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Assessment of In-Plant Particulate Matter and its Toxic Metals Contents of Sponge Iron Industry in Goa, India

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Abstract The present study attempted to assess toxic metal contents (Arsenic, Cadmium, Copper, Cobalt, Chromium, Iron, Manganese, Nickel, Lead and Zinc) in Total Suspended Particulate (TSP) and Particulate Matter less than ten micron (PM_{10}) in three sponge iron industries in Goa (India), one of the famous tourist place on the World map. TSP and PM_{10} average concentration in all three sponge iron industries were found to be in the range 401–485 μg/m^3 and 135–270 μg/m^3 respectively. Amongst all the metals, concentration of iron was the highest in TSP as well as in PM_{10}. Statistical results indicate that proportion of specific metals were found higher in PM_{10} as compared to the ratio of PM_{10}/TSP ratio. Value of correlation coefficient was found to be significant for Cr–Pb indicating coal burning was the major source contributor.

Keywords TSP · PM_{10} · Toxic metal · Sponge iron industry

Monitoring and assessment of particulate pollution is an important step in determining the levels and its impact on nearby environment. Number of studies involving characterization of airborne particulate matter have been reported in the past for urban and industrial locations (Gajghate et al. 2005; Toledo et al. 2008). In addition, studies on emission inventory with respect to particulate matter and toxic metal emissions from industrial sources have also been reported by Bhanarkar et al. (2005). The toxic metal characterisation of RSPM in the ambient air was conducted in different regions (Mugicaa et al. 2002; Gajghate and Bhanarkar 2004). Levels of toxic metal in particulate matter in the industrial environment viz. steel industries (Yaghi and Wahab 2003; Chai et al. 2008), foundry (Liu et al. 2009), galvanizing industry (Yaghi and wahab 2003), aluminum smelter (Kuo et al. 2007) in different parts of the World have been reported.

Goa is the smallest state of India and lies between 28° 38′ North latitude and 72° 12′ East longitude having land area of 3,702 Sq kms. with total forest area of 1,425 Sq kms. It is one of the famous and popular tourist attraction place in India for Indian as well as for foreigners. Rapid industrialization in various regions of the State raises serious environmental pollution issues in the vicinity as well as degrade pristine environment. The major polluting sources in different industrial estate are Sponge Iron (SI) plants, iron ore mines, stone crusher units etc. Sponge iron is one the major input material for steel production. Total number of sponge iron industries in India are 222 including four SI industries in Goa. India produces 13.9 million tons of sponge iron, out of which only 4.2 million tons is gas based and the rest 9.7 million tons is coal based (Battacharjee 2007). Sponge iron industry is considered as one of the major source of air pollution. In sponge iron industries, iron ore (hematite), non-coking coal and dolomites are crushed and then charged in requisite proportions into rotary kiln. Thermal treatment to optimally blended raw materials for fixed duration produces, sponge iron. Various air pollutants including Total Suspended Particulate Matter (TSP), Particulate Matter less than ten micron (PM_{10}),

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Sulphur dioxide (SO_2), Nitrogen dioxide (NO_2), Carbon dioxide (CO_2) are generated during sponge iron production. In India, data on status of air pollution in and around sponge iron industry is very scanty. The present study aims to highlight the fugitive air quality with respect to pollutants such as TSP, PM_{10} and its toxic metals contents for SI industries in Goa (India).

Materials and Methods

Three major SI industries of Goa state having different capacities and different Air Pollution Control (APC) equipment have been selected for in-plant air quality monitoring. SI industries A & B are situated in Sanguem while industry C is situated in Pissurlem Industrial Estate as shown in Fig. 1.

Fig. 1 Locations of sponge iron industries

Production capacity, APC equipment and other details about the SI industries are given in Table 1. In-plant air quality monitoring in the identified SI plants was carried out during winter, 2007. In each SI plant, TSP and PM_{10} (both at the same location) were monitored considering various in-plant activities. The process/activities around the monitoring locations in all SI plants are similar that is crushing/grinding, screening, and feeding raw material to rotary kiln. High volume and PM_{10} samplers were used to collect TSP and PM_{10} respectively. Samplers were placed at a height of about 2–3 m and run continuously for a period of 8 h with flow rate of 1.15 m^3/min, at all monitoring sites.

Total 24 samples were collected from each SI plant (12 samples for each TSP and PM_{10}). Whatman GF/A glass fiber filter papers of the size $8'' \times 10''$ were pre-baked at 100°C in oven, cooled in desiccator and weighed, prior to its use. The exposed filter papers were kept in desiccator to remove the absorbed moisture and weighed (Mettler AE 163). Concentration of particulate matter was calculated using volume of air at STP.

Filter paper samples were digested with nitric acid and hydrogen chloride for 20 min in microwave oven (Milestone). The samples were then cooled and filtered through a filter paper (Whatman filter paper No. 42 of 125 mm-diameters). The volume was then made up to 100 mL with de-ionized water. The same procedure was adopted for preparation of blank sample. The atomic absorption spectrometry (AAS- Perkin Elmer 8000) instrument was used to analyze the toxic metals viz. Arsenic (As), Cadmium (Cd), Copper (Cu), Cobalt (Co), Chromium (Cr), Iron (Fe), Manganese (Mn), Nickel (Ni), Lead (Pb) and Zinc (Zn).

Quality assurance and quality control was achieved by using high quality glass wares throughout the sampling, digestion and analysis steps, to prevent any metal contamination. The calibration was performed by using the superior AAS single element standard for respective toxic metals (CertiPUR- Merck). Laboratory and field blank filter papers were processed similarly for background correction. The recovery was calculated by spiking with a known amount of element concentration on blank filter paper. The recovery tests of trace metals were 93.06%, 91.51%, 94.53%, 96.80%, 92.42% and 96.06% for Pb, Co, Cr, Cu, Mn and Fe respectively. The recoveries of these

Table 1 Details of sponge iron plants and their locations

SI Plant	Production capacity (MTPD)	Air pollution control equipment installed	Location area	Monitoring site description
A	200	Electrostatic precipitator	Sanguem	Industrial Estate close to iron ore mine and highway
B	250	Electrostatic precipitator	Sanguem	Industrial Estate close to iron ore mine
C	200	Venturi Scrubber	Pessurlem	Industrial Estate close to residential area

elements were in the range of 91.5% – 96.8% with relative standard deviation 2.08%. The limits of detection for Co, Cr, Cu, Fe, Mn and Pb are 5, 6, 3, 6, 2 and 10 μg/L respectively.

Results and Discussion

In all three SI units, average TSP concentration was found in the range of 401 μg/m^3 to 485 μg/m^3 and PM_{10} concentration was found in the range of 135 μg/m^3 to 270 μg/m^3 (Figs. 2, 3). These observed values are comparatively lower than the other reported studies (Table 2).

Figure 4 and 5 present average toxic metals concentration in TSP and PM_{10} respectively. Metals concentration in TSP ranged from 64–45,225 ng/m^3 while in PM_{10} the concentration ranged from 49–33,522 ng/m^3. The ascending trend of the metal concentration was Co < Cr < Pb < Cu < Mn < Fe. Average Pb concentration in different industries was in the range of 1,015–1,779 ng/m^3 in TSP while it was 767 to 1,645 ng/m^3 in PM_{10}. Average Co and Mn concentration in TSP were found between 64 and

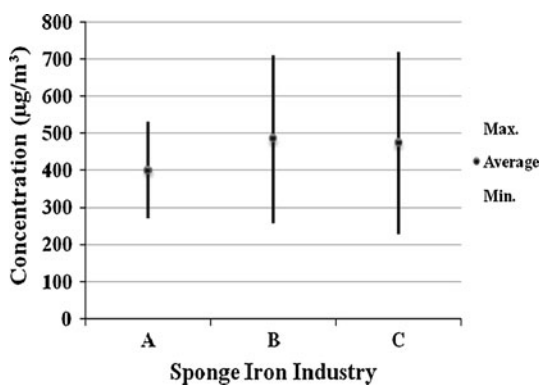

Fig. 2 TSP concentration in SI industries

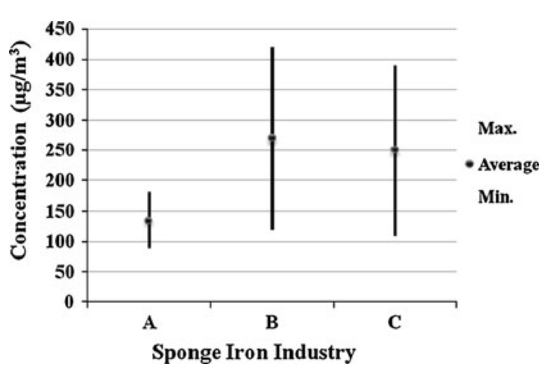

Fig. 3 PM_{10} concentration in SI industries

134 ng/m^3 and 3,184–5,015 ng/m^3 respectively while they were 49–103 ng/m^3 and 1,960–3785 ng/m^3, respectively in PM_{10}.

Cr concentration was in the range of 250–565 ng/m^3 and 209–515 ng/m^3 in TSP and PM_{10} respectively. The major source for Cr emission is coal combustion (Hlavay et al. 1998). Concentration of Cu and Fe in TSP ranged from 860 to 731 ng/m^3 and 30,167–45,226 ng/m^3 respectively while it was found between 731 and 950 ng/m^3 and 20,156–33,522 ng/m^3 in PM_{10}. The concentration of metals in PM_{10} are comparable to the values reported by Liu et al. (2009) while these are higher than the values reported by Chai et al. (2008) and Kinyua et al. (Kinyua et al. 2008). Iron ore is the main source for Fe in particulate matter and higher concentration of Fe may be due to resuspension of iron ore dust from its open stock piles.

Total mass of analysed metals and their percentage in TSP and PM_{10} were estimated separately for each industry. Percentage of total metals in PM_{10} was found higher as compared to percentage of total metals in TSP in each case. The mean percentage of total metals for all industries was 19.6 and 25.2 in TSP and PM_{10} respectively. Fe content in the particulate matter was estimated to be 17.3% and 21.2% respectively in TSP and PM_{10}.

The fraction of metal species in PM_{10} and TSP was estimated for various industries. Fig. 6 presents ratio of metal fraction in PM_{10} and metal fraction in TSP in various industries. Result indicates that although PM_{10} fraction in TSP is lower than 60%, proportions of all the metals are higher in PM_{10} in all the SI industries. Proportion of most of the metals is more than 70% in PM_{10} in comparison with the PM_{10}/TSP ratio.

The correlation between TSP and PM_{10} shows that there is a higher proportion of metal in the respirable fraction than in the particles with bigger diameter (Mugicaa et al. 2002). The sources of toxic metals are different depending on the raw material and production process of the industry. The Pearson correlation coefficient value obtained among the metals helps to predict, either two or more elements emitted from the same source or different sources.

Table 3 shows the correlation coefficient of toxic metals in PM_{10}. The result reveals that correlation coefficient value for Cr–Pb was 0.99, for Cu-Mn was 0.93 and for Fe-Co it was 0.90. The Cr and Pb are generated from the same source that is from coal (Hlavay et al. 1998) as coal is one of the main raw materials used in rotary kiln of SI industry. Pereira et al. (2007) suggested that Cu and Mn are associated with fossil fuel combustion.

The higher values of TSP and PM_{10} were observed at all sampling locations which is due to in-plant activities of sponge iron units. The results of toxic metals show higher concentrations as compared to other reported studies. Ratios of metals in PM_{10} and TSP indicate higher

Table 2 Comparative results of TSP, PM_8, PM_{10} and toxic metal (ng/m^3) concentration in various industries

Industry	PM (μg/m^3)	Pb	Cr	Co	Cu	Mn	Fe
TSP							
Steel[a]	39–800	4–6900	16–133	–	6–81	–	–
Galvenised steel	701	4420	24	–	3	–	–
PM_{10}							
Foundry[b]	340–990	590–1500	400–660	–	440–860	4850–14270	18890–83030
PM_8							
Capital Iron and Steel Company[c]	230	210	92	3.4	120	337	12700
Various Industries[d]	62–108	170–340	–	–	120–170	380–790	3490–6030
Present study (Sponge Iron Industry)							
TSP							
A	401	1779	564	64	1553	3025	30167
B	485	1146	347	126	860	3183	42456
C	474	1015	250	134	1279	5015	45256
PM_{10}							
A	135	1644	515	49	751	1960	20156
B	270	1029	326	103	731	2479	33522
C	250	767	209	100	950	3785	33124

[a] Yaghi and Wahab (2003)

[b] Liu et al. (2009)

[c] Chai et al. (2008)

[d] Kinyua et al. (2008)

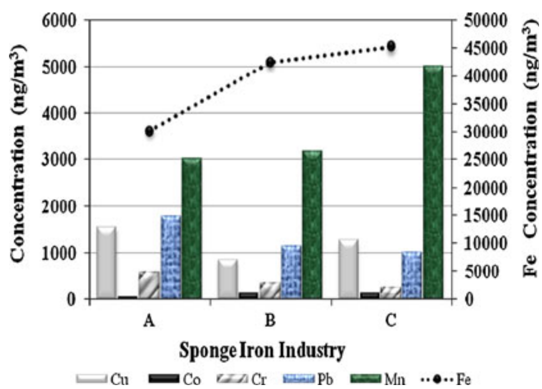

Fig. 4 Toxic metals concentration in TSP

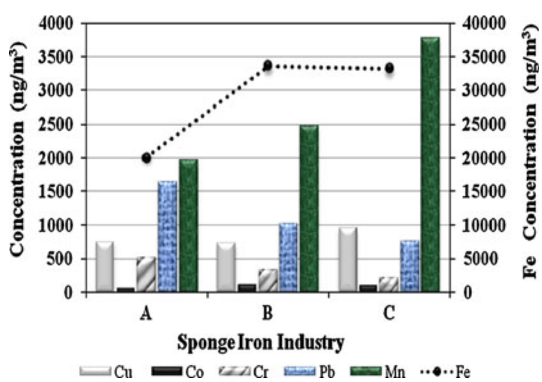

Fig. 5 Toxic metals concentration in PM_{10}

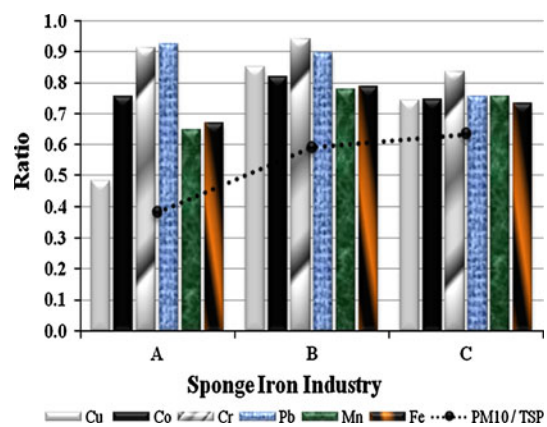

Fig. 6 Metal fraction in PM_{10}/TSP ratio

Table 3 Correlation coefficient of PM_{10}

Metals	Pb	Co	Cr	Cu	Mn	Fe
Pb	1					
Co	−0.721	1				
Cr	0.996	−0.653	1			
Cu	−0.670	−0.030	−0.737	1		
Mn	−0.890	0.327	−0.930	0.935	1	
Fe	−0.949	0.903	−0.915	0.402	0.701	1

proportion of metals in PM_{10}, which can cause serious health problem to workers due to inhalation of finer particles. Regular practice of water sprinkling, stock piles covering and converting dusty roads into tar roads in the plant premises will help to minimize the higher concentration of TSP and $PM_{10.}$

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