPA 1997), the total Hg emission to the atmosphere from this source is estimated to be 6.6 Mg per year. The average health care waste generation per bed per day in India has been estimated at 1 – 2 kg (Table 4.8). According to law experts in India there is no lack of legislation, but the problem lies with implementation. Often medical waste is disposed of together with MSW, due to which the waste stream becomes hazardous. Technologies available for handling medical waste include: a) incineration; b) autoclave; c) microwave; d) chemical disinfection and e) plasma pyrolysis. In India there are incineration plants at some hospitals to handle medical wastes. The capacity of these varies from 50 to 175 kg hr^{-1} of infectious and non-infectious wastes generated. In Delhi, there are 61 medical waste incinerators, but there is no information regarding the handling of hospital wastes in other parts of the country.

4.6.3 Electronic Waste (E-waste)

In recent years, discarded electronic waste known as “E-waste” often enters into the waste streams in India as in many other (Asian) countries. Automation, increased demand for electronic equipment including computers and increased consumer

Table 4.8 Estimated medical waste generation in selected Asian countries (Visvanathan, 2006)

Country	Waste *(kg* $bed^{-1}day^{-1}$*)*	Total wastes *(Mg* yr^{-1}*)*
Bangladesh	0.8 – 1.67	93,075 (only in Dhaka)
Bhutan	0.27	73
China	-	730,000
India	1 – 2	330,000
Malaysia	1.9	-
Nepal	0.5	365
Pakistan	1.06	250,000
Sri Lanka	0.36	6,600 (Only in Colombo)
Thailand	0.68	-
Metro Manila (Philippines)	-	17,155
Vietnam	2.27 (Hanoi)	60,000

choice are believed to be the major reasons for growing quantities of E-waste. Recently its production in India has increased to 380 Gg in 2007 and it has been forecast by the authorities that its production will increase to 470 Gg in 2011. There is also a huge amount of E-waste imported from the West, possibly as much as 50,000 Mg annually; mainly discarded computers and accessories (http://www.physorg.com/news116912274.html accessed January 21, 2008). Before or while burning E-wastes, scrap dealers can recover valuable metals, which is however not without impact on health and the environment. In India, there is a general lack of recycling technology. Computer scrap is often reused and many different types of E-waste end up in landfills, creating health and environmental problems since this method of disposal is not well developed. In addition, India has dumped E-waste in other countries.

Sarkar (2007) studied E-waste generation (excluding imported) in India and observed that 146 Gg electronic wastes were generated from PCs, refrigerators, TVs and washing machines in 2006, and the amount is expected to rise to 1.6 Tg in 2012. In addition, India receives a large volume of E-wastes. As there is no national level policy for management of E-waste, most of the recycling facilities are unorganised and do not use suitable, state-of-the-art technologies for the recovery of toxic metals. Selected trace elements from E-wastes in India have been addressed by Sarkar (2007), indicating that 0.82 Mg Hg yr^{-1} escapes into the environment (Table 4.9), and the values will increase due to increased annual E-waste and the lower lifetimes of newer computers. The total Hg released from the above mentioned three types of wastes is given in Table 4.6.

4.7 Biomass Burning

We consider Hg emissions from biomass burning to be anthropogenic and it is therefore necessary to understand its effects on the atmosphere on a regional (i.e. in Asia) and global scale (Reddy and Venkataraman, 2002; Streets et al. 2003). Venkataraman et al. (2006) focused forest and crop waste burning in India between

Table 4.9 Mercury in electronic wastes in India (from Sarkar, 2007)

Waste type	2004 *(Tg)*	Total Hg *(Mg* yr^{-1}*)*
E-waste	0.146	0.82•

E-waste in India – annual and total production and entry into environment (Referring to the estimated number of annual production of obsolete computers (1.38 million), total market size (15.5 million), MCC data on average weight of computer (27 kg), proportion of presence of toxic chemicals in each computer and recycling efficiency - annual and total production of various toxic substances from e-waste generated from discarded computers and related materials have been estimated.

	TW (%)	AW *(mg)*	RE	YP *(Mg)*	AR *(Mg)*	EE *(Mg)*	TP *(Mg)*	TR *(Mg)*	TE *(Mg)*
				A	B	A-B	C	D	C-D
Hg	0.0022	0.00059	0	0.82□	0.00	0.82	9.19	0.00	9.2

Source (adapted): MCC (Microelectronics and Computer Technology Corporation), 1996, Electronics Industry Environmental Roadmap, Austin, Texas, details available at www.svtc.org/cleancc/pubs/sayno.htm (last accessed on 20th March 2006) and Boralkar D.B. (2006), Perspective of electronic waste management, Green Business Opportunities, Vol 12 (1), pp 7 – 10.

TW = Total weight of Hg in each computer; AW = Average weight of Hg in each computer; RE = Recycling efficiency; YP = Yearly production of toxin material; AR = Max recycled annually; EE = Entry into environment; TP = Tot production (based on market size); TR = Total max recycled possible; TE = Total entry into environment.

1995 – 2000 using forest burnt areas and biomass density for Indian ecosystems. It has been estimated that Indian forest is burned at a rate of 32 (16 – 61) Tg yr^{-1} and in open and dense forest with low density biomass cover (Streets et al. 2003). Crop waste burning, including cereal, sugarcane waste, oilseeds, fiber crops and pulses were also estimated at 116 (58 – 289) Tg yr^{-1} (Venkataraman et al. (2006). Mercury emissions during biomass burning have been shown in Table 4.6. However, biomass is the main source of energy for villagers and about half of all energy in India used for cooking food. It is interesting to note that the firewood consumption (kg/capita/yr) increases with increased altitude in the region of Garwal Himalaya. The summer time average consumption at 500 altitudinal range (m a.s.l.) is 392.28 kg/person/year whereas at 2000 altitudinal range it is 1019 kg/person/year (Bhatt and Sachan, 2004). It means Hg emissions will be higher as well when firewood is burnt at higher altitude in the mountain region.

4.8 Miscellaneous

4.8.1 Brick Industry

The Indian brick industry is the second largest in the world after China. The Energy and Resources Institute (TERI) has estimated over 100,000 units producing 140 billion bricks per year. There are three types of brick works, based on production capacity i.e. small (<1 million bricks per year); medium (1 – 2.5 million bricks per years) and large facilities (>2.5 million bricks per year). Smaller brick facilities are generally situated in the village areas whereas the medium and larger types are located near urban areas. It is an energy intensive process and coal is the major fuel used. It has been estimated by TERI that about 24 Tg of coal, containing 0.376 g Hg Mg^{-1}, are fed to the brick kilns for the production of 140 billion bricks (e.g. 350 Tg of bricks considering the weight of a brick in India to be 2.5 kg, based on TERI, 2008). In addition, Indian brick kilns consume a considerable amount of biomass and fuel oil, but the amounts of these are not known (Garg et al., 2006). Based on the use of low grade coal, the uncontrolled emissions of Hg from these processes to the atmosphere are 7.5 t Hg yr^{-1} (Table 4.6). In addition there are PIC (product of incomplete combustion) emissions. In 1996, the Indian government enforced regulations which have caused some technological improvements e.g. reduced dust emissions, and improvement of firing technology, especially in large brick works (Maithel and Uma, 2000). It has been reported by TERI that new technologies such as vertical shaft brick kilns (VSBK) has been introduced in several brick production facilities. The process claims to both lower investment and to meet emission standards.

4.8.2 Instruments, Batteries and Thermometers

Substantial amounts of Hg are used in the production of instruments, batteries and clinical thermometers. Table 4.2 indicates the amount of Hg used in the manufacture of instruments between 1998 and 2001. Clinical thermometers and barometers may often be broken during manufacture. Broken products are put aside and often cause fugitive emission of Hg. However, there are no measurements by which the total amount of Hg thus lost to the environment can be detected. In addition, bookkeeping is quite poor. One of the largest thermometer companies, at Kodaikanal in the Tamil Nadu state, was forced to close due to illegally dumping Hg-bearing waste into the surroundings. Before closing the estimated Hg emission from broken pieces at the plant, was 3.5 to 4.2 t yr^{-1} (Each thermometer contains 1.0 g Hg; total production 10-12 million pieces per year; breakage during production and handling 35%.) The Hg consumption in different instruments is shown in Table 4.10.

Table 4.10 Total mercury consumption in instrument manufacturing Industry (from different sources)

Instruments	Unit *(kg)*	Used/unit *(g)*
Clinical thermometers	3,100	0.61
Lab thermometer	900	3.0
Blood pressure monitors	12,000	60.0
Barometers (in kg)	125	5
Total	16,125	

4.9 Mercury in the Indian Environment and the Cycling in the Bio-geosphere

The soil, water and air are not only a part of the ecosystem but also play an important role for humans, animals and aquatic species because the survival of human, aquatic species and plants is tied up with uncontaminated soil, water, and air. Releases of the non-essential element Hg from industrial sources are well documented in developed countries. This study addresses emission of this element in the Indian ecosystem and indicates that its presence in soils, plants, air and water and aquatic species and sediments are at alarming levels, which is also supported by the work of Srivastave (2003) and many other authors in the West (Hylander and Meili, 2003; Pacyna and Pacyna, 2001, 2002; Pirrone et al. 1998). Coastal areas are often contaminated by the discharge of Hg from all Hg-cell chlor-alkali plants. At one well known clinical thermometer works in Tamil Nadu, an ambient air concentration of 1.32 μg Hg m^{-3} was reported. Outside the factory, lichen (Parmelia sulcata) and moss (Funaria hygrometrica) samples contained 7.9 μg kg^{-1} and 8.3 μg kg^{-1}, respectively. Fish in lake waters contained 120 to 290 mg kg^{-1}, whereas total Hg and MeHg in waters were measured to be 356 – 465 ng L^{-1}, and 50 ng L^{-1} respectively (Karunasagar et al., 2006). Concentration of Hg_T in sediments in the same lake near the factory situated 2130 m above mean sea level, varied from 279 to 350 mg kg^{-1}.

High concentrations of Hg are reported in fish that grow in saline or fresh water in coastal areas (1.1 – 700 mg kg^{-1}) Table 4.11) for many states of India (WHO's permissible value is 0.5 mg Hg kg^{-1}). Sinha et al. (2007) studied the Hg concentration in different samples from the river Ganges (Table 4.12) and a high concentration was reported for various species although not in the water samples themselves.

Seasonal variation was also reported by these authors. These authors collected about 61 fish samples for the river Ganges near Varanasi, where they found that the Hg concentration in the fish (*Macrognathus pancalus*) varied up to 91.7 mg kg^{-1}.

Table 4.11 Average and maximum mercury concentration in fish and other species

Place	Fish/species	Hg *(mg kg^{-1})*	Hg max. *(mg kg^{-1})*	Reference
North Koel river, Jharkhand	Fish		600 - 700	1
Mumbai, East Coast,	Fish	0.03 – 0.082	1.6	2
Maharashtra	Bivalves	0.13 – 10.82	21.6	2
Sagar Island,	Gastropods	1.05 – 3.60	7.2	2
East coast West Bengal	Crabs	1.42 – 4.94	9.9	2
	Bivalves	0.06 – 2.24	4.5	2
Binage, Karwar, Karnataka	Oysters	0.18 – 0.54	1.1	3

1. "Mercury concentration of fishes in north koel river, Rehela, Bihar, India". Indian Biologist 23(2) 1992; 58 – 60.
2. Chemosphere, vol 33 147 – 158 (1996), cited in Global Mercury Assessment, UNEP Chemicals, 2002.
3. "Heavy metal distribution in the biotic and abiotic matrices along Karnataka coast, West coast of India". Indian Journal of Marine Sciences, 27, June 1998, 201–205.

Table 4.12 Mercury concentration of different samples of the Ganges River collected at Varanasi, India (Sinha et al., 2007)

Season	Water ($\mu g\ kg^{-1}$)	Sediment ($\mu g\ kg^{-1}$)	Benthos ($\mu g\ kg^{-1}$)	Fish ($mg\ kg^{-1}$)	Soil ($\mu g\ kg^{-1}$)	Vegetation ($\mu g\ kg^{-1}$)
Winter	0	106 ± 113	144 ± 252	4.048 ± 18.676	95± 114	254 ± 397
Summer	0.37 ± 0.29	80 ± 87	108 ± 167	0.205 ± 0.531	126 ± 111	98 ± 81
Post monsoon	0.32 ± 0.48	0	92 ± 129	4.369 ± 16.067	0	245 ± 127

The observed Hg concentration in their study was more than that in the fish samples collected from the western coast, Mumbai (0.03 – 0.82 mg kg^{-1}). Mercury in fish resides as MeHg (which affects humans) bound to the proteins and muscle tissues of the fish. Besides MeHg, concentration of elemental Hg is also observed in fish and shellfish species. It was reported also that rice fields contaminated by Hg from coal combustion power plants contain MeHg. In many parts of the world, including India, high concentrations of MeHg and Hg have been demonstrated in oceans, rivers, lakes and reservoirs. Pirrone and Mahaffey (2005) reviewed Hg in global fish populations. In many regions of India, fish is an important daily food item and the authorities should make people understand the effects of high concentrations of Hg and MeHg in fish. In the 1960s in Japan, Minamata disease was caused by consuming Hg contaminated fish and rice. It has been reported in the panel discussion of the 8th International Conference on Mercury as a Global Pollutant at Madison, WI, USA that MeHg in human hair is 250 to 300 times more than Hg in the blood for those who eat fish regularly or frequently. Patel (2003) studied the health impacts on humans at contaminated sites of the central region, Chhattisgarh state of India where 50 Tg of coal and minerals are exploited annually by various industries and thermal power plants. In addition over 600 rice mills are in operation producing > 2 Tg of rice contaminated by Hg, As and Pb. Twenty-two human hair samples were analysed from the contaminated areas and were found to contain Hg from 2.6 – 37.8 mg kg^{-1} with mean and median values of 12.3 and 10.4 mg kg^{-1}, respectively. This author believes that in this region, the toxic effects of Hg due to contaminated of food and water are expected to show up shortly. However, scientific knowledge on MeHg exposure and its effects on humans are still not complete.

Das et al. (1998) indicated that 90% of MSW in India is directly dumped on the land in an improper manner and the problem with disposal facilities in towns and cities is that they cannot keep pace with the quantity of waste generated. It has also been forecasted that by the middle of the 21st century, MSW will be generated at a rate of 250 – 300 Tg yr^{-1} (Sharholy et al., 2007; Das et al. 1998). Sewage sludge, pesticides, composts and fertilizers are often used on agricultural lands and these are also sources of Hg in soils and groundwater. Often, untreated effluent is pumped into rivers, lakes and groundwater, and through bore wells, (such as in Andhra Pradesh and Gujarat states). The Hg leached from landfills contaminates groundwater and streams, from which it moves into soils, and agricultural lands.

Mercury emission scenarios for coal combustion, MSW, and the non-ferrous metallurgical industry are alarming. The highest Hg emission from coal combustion has been estimated in this document for the year 2004.

4.10 Discussion

This study indicates that the atmospheric Hg emissions in India from industrial sources ranged between 321 to 253 Mg annually during the past years. Occasionally, Hg emissions have been given for a single year, e.g. in brick manufacturing, medical wastes and E-wastes. The highest Hg emissions occurred from the combustion of fossil fuels in power plants, followed by three types of waste. The Hg emissions given for Chlor-alkali plants should be used with caution. In addition, the Hg emissions from residual fuel oil use over the period 2001 to 2004 were negligible e.g. 0.54 – 0.47 Mg (based on the uncontrolled emission factor 0.065 g Mg^{-1}). No information was available from the pulp & paper industry or the oil and petrochemical industry in India. It has been reported by the Ministry of Environment and Forests, New Delhi, that major Hg-cell plants have been converted to the Membrane Cell process (Pandey, 2006) which means that Hg use and emission in chlor-alkali plants are expected to drop. At the end of the 1990s, Indian chlor-alkali plants discharged Hg-contaminated wastewaters containing Hg in the range of 0.08 to 2 mg L^{-1} (the Indian standard for Hg in industrial waters is 0.001 mg L^{-1}). Mercury is used often in electrical and electronic devices, fluorescent lamps, laboratory and medical equipment, clinical thermometers and computer components. However, strict enforcement of the regulations inside the country is needed. If necessary, a trade ban should be implemented to curb the use of Hg in India. Mercury emissions vary widely from one region to another in India, based on industrial activities. Often, activities such as coal mining and the burning of coal in power plants, metallurgical industry, chlor-alkali facilities, and waste disposal will produce trace element problems, including Hg, in the region. We have also identified Hg emissions from the cement industry and brick manufacturing, where 24 Tg of coal are used. In addition, Hg containing E-waste, medical waste and the MSW add Hg to the ecosystem of India.

Two scientists from the Department of Botany, Sri Krishnadevaraya University, Anantapur, India studied Hg in plant species (*Tephrosia purpurea, Cassia auriculata* and *Arachis hypogaea*) near a cement works at Bethamacharla, Andhra Pradesh. They found more Hg, 0.76±0.04 (SD) ng/mg in the leaves than roots (0.750±0.02) or stem (0.541±0.01) in *Cassia auriculata*. It is also confirmed that the mobility of Hg is greater when it enters the plants through the stem or leaf. The accumulation of Hg indicates that the cement industry emits Hg to the vicinity of the plants, but the accumulation levels vary with species, wind direction, soil pH, aeration as well as soil moisture.

Villagers and ordinary people in cities or towns are often not aware of the toxicity of Hg and how this element enters into human food chain. Hence proper education is necessary so that people in India can understand the effects of Hg concentration in fish or in drinking water. Mercury is notorious for its toxicity to biological organisms. Excessive releases of Hg and its compounds may lead to severe environmental and health consequences (Wong et al., 2006).

In India Hg emissions from most industrial sources are still increasing. The coastal areas as well as the inside of the country are highly polluted due to chlor-alkali plants and the process by which Cl_2/NaOH have been produced since the 1940s

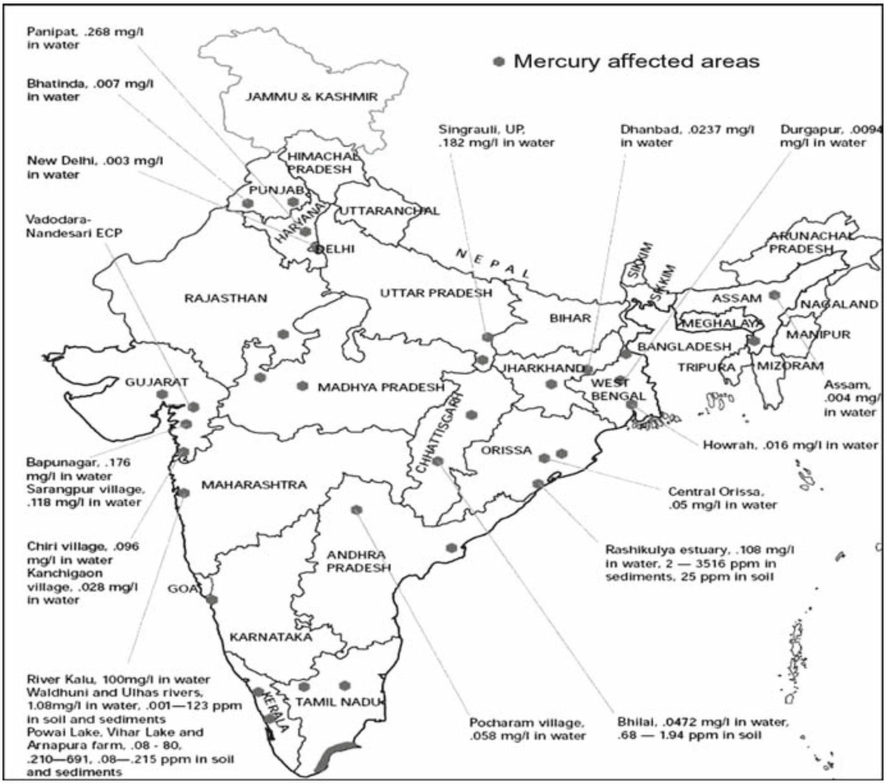

Figure 4.8 Mercury pollution due to use of Mercury-Cell Chlor-alkali plants in India in the 20th entury (Reproduce with permission, Center for Science and Environment, New Delhi 2008)

(Figure 4.8). The six Asian countries, India, China, Pakistan, Bangladesh, Japan, and Indonesia are all densely populated. Mercury emissions from industrial sources may cause future epidemics among the population. Over time, excessive Hg emissions will cause bioaccumulation and bio-magnification in the food chain, which may create serious problems with human health in India and surrounding countries. It has already been mentioned regarding the high concentration of Hg^0 and MeHg in fish, shellfish and seafood, that there are signs of Hg in the human hair when Hg - contaminated fish is eaten often. Excessive Hg emissions in India can cause Hg deposition problems on a global scale.

Industrial progress is necessary if the economic growth of a country is to be maintained. If India follows this pattern, the country must adopt the best available technology to control Hg emissions from industry. In coal fired power plants, electrostatic precipitators are not enough. This gas cleaning equipment does not capture vapour - phase Hg^0 from the process. Management in India should understand that there is a lack of scientific information concerning the emission, distribution, and biogeochemical behaviour of Hg in India. The imbalance between India and the

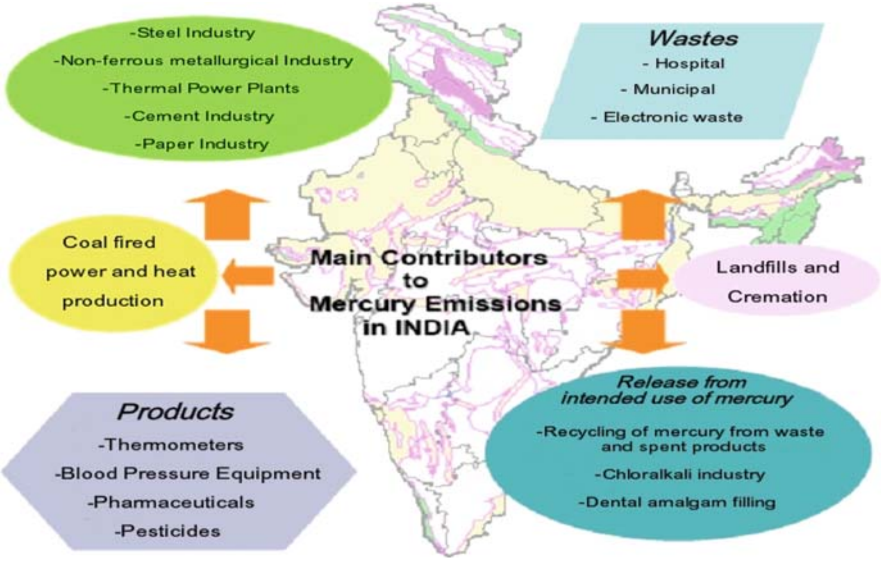

Figure 4.9 Sources of mercury in India (Modified from Srivastava, 2003)

developed countries regarding Hg emissions from industrial sources is due to technical motivation, environmental awareness and socio-economic conditions. India is, however, trying to curb environmental trace elements including Hg, by the formulation of discussions, mass education, strict regulations and effective control technologies.

On this subcontinent, detailed studies on e.g. Hg emission rates from specific industries, improved analytical techniques especially for Hg in coal, data bases, studies of biogeochemical properties of Hg, should all be encouraged for environmental and health reasons. In addition, there should be intense and continuous exchange programs among researchers and scientists between the developed countries, India and other countries in the region.

It should also be stated here that due to the lack of true emission data there will be uncertainties in the estimation of anthropogenic emissions of Hg not only in India but also in other parts of the globe. In India the Hg emissions from certain industrial sources, such as the chlor-alkali industry, has decreased very recently. However, the summary of the estimated Hg emissions is depicted in Table 4.6 and sources are shown in Figure 4.9.

4.11 Future Directions

Our knowledge of Hg and its compounds has improved quite a lot since the 1st International Conference on Mercury as a Global Pollutant, held in Gävle, Sweden in 1990. The European Union (especially EU-15), the U.S., Canada and Japan have formulated rules and regulations to curb Hg emissions from industry and the results can be seen now in many parts of these countries. The technology for gas cleaning equipment such as the flue gas desulphurisation process and others have been improved and the improvements also implemented. Local emissions of Hg have been reduced, but cross-boundary deposition of Hg by dry and wet methods is increasing. This means that increased economic development in India or in Asia and the burning of large amounts of coal and other industrial developments associated with this will result in long range transport of elemental Hg and MeHg from Asia to America and Europe. At present we understand the speciation of Hg and its role in the ecosystem, but the behaviour of MeHg in the environment is less clear.

In India, it is vital that scientists determine the sources of Hg and its emissions. Based on reliable measurements, it is possible to build up emission factors from which emissions of an element can be calculated. Stack measurements are expensive, but material balances can be applied to calculate emissions of Hg. This is not 100% correct but shows the path of how emissions of an element like Hg are developing. In the 20th century the Hg-cell process was used for the production of $NaOH/Cl_2$, and Hg emission was reported to be 150 – 200 Mg yr^{-1}. During the course of this study, we have understood that the majority (86%) of Indian chlor-alkali pants have been converted to the membrane-cell process with the remaining 8-10 plants still using the Hg-cell process. The Ministry of Environment and Forests, New Delhi, has stated that the total Hg release to the environment should be <2.0 g Mg^{-1} of product by December 2005 (Pandey, 2006). This information is encouraging. It is necessary for India to generate more reliable data, which can be used by scientists during modeling and formation of emission inventories. Computer modeling is often used in simulating global Hg scenarios. Often information on emissions from India and other Asian countries report emissions that are too low, as a result of which large differences occur between expectation and reality with respect to Hg cycles. Hence lack of scientific data in Asia has caused inaccurate assessments on Hg amounts and its association with environmental and health effects.

Asia is a region in which great diversity in climate is found. One area may be hot and humid while another region has very high precipitation such as in Bangladesh (1400 mm rain per year). In addition there is acid rain (pH < 4.5) SO_4^{2-} loading on soils and the aquatic environment. These diversities will have their effect on the bio-accumulation, bio-magnification and the uptake of Hg. There have been few studies, or none at all, carried out in Asian countries and these now have more focus on the Hg question than the Western countries. We have known for quite some time that high concentrations of Hg occur in pike in lakes in Sweden, Finland and Norway and that many lakes have been blacklisted. Scientists are working to understand the cause of this and produce remedies. In India, however people eat fish caught in lakes, rivers and the sea, unaware of the Hg problem in the fish and of how high concentrations may affect, particularly the high risk population i.e. pregnant women, and children. Remedial measures can be promoted by introducing non-Hg medical equipments such as digital thermometers, blood pressure equipment, avoiding amalgam fillings and for the large-scale use of alternative energy sources (solar, hydro etc.) to reduce coal use in the thermal power industry.

The scientific community has largely overlooked Hg emissions from the brick industry, which has been in operation now for decades. In our present study, we have observed that India, after China, is the second highest producer of bricks. In this industry 24 Tg of poor quality coal and bio-fuels (accurate amounts unknown) are consumed. Detailed study is necessary to improve the processes and to determine emissions of Hg and unburned particulates and their effects on the environment.

Appendix 1 Current lists of chlor-alkali plants in India (Personal communication with Toxicslink, New Delhi on 01.17. 2008)

No.	Name of the Unit	Location	Technology Adopted
A	**Eastern Region**		
1	Bihar Caustic & Chem.	Jharkhand	Membrane
2	Durgapur Chemicals	Durgapur, WB	Mercury
3	Hindustan Heavy Chem.	Kolkata	Mercury
4	Hindustan Paper (Nagaon & Cachar)	Assam	Mercury
5	HJI-Prop: GMMCO Ltd	Amlai, MP	Membrane + Mercury
6	Jayshree Chemicals Ltd.	Ganjim, Orissa	Mercury
7	Kanoria Chemicals Ltd.	Renukoot, UP	Membrane + Mercury
B	**Western Region**		
8	Atul Ltd.	Valsad, Gujarat	Membrane + Mercury
9	Ballarpur Industries	Ballarshah	Membrane
10	Century Rayons	Thane, Maharashtra	Membrane
11	Grasim Industries	Nagada, MP	Membrane
12	Gujarat Alkalies & Chem.	Dahej & Baroda, Gujarat	Membrane
13	Indian Rayon	Veveral, Gujarat	Membrane
14	NRC Ltd.	Thane, Maharashtra	Membrane
15	Reliance (IPCL)	Dahej, Gujarat	Membrane
16	Standard Industries	Mumbai, Maharashtra	Membrane
17	Shriram Alkalies	Jhagadia, Gujarat	Membrane
18	Tata Chemicals	Jamnagar, Gujarat	Membrane
19	United Phosphorus	Bharuch, Gujarat	Membrane
C	**Northern Region**		
20	Lords Chloro Alkarli Ltd.	Alwar, UP	Membrane
21	Punjab Alkarlies & Chem.	NayaNangal, Punjab	Membrane
22	Shriram Vinyl Chemicals	Kota, Rajasthan	Membrane
23	Siel Chemicals Complex	Rajpura, Punjab	Membrane
D	**Southern Region**		
24	Chemplast Sanmar (Mettur)	Mettur Dam, Tamil Nadu	Mercury
25	Chemplast Sanmar (Karaikal)	Karaikal	Membrane
26	Chemfab Alkalis	Pondicherry	Membrane
27	DCW Ltd.	Sahupuram, Tamil Nadu	Membrane
28	Solaris Chemtech.	Karwar, Karnataka	Mercury
29	Sreee Rayalaseema	Kurnool, AP	Membrane
30	Tamilnadu Petroproducts	Chennai, Tamil Nadu	Membrane
31	The Andhra Sugars	Kovvur & Saggonda, AP	Membrane
32	The Travancore Cochin Chem.	Kochi, Kerala	Membrane

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