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21TH CENTURY MERCURY EMISSION BY DIFFERENT SOURCES AFFECTS THE ENVIRONMENT IN INDIA

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ABSTRACT:
The global cycling of Mercury (Hg), leads to increase Hg concentrations and contaminate environmental compartments and reservoirs. The global inventory of mercury emissions to the atmosphere from anthropogenic sources in 2015 is 2220 tonnes. Such emissions account for 30% of mercury emitted annually to the atmosphere. It is 20% more than in 2010. The atmospheric mercury (Hg) emissions increases due to cement production, coal combustion in power plants, non ferrous metal production, primary iron and steel production and waste associated with mercury added products. 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 21 st 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 widerange 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 now a day's quite high in coastal areas. 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. Mercury travels well through the atmosphere, eventually making its way into plants, glacial ice, and soils. As glaciers melt, ice-trapped mercury is released into the atmosphere as well as downstream ecosystems.

Key words: - *Global environment, emission of mercury, anthropogenic sources, Cycling of Mercury, Climate change.*

INTRODUCTION:

Our understanding of the critical processes driving global mercury (Hg) cycling, in particular those that affect large-scale exchange of Hg among major environmental compartments, has advanced substantially over the past decade. Progress has been driven by major advances in three interconnected areas: new data, new models, and new analytical tools and techniques. In this paper, we summarize the state of knowledge of the major global Hg reservoirs in the Earth system: the atmosphere, terrestrial ecosystems, and aquatic ecosystems.

We describe the constraints on processes that control Hg exchanges between these reservoirs, and the relative influences of policy, land use, climate change, and anthropogenic disturbances on Hg cycling. Overview of global Hg cycling and impacts of policies and global change. Yellow numbers are estimated pool sizes in global reservoirs, and arrows indicate exchange processes between major environmental reservoirs. Pool sizes and exchanges are strongly modulated by anthropogenic emissions and releases (blue arrows) which transform in the atmosphere and deposit to aquatic and terrestrial ecosystems (green arrows). The Hg cycle will continue to experience disturbances due to changes in anthropogenic emissions and will be increasingly affected by land use and climate change, which remobilize (orange arrows) Hg that has accumulated in environmental reservoirs from previous Hg emissions and releases. 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. 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. [3] During the course of development, industrial management and the government authorities did not pay adequate attention at the regionalor 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. In the industrial area of Chhattisgarh state, water discharged from different industries such as thermal power plants, the steel industry, the cement industry, sulphuric 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[1]. Human activities redistribute Hg in a manner that causes elevated concentrations of pollutants in the human food chain.

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[2]. This imported Hg is generally used in chlor-alkali plants and the leading Hg users. There is no information of cross-boundary flow of Hg vapour from India to other parts of the world except for the Himalayas. 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. 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 or dry deposition. But the enhanced wet deposition rates close to major Hg sources through cloud-droplet activation and precipitation scavenging have been confirmed. 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. [5]

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. 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. 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.

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), India is the third largest hard coal producer in the world after the PR[3]China and the USA. Coal production has increased from 310 Tg in 2000 to 373 Tgin 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 ofsteam and coking (19 Tg) coals (GOI, 2006) . Coking coals are primarily consumedin the iron and steel industry. There are 81 thermal power plants in India, three ofwhich are not operating currently.

2. Iron and Steel industry

In the 21 st century, iron and crude steel production in India has increased from 21.3Tg 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 °Cor 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. 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 isquite 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.

3. Non-ferrous Metallurgical Iindustry in India

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 Au smelt process and the Imperial Smelting are practiced. In addition, there is one zinc production plant where Zn is produced by the hydro metallurgical process. The Cu-smelters are situated at Khetri, (Rajasthan), Ghatsila, (Jharkhand),Dahej (Gujarat), Tuticoran, (Tamil Nadu) where the Copper Flash Smelting Process and the Au smelt 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, December13, 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. 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).

4. Chlor-alkali Industry in India

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 + 2H2O ® Cl2 + H2 + 2NaOH (2) 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.

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.

6. Wastes Disposal

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) [(9)]. 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.

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 4 Mercury Emissions from Industrial Sources in India and its Effects 101 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). [(7)] 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. [(8)] 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 392.28kg/person/year whereas at 2000 altitudinal range it is 1019 kg/person/year. It means Hg emissions will be higher as well when firewood is burnt at higher altitude in the mountain region.

8. Miscellaneous

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. [(4)] There are three types of brick works, based on production

Instruments, Batteries and Thermometers

Substantial amounts of Hg are used in the production of instruments, batteries and clinical thermometers. 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, book keeping 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%.[(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, 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 . 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. [(6)]

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 Me Hg 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 20 th 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.

REFERENCES:

CPCB, 2000. Status of municipal solid waste generation collection and disposal in Class 1-cities. Central Pollution Control Board, Ministry of Environment & Forests, new Delhi. India AMA (Alkali Manufactures Association) 2007. http://www.ama-india.org/

Karunasagar, D., Balaram Krishna, M.V., Anjaneyulu, Y. and Arunachalam, J. 2006. Studies of mercury pollution in a lake due to thermometer factory situated in a tourist resort: Kodaikkanal, India. Environ. Pollut.

Prosun Bhattacharya KTH Royal Institute of Technology Arun B. Mukherjee N. Pirrone and R. Mason (eds.), *Mercury Fate and Transport in the Global Atmosphere*,

UNEP, 2005. Toolkit for identification and qualification of Hg release.

Subramianium, V., Madhavan, N., Saxena, R. and Lundin, L.C. 2003. Nature of distribution of mercury in the sediments of the River Yamuna (tributary of the Ganges), India. *J. Environ. Monit.*

Streets, D.G., Bond, T.C., Carmichael, G.R., Fernanes, S.D., Fu, Q., He, D. et al. 2003. An inventory of gaseous and primary aerosol emissions in Asia in the year 2000. J. Geophys. Res.,108 (D21), 8809.

Venkataraman, C., Habib, G., Kadamba, D., Shrivastava, M., Leon, J.-F., Crouzile, B., Boucher, O., Streets, D.G. 2006. Emissions from open biomass burning in India: Integrating the inventory approach with high-resolution Moderate Resolution Imaging Spectroradiometer (MODIS)

active-fire and land cover data. Global Biogeochemical Cycles

Singhal, S. and Pandey, S. 2001 Solid waste management in India: Status and future directions.

TERI Information Monitor on Environmental Science.