

Distribution of trace elements in coal and combustion residues from five thermal power plants in India

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ABSTRACT

The rapid increase of coal fired thermal power generation in India has resulted in increased generation of fly ash and bottom ash of various properties. In this study, coal and ash samples collected from five different thermal power plants across India were characterized and quantified to determine trace element concentration so as to understand their distribution, enrichment, and partitioning behavior. Concentrations of Pb, Cu, Cd, Zn, Fe, Mn, Cr, Ni, Mg, Li, Co, Hg, and As, were estimated in fly ash, bottom ash, and coal samples. The concentrations of toxic elements, such as As, Hg, Pb, and Cd in fly ash were in the range of 0.19–0.35 µg/g, 0.51–2.13 µg/g, 7.6–35.3 µg/g, and 0.6–0.93 µg/g, respectively, whereas in bottom ash, concentrations of these toxic elements were in the range of 0.1–0.29 µg/g, 0.41–1.58 µg/g, 8.8–28.28 µg/g, and 0.49–0.79 µg/g, respectively. Cadmium and As were the lowest in both coal and ash samples, whereas Fe, Mn, and Zn were found to be the highest. The elements were classified into three groups based on their volatility. All the elements were found to be enriched more in fly ash than in bottom ash. To evaluate the influence of the elements on local environment, enrichment factor with respect to Fe was calculated for all the elements in fly ash and bottom ash. The enrichment ratio, relative enrichment index, and partitioning behavior were used to describe the differences of trace-element concentrations in coal, fly ash, and bottom ash. Among the elements, maximum enrichment was observed for Mn in both fly ash and bottom ash.

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1. Introduction

Coal is an important source for power generation in India. The rapid increase of power demand and at the same time the exploitation of poor-quality coal with high ash yield, result in the generation of fly and bottom ash amounts of various properties from coal-fired power plants. Indian coal used in power plants generally has high ash yield (35–45%) and is of low quality (Mathur et al., 2003). Presently about 110 Mt of coal ash is generated in India from more than 70 thermal power plants per year (Sarkar et al., 2005). By the year 2012, this is predicted to increase to 170 Mt per annum (Rajamane, 2003).

Formation mechanisms of coal ash under pulverized-fuel firing conditions have been described extensively in the literature (Clarke and Sloss, 1992). The physical and chemical properties of this industrial waste product, in general, are quite variable, as they are influenced by coal source, moisture, particle size, type of coal-burning process, and the techniques applied for handling and storage (Ahmaruzzaman, 2009; Soco and Kalembkiewicz, 2009). In the burning process of coal, minerals undergo thermal decomposition, fusion, disintegration, and agglomeration. Many elements present in a volatile form may vaporize. A major

portion of elements in the boiler enter into slag or bottom ash, and the rest of the inorganic materials find their way into the flue gas, in fly ash or vapor. Fly and bottom ashes are significant sources of exposure to toxic elements that affect especially the population in the vicinity of industrial areas. The chemical characteristics of coal ash depend largely on geological factors related to the coal formation and on the operating practices employed at the power plant. Thus, each individual coal-fired plant has its own chemical ash characteristics. A large portion of coal ash consists of relatively inert material, such as silica and other compounds of trace elements, some of them being toxic (Dai et al., 2011; Finkelman et al., 2002). Selective partitioning of trace elements between the various exit streams classifies the elements into three groups: (I) Elements which are condensed equally between bottom and fly ashes but not in the fugitive fly ash; (II) Elements which are more concentrated in the fly ash collected on electrostatic precipitators and the fugitive fly ash than in the bottom ash; and (III) elements which are mainly present in gas phase and in minor concentration in fly and bottom ashes (Clarke, 1993). There is a considerable overlap among these groups due to the wide variations in operating conditions (especially temperature) that control element volatility, and the form of trace elements in coal (salts and oxides of high vapor pressures, organically bound elements, etc.) that may also suppress or enhance vaporization (Senior et al., 2000).

Although particle emission controls in power stations may reach high retention efficiency (99.9%) by using electrostatic precipitators,

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considerable amounts of fine fly-ash particles are emitted to the atmosphere because of the high rate of coal consumption (Querol et al., 1995). On the other hand, the major portion of fly ash produced in India goes for disposal in ash ponds and landfills; only a small part of it is used in construction material or as soil amendment (Bhattacharjee and Kandpal, 2002), while the major amount is stockpiled in open areas. Resuspension of the finest fly-ash fraction (typically of particles with diameters $\leq 60 \mu\text{m}$) might, therefore, cause atmospheric pollution, also when these elements leach, they cause serious atmospheric and subsurface contamination (Baba, 2000). In the present study, coal and ash samples collected from five thermal power stations of different capacities were characterized and analyzed to determine their elemental concentration in order to understand their partitioning behavior.

2. Materials and methods

2.1. Sample collection

The feed coal at all power stations was sampled on 5 different days over a period of one month. The samples were obtained in duplicates from samplers located at the coal feeder of the boilers. The samples were further homogenized to obtain a gross sample. The details of coal grading of individual power stations are given in the following paragraph. The fly ash and bottom ash samples from the 5 power stations were also sampled in parallel (about 10 samples of each from individual power stations). Bottom ash samples were collected from the ashers of the boiler and fly ash from the hoppers of the electrostatic precipitators. The gross samples were air-dried, milled, and split carefully in accordance with ISO recommendations to obtain a representative subsample of particle size $< 250 \mu\text{m}$ for further chemical analyses.

Most of the power stations under study use Indian coal as the feed material. The location details of individual power plants along with the generation capacity are shown in Fig. 1.

2.2. Sample extraction

2.2.1. Reagents and chemicals

Stock solutions (1000 mg/l) of all the trace metals obtained from Fluka were prepared by dissolution of appropriate amount of salt in HCl or HNO_3 . Working standards of all trace metals, were prepared by serial dilutions of the 1000 mg/l stock solution using deionized MilliQ water acidified to 1% v/v by electronic grade HNO_3 . Sodium borohydride solution (NaBH_4 , 95%) used for total mercury and total arsenic content determination was obtained from SISCO Research Lab. Pvt. Ltd. (India).

2.2.2. Sample extraction for non-volatile trace elements

Fly ash aliquots of 0.5 g were weighed in Teflon beakers. The mixture of $\text{HNO}_3 + \text{HClO}_4$ (5:2) was added to the samples, and the beakers were placed on a hot plate and evaporated to near dryness. The treatment was repeated to get a sponge like mass. Then, the mass was dissolved in 0.25% (w/w) HNO_3 filtered and eluted to 100 ml with the same solvent.

2.2.3. Sample extraction for volatile trace elements

A 0.25 g coal or 0.1 g ash sample was transferred into a pressure-resistant PTFE vessel (volume 100 ml), and the mixture $\text{HNO}_3 + \text{HF}$ (5:1) was added. The vessel was then sealed and mounted in a sleeve (outer vessel). The sample with the acid mixture was digested in a microwave oven. As HF was used in the digestion acid mixture, the removal of HF was needed for the following analytical procedure. The reaction mixture was subjected to an evaporation procedure by use of the evaporation module in order to remove the acids after the final

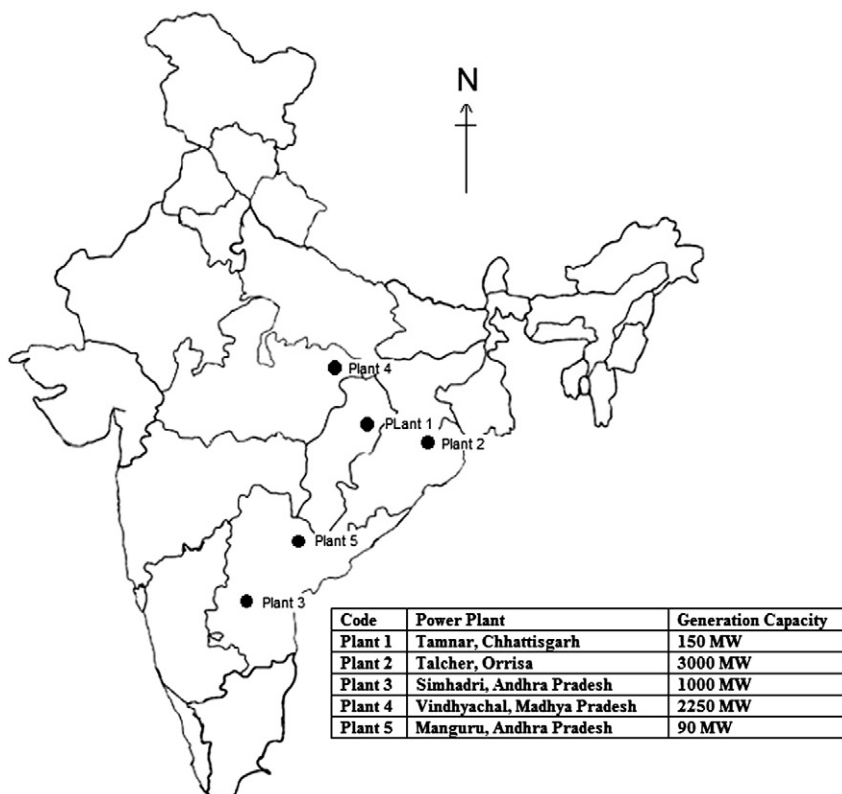


Fig. 1. Map showing locations of the thermal power plants studied.

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