Evaluation of the emission characteristics of trace metals from coal and fuel oil fired power plants and their fate during combustion

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Abstract

Coal as well as fuel oil combustion generates emissions of potentially toxic trace pollutants including organic and inorganic chemical compounds besides major pollutants. A study on As, Cd, Co, Cr, Cu, Hg, Fe, Mn, Ni, Pb, Se, and Zn emissions from a 220 MW coal-fired power plant equipped with a electrostatic precipitators (ESPs) and 6 MW oil fired-power plant was carried out, using stack monitoring kit, Envirotech APM 620, which is similar to EPA Method 29. Simultaneous sampling of coal, fuel oil, oil waste, bottom ash, fly ash, flue gases, and particles associated with the gas phase has been performed. This sampling method was used for trace metal sampling. The content of all these metals in coal, oil, oil waste, bottom ash, fly ash have been determined by XRF, whereas their contents in the flue gases, and particles associated with the gas phase has been analyzed with ICP-AES. The mass balances obtained for trace elements were satisfactory in case of fuel oil based power plant, whereas in case of coal fired power plant, the mass balance for all the trace elements were below 50% except for the As, Se, and Hg. The enrichment factors for all trace metals was <1 in both cases. The above sampling method is moderately adequate method for trace element sampling in coal as well as oil fired power plants except for Hg. The results indicate that trace metals emissions were higher in coal-based power plant than the fuel oil-fired power plant.
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1. Introduction

Beside major pollutants (particulates, carbon, sulfur, and nitrogen oxides), coal as well as fuel oil combustion generates emissions of potentially toxic trace elements [1]. Trace metals refer both to those metals present as metallic compounds in solution and to metals present in particles such as rust. They can be dissolved or suspended in the fuel hydrocarbons or in free water present in the fuel. The fate of potentially toxic trace elements in combustion systems has received an increasing interest from both regulatory authorities and scientists. Proposed legislation to regulate these trace element emissions must be based on an understanding of the chemistry of these elements since specific chemical species will account for differences in human toxicity, rate of transport through the ecosystem, and the design variations in possible emission control schemes. These elements differ in their behavior in power plants. Some are emitted from coal or fuel oil combustion in the gaseous form, some are attached to fine particles and some are retained within the heavier ash and do not leave the power plant at all. An additional layer of complexity results from the fact that these elements may or may not be associated with fine particulate matter (PM2.5 and PM10) during or after emission from the stack. Since the concerns over the formation and emission of hazardous heavy metals have been increased, several review articles have dealt with the governing factors with human health [2–5]. In view of the predicted increase in coal as well as fuel oil use, an

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Table 1
Proximate and ultimate analysis of the burned coal and fuel oil during sampling

	Coal			Fuel oil		
	Sampling 1	Sampling 2	Sampling 3	Sampling 1	Sampling 2	Sampling 3
Gross calorific value	4337.2[a]	4215.3[a]	4289.6[a]	9941.9[b]	9714.3[b]	9625.4[b]
Specific consumption (kg/MWH)	738.2	743.2	745.6	0.231	0.261	0.245
Moisture (wt.%)	7.8	8.2	7.9	0.05	0.05	0.04
Ash (wt.%)	34.67	32.51	36.25	0.033	0.031	0.029
Carbon (wt.%)	41.5	38.4	40.6	89.1	86.8	87.4
Hydrogen (wt.%)	3.33	3.21	3.79	2.5	2.4	2.5
Nitrogen (wt.%)	0.94	0.78	0.84	0.42	0.39	0.41
Sulfur (wt.%)	0.76	0.68	0.71	0.38	0.35	0.37
Oxygen (wt.%)	11	10.2	9.9	7.51	6.97	7.65

[a] $(kcal\,kg\,coal^{-1})$.
[b] $(kcal\,l\,oil^{-1})$.

understanding of the behavior of chemical species during combustion, emission, and environmental transport is of critical importance.

In general, the less volatile such as cadmium, cobalt, copper, chromium, iron, manganese, nickel, lead and zinc and oxidized mercury, are likely to be associated with fine particulate matter as well as fly ash and bottom ash [6]. As and Se present an intermediate volatility, and they will be emitted to the atmosphere to a large extent [7,8]. Many investigations on heavy metals that were regulated by law, such as lead, cadmium, chromium, arsenic, and mercury, have been made on their formation, enrichment in different size particles, removal by absorption and adsorption, reaction and so on. However, the real behavior of these elements cannot be predicted in a laboratory, because of the fact that coal combustion is conditioned by high complexity process, such as combustion temperature, halogen species concentration [3], redox conditions [9], and interaction between different species [10]. To consider the environmental consequences of these trace metal emissions, sampling methods based on solid sorbents is needed. At present, several methods for sampling and quantifying trace metals in flue gas are used. These methods are classified into two groups: methods based in solid sorbents and methods that employ impingers with oxidant solutions. The first group is easier to use and safer than the second one. However, salt blocking layer and preference canals formation on the sorbent surface is possible. Furthermore, several impinger-based methods have been used for the trace elements sampling for emissions of coal- as well as fuel oil-fired power plants [11,12].

The available literature indicates that little work has been done to describe trace element emission and their fate from coal- as well as oil-fired power plants in India. Nearly 73% of India's total installed power generation capacity is thermal, of which 90% is coal-based generation, with fuel oil, diesel, wind, and gas making up the rest. The overall objective of the work is to quantitatively evaluate the trace metal emissions and their fate from two Stationary sources. In this work, stack monitoring kit, Envirotech APM 620, which is similar to EPA method 29, for sampling trace metals As, Cd,

Co, Cr, Cu, Hg, Fe, Mn, Ni, Pb, Se, and Zn is employed. For this purpose, samples were collected from all the relevant input and output coal- and fuel oil- based power plant streams: coal, oil, oil residue waste, bottom ash, fly ash, flue gas, and particles associated with the gas phase. Finally, overall mass balances have been performed to determine the efficiency of the method employed.

2. Power Plants data

The coal-fired power plant located in Western India has an independent bituminous coal generation unit with 220 MW installed capacity and equipped with tangential burners. The power plant burns indigenous high ash and low sulphur bituminous coal. The fuel oil-based power plant is also located in Western India, with 6 MW-installed capacity. Proximate and ultimate analysis of the burned coal and fuel oil are shown in Table 1.

3. Experimental

3.1. Summary of method, stack monitoring kit APM 620

3.1.1. Gaseous samples

In this study, real samples coming from a bituminous 220 MW coal-fired and 6 MW oil-fired power plants have been used. Fig. 1 shows a scheme of the sampling method. One m^3 of the flue gas was sampled for a period of 1 h. The sample is withdrawn from the flue gas stream iso-kinetically through a filter system, maintained at 120 °C, followed by a series of impingers in an ice bath. Particles associated with the gas phase are collected in a filter placed in a heated area (Fig. 1) of the sampling train. All trace metals were collected in 6% HNO_3 in 10% H_2O_2. Flue gas sampling conditions of the two power plants are given in Table 2. The recovered samples were analyzed for As, Cd, Cr, Co, Cu, Pb, Mn, Hg, Ni, Se, and Zn by inductively coupled plasma atomic emission spectrometry (ICP, Perkin-Elmer, Optima 2000).
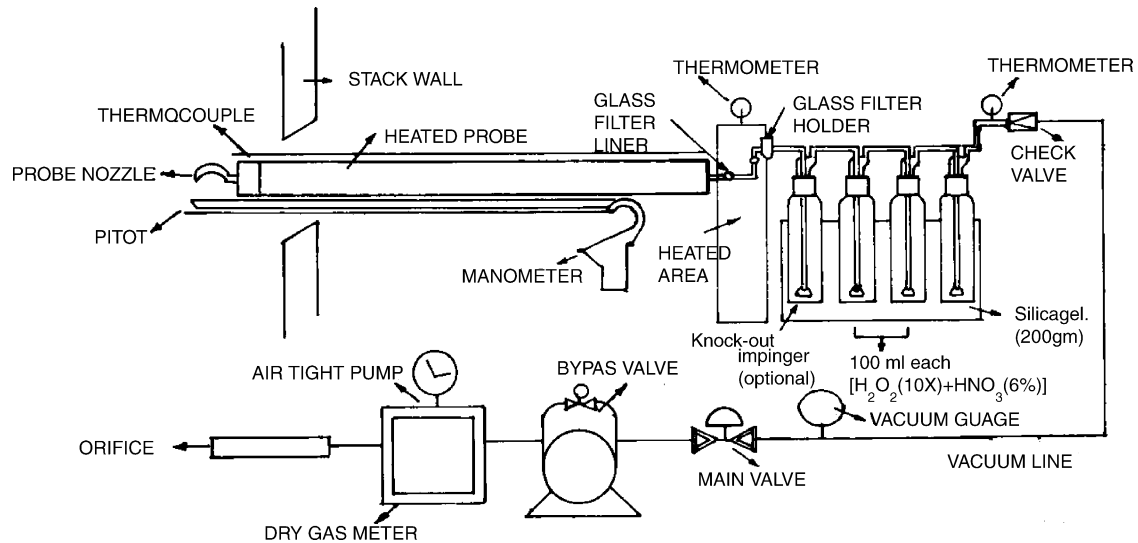
Fig. 1. The envirotech APM 620 sampling train.

3.1.2. Solid samples

Sampling of solid samples was carried out simultaneously to the sampling of gases emissions. The conveyor belt must run continuously during sampling (30 min). The coal, fuel oil, bottom ash, fly ash and oil residue masses sampled were 250 kg, 50 l, 100, 40 and 25 kg, respectively. To collect representative samples, solids were quartered and the particle size reduced until obtaining 500 g of each type of sample except fuel oil, which was used directly as collected. Fly ash samples were collected from ESPs.

3.2. Microwave acid extraction for particle associated with gas phase samples

The microwave acid extraction procedure employed for these samples has been described by Moreda-Pineiro et al.

[13]. The particles associated filter placed into the poly tetra fluoro ethylene (PTFE) bombs, the aqua reagent mixture (AR). Six millilitre of HCl (c), 2 ml HNO_3, 4 ml HF and 1 ml H_2O was added in order to dissolve Al–Si bearing particles as well as glass fiber of filters; and the mixture was subjected to microwave energy. The microwave program: 5 min (300 W) → 3 min (650 W) → 3 min (450 W) → 3 min (0 W). HBO_3 (0.2 g) was added to neutralize the excess of HF. After microwave extraction, the bombs were cooled in a water bath. Then the acid liquid phase was filtered using Whatman No. 40 paper filter (Whatman International Ltd., Maidstone, UK). The solutions were made up to 25 ml volume with ultra pure water, and then they were stored in polyethylene bottles at 4 °C before measurements. Blank glass fibre filters were also dissolved, analyzed and values subtracted to the actual samples.

Table 2
Flue gas sampling conditions

Stack description	Coal			Fuel oil		
	Sampling 1	Sampling 2	Sampling 3	Sampling 1	Sampling 2	Sampling 3
Stack height (m)	220	220	220	90	90	90
Stack diameter (m)	2.8	2.8	2.8	1.5	1.5	1.5
Primary fuel	Coal	Coal	Coal	Fuel Oil	Fuel Oil	Fuel Oil
Supporting fuel	Oil	Oil	Oil	–	–	–
Monitoring date	5/12/2003	5/12/2003	5/12/2003	3/01/2004	3/01/2004	3/01/2004
Load, MW	220	220	220	6	6	6
Coal mills in service	All (5 out of 5)	All (5 out of 5)	All (5 out of 5)	–	–	–
Oil guns in service	Nil	Nil	Nil	–	–	–
ESP fields in service	28	28	28	–	–	–
ESP fields out of service	Nil	Nil	Nil	–	–	–
Velocity in stack ($m s^{-1}$)	16.9	18.2	15.6	215.5	23.7	19.8
Volumetric flow rate (Nm^3/s)	360.1	374.5	340.2	395.5	415.6	378.5
Flue gas temp. (°C)	120	110	132	334	310	295
Moisture (%)	1.9	2.3	1.7	1.3	1.5	1.8
Flow rate set for PM ($l min^{-1}$)	92	89	75	102	92	82
PM emission rate ($kg h^{-1}$)	263	252	243	209	199	185

PM: Particulate matter.

3.3. Solid samples preparation for XRF

The coal, bottom ash, fly ash and oil residue samples were dried then fine powered using mortal piston and these samples were analyzed by XRF (Bruker AXS Spectrometer S4 Pioneer XRF).

3.4. Reagents and standard solutions

H_2O_2 (Merck, Darmstad, Germany), 70% HNO_3, 38% HCl (<0.01 $\mu g\,L^{-1}$ As, 0.001% Heavy metals), 51% HF (<0.01 $\mu g\,L^{-1}$ As and <0.001 $\mu g\,L^{-1}$ Hg) (Baker), and HBO_3 (Aldrich, Milwaukee, USA), 15474 ICP multimetal standard I (Merck, Darmstad, Germany), were used. These solutions were prepared daily. Whatman GF/A filters were employed for particles associated with gas phase with the gas phase sampling. Filter weights, and the weights and volumes of the impingers and their contents were recorded before and after each sampling run. The reference materials NIST-1632b (bituminous) NIST-1635 trace elements in coal, NIST-1633b trace elements in fly ash, and fuel oil as per International fuel specification ISO 8217 (Kittiwake GmbH, Germany) were analyzed in order to assess the accuracy of the employed method.

3.5. Optimization of operating conditions

Acid microwave extraction analysis recovery. Acid extraction induced by microwave energy was used in order to extract the trace metal content in the solid samples studied. The reference materials NIST-1632b (bituminous) and NIST-1635 (sub-bituminous) trace elements in coal, NIST-1633b trace elements in fly ash were analyzed by both ICP-AES and XRF, and fuel oil as per International fuel specification ISO 8217 (Kittiwake GmbH, Germany) was analyzed by ICP-AES in order to assess the accuracy of the employed method. The recoveries obtained by both ICP-AES and XRF for coal and fly ash were comparable. Adequate analytical recoveries (98%) for coal, fly ash and fuel oil reference materials by using aqua regia were obtained for As, Cd, Co, Cr, Cu whereas 86.5% recoveries were obtained for Fe, Mn, Ni, Pb, Se, and Zn. Similar analytical recoveries were calculated using an information Hg value (a value given by NIST as additional information but not certified) offered by the NIST-1632b coal reference material. Thus, it may be assumed that there are no trace metal losses during extraction procedure.

4. Results and discussion

As shown in Table 3, the particulate emissions from coal combustion showed greater values than oil combustion. The physico-chemical characteristics of solid waste like fly ash, bottom ash from coal combustion and oil residue from fuel oil combustion are presented in Table 3. Except moisture content

Table 3
Characteristics of solid waste

	Fly ash	Bottom ash	Oil residue (waste)
pH	7.80 ± 0.9	7.90 ± 0.92	8.10 ± 1.2
Moisture content %	1.80 ± 0.06	2.60 ± 0.09	2.30 ± 3.2
Sp. gravity	0.92 ± 0.02	0.94 ± 0.05	0.98 ± 0.06
Loss on ignition %	3.3 ± 0.23	4.10 ± 0.75	25.6 ± 2.8
Al_2O_3 %	13.7 ± 3.3	14.8 ± 4.3	11.0 ± 3.6
Fe_2O_3 %	4.80 ± 1.3	2.90 ± 1.4	7.50 ± 2.8
SiO_2 %	39.5 ± 4.6	42.5 ± 4.8	30.7 ± 5.6
CaO %	13.6 ± 3.8	11.8 ± 2.8	6.30 ± 1.6
MgO %	7.70 ± 2.8	8.80 ± 1.9	9.60 ± 2.1
Na_2O %	0.58 ± 0.08	0.80 ± 0.05	0.20 ± 0.08
K_2O %	1.40 ± 0.4	1.80 ± 0.6	1.36 ± 0.9
SO_3^- %	0.04 ± 0.002	0.03 ± 0.007	0.07 ± 0.009

and loss on ignition values, all others are characteristics of oil residue are more or less comparable with fly ash and bottom ash. The high loss on ignition of oil residue may directly be attributed to high gross calorific value of the fuel oil.

4.1. Trace metal concentrations in coal, oil, fly ash, bottom ash, oil residue, flue gas, and particles associated with the gas phase

Trace metal concentrations found in the different samples studied are shown in Table 4 and the standard deviation of concentrations of each element is given ($N = 3$). Invariably, the trace metal concentrations in all the samples of oil combustion are less than the corresponding samples of coal combustion. Metal concentrations in coal are in agreement with the ranges of concentrations reported by several others [1,14] whereas Se concentrations found are larger in all cases. On the other hand, concentrations of these elements in coal combustion of this power plant are in agreement with the values reported [15–17].

4.2. Trace metal mass balances

To evaluate efficiency of Envirotech APM 620 method for trace metal sampling in the gas of coal- and fuel oil-based power plants, mass balances were calculated. For this reason, a comparison was established for each compound as follows for coal-fired power plant (Eq. (1))

$$C_c F_c = C_s F_s + C_a F_a + C_g F_g \qquad (1)$$

where C_c, C_s, C_a, and C_g represent the concentration, expressed in $\mu g\,kg^{-1}$ or $\mu g\,m^{-3}$ of each element in coal, bottom ash, fly ash and flue gas, respectively. F_c, F_s, F_a, and F_g are the input/output flow rates in coal, bottom ash, fly ash and flue gas, respectively. These flow rates are expressed in kg kg coal^{-1}, except for F_g, which is expressed in m^3 kg coal^{-1}

$$F_s = \%\ \text{mineral residue} \times 0.20,$$

$$F_a = \%\ \text{mineral residue} \times 0.80$$

Table 4
Heavy metal concentrations in coal and fuel oil and its combustion products

	Coal mg kg⁻¹	Fly ash (mg kg⁻¹)	Bottom ash (mg kg⁻¹)	Flue gas (µg Nm⁻³)	Particle associated to gas phase (µg Nm⁻³)	Oil (mg kg⁻¹)	Oil residuce (Waste) (mg kg⁻¹)	Flue gas (µg Nm⁻³)	Particle associated to gas phase (µg Nm⁻³)
As	41.9 ± 2.4	172.3 ± 12.3	9.8 ± 1.7	19.5 ± 2.4	62.5 ± 5.8	13.2 ± 3.5	25.8 ± 3.5	6.5 ± 1.6	22.5 ± 2.5
Cd	4.31 ± 0.6	1.57 ± 0.27	2.58 ± 0.8	1.2 ± 0.54	0.62 ± 0.14	1.85 ± 0.54	0.84 ± 0.24	0.6 ± 0.07	0.32 ± 0.08
Co	4.1 ± 1.1	0.31 ± 0.005	0.24 ± 0.07	0.08 ± 0.004	0.29 ± 0.08	2.3 ± 0.65	2 ± 0.54	0.2 ± 0.006	0.21 ± 0.08
Cr	21 ± 2.8	13.4 ± 1.7	10.5 ± 1.2	0.75 ± 0.14	1.8 ± 0.25	3.2 ± 0.98	7.0 ± 1.1	2.7 ± 0.85	0.62 ± 0.14
Cu	43 ± 4.4	328.4 ± 28.4	389.4 ± 79.4	6.7 ± 2.4	16.7 ± 2.5	8.9 ± 1.5	148.3 ± 11.5	3.9 ± 0.95	11.2 ± 0.85
Fe	9432 ± 89	54326.5 ± 147	64325.5 ± 168	16.8 ± 4.2	230 ± 12	7439 ± 95	4300 ± 90	9.8 ± 1.3	18.5 ± 0.41
Hg, total	0.2 ± 0.007	0.29 ± 0.007	ND	22.3 ± 8.9	0.42 ± 0.08	0.02 ± 0.001	0.42 ± 0.005	14.6 ± 2.5	0.01 ± 0.004
Mn	98.5 ± 11.5	4.5 ± 0.89	3.5 ± 0.84	0.98 ± 0.14	3.4 ± 0.65	16.8 ± 3.2	124.5 ± 6.5	0.43 ± 0.05	1.2 ± 0.08
Ni	16 ± 4.2	73.9 ± 10.8	69.8 ± 11.8	3.8 ± 0.98	1.9 ± 0.87	9.9 ± 1.6	94.2 ± 9.9	1.6 ± 0.98	1.7 ± 0.65
Pb	29.4 ± 8.6	266.1 ± 18.9	325.6 ± 21.7	1.3 ± 0.75	0.89 ± 0.14	22.4 ± 3.1	342.2 ± 21.5	0.65 ± 0.24	0.63 ± 0.054
Se	12.1 ± 3.1	32.4 ± 9.5	8.9 ± 1.2	51.8 ± 11.5	0.78 ± 0.11	4.8 ± 0.86	3.8 ± 0.88	25.8 ± 2.5	0.6 ± 0.008
Zn	30 ± 12.4	465 ± 65.7	514 ± 18.6	19 ± 3.5	28 ± 6.4	14.2 ± 3.2	72.5 ± 0.63	12.8 ± 3.1	21 ± 4.8

In these equations, it is assumed that 20% of the mineral residue generated in coal combustion is present in bottom ash form and 80% in fly ash form. These values are estimated from coal power plant historical data.

On the other hand, $C_c F_c$: µg of element in coal by kg of burned coal, $C_s F_s$: µg of element in bottom ash by kg of burned coal, $C_a F_a$: µg of element in fly ash by kg of burned coal; finally, F_g was calculated by the following multiplication—F_g is the total gas emission value (m³ kg coal⁻¹). Then $C_g F_g$: µg of element in flue gas by kg of burned coal. Similarly, for fuel oil-based power plant (Eq. (2))

$$C_o F_o = C_r F_r + C_g F_g \tag{2}$$

Where C_o, C_r and C_g represent the concentration in µg g⁻¹ or µg m⁻³ of each compound in fuel oil, oil residue and flue gas, respectively. F_o, F_r and F_g are the input/output flow rates of oil, oil residue and flue gas, respectively, and are expressed in kg l oil⁻¹, except for F_g, which is expressed in m³ l oil⁻¹.

$$F_r = \%\ \text{oil residue}$$

Here, it is assumed from fuel oil based power plant historical data that 100% of waste generated in fuel oil combustion is oil residue. $C_o F_o$: µg of element in fuel oil by litre of burned oil, $C_r F_r$: µg of element in oil residue by litre of burned oil; finally, F_g was calculated as similar to coal fired power plant, $C_g F_g$: µg of element in flue gas by liter of oil burned.

Once all factors of Eqs. (1) and (2) were known, mass balances of trace metals were calculated for coal, bottom ash, fly ash and flue gas for coal-fired power plant, whereas in case of fuel oil-based power plant, the mass balances were calculated for fuel oil, oil residue and flue gas. Particles associated with gas phase were included in metals flue gas mass balances. The mass balances are shown in Table 5. Acceptable results were obtained for all the metals in case of fuel oil- based power plant where as in case of coal fired power plant, the mass balance were less than 50% for all the metals except As, and Hg; the values of these were 84, and 76%, respectively. The high number of factors involved on the mass balances originate that the summation of these small deviations on the trace metals concentrations may give error estimations around 25%. Therefore, mass balances less than 50% were obtained for certain elements.

These results improve earlier studies [18] reporting the mass balances of 67, 113, and 68% for As, Hg, and Se, respectively, using Ontario Hydro method sampling train. Yokonama et al. [19] reported values of 138% for adjustments of Hg mass balances in a Japanese coal-fired power plant, employing KMNO4/H2SO4 for Hg sampling. Senior et al. [20] studied several coals by Nemtron Activation analysis, obtaining mass balances of 29% for As and 190% for Se in American coals.

Table 5
Trace metal mass balances

		Coal- based power plant				Fuel oil- based power plant		
		Bottom ash % total	Fly ash % total	Flue gas % total	Mass balance %	Oil residue % total	Flue gas % total	Mass balance %
As	Sample 1	0.5	97.4	2.1	83.47	65.3	34.7	59.14
	Sample 2	1	97.8	1.2	84.20	72.1	27.9	61.49
	Sample 3	0.9	97.6	1.5	83.26	68.6	31.4	59.33
Cd	Sample 1	21	60.4	18.6	32.02	56.3	43.7	51.05
	Sample 2	23.7	59.8	16.5	32.09	50.1	49.9	50.00
	Sample 3	24.2	63.5	12.3	32.91	61.3	39.7	49.30
Co	Sample 1	42.5	46.8	10.7	40.58	92.5	7.5	84.77
	Sample 2	44.7	49.3	6	43.71	96.7	3.3	77.04
	Sample 3	43.8	47.6	8.6	40.17	89.8	10.2	66.21
Cr	Sample 1	39.4	58.7	1.9	48.75	71.8	28.2	59.66
	Sample 2	36.7	60.4	2.9	48.53	83.4	16.6	62.79
	Sample 3	43.2	55.8	1	50.08	76.9	23.1	64.24
Cu	Sample 1	49.8	42.5	7.7	46.10	92.1	7.9	89.94
	Sample 2	56.6	40.3	3.1	48.76	85.6	14.4	83.67
	Sample 3	54.3	43.5	2.25	48.89	90.9	9.1	89.05
Fe	Sample 1	44.3	55.6	0.1	49.47	97.9	2.1	97.68
	Sample 2	43	56.7	0.3	44.05	98.2	1.8	97.99
	Sample 3	44.9	54.8	0.3	49.43	95.6	4.4	95.40
Hg, total	Sample 1	0.1	23.1	76.8	76.11	13.4	86.6	84.55
	Sample 2	0.4	19.5	80.1	79.56	7.2	92.8	89.63
	Sample 3	0.3	27.1	72.6	72.07	4.3	95.7	91.88
Mn	Sample 1	52.3	42.5	5.2	42.25	97.3	2.7	96.97
	Sample 2	49.8	41.7	8.5	42.15	98.5	1.5	98.13
	Sample 3	57.3	37.3	5.4	41.14	98.3	1.7	97.69
Ni	Sample 1	46.7	49.2	4.1	46.86	93.6	6.4	92.14
	Sample 2	45.9	52.7	1.4	48.30	95.8	4.2	94.66
	Sample 3	43.1	55.9	1	47.63	94.1	5.9	92.60
Pb	Sample 1	60.5	39.3	0.4	50.86	98.5	1.5	98.32
	Sample 2	58.6	40.9	0.5	50.91	99	1	98.72
	Sample 3	57.8	41.8	0.4	51.30	98.7	1.3	98.45
Se	Sample 1	30.8	2.7	66.5	40.88	10.4	89.6	79.43
	Sample 2	29.5	5.8	64.7	42.90	7.5	92.5	80.64
	Sample 3	26.9	3	70.1	43.23	13.5	86.5	78.72
Zn	Sample 1	48.6	43.9	7.5	45.63	79.8	20.2	70.86
	Sample 2	50.3	44.8	4.9	46.99	80.9	19.1	69.92
	Sample 3	55.2	43.1	1.7	48.58	89.3	12.3	76.19

4.3. Relative distribution of trace metals in the power plants

During coal combustion, trace elements bound in coal are distributed into bottom ash, fly ash and flue gas whereas trace elements in fuel oil are distributed in oil residue and flue gas during fuel oil combustion. They are broadly classified in to three groups depending on their partitioning behavior:

- Class 1
  - Coal combustion: they are readily incorporated into bottom ash, in this group Cd, Mn, Ni, Pb and Fe are included [18].

- Fuel oil combustion: they are readily enriched in oil residue, in this group Cd, Co, Cr, Cu, Fe, Mn, Ni, Pb, Zn are included [18].
- Class 2
  - Coal combustion: they are concentrated in fly ash compared to bottom ash, in this group are As, Se, Co, Cr, Cu, and Zn are included [18].
- Class 3
  - Coal and fuel oil combustion: they remain essentially in gas phase, in this group Hg is included [18].

Results are agreement with this study except for Mn, Se, and Zn, in case of coal combustion. In the present study the proportion of Mn, Zn in fly ash, Se in flue gas and Zn in bottom

Table 6
Enrichment factors

	Fly ash	Bottom ash	Oil residue
As	0.868	0.069	0.242
Cd	0.539	0.429	0.363
Co	0.022	0.572	0.608
Cr	0.488	0.247	0.271
Cu	0.253	0.662	0.878
Fe	0.166	0.532	0.717
Hg, total	0.426	NIL	0.060
Mn	0.032	0.992	0.919
Ni	0.182	0.520	0.988
Pb	0.261	0.556	0.894
Se	0.787	0.022	0.098
Zn	0.557	0.472	0.633

Table 7
Emission factors

	Coal-based plant Min./max., g/GJ	Flue oil-based plant Min./max., g/GJ
As	8.97×10^{-4} /2.87×10^{-3}	1.26×10^{-4} /4.37×10^{-4}
Cd	2.85×10^{-5} /5.52×10^{-5}	6.12×10^{-6} /1.17×10^{-5}
Co	3.17×10^{-6} /1.34×10^{-5}	3.91×10^{-6} /4.11×10^{-6}
Cr	3.45×10^{-5} /8.29×10^{-5}	1.20×10^{-6} /5.25×10^{-5}
Cu	3.08×10^{-4}/7.68×10^{-4}	7.58×10^{-5} /2.17×10^{-4}
Fe	5.89×10^{-5} /7.73×10^{-4}	1.91×10^{-4} /3.59×10^{-4}
Hg, total	1.93×10^{-5} /1.02×10^{-3}	2.01×10^{-7} /2.83×10^{-4}
Mn	4.51×10^{-5}/1.56×10^{-4}	8.41×10^{-6} /2.33×10^{-5}
Ni	8.75×10^{-5} /1.75×10^{-4}	3.11×10^{-5} /3.30×10^{-5}
Pb	4.10×10^{-5} /5.99×10^{-5}	1.22×10^{-6} /1.26×10^{-5}
Se	3.59×10^{-5} /2.38×10^{-3}	1.17×10^{-5} /5.01×10^{-4}
Zn	8.74×10^{-4} /1.28×10^{-3}	2.48×10^{-4} /4.08×10^{-4}

ash are larger (36, 55, and 50%, respectively). Hg is more volatile among the trace metals; therefore, the proportion of this element in the gas is larger (97% both in coal and fuel oil combustion). Other metals are distributed in fly ash, bottom ash or oil residue.

4.4. Enrichment factors

The enrichment factor expresses the elemental behavior, during coal/fuel oil combustion, in the different streams of the coal/fuel oil based power plant. Generally, volatile elements tend to condense in fly ash producing an enrichment of these elements in this stream. Following expression was established based on Meij et al. [21].

Enrichment factor, $r = (C_{ZY})/(C_{ZC}) \times$ percentage mineral residue in coal/oil, where $Y =$ fly ash (coal) = bottom ash (coal) = flue gas (coal) = oil residue (fuel oil) = flue gas (fuel oil), C_Z: concentration of trace element, C_{ZC}: concentration of trace element in coal/oil.

The enrichment factors are shown in Table 6. The enrichment factors of the trace elements, Cd, Cr, Fe, Se, Zn for fly ash are larger than for bottom ash. This may be due to high affinity of these elements for the small particles (fly ash) [15,18]. Furthermore, a phenomenon of vaporization–condensation may be considered. Co, Cu, Mn, Ni, and Pb showed higher enrichment factors for bottom ash. Hg enrichment factor for flue gas is high in both coal and fuel oil based power plants, whereas enrichment factor is greater for particle associated gas phase in case of coal based plant and fuel gas in case of fuel oil based plant. However, the enrichment for all the trace metals were <1 in all cases. This fact could be due to small error (10–15%) estimation on the trace metal concentrations in the different type of samples analyzed.

Among the trace metals, enrichment factor for Se < 1 was referenced in literature [22] and this fact is attributed to the releasing of Se in the gas phase is around 20–30% [14,15,20,22–27]. In our study, Se released in the gas phase is 37%. Thus we can conclude that Se in the flue gas is more efficiently collected using Envirotech APM 620 method. And,

also the percentage of As released in our study (1.5%) is in agreement with the literature. As expected, the other trace metals were distributed in fly ash, bottom ash and oil residue except Hg. Therefore, the results indicate that Envirotech APM 620 is an adequate method for trace elemental sampling except for Hg. Many parameters (temperature, % oxidant species in flue gas, etc.) must be considered in order to understand the behavior of mercury in a power plant.

4.5. Volatile trace elements in particles associated with gas phase

Despite the high efficiency of air pollution control equipment like ESP to remove particles, a small portion of this comes to stack, mainly smallest particles (<0.3 μm) [21]. These particles act as condition nucleons for elements such as As, Hg, and Se. Hg is more volatile among all trace elements, thus a larger portion of this metal is released in gas phase than As, Se, and also other metals. Yokoyama et al. [19] reported that more than 99.5% of Hg in the stack emission was gaseous form, and the proportion of particles form was extremely low during coal combustion. Andren et al. [23] reported that 93% Se in the flue gas of coal fired power plant existed in the gas phase. Results from the present study are more or less in agreement with relative volatility of these elements; about 98% of the Hg in stack leaves it in the gas phase in both coal and oil fired power plants 94 and 75% of Se in stack for coal and fuel oil based power plants, respectively, leave it in the gas phase too. However, As contribution to the gas phase was less compared to Hg and Se.

4.6. Emission factors

Table 7 shows calculated emission factors in the stack. Most of the emission factors from this study were higher than the USEPA [28], even though the emission factor was a controlled value. The emission of heavy metals is mainly affected by their content in the fuel. Also, off-gas temperature and the amount of dust in off-gas affect their emission. In the

present study, the emission factor was comparatively higher in coal combustion than in fuel oil combustion for all the metals. However, the variation was greater in case of mercury.

5. Conclusions

A study of trace metal emissions from a 220 MW coal fired power plant and a 6 MW fuel oil based power plant was carried out. Potential toxic trace elements are distributed in the flue gas from coal as well as from oil-fired power plants. The mass balances obtained for trace elements were satisfactory in case of fuel oil based power plant, whereas in case of coal fired power plant, the mass balance for all the trace elements were below 50% except for the As, Se, and Hg. The enrichment factors for all trace metals were <1 in both cases. Envirotech APM 620 method is an adequate method for trace element sampling in coal as well as oil fired power plants except for Hg. The results indicate that trace metals emissions were higher in coal-based power plant than the fuel oil fired power plant. Total Hg was the predominant metal in flue gas of both power plants. Among the volatile trace metals, it has been proved that Hg and Se were more emitted in the gas phase in stack than the As.

Acknowledgements

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