



Hazards of Mercury – Safety Perspectives and Measures

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Mercury is one of the most hazardous contaminants emitted to the atmosphere due to its toxic effects on the environment and human health. Anthropogenic and geological sources account for 30 % and 10 % respectively, whereas the rest is from re-emissions. Consumption of fossil fuels for power generation and heating purposes is still the main source of anthropogenic emissions of mercury. The mercury emissions from industrial sources not only affect equipment and processes but are also a potential hazard for plant and operator's safety. High reactivity and volatility of mercury make its capture rather difficult. Mercury in the atmosphere is in three primary forms i.e. elemental, inorganic and organic. Gaseous elemental mercury is the most common in anthropogenic and natural emissions to the atmosphere. The transport and deposition of atmospheric mercury depend greatly on whether it is elemental or oxidized. The global cycle of mercury is mainly controlled by oxidation–reduction reactions in the atmosphere and aquatic ecosystem that readily convert volatile Hg⁰ into soluble Hg²⁺ and vice versa. A small fraction of mercury is converted to methyl mercury by bacteria in anoxic environments. Exposures to mercury can affect the human nervous system and harm the brain, heart, kidneys, lungs, and immune system. The only way to reduce mercury pollution is to capture it from emission sources by effective technologies and safety measures. The paper highlights the mercury sources, which increase health hazards in Europe and Asia along and discusses the transport of mercury and viable preventive measures. The progress in mercury removal technologies is also discussed with their limitations.

1. Introduction

The rapid pace of industrialization and its by-products has been changing the environment due to hazardous waste discharges and poisonous gas fumes and smokes into the environment. All these by-products adversely affect terrestrial ecosystems, e.g., water, air, vegetation, forestry resources, and other forms of life (Dubey et al., 2003). The boom in world's heavy industry has greatly increased the consumption of energy. Fossil fuels are still used to support more than 80 % of world energy consumption. However, one of the main concerns arisen from the use of fossil fuels is the emission of gases that are considered detrimental to the environment such as carbon dioxide, sulphur dioxide, nitrogen dioxide, unburned hydrocarbon etc. and heavy metals such as mercury etc.

Mercury is a toxic, bio-accumulating trace metal whose emissions to the environment have increased significantly as a result of anthropogenic activities such as mining and fossil fuel combustion. It is released the environment either naturally or through human activities in three forms such as elemental (Hg⁰), oxidized (Hg²⁺) and particulate (Hg^p).

During the post-industrial era, combustion of fossil fuels combined with long-range, atmospheric transport have increased the mercury in soils and sediments by a factor of 3 to 10, and the global mercury emission into the atmosphere was reported to amount to 3,000 t in 2005 (Xu et al., 2015). A recent study (Lamborg et al., 2014)

reported that anthropogenic perturbations to the global mercury cycle have led to an approximately 150 % increase in the amount of mercury in thermocline waters and have tripled the mercury content of surface waters compared to pre-anthropogenic conditions. Most mercury forms are highly toxic for highly exposed humans, but even low exposure can seriously and adversely affect the central nervous system. The presence of mercury not only affects the environment but also has detrimental effects on industrial equipment. Mercury in natural gas is present predominantly as elemental mercury.

Elemental Mercury forms an amalgam with the surface layer of the metal it contacts (Abbas et al., 2014). A very small amount of mercury is sufficient to destroy the aluminum heat exchangers often used in the cryogenic processes at LNG plants or naphtha crackers for olefin production. Moreover, mercury deposition in equipment poses a health and safety risk for workers involved in maintenance or inspection activities. Mercury in gas plant products affects downstream processes as well.

The only way to reduce the mercury hazards is to deal with it by adopting proper safety and remove it from process streams efficiently. The paper highlights mercury emission sources in Europe and Asia, and provides an over view of health hazards and safety measures in mercury removal technologies.

2. Mercury Sources

Mercury is released by natural and anthropogenic sources throughout the world. Mercury emissions to the atmosphere from natural sources are estimated at about 80–600 t/y. According to UNEP (UNEP, 2013a), the flow of mercury through the environment suggests that natural sources account for about 10 % of the estimated 5,500–8,900 t of mercury currently being emitted and re-emitted to the atmosphere from all sources. Anthropogenic sources of mercury emissions account for about 30 % of the total amount of mercury entering the atmosphere each year.

Current anthropogenic sources, which include numerous industrial point sources, are estimated to release about 1960 t of mercury on an annual basis (UNEP, 2013a). The major source regions are Asia and Africa (47.5 % and 16.8 % of the global total, respectively). The main sectors identified are artisanal and small scale gold mining, coal combustion, production of non-ferrous metals (including copper, lead, zinc, aluminum and large-scale gold production), cement production, and disposal of wastes containing mercury (AMAP/UNEP, 2013). Figure 1 shows the mercury emission sources (2005-2010) in Europe and Asia.

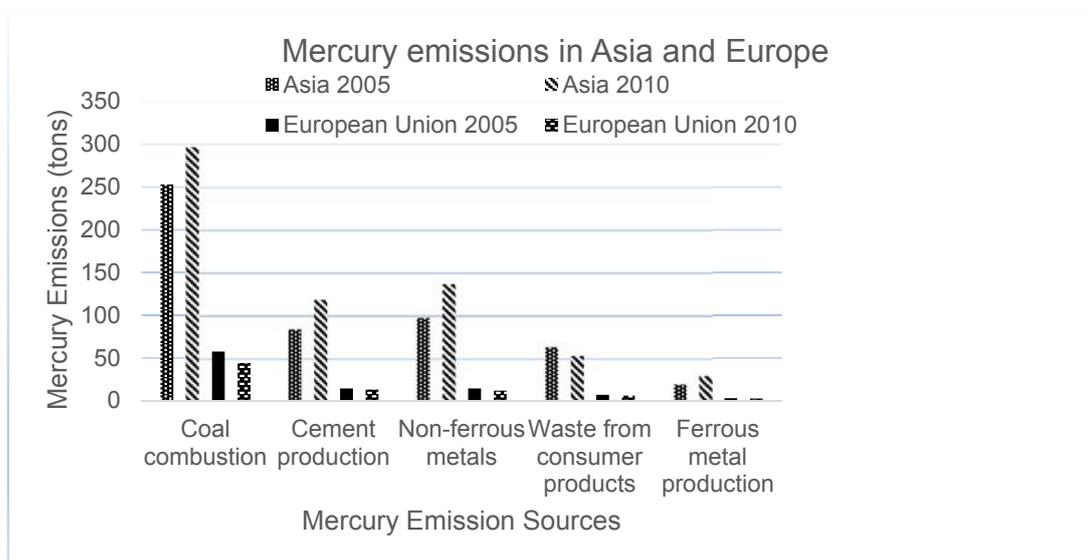


Figure 1: Mercury emissions sources in Asia and Europe data extracted from (UNEP, 2013a)

Overall, coal burning is still the main source of mercury emissions in Asia and Europe. However, the trend continues to increase in Asia, but at the same time improvements are taking place in Europe. The reason of increasing mercury emissions in Asia is predominantly due to increasing energy demand and improvements in infrastructure that lead to more cement production, mainly in China and India.

Strict regulations in Europe on mercury imports and slight shift towards renewable energy resources are the major factors in reduction of mercury emissions. The area coverage by Hg emissions depends on the chemical formulation of that substance. As Hg^0 in gaseous form it can remain in the atmosphere for long periods (e.g., one year) and be transported over long distances. Conversely, as Hg^{2+} and Hg^p mercury is short lived, resulting

in localized deposition. For instance, in industrial areas of Europe, the deposition of mercury emissions from European sources constitutes up to 60 %, whereas in the Mediterranean area it is just 20 % or even less (Elsie M, 2013).

Furthermore, the growing population and expansion of industrial sector will influence the increase of the demand for energy. Thus, in the near future, we can expect a growth in mercury emissions due to anthropogenic sources, such as power generation from coal and natural gas.

3. Health Hazards of Mercury

Mercury is mainly classified in three distinct forms in flue gases from coal power plants: (Hg^0), (Hg^{2+}) and (Hg^p) (Pavlish et al., 2003). The Hg^{2+} and Hg^p are soluble in water and hence they are deposited on a local and regional scale, whereas Hg^0 is present in vapour phase that enables its transportation worldwide (Rao, 2010). As a result, most of mercury in the air is in the gaseous elemental phase. When mercury moves from air to water and land, it is generally in an oxidized gaseous or particulate form, whereas when it is re-emitted to air it has been converted back to gaseous elemental mercury.

The pathways and fate of mercury in aquatic environments are important because it is in waters, sediments, and wetland soils. Usually, that inorganic form of mercury is converted into methyl mercury (MeHg) by sulfur reducing bacteria in anoxic environments.

MeHg bio accumulates in the bodies of aquatic animals, so people are exposed to it mainly by consuming contaminated fish and sea food. Recently, it was found that mercury is coming from human activities, including burning fossil fuels like coal. Mining for gold and coal, are deemed as the main drivers for the increase in the ocean's mercury, causing the substance to increase by a factor of 3.4 in the ocean's upper levels since the beginning of the Industrial Revolution (Lamborg et al., 2014).

Mercury is a neurotoxin, and ingesting too much of it can cause developmental defects in foetuses and, at extreme levels, death. Typically, people ingest mercury by eating fish, with larger, predatory fish containing more mercury than smaller prey fish. However, the main exposure to methyl mercury is not only restricted to fish, but also to rice meals (Feng et al., 2007).

Apart from MeHg, Hg^0 vapors are also quite dangerous for humans if exposed to. In industrial settings such as chloralkali and power generation plants, workers and local residents are also likely be exposed to mercury through the respiratory tract (Li et al., 2009). In humans, approximately 80 % of mercury vapour (Hg^0) is readily absorbed through the respiratory tract, but only 0.01 % by the gastrointestinal tract and to a limited extent via the skin (0.024 ng Hg/cm^2 skin per 1 mg/m^3 of Hg present in air) (Holmes et al., 2009). On one hand, when organic Hg vapors are absorbed, they get distributed to fat-rich tissues and their high lipophilicity enables the transfer across placental and blood-brain barriers.

On the other hand, the inorganic forms of mercury allow reaching most human organs, but their reduced lipophilicity limits the ability to penetrate the blood-brain and placental barriers (Holmes et al., 2009). Figure 2 shows the impact of mercury toxicity on various organs.

New estimates suggest that between 1.5 and 2 million children in the Europe are born each year with MeHg exposures above the safe limit of 0.58 $\mu\text{g}/\text{g}$ and 200,000 above the WHO's recommended maximum of 2.5 $\mu\text{g}/\text{g}$ (Bellanger et al., 2013). Figure 3 shows detailed facts on the number of annual births having excess Hg levels in different European countries with MeHg exposure distributions.

4. Safety measures for dealing Hg Hazards

As aforementioned that the most efficient method of removal of Hg is to eliminate it from the source. At the same time, the awareness of the hazards of Hg can play an important role in the mitigation process into the biogeochemical cycle (UNEP, 2013b). Advanced training methods (see for instance Nazir et al. (2012)) can be used to improve the understanding, knowledge, and awareness of specific operators dealing with Hg. To reach an optimal point between investments on Hg related Hazards and overall profitability, it is essential to involve decision/policy makers. An overview of mercury removal methods is provided in the following section.

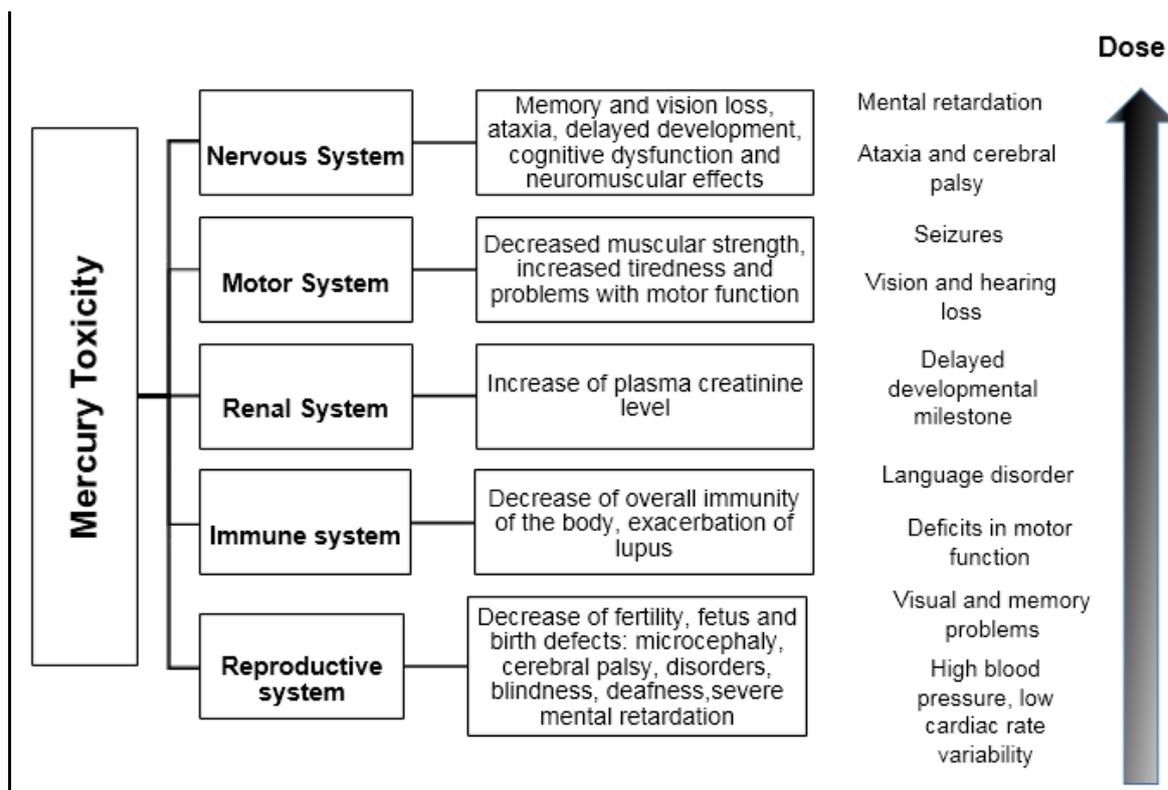


Figure 2: Impact of mercury toxicity on organ systems (modified from (Zahir et al., 2005) and (Bose-O'Reilly et al., 2010)) with permission from Elsevier, 2014

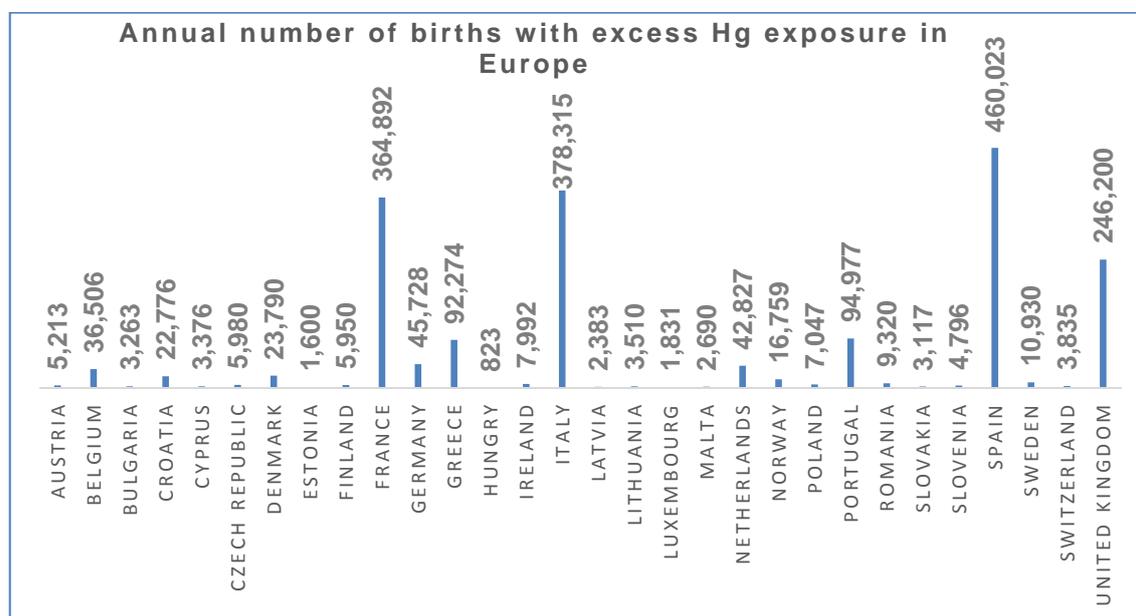


Figure 3: Annual number of births with excess ($>0.58 \mu\text{g/g}$) Hg exposure in Europe, data extracted from (Bellanger et al., 2013)

5. Mercury Removal Technologies

As discussed above, fossil fuels are being used mostly for energy generation, thus emitting mercury to the atmosphere. Hg^0 is mainly present in flue gases of coal power plants ((others: Hg^{2+} and Hg^{p}) and natural gas ((others: Hg^{2+}). However in crude oil and condensate, organic mercury is mainly present. Virgin activated

carbon, sulfur, chloride, iodine and brominated carbons are being used to capture mercury from emission sources (Yang et al., 2007). Furthermore, a number of technologies and products, which meet the specifications for down- stream processing, are commercially available. However, not all systems are capable to treat the full range of mercury emissions in a single action (Mahpuzah et al., 2011). The limitations of some of mercury removal technologies are summarized in Table 1 (Abbas et al., 2014).

Table 1: Mercury removal systems with their limitations

Mercury Removal Systems	Limitations
Adsorption on activated carbon	Low saturation loading but cheap, disposal problem and cant remove all types of mercury in one step
Sulfur impregnated carbon	Less efficient and lose of sulfur in contact with liquid hydrocarbons
Adsorption on molecular sieve	Common sieves have low capacity; big beds
Adsorption on metal sulphide impregnated on mesoporous Alumina	Low resistance to both capillary condensation and liquid carry-over, only capable to remove elemental mercury
Adsorption by amalgamation with a metal such as aluminium, silver Zeolites etc.	High investment cost, lower capacities
Oxidising solutions- potassium permanganate, sodium hypochlorite, and sodium vanadate	Regeneration problems; system contamination
Acid absorption of mercury-acidic permanganate and chromic acid	Increased corrosion, low saturations, system contamination
Condensation and separation	Poor removal efficiency, liquid contamination

Abu Daabes (Abu-Daabes, 2005) synthesized and evaluated chelating adsorbents to remove oxidized mercury from flue gas. Moreover, it is also proven that ionic liquids, particularly solid supported ionic liquids (SSILs), can capture different types of mercury in a single step more efficiently than other techniques (Mahpuzah et al., 2011). Ji and coauthors (Ji et al., 2008) used a ionic liquid 1-butyl-1-methyl pyrrolidinium bis(trifluoromethane sulfonyl) imide (P14), as a coating on both a silica substrate and on a chelating adsorbent, for the capture of elemental mercury from flue gas at 160 °C. Fixed-bed experiments done using P14 and P14-KMnO₄ ionic liquids coated adsorbents showed high capacity for the capture of vapor phase elemental mercury. P14-KMnO₄ coated based adsorbents showed a capacity to capture elemental mercury greater than 7.2 mg/g due to their ability to oxidize Hg⁰ (Ji et al., 2008). Silica coated with 1-butyl 3-methyl imidazolium chloride showed 10mg/g and 38mg/g of adsorption capacity for Hg⁰ and Hg²⁺ respectively (Ji et al., 2008). SSILs can adsorb mercury three times more than other commercially available adsorbents from natural gas even without modifications of the plant infrastructure (Mahpuzah et al., 2011). First author found in his experiment that carbon supported ionic liquids are more promising than silica supported ionic liquids, it will definitely help to reduce the adsorbent cost for its practical application on large scale. The research is in progress to understand the mechanism of mercury adsorption on carbon supported ionic liquids that will help to further improve the efficiency.

6. Conclusions

The hazards of mercury were illustrated with help of recent literature and some statistics. In spite of the limitations of existing removal methods, it is necessary to integrate the safety awareness of mercury in the industry as well as for those who may get exposed to it. The immediate way to reduce mercury pollution is to capture it efficiently from anthropogenic sources especially from power plants. SSILs have proven better ability to remove mercury from process streams efficiently in a single step. Future studies and investigations are required to understand the mercury adsorption mechanism on SSILs, it will surely help researchers to come up with best pair of ionic liquids and solid support.

References

- Abbas, T., Abdul Mutalib, M. I., Azmi Bustam, M., 2014, Developments in Mercury Removal from Natural Gas- A Short Review. *Applied Mechanics and Materials*, 625, 223-228.
- Abu-Daabes, M. A. 2005. *Synthesis and characterization of nano-structured chelating adsorbents for the direct removal of mercury vapor from flue-gases*. University of Cincinnati.

- Amap/Unep, 2013, Technical Background Report for the Global Mercury Assessment 2013. UNEP Chemicals Branch, Geneva, Switzerland.
- Bellanger, M., Pichery, C., Aerts, D., Berglund, M., Castaño, A., Čejchanová, M., Crettaz, P., Davidson, F., Esteban, M., Fischer, M., Gurzau, A., Halzlova, K., Katsonouri, A., Knudsen, L., Kolossa-Gehring, M., Koppen, G., Ligočka, D., Miklavčič, A., Reis, M., Rudnai, P., Tratnik, J., Weihe, P., Budtz-Jørgensen, E., Grandjean, P., 2013, Economic benefits of methylmercury exposure control in Europe: Monetary value of neurotoxicity prevention. *Environmental Health*, 12, 1-10. doi: 10.1186/1476-069X-12-3
- Bose-O'reilly, S., Mccarty, K. M., Steckling, N., Lettmeier, B., 2010, Mercury Exposure and Children's Health. *Current problems in pediatric and adolescent health care*, 40, 186-215. doi: 10.1016/j.cppeds.2010.07.002
- Dubey, B., Upadhyay, R. K., Hussain, J., 2003, Effects of industrialization and pollution on resource biomass: a mathematical model. *Ecological Modelling*, 167, 83-95. doi: [http://dx.doi.org/10.1016/S0304-3800\(03\)00168-6](http://dx.doi.org/10.1016/S0304-3800(03)00168-6)
- Elsie M, S., Noelle E, Selin, 2013, Future trends in environmental mercury concentrations: implications for prevention strategies. *Environmental Health*, 12.
- Feng, X., Li, P., Qiu, G., Wang, S., Li, G., Shang, L., Meng, B., Jiang, H., Bai, W., Li, Z., Fu, X., 2007, Human Exposure To Methylmercury through Rice Intake in Mercury Mining Areas, Guizhou Province, China. *Environmental Science & Technology*, 42, 326-332. doi: 10.1021/es071948x
- Holmes, P., James, K., Levy, L., 2009, Is low-level environmental mercury exposure of concern to human health? *Science of the total environment*, 408, 171-182.
- Ji, L., Thiel, S. W., Pinto, N. G., 2008, Room temperature ionic liquids for mercury capture from flue gas. *Industrial & engineering chemistry research*, 47, 8396-8400.
- Lamborg, C. H., Hammerschmidt, C. R., Bowman, K. L., Swarr, G. J., Munson, K. M., Ohnemus, D. C., Lam, P. J., Heimbürger, L.-E., Rijkenberg, M. J. A., Saito, M. A., 2014, A global ocean inventory of anthropogenic mercury based on water column measurements. *Nature*, 512, 65-68. doi: 10.1038/nature13563
<http://www.nature.com/nature/journal/v512/n7512/abs/nature13563.html#supplementary-information>
- Li, P., Feng, X. B., Qiu, G. L., Shang, L. H., Li, Z. G., 2009, Mercury pollution in Asia: A review of the contaminated sites. *Journal of Hazardous Materials*, 168, 591-601. doi: <http://dx.doi.org/10.1016/j.jhazmat.2009.03.031>
- Mahpuzah, A., Martin P. Atkins., Amiruddin, Hassan., John D. Holbrey., Yongcheun, Kuah., Peter, N., Alexander A. Olifrenko., Natalia V. Plechkova., Syamzari Rafeen., Adam A., Rahman., K. R. S., Shahidah M. Shariff., Geetha, Srinivasan., Yiran, Zoub, 2011, Mercury removal from gas streams using new solid adsorbents. *International Gas Union Research Conference*. Korea.
- Nazir, S., Totaro, R., Brambilla, S., Colombo, S., Manca, D., 2012, Virtual Reality and Augmented-Virtual Reality as Tools to Train Industrial Operators. *Computer Aided Chemical Engineering*, 30, 1398-1401.
- Pavlish, J. H., Sondreal, E. A., Mann, M. D., Olson, E. S., Galbreath, K. C., Laudal, D. L., Benson, S. A., 2003, Status review of mercury control options for coal-fired power plants. *Fuel Processing Technology*, 82, 89-165.
- Rao, P. S. 2010. *Advanced adsorbents for warm gas capture of mercury in coal gasification*. University of Cincinnati.
- Unep, 2013a, Global Mercury Assessment 2013: Sources, Emissions, Releases and Environmental Transport. UNEP Chemicals Branch, Geneva, Switzerland.
- Unep, 2013b, Minamata Convention on Mercury. UNEP Geneva, Switzerland.
- Xu, J., Bravo, A. G., Lagerkvist, A., Bertilsson, S., Sjöblom, R., Kumpiene, J., 2015, Sources and remediation techniques for mercury contaminated soil. *Environment International*, 74, 42-53. doi: <http://dx.doi.org/10.1016/j.envint.2014.09.007>
- Yang, H., Xu, Z., Fan, M., Bland, A. E., Judkins, R. R., 2007, Adsorbents for capturing mercury in coal-fired boiler flue gas. *Journal of Hazardous Materials*, 146, 1-11. doi: <http://dx.doi.org/10.1016/j.jhazmat.2007.04.113>
- Zahir, F., Rizwi, S. J., Haq, S. K., Khan, R. H., 2005, Low dose mercury toxicity and human health. *Environmental toxicology and pharmacology*, 20, 351-360.