Environmental pathways and distribution pattern of total mercury among soils and groundwater matrices around an integrated steel plant in India

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Coal burning in steel industries is chief source of Hg presence in surrounding environment. This study focused on spatial distribution of total Hg content in soils and groundwater matrices along with its temporal variation within a decade around an integrated steel plant; plant, Bhilai, India. All collected samples of soils and groundwater were analyzed for total Hg content using Inductive coupled plasma atomic emission spectrophotometer (ICPAES). Highest annual average Hg content found in soils (16.58±5.32 ppm) and groundwater (0.44±0.12 ppm) has shown 4-5 fold higher concentration compared to background levels. Similar pattern of spatial distribution and seasonal trends of soil and groundwater Hg has been obtained. Regression analysis has shown that significant contribution of Hg from air matrix to soils and groundwater was occurred. Significant temporal variation has also been occurred.

Keywords: Ground water, Industrial environment, Mercury pollution, Soil, Spatial variability, Temporal variation

Introduction

Processing of mineral resources at high temperatures (combustion of coal, roasting and smelting of iron ores, incineration of wastes and production of steel) release mercury (Hg) to the environment. Majority of emissions originate from coal combustion, particularly in Asian countries including China, India and Korea. Hg is present in coal in appreciable quantities¹,². In Germany, for every 1000 kg of coke produced, 0.01-0.03 g Hg is released³. The quantity released by burning coal is estimated to 3,000 tonnes per year worldwide, which is about the same amount released through all industrial processes. Hg concentration in coal varies from as low as 70 µg/g up to 22,800 µg/g⁴. On an average, India annually consumes 325 million tonnes of coal in sectors such as coal-fired thermal power plants, iron and steel plants, cement plants, foundries, fertilizer production, paper manufacturing, etc. Total Hg pollution potential from coal in India is estimated to be 77.91 tonnes per annum, considering average concentration of Hg in coal as 0.272 ppm. Hg concentrations in Indian coal are reported to be 0.17-0.32 ppm⁵. It should be noted, however, that the major source of atmospheric Hg in vicinities of steel plant environment is production of metallurgical coke. Main contributors⁶ to Hg emission in India include coal using industries, incineration plants at hospitals and municipalities, products like thermometer, blood pressure equipment, pharmaceuticals, pesticides, landfill and cremation activities.

Gaseous Hg²⁺ and particulate Hg emissions generally undergo direct wet or dry deposition to the earth’s surface locally. Site-specific deposition⁷ of Hg is variable, and is affected by conditions like meteorology, temperature and humidity, solar radiation and emission characteristics (speciation, source, stack height etc.). Fallout of elemental Hg (60.36-836.18 g/km²/month) over the soil horizon in vicinity of a steel plant has been reported⁶. Another report⁶ has shown Hg presence as high as 56 ppm in dust fall out and 40-72 ppm in surface soils. Most of total atmospheric Hg reaches directly or indirectly to groundwater⁸. Hg concentration in soil has increased with at least a factor of 5 during the 20th century⁹-¹¹. Highest Hg concentration in soil samples of New Jersey, USA has been found to be 153 µg/kg, while it was reported¹² very low (0.00015 to 3.8 µg/l) in groundwater samples of the same area.

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Inhalation of Hg (1-3 mg/m³) for 2-5 h may cause headaches, salivation, metallic taste in the mouth, chills, cough, fever, tremors, abdominal cramps, diarrhea, nausea, vomiting, tightness in the chest, difficulty in breathing, fatigue, or lung irritation. Hg exposure in children can cause a severe form of poisoning called acrodynia. Present work is focused on spatial distribution of total Hg in major routes of its human exposure around an integrated steel plant, Bhilai, District Durg, Chhattisgarh, India.

**Materials and Methods**

**Study Design**

Hg monitoring was undertaken in soils and groundwater around an integrated steel plant, Bhilai, India. Major environmental routes of exposure are steel plant emissions, re-suspended soils and groundwater of study area. Total availability of groundwater in the state is 432 m³ and nearby population (60%) use it for drinking purpose. Study area (Fig. 1) is located at global scale (longitude 81°23′6″E, latitude 21°11′0″N). Land use distribution is: residential, 27.8%; commercial, 5%; industrial, 31.5%; public utility, 7.7%; recreation, 1%; and traffic use, 27%. A total of 740 ha of land (5.6% of total land) has been utilized for recreation, 1%; and traffic, 27%. Of yearly wind direction.

**Sample Collection and Digestion**

All containers and equipment used for water and soils sampling were cleaned using a dilute liquid soap followed by a HCl solution and multiple rinses in ultrapure, deionized (DI) water, following standard protocols. Ground Water samples (250 ml) and respective soils (250 g) of identified regions were collected in pre-washed polyethylene bottles and polyethylene bags, respectively. In each sampling region, 4-5 random points were chosen to collect groundwater and soil samples. Samples of all sampling points in a specific region were mixed to form one representative sample of the region. In case of groundwater sampling, bore-well pumps were operated for 3-5 min before collection of samples to obtain representative samples. Bottles were filled up to neck and then added few drops of acid mixture (H₂SO₄ and HCl, 1:1) to maintain pH at 1-2. In case of soil sampling, surface of soils were digging up to a depth of 6 cm because atmospheric Hg moves inner soils (3-6 cm depth) due to atmospheric pressure. Soil samples, collected using stainless steel spoons, were transferred to zippered polyethylene bags using acid-cleaned stainless steel spatulas. All collected samples were chilled immediately on wet ice and stored at 5°C or less until chemical analysis and transported to laboratory for further analysis.

Powdered soil (1 g) samples were digested in Teflon digestion bomb and added nitric acid (HNO₃) and hydrogen peroxide (H₂O₂) (3:1). Teflon bomb was then kept in an electric oven at 60°C for 8 h, cooled, and contents filtered in a volumetric flask and washed with dilute HNO₃. Final volume of digested sample was made up to 25 ml using distilled water. Digested samples of soil and groundwater were analyzed for total Hg content using Inductive coupled plasma atomic emission spectrophotometer (ICP-AES) (JOBIN–YVON HORIBA ICP Spectrometers Version 3.0). An Argon gas (ionization energy, of 15.6 eV) was used as plasma. Hg analysis was carried out at a wavelength of 194.227 nm to avoid interferences. Calibration of instrument was done using HgC₁Cl₁⁻ (AR, Merck) of concentration range 0.001-0.1 ppm.
The data was utilized for assessment of spatial distribution (Fig. 3). Seasonal trend of Hg data across sampling regions has been shown (Fig. 4). The data was utilized for correlation studies with air-Hg data of similar sampling region. Mean/median and standard deviation of Hg data of all regions around steel plant along with data of 1997 has been presented. Mann Whitney test was applied for comparison of mean of data of two sampling program.

**Results and Discussion**

**Assessment of Annual Measurements in 2006 Sampling Program**

In case of current sampling program (2006), most of the sampling locations were within 3 km radius around steel plant. All sites have shown comparable pattern of soils mercury (S-Hg) and groundwater mercury (GW-Hg) content (Table 1). Prevailing wind site No. 1 located southwesterly from the steel plant have shown highest annual average levels of S-Hg (16.58±5.32) and GW-Hg (0.44±0.12). Prevailing wind sites (1, 2 and 3) and other site (4, 5, 6 and 8) have shown 2-4 fold higher concentration of S-Hg and 4-5 fold higher concentration of GW-Hg compared to background levels (Site No. 9). Wind direction from steel plant is favorable to sites 4 and 5 during winter season of sampling year. Lower concentration of S-Hg and GW-Hg at Site No. 7 was due to the presence of high soil organic content resulted from deposition of coke oven effluent litter in a large
land. Higher soil organic content is reported for higher rate of conversion of inorganic/elemental Hg to vaporizable organic mercury. GW-Hg levels are also lower at same Site. Black soils are visibly observed at Site Nos 7 and 8 while sandy soils is observed in other Sites. Deviations from annual mean of S-Hg and GW-Hg across all Sites (except Site No. 04) observed to be higher compared to background Site. Lower mean deviations of S-Hg at Site Nos 3, 7 and 8 might be due to their location in upwind from steel plant and free from any other source of Hg emission. Higher mean deviation of GW-Hg at Site Nos 4 and 5 compared to other Sites might be due to their close proximity to many other potential sources of Hg emission (many hardware shops, nursing homes, electrical appliances shops, automobile

Fig 2 — Windrose diagram of Durg-Bhilai region for March 2005-February 2006 (avg wind speed, 3-5 km/ h)

Fig 3 — Annual spatial distribution of total Hg around Bhilai Steel Plant in: A) soil; B) ground water

Fig. 4 — Seasonal variation of total Hg in soil and ground water around Bhilai Steel plant during: a) summer; b) post rainy; and c) winter
work-shops and National Highway etc.). As per Indian Standards, S-Hg levels (2006) are found to be 180-330 fold higher than permissible limit (0.05 ppm), which was only 2-40 fold higher than permissible limits in 1997. In case of GW-Hg concentration (2006), levels across sampling sites were found to be 10-450 fold higher than permissible limit (0.001 ppm), which were only 4.5-30 fold higher than permissible limit in 1997. A strong increase in Hg among selected environmental matrices has been observed compared to previous reported values of 0.058-0.268 ppm Hg in water due to contamination of industrial effluent.

Spatial Distribution and Seasonal Trends
Annual spatial distribution of S-Hg and GW-Hg around steel plant at a distance of 3 km (Fig. 3) indicated that origin of Hg is same in both matrices. Both matrices have shown similar pattern of variation across all Sites in winter season more precisely compared to summer and post-rainy season (Fig. 4). S-Hg have shown continuously higher level of occurrence compared to GW-Hg in summer and post-rainy season, while GW-Hg is slightly higher than S-Hg up to Site No.4 (prevailing wind locations) in winter season. Site Nos 5-8 have shown different pattern of variation in both S-Hg and GW-Hg during post-rainy season.

Correlation with Air-Hg Data
Strong positive correlation between Tair-Hg [Total air Hg=Air-Hg+particulate (PM$_{10}$)-Hg)] and S-Hg has been occurred at Site Nos 1 and 4, which are prevailing wind sites and close proximity to steel plant (Table 2). Site No. 2 is also prevailing wind site but located 10 km away from the plant. Site Nos 4 and 5 are also located in close proximity to steel plant but lower values of correlation are attributed to contribution from other local sources apart from the steel plant. Site Nos 6-8 have not shown good correlation between Tair-Hg and S-Hg.

Using slope and intercept values of regression between Tair-Hg and S-Hg, calculated value (intercept) gives clear agreement with measured values. Most sites (located 3 km away from steel plant) have shown that 30-50% contribution of S-Hg is from their respective Tair-Hg accept Site Nos 7 and 8, which have shown 8-20% contribution from Tair-Hg in S-Hg. In case of regression between Tair-Hg and GW-Hg, slope values have shown that GW-Hg (Site Nos. 3-5) is significantly affected by Tair-Hg (54-89% contribution), which is also reported that most of the Hg in groundwater is derived from atmospheric sources. In other Sites, lower contribution from Tair-Hg in GW-Hg has been observed. Slope values are known for contribution factor of independent variable to dependent variable (in case of regression between both Tair-Hg and S-Hg, Tair-Hg is independent variable). Lower values of contribution factor has been observed in regression between Tair-Hg and GW-Hg compared to regression between Tair-Hg and S-Hg. Correlation values between S-Hg and GW-Hg (S-Hg is taken as independent variable) have shown strong positive correlation between them across all sites.

Temporal Variation of Hg Data Measured in Selected Matrices
Box-plot statistical graph of S-Hg (Fig. 5a) and GW-Hg (Fig. 5b) levels measured in two monitoring programs [1997 (n=36) and 2006 (n=270)] indicated that in 2006 distribution was highly skewed with outlier of higher concentration confirming the usage of non-

### Table 1 — Yearly average of mercury content in soil and ground water in selected sampling programs around an integrated steel plant

<table>
<thead>
<tr>
<th>Site No.</th>
<th>Name of site</th>
<th>2006 Soil Mean±Std</th>
<th>2006 Ground water Mean±Std</th>
<th>1997 Soil Mean±Std</th>
<th>1997 Ground water Mean±Std</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Maroda</td>
<td>16.58±5.32</td>
<td>0.44±0.18</td>
<td>1.94±0.032</td>
<td>0.0124±0.086</td>
</tr>
<tr>
<td>2</td>
<td>Rouvabandha</td>
<td>15.09±5.12</td>
<td>0.38±0.33</td>
<td>1.12±0.039</td>
<td>0.0125±0.083</td>
</tr>
<tr>
<td>3</td>
<td>Sector</td>
<td>9.52±2.04</td>
<td>0.31±0.49</td>
<td>0.81±0.045</td>
<td>0.0032±0.065</td>
</tr>
<tr>
<td>4</td>
<td>Power house</td>
<td>12.22±3.56</td>
<td>0.37±0.67</td>
<td>1.16±0.051</td>
<td>0.013±0.089</td>
</tr>
<tr>
<td>5</td>
<td>Bhilai-3</td>
<td>12.88±4.70</td>
<td>0.39±0.85</td>
<td>1.89±0.033</td>
<td>0.0043±0.140</td>
</tr>
<tr>
<td>6</td>
<td>Somani</td>
<td>10.63±3.59</td>
<td>0.20±0.19</td>
<td>0.69±0.039</td>
<td>0.0008±0.190</td>
</tr>
<tr>
<td>7</td>
<td>Pureina</td>
<td>3.59±0.96</td>
<td>0.08±0.04</td>
<td>0.03±0.046</td>
<td>0.0052±0.099</td>
</tr>
<tr>
<td>8</td>
<td>Big tank</td>
<td>8.96±2.73</td>
<td>0.11±0.03</td>
<td>0.16±0.059</td>
<td>-</td>
</tr>
<tr>
<td>9</td>
<td>Housing board colony</td>
<td>4.46±0.88</td>
<td>0.09±0.06</td>
<td>0.10±0.061</td>
<td>-</td>
</tr>
</tbody>
</table>
parametric method, whereas in 1997, data was closer to normal distribution although still skewed. Number of sampling sites in two monitoring programs was 08 (ground water monitoring) and 09 (soil monitoring) in 1997, while it was 09 for both matrices in 2006. GW-Hg concentration in both two programs occurred between 0.00-0.0124 ppm (1997) to:20 0.00- 0.61 ppm (2006). S-Hg content has shown concentration between 0.00-1.94 ppm (1997) to:20 0.00-22.4 ppm (2006). Site wise comparison between two monitoring program (from 1997 to 2006) has shown that value of S-Hg increases 8-fold (Site No.1), 13-fold (Site No. 2), 12-fold (Site No. 3), 7-fold (Site No. 4 and 5), 15-fold (Site No. 6), 119-fold (Site No. 7), 66-fold (Site No. 8) and 44-fold (Site No. 9). In case of GW-Hg, it was found to be: 35-fold (Site No.1), 30-fold (Site No. 2), 10-fold (Site No. 3), 28-fold (Site No. 4), 90-fold (Site No. 5), 250-fold (Site No. 6) and 15-fold (Site No. 7).

Mann-Whitney test U test (MW) has shown significant differences (Table-3) in annual average Hg levels of soils and ground water across sampling sites in both monitoring programs (1997 and 2006). In case of S-Hg monitoring, same sites of 1997 program were covered up in 2006. Higher soil median difference was found to be 15.36 (Site No. 1), 14.24 (Site No. 2) and 12.39 (Site No. 4). Lowest soil median difference was found to be 3.37 at Site No. 7. In case of GW-Hg, 07 sites out of 09 sites of 2006 monitoring program were

<table>
<thead>
<tr>
<th>Site No.</th>
<th>Correlation between TAir Hg - Soil Hg</th>
<th>Correlation between TAir Hg - gw Hg</th>
<th>Correlation between soil Hg - gw Hg</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$r$</td>
<td>$r^2$</td>
<td>Slope</td>
</tr>
<tr>
<td>1</td>
<td>0.91</td>
<td>0.88</td>
<td>0.41</td>
</tr>
<tr>
<td>2</td>
<td>0.48</td>
<td>0.23</td>
<td>0.39</td>
</tr>
<tr>
<td>3</td>
<td>0.71</td>
<td>0.51</td>
<td>0.25</td>
</tr>
<tr>
<td>4</td>
<td>0.52</td>
<td>0.27</td>
<td>0.35</td>
</tr>
<tr>
<td>5</td>
<td>0.56</td>
<td>0.31</td>
<td>0.26</td>
</tr>
<tr>
<td>6</td>
<td>0.61</td>
<td>0.37</td>
<td>1.2</td>
</tr>
<tr>
<td>7</td>
<td>0.43</td>
<td>0.18</td>
<td>0.22</td>
</tr>
<tr>
<td>8</td>
<td>0.2</td>
<td>0.04</td>
<td>0.05</td>
</tr>
<tr>
<td>9</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
</tbody>
</table>

Table 2 — Correlation data of air-Hg levels with soil-Hg and GW-Hg levels

Fig.5 — Levels in selected yearly monitoring programs around an integrated steel plant of: A) soil-Hg; and B) ground water -Hg

*Table 2 — Correlation data of air-Hg levels with soil-Hg and GW-Hg levels*
covered up in monitoring program of 1997. Higher Ground water median difference is found to be 0.37 (Site No. 1), 0.28 (Site No. 2) and 0.23 (Site No.4). Lowest soil median difference is found to be 0.074 at Site No. 7. In case of overall comparison across all sites between two monitoring programs, soil and groundwater median differences are found to be 9.16 and 0.159 respectively.

Conclusions
The sites with Black soils have shown lower range of S-Hg content compared to sites of sandy soils. Higher degree of annual mean deviations across all sites compared to background site and as well as previous monitoring program (1997) has been observed. Under spatial distribution of total Hg in both matrices around the steel plant, soil is major route of GW-Hg and also major reservoir of Hg content emitted from steel plant. Seasonal trends across monitoring sites have also shown similar pattern of variation in summer, post-rainy and winter season throughout the sampling year. Prevailing wind sites have shown strong correlation between Tair-Hg and S-Hg while it is poor between Tair-Hg and GW-Hg. Significant contributions of Tair-Hg in S-Hg and GW-Hg has been obtained by regression analysis. Contribution of Tair-Hg to S-Hg and GW-Hg vary significantly across sampling sites and independent from wind conditions. Strong positive correlation between S-Hg and GW-Hg has been obtained. Significant temporal variation in S-Hg and GW-Hg has been observed in monitoring programs carried out in 1997 and 2006. Significance in mean differences has been obtained by application of Mann Wittney U test.

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