Estimation of Particulate Mercury Emission in the Ambient Air Around the Plant Area

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Abstract

Mercury is unique in being the only metal in liquid form at ambient temperatures. Present study involves about mercury in the Suspended Particular Matter (SPM), it detect with the help of Direct Mercury Analyzer-80 (DMA-80). Mercury is released in the atmosphere through coal-based power plant. During coal combustion, two forms of mercury are released from a power plant, oxidized (or ionic) mercury, which is water-soluble and elemental mercury, which is not very water-soluble. Mercury can cause long lasting effects to all living as well as non-living.

Keywords: Mercury; Coal Based Power Plant; Effects of Mercury, DMA-80

Introduction

The purpose of this study is to evaluate the industrial and urban pollutants from the thermal power plant. Many models have been used to calculate the amounts and movements of mercury in the world [1]. A large proportion of the mercury found in the environment is derived from industrially produced mercury and amounts to approximately 10000 tons per year [2]. Toxic pollutants are routinely emitted in to the atmosphere by either natural or anthropogenic activities: such as combustion of coal, mining of ores and cement plant, industrial sources (stationary sources), motor vehicles (mobile sources). There are also many sources of mercury, chlorine industry, the preparation of chlorine by the Hg-cell process contains mercury, the burning of fossil fuels, compost incinerators, mining and extraction of mercury from cinnabar, the chlor-alkali industries, paper pulp, paints, fungicides, electrical equipments, instrumentation, amalgamation, medical waste, residential boiler, municipal waste, hazardous waste etc.

Toxic pollutant like mercury is of current interest as it has effects on human health such as inhalation of high concentration of mercury vapor cause pulmonary deposition, damage to lower parts of bronchial tree and peripheral lung tissues [3,4,5]. In animals elemental mercury vapor is slightly soluble in water, it could be expected to penetrate far down the bronchial tree. This expectation fulfilled experimentally [6] it was shown that only about 30% of the whole body burden of the mercury was in the lung. The analysis of mercury in the air is of great importance for evaluating health hazards of industrial atmosphere. Almost all mercury compounds are toxic and can be dangerous at very low levels in both aquatic and terrestrial ecosystem. Organic mercury has been determined in biological material [7]. Mercury is easily vaporized at normal temperature; the vaporization of metallic mercury constitutes the easiest way of transport in to the atmosphere. The vapor pressure even high at normal temperature 1.2x10⁻³ mm Hg at 20°C [8]. In the environment mercury observe in various forms, elemental mercury or metallic mercury (Hg⁰), inorganic and organic mercury. Metallic mercury is usually referred to as mercury vapor when present in the atmosphere or as metallic mercury in liquid form, Hg²⁺ (divalent mercury) and particulate mercury. The environmental behavior of mercury and its impacts and concentration on air quality, was monitored on a routine basis at an industrial site [9].

Figure 1: Mercury concentration from various sources.

Methyl mercury (CH₃Hg) which is concentrated in fish and birds. Most of the Oxidized mercury and all of the elemental mercury are

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carried away by the wind. A small amount of the oxidized mercury ends up in water and may be formed into an organic form called Methyl mercury [10].

The objective of the proposed study during Dec-2007 to Feb-2008 is to investigate the mercury concentration in ambient particulate matter around a large coal-fired power station located near the coastal belt. The topography as the regions shows that the beaches and fishery folk villages in one side and on other side being hilly terrain.

**Material and Method**

**Sampling Method**

Different types of filters for air sampling are available today. They are Glass Microfibre filters like GF/A and EPM 2000 as well as quartz filters QM-A. The filter shall be selected based on the kind of further analysis like trace metals etc. required from the Suspended Particulate Matter (SPM) samples. The GF/A filter is suitable for analysis of mercury and trace metals. The SPM was collected under different weather condition on a glass microfibre filters GF/A 20.3x25.4cm (Whatman) for 24 hours using a High Volume air sampler.

**Analytical Instrumentation**

Mercury in the SPM was solubilized by extraction with concentrated nitric acid. The mercury content of the sample is determined by direct mercury analyzer-80 (Milestone) at 253.65 nm mercury absorption line [11].

**Direct Mercury Analyzer (DMA-80)**

The instrumental conditions are to be optimized as recommended in the operation manual. The thermal decomposition technique employed by the DMA-80 is best exemplified in EPA Method 7473 for analysis of environmental samples. Methods like Cold Vapor Atomic Absorption Spectroscopy require chemical reduction of the mercury to its elemental state. It also needs sample preparation which takes several hours. On the other hand the DMA-80 analyzes samples directly, fast- approximately 5 minutes per sample, sample is thermally decomposed, chemical pretreatment (mercury is reduced by the catalysts in the decomposition tube) and waste disposal (no reagents).

Each sample with bodies(boat) is dried for about 10 to 60 seconds at 300°C and then thermally and chemically decomposed within the decomposition furnace (Controlled heating in an oxygenated decomposition furnace is used to liberate mercury from solid and liquid aqueous samples in an instrument at about 850°C for 150 seconds). The decomposition products are carried by oxygen to the catalytic section of the furnace (here oxidation is completed and halogens, sulfur, nitrogen oxides are trapped) [11]. Remaining decomposition products are then carried to an amalgamator that selectively traps mercury. After the system is flushed with oxygen to remove any remaining gases or decomposition products, the amalgamator is rapidly heated releasing mercury vapors. Flowing oxygen carries the mercury vapors through absorbance cell positioned in the light path of a single wavelength atomic absorption spectrophotometer. Absorbance is measured at 253.65 nm as a function of mercury concentration. The results of mercury concentration are recorded in nanogram as well as microgram per kilogram. The working range for this method is 0-35ng Hg in lower range and 35-600 ng Hg in higher range in each sample of about 0.2g. The instrument minimum detection limit is 0.01ng Hg in each sample. At least a high and low concentration standard for each working range is analyzed using the analytical parameters as recommended by the manufacturer. The working calibration standards must be measured within 10% of their true value for the curve to be considered valid.

**Interferences**

Instrumental memory (previous sample concentration) effects in between different sample analyses may be encountered, eg. Analyzing a sample containing high mercury content (≥600ng) prior to analyzing one of low concentration (≤35ng) samples. Typically to minimize memory effect, the samples are analyzed in batches of low and high concentration, always analyzing those of low concentration first. A blank analysis with an extended decomposition time may be preferred following the analysis of a high concentration samples to minimize memory effects.

**Safety Measures**

Many mercury compounds are highly toxic if swallowed, inhaled or absorbed through the skin. Extreme care is required in the handling of concentrated mercury reagents. Concentrated mercury reagents should only be handled by analysts having prior knowledge about the risks and required safe handling procedures.

**Calibration and Standardization**

**Reagent Water**

Double distilled water to remove probable interference.

**High Purity Oxygen**

The oxygen required for DMA instrument should be interference and Hg free. (If the oxygen is possibly contaminated with Hg vapor a gold mesh filter should be insulated between the gas cylinder and the mercury analysis instrument to prevent any mercury from entering the instrument.)

**Hg Standard (Stock Solution)**

Dissolve 0.1354g of AR grade Mercuric chloride (HgCl₂) in 75ml
of reagent water. Add 10ml of concentrated nitric acid (AR grade) and adjust the volume up to 100 ml with reagent water (1ml=1mg Hg).

**Working Standard**

Make successive dilutions of the stock solution with reagent water to obtain known standards of 10ppm and 1ppm. For calibration of the instrument in high range, standards of 1,2,3,4,5 and 6ppm Hg concentrations are recommended. These are prepared by dilution of the 10ppm standard. However for calibration of the instrument in low range, standards of 0.00, 0.05, 0.1, 0.2, 0.3, 0.4, 0.5 ppm are recommended [11]. Standard was prepared by dilution of the 1ppm standard solutions and results are summarized in Table 1.

<table>
<thead>
<tr>
<th>Volume of 1 ppm solution( ml )</th>
<th>Final volume (ml)</th>
<th>Concentration (ppm)</th>
<th>Mercury result and calibration (ng)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.25</td>
<td>25</td>
<td>0.05</td>
<td>5.03</td>
</tr>
<tr>
<td>2.5</td>
<td>25</td>
<td>0.1</td>
<td>8.66</td>
</tr>
<tr>
<td>5</td>
<td>25</td>
<td>0.2</td>
<td>12.46</td>
</tr>
<tr>
<td>7.5</td>
<td>25</td>
<td>0.3</td>
<td>32.82</td>
</tr>
<tr>
<td>10</td>
<td>25</td>
<td>0.4</td>
<td>41.22</td>
</tr>
<tr>
<td>12.5</td>
<td>25</td>
<td>0.5</td>
<td>74.34</td>
</tr>
</tbody>
</table>

Note: 1 ppm= 1 mg/lit=1µg/ml= 1 ng/µl

[The known sample/standard of 0.05ppm HgCl₂ shall get DMA result of about 5ng and the concentration of 50µg/kg]

Fill about 100µl of known/prepared (refer Table-1) standard solution in the sample boat. Analytical parameters for drying, decomposition and Wait times as recommended by the instrument manufacturer shall be chosen for the analysis. Each standard solution should be analyzed twice. For the DMA 80, parameters of 70 seconds drying, 100 seconds decomposition and 40 second wait time for each sample analysis are pre-set by instrument manufacturers.

**Sample Preparation and Analysis**

About 20-30% area of exposed filter paper (for example 16 circles of 1.5 cm diameter are cut using a stainless steel punch) from each sample is taken for analysis. These circles are put in a reaction vessel and 10 ml of concentrated HNO₃ is added. The reaction vessels are kept in a microwave oven for digestion after setting following programmed.

The digestion was carried out in three steps each of five minute interval so as to obtain power of about 250, 400, 500 watt and ventilation time of 15 minute was given. The samples are taken out and kept at room temperature. The digested samples filter with the help of whatman filter paper and make up the volume up to 100 ml with reagent water in the volumetric flask. Measure about 100 µl of the sample by a micropipette with disposable tip (use new tip for each sample) fill in quartz boat and introduce in the instrument. The results of mercury concentration in nanograms and microgram per kilogram are recorded.

**Data Analysis and Calculations**

Mercury concentration in suspended particulate matter

\[
\text{Hg content in total sample} = \frac{\text{conc.of } Hg(\mu g/kg) \times 0.1(100ml=100gm=0.1kg) \times M.F}{\text{Volume of air sample (m}^3\text{)}}
\]

\[M.F= \frac{A(f)}{A(s)}\]

Where,

A (f) is the area of exposed total filter
A(s) is the area of sample filter digested in HNO₃

**Result and Discussion**

The concentrations of particulate laden mercury is summarized in Table-2. It is observed that mercury concentrations at various sites around the power plant in the 10 km region varied between 0.0002 to 0.0224 µg/m³. The minimum particulate mercury concentration was observed at site 11 which 8 Km away from the plant site and in the SSE. The location was very near to the forest area and no other mercury source was observed in the vicinity. Hence the
concentration of mercury was minimum.

The sampling locations at 1, 3 and 10 in the N, NNW and ENE direction recorded the maximum concentrations. These sites are very near to the boundary walls of the power plant. Most of the sampling sites (4-14) were in rural areas surrounded by agriculture fields. Extensive use of pesticides, fungicides was observed. Agricultural activities make use of organomercurial fungicides. It has been reported that residual mercurial fungicides can firmly bound to the soil and small fractions vaporize and enter the atmosphere. The site 2,12 and 13 showing concentration of mercury 0.0065, 0.0079, and 0.0080 µg/m³ which is 1.5, 9 and 9.5 Km respectively in the direction NE, NNE, NNW. It is much away from plant site but site 12 and 13 is near to railway line. Concentration of mercury in petroleum can be saturated with mercury vapor [12] approximately half of the side shown under study area is villages. So the source of mercury other than the plant which is anthropogenic and natural. Anthropogenic source is coal burning, burning of fossil fuels and natural from rock, minerals. The present site 9 and 10 shown under hilly region. Site 9 and 10 which is NE, ENE direction respectively and their concentration shows 0.0071 and 0.0091µg/m³. This site shows higher concentration of mercury because in it was very near to the manufacturing medicinal capsule. It is reported that industries releases of substantial mercury primary processes of mercury production and other industrial processes where mercury vapors are generated as a side product. Ministry of Environment and Forests, Government of India, wide notification declared this area is an ecologically fragile area [13].

Considering site 3,4 and 5 which is 4 Km away from the power plant, the concentration of mercury at that site were found to be 0.0090, 0.0013 and 0.0060 µg/m³ as, respectively. Site 3 show higher concentration of mercury than site 4 and 5 as it was near to a traffic with National/State highways there are automobile exhaustion. Site 6 is nearer to the reserved forest and 3.5 Km away from plant site, 0.0044 µg/m³ mercury in E direction. From the project site SE direction shows the site i.e. site 8. The site 8 is 8 Km away from plant site, bearing 0.0036 µg/m³ mercury concentration.

**Conclusion**

The observed data for the industrial areas show that the concentration of mercury in the range of 0.00021-0.0224 µg/m³. Industry should adopt the appropriate measure for reducing mercury concentration in ambient air of villages around power plant. The presence of mercury at different sites are shown in the Table-2. The majority of reported toxic effects that can result from exposure to mercury affect to central nervous system. The organic chemical used in laboratory and in daily life has indicated that they have an effect on human health. Longer exposure of mercury in workplace area is responsible various types of physiological effect.

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**Table 2: Ambient Air Quality Monitoring Stations**

<table>
<thead>
<tr>
<th>Sr. No.</th>
<th>Sampling location</th>
<th>Direction (From project site)</th>
<th>Distance(Km) (From project site)</th>
<th>Hg conc. (µg/m³)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.</td>
<td>Site-1</td>
<td>NW</td>
<td>1.5</td>
<td>0.0224 ± 0.0002</td>
</tr>
<tr>
<td>2.</td>
<td>Site-2</td>
<td>NE</td>
<td>1.5</td>
<td>0.0065 ± 0.0002</td>
</tr>
<tr>
<td>3.</td>
<td>Site-3</td>
<td>NNW</td>
<td>4.0</td>
<td>0.0090 ± 0.0015</td>
</tr>
<tr>
<td>4.</td>
<td>Site-4</td>
<td>NNE</td>
<td>4.0</td>
<td>0.0013 ± 0.0002</td>
</tr>
<tr>
<td>5.</td>
<td>Site-5</td>
<td>ENE</td>
<td>4.0</td>
<td>0.0060 ± 0.0015</td>
</tr>
<tr>
<td>6.</td>
<td>Site-6</td>
<td>E</td>
<td>3.5</td>
<td>0.0044 ± 0.0002</td>
</tr>
<tr>
<td>7.</td>
<td>Site-7</td>
<td>SW</td>
<td>3.5</td>
<td>0.0065 ± 0.0003</td>
</tr>
<tr>
<td>8.</td>
<td>Site-8</td>
<td>SE</td>
<td>8.0</td>
<td>0.0036 ± 0.0003</td>
</tr>
<tr>
<td>9.</td>
<td>Site-9</td>
<td>NE</td>
<td>6.5</td>
<td>0.0071 ± 0.0002</td>
</tr>
<tr>
<td>10.</td>
<td>Site-10</td>
<td>ENE</td>
<td>6.0</td>
<td>0.0091 ± 0.0002</td>
</tr>
<tr>
<td>11.</td>
<td>Site-11</td>
<td>SSE</td>
<td>8.0</td>
<td>0.0002 ± 0.00002</td>
</tr>
<tr>
<td>12.</td>
<td>Site-12</td>
<td>NNE</td>
<td>9.0</td>
<td>0.0079 ± 0.0002</td>
</tr>
<tr>
<td>13.</td>
<td>Site-13</td>
<td>NNW</td>
<td>9.5</td>
<td>0.0080 ± 0.0015</td>
</tr>
<tr>
<td>14.</td>
<td>Site-14</td>
<td>SSW</td>
<td>10.0</td>
<td>0.0030 ± 0.0015</td>
</tr>
</tbody>
</table>
References