

ATMOSPHERIC EMISSIONS OF TRACE ELEMENTS AT THREE TYPES OF COAL-FIRED POWER PLANTS

I. Demir¹, R. E. Hughes¹, J. M. Lytle¹, and K. K. Ho²

¹Illinois State Geological Survey, Champaign, IL 61820

²Illinois Clean Coal Institute, Carterville, IL 62918

INTRODUCTION AND BACKGROUND

A number of elements that occur in coal are of environmental concern because of their potential toxicity and atmospheric mobility during coal combustion. Sixteen of these elements (As, Be, Cd, Cl, Co, Cr, F, Hg, Mn, Ni, P, Pb, Sb, Se, Th, U) are among the 189 hazardous pollutants (HAPs) mentioned in the 1990 Clean Air Act Amendments (CAA) [U.S. Public Law 101-549, 1990]. The HAPs provisions of the 1990 CAA presently focuses on municipal incinerators and petrochemical and metal industries; a decision on whether to regulate HAPs emissions from electrical utilities will not be made until the U.S. Environmental Protection Agency (EPA) completes its risk analysis.

Numerous studies on environmental aspects of trace elements in coal were reviewed by Swaine [1990], Clarke and Sloss [1992], Wesnor [1993], and Davidson and Clarke [1996]. These reviews indicated a high variability of data on trace element partitioning among various phases of coal combustion residues (fly ash, bottom ash, flue gas). Such high variability results from the variations of types and operational conditions of combustion units, the characteristics of coal, and the modes of occurrence of trace elements in the coal. Difficulties in obtaining representative samples and analytical errors also add to the variability of data on trace element emissions from power plants.

In this study, the atmospheric emissions of 12 elements (As, Co, Cr, F, Hg, Mn, Ni, P, Sb, Se, Th, and U) of environmental concern from three types of power plants burning Illinois coals were inferred from the analytical data on the feed and combustion residues from the plants.

EXPERIMENTAL

Samples and Sample Preparation

Samples of feed coals and coal combustion residues were collected from a fluidized bed combustion (FBC) plant, a cyclonc (CYC) plant, and a pulverized coal (PC) plant burning Illinois coals (Table 1). A sample of limestone used in the FBC plant was also collected. To prepare for chemical and mineralogical analysis, representative splits of the coal and coarse-grained coal combustion residues were ground to -60 mesh; representative splits of the fine-grained coal combustion residues were prepared by riffing and splitting.

Chemical and Mineralogical Analysis

The samples of coal and coal combustion residues were analyzed for major, minor, and trace elements following the procedures of Demir et al. [1994]. The samples were also analyzed for mineralogical composition using x-ray diffraction (XRD) methods. The XRD analysis procedures were described in Demir et al. [1997].

RESULTS AND DISCUSSION

Mass balances, emissions, and relative enrichments in the combustion residues were calculated for the 12 elements using the chemical analysis data (Table 2).

Mass balances and emissions. The mass balance value of an element was calculated by comparing the amount of the element in the feed (coal or, in the case of the FBC unit, coal (75%) + limestone (25%)) with the amount of the same element recovered in the combustion residues. The mass balance calculations took into consideration the mass ratios of fly ash to bottom ash, as well as the measured concentrations of ash and elements in the samples. The fly ash to bottom ash ratios were 80/20 for the FBC plant, 25/75 for the CYC plant, and 75/25 for the PC plant.

The mass balances of the 12 elements were normalized to that of Al to eliminate analytical errors. The reason is that Al is a refractory element with relatively high concentration in coal and expected to be retained almost completely in the combustion ashes; less than 5% of Al is expected to escape the particulate collection systems with ultra fine, air-borne fly ash particles. Mass balances of about 100% for Al for the CYC and PC units (Table 2) indicated that the mass balance calculations performed in this study were reliable. The Al mass balance for the FBC unit (76%) was not as good as the Al mass balance for the CYC and PC units; this can perhaps be attributed to the variability in the characteristics of the feeds used in the FBC plant. Both the limestone and the coal used in the FBC unit are blends of products from many different quarries

and mines in Illinois. Therefore, future studies should collect at least several sets of samples over a period of several months of operation from the FBC plant, and the average mass balance data on these samples should be used to smooth out the variance.

If the amount of an element recovered from the combustion residues accounted for 100% of the amount in the feed, then the emission of the element was assumed to be zero. If the mass balance of an element was less than 100%, then the difference was considered to indicate the percentage of the element emitted into the atmosphere through the gas phase or condensation on the ultra fine, air-borne fly ash particles.

For convenience, the emission values were divided into three categories:

Low:	<25%
Moderate:	25-50%
High:	>50%

Negative emission values resulting from the excess mass balance (101-135%) in some cases (Table 2) probably resulted partly from analytical error and partly from contamination of the combustion residues due to the erosion of hardware in the combustion process. Therefore, the negative emission values were assumed to be in the low emission category.

For the FBC plant, the emission of all elements, except F (85%) and Mn (58%), was low (Table 2). The low emission of normally volatile elements Hg (18%) and Se (13%) was somewhat surprising. Apparently, low combustion temperature required in the FBC process or the chemical environment created by the addition of limestone at the FBC unit generally reduced the emission of the elements investigated in this study. The FBC fly and bottom ashes naturally contain large amounts of Ca-bearing mineral phases, namely anhydrite and lime (Table 3). Several authors [Clarke and Sloss, 1992; Meij, 1993, 1994a; Gullet and Ragnunathan, 1994; Querol et al., 1995; Bool and Helble, 1995] reported that lime, limestone, or Ca has the ability to capture substantial amounts of As, Hg, Sb, and Se during combustion. Suarez-Fernandez et al. [1996], on the other hand, did not find any major difference between the combustion behavior of trace elements in a laboratory-scale FBC unit with and without the addition of limestone.

For the CYC plant, the emission of highly volatile elements F (89%), Hg (75%), and Se (53%) was high, as expected (Table 2). Arsenic, Co, Mn, Sb, and U were emitted in moderate amounts (29-46%) from the CYC plant; emissions of other elements from the CYC plant were low.

For the PC plant, high emissions were observed for the highly volatile elements F (92%), Hg (90%), and Se (79%), and moderate emissions were observed for Co (40%), Mn (38%), Ni (27%), and U (31%). The emission of other elements from the PC plant was low (0-13%).

Querol et al. [1995] reported that Mn has an affinity for Fe-oxide in the combustion residues. The feed (coal) from the CYC and PC plants contains less Mn than the feed (coal + limestone) from the FBC plant (Table 2). Furthermore, combustion residues from the CYC and PC plants contain more magnetite than the combustion residue from the FBC plant (Table 3). This may be the reason why the Mn emission from the CYC and PC plants was lower than that from the FBC plant.

According to the literature review [Clarke and Sloss, 1992; Davidson and Clarke, 1996], among the 12 elements investigated here, substantial portions of only F, Hg, and Se, are emitted in the gas phase during coal combustion. The emission of other elements generally takes place through their enrichment in the submicron size fly ash particles that pass through the particulate control systems.

Enrichment in combustion residues. The enrichment of trace elements in various coal combustion residues affects the emissions of the elements during coal combustion. A relative enrichment factor (RE) was calculated for each element using the formula of Meij [1992]:

$$RE = (C_{el-combustion\ ash} / C_{el-feed}) \times (\%Ash_{feed} / 100)$$

where $C_{el-combustion\ ash}$ and $C_{el-feed}$ are the concentrations of an element in the combustion residue (fly ash or bottom ash) and feed, respectively, and $\%Ash_{feed}$ is the percent ash in the feed. The feed refers to coal or, in the case of the FBC unit, mixture of coal (75%) and limestone (25%).

The RE values of all elements, except Mn and F, were higher for the fly ash than for the bottom

ash samples from all three plants (Table 2). The RE value of Mn for the fly ash samples were smaller than or about equal to the value for the bottom ash samples. Fluorine had the same RE value for both the fly ash and bottom ash samples from the FBC unit. The comparison of the RE data of the elements investigated here indicated that a portion of most of these elements were volatilized during combustion and then upon cooling condensed on the fly ash particles or stayed in the gas phase, or partitioned between the fly ash particles and the gas phase.

Elements that are neither enriched nor depleted in the combustion residue should ideally have RE values of 1. Elements with RE values of greater or less than 1 are enriched or depleted, respectively, in the combustion residue. Based on the literature [Meij, 1992] and for convenience, the RE values in this study were divided into three categories as follows:

No enrichment or depletion:	RE = 0.7-1.3
Enrichment:	RE > 1.3
Depletion:	RE < 0.7

The RE values in the combustion products were used in the past to assign the inorganic elements in coal to differing volatility classes [Clarke and Sloss, 1992; Meij, 1992; Davidson and Clarke, 1996]. However, such a task is often complicated because of substantial variations in the combustion behavior of elements depending on the characteristics of coal, type and operation conditions of power plants, and the degree of sampling and analytical errors.

Only a few trends common to all three types of plants were apparent from the results of this study (Table 2):

- (1) no elements were enriched in the bottom ashes,
- (2) As, F, Hg, Sb, and Se were depleted in the bottom ashes, and
- (3) Co, F and Mn were depleted in the fly ashes.

The RE values of other elements varied depending on the ash and plant types investigated. The reason why Al, a conservative element, was depleted in the bottom ash of the FBC unit is not clear although analytical error is a suspect. This study has not examined the enrichment of the trace elements in particle size fractions of the fly ash samples. Previous studies [Meij, 1994b; Tumati and DeVito, 1991, 1993; Dale et al., 1992; DeVito and Jackson, 1994; Helble, 1994; Querol et al., 1995; Cereda et al., 1995; Suarez-Fernandez et al., 1996] indicated that there is generally a positive correlation between ash particle size and the concentration of As, Co, Cr, Hg, Mn, Ni, Sb, and Se.

SUMMARY AND CONCLUSIONS

Mass balances, emissions, and relative enrichment factors (RE) were calculated to determine the combustion behavior of 12 elements (As, Co, Cr, F, Hg, Mn, Ni, P, Sb, Se, Th, U) of environmental concern at three types of power plants burning Illinois coals.

For convenience, the percentage of an element emitted from the power plants was classified as either low (<25%), moderate (25-50%), or high (>50%). Based on this classification, the emission results for the 12 elements were as follows:

	<u>low emission</u>	<u>moderate emission</u>	<u>high emission</u>
FBC plant	As, Co, Cr, Hg, Ni, P, Sb, Se, Th, U	none	F, Mn
CYC plant	Cr, Ni, P, Th	As, Co, Mn, Sb, U	F, Hg, Se
PC plant	As, Cr, P, Sb, Th	Co, Mn, Ni, U	F, Hg, Se

Overall low emissions at the FBC plant relative to the other plants likely resulted from either the lower operating temperature compared with other combustion methods or from the creation of a favorable chemical environment as a result of the addition of limestone.

The atmospheric emissions of trace elements are controlled by their volatility and affinity for various coal combustion phases. The elements investigated in this study had higher concentrations in the fly ash than in the bottom ash with a few exceptions. This results from the partial volatilization of the elements from the bottom ash and their subsequent condensation on the fly ash particles upon cooling.

Relative enrichment (RE) values calculated from the composition of feed, fly ash, and bottom ash showed only few trends common to all three plants: (1) no element was enriched in the bottom ashes, (2) As, F, Hg, Sb, and Se were depleted in the bottom ashes, and (3) Co, F and Mn were

depleted in the fly ashes. The RE of other elements varied depending on the ash and plant types.

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Table 1. Amounts and description of coal and coal combustion residues from three types (FBC, CYC, PC) of power plants.

Plant type	Sample type	Amount (lb)	Sample Description*
FBC	coal	25	<3/8" size coal
	fly ash	18	Very fine particle size, light gray color
	bottom ash	24	<1/4" particle size, mostly yellowish and grayish particles, and small number of black particles.
	limestone	25	Crushed and off-white color
CYC	coal	9	Crushed coal
	fly ash	8	Fine particle size, dark gray color
	bottom ash	12	<3/8" particle size, black color, and high moisture content because of quenching in water
PC	coal	12	Crushed coal
	fly ash	8	Fine particle size, light gray color
	bottom ash	15	<3/8" particle size, dark gray to black color, and high moisture content because of quenching in water

* The size ranges are semiquantitative values based on visual examination.

Table 2. Chemical analysis of coal, coal combustion residues, and limestone samples from three types of power plants, and emission and relative enrichment (RE) values of Al and the 12 elements of environmental concern. The concentration values are in mg/kg unless indicated otherwise. All the values are on a dry basis.

Plant type	Sample type	1000°C														
		ash,%	Al,%	As	Co	Cr	F	Hg	Mn	Ni	P	Sb	Se	Th	U	
FBC	coal	10.73	1.00	1.8	4.6	25	137	0.10	77	18	131	0.4	5.5	1.8	1.9	
	fly ash	97.40	3.39	6.1	12.3	75	53	0.25	620	66	567	1.3	14.4	5.6	7.1	
	bottom ash	97.49	1.09	4.0	4.3	35	48	0.01	310	14	480	0.8	<1	1.9	4.0	
	limestone	59.18	0.63	3.3	3.5	11	5	<0.01	1394	9.4	262	0.2	<0.5	1.0	2.8	
	%Mass balance		76	81	76	96	15	82	42	108	104	106	87	94	94	
	%Emission*		24	19	24	4	85	18	58	0	0	0	13	4	6	
	RE for fly ash		0.9	0.6	0.6	0.8	0.1	0.7	0.3	1.0	0.8	0.8	0.8	0.8	0.8	
	RE for bottom ash		0.3	0.4	0.2	0.4	0.1	0.0	0.2	0.2	0.7	0.5	0.0	0.3	0.4	
	CYC	coal	10.48	0.80	2.6	4.0	17	63	0.08	77	8	44	0.7	2.7	1.2	2.0
		fly ash	87.52	7.02	50.6	24.2	227	230	0.73	310	173	742	13.6	43.3	14.6	21.7
bottom ash		100.4	8.01	1.2	20.2	112	15	0.02	542	70	524	1.1	2.1	11.3	11.1	
%Mass balance			102	54	54	85	11	25	65	123	135	62	47	104	71	
%Emission*			0	46	46	15	89	75	35	0	0	38	53	0	29	
RE for fly ash			0.9	2.0	0.6	1.4	0.4	1.0	0.4	2.3	1.8	2.0	1.7	1.3	1.1	
RE for bottom ash			1.0	0.0	0.5	0.7	0.0	0.0	0.7	0.9	1.2	0.2	0.1	1.0	0.6	
PC		coal	10.66	0.82	2.2	3.5	17	63	0.08	77	11	44	0.6	2.9	1.4	2.3
		fly ash	97.48	8.47	34.0	20.2	175	67	0.10	468	77	524	7.9	7.4	12.6	16.8
		bottom ash	99.96	6.91	3.0	22.2	136	5	<0.01	468	85	262	2.2	2.2	10.4	12.5
	%Mass balance		105	121	60	99	8	10	62	73	106	110	21	87	69	
	%Emission*		0	0	40	1	92	90	38	27	0	0	79	13	31	
	RE for fly ash		1.1	1.6	0.6	1.1	0.1	0.1	0.6	0.7	1.3	1.4	0.3	1.0	0.8	
	RE for bottom ash		0.9	0.1	0.7	0.9	0.0	0.0	0.6	0.8	0.6	0.4	0.1	0.8	0.6	

*%Emission = 100-mass balance. Negative trace element emission values resulting from greater than 100% mass balance were assumed to indicate no emissions (see text).

Table 3. Mineralogical composition of coal combustion residues and limestone from the three power plants.

Plant Sample type type	Mineral content (wt%)										
	mullite	quartz	calcite	hematite	magnetite	anhydrite	gypsum	lime	portlandite	amorphous	
FBC fly ash	0.0	8.4	0.0	3.0	4.1	31	0.0	2.3	11	40	
FBC bottom ash	0.0	8.2	1.9	0.0	0.0	29	2.0	40	13	6.1	
CYC fly ash	1.9	7.6	0.8	3.0	14	0.0	5.0	0.0	0.0	68	
CYC bottom ash	0.0	1.3	0.0	0.0	1.3	0.0	0.5	0.0	0.0	97	
PC fly ash	5.1	trace	0.0	2.1	15	1.3	0.0	0.0	0.0	77	
PC bottom ash	0.0	1.0	0.4	2.0	16	0.0	0.0	0.0	0.0	81	
FBC limestone	3.4 % illite, 1.5% kaolinite and chlorite, 5.0% quartz, 86% calcite, and 4.0% dolomite.										