



# Partitioning of selected trace elements in coal combustion products from two coal-burning power plants in the United States



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## ABSTRACT

Samples of feed coal (FC), bottom ash (BA), economizer fly ash (EFA), and fly ash (FA) were collected from power plants in the Central Appalachian basin and Colorado Plateau to determine the partitioning of As, Cr, Hg, Pb, and Se in coal combustion products (CCPs). The Appalachian plant burns a high-sulfur (about 3.9 wt.%) bituminous coal from the Upper Pennsylvanian Pittsburgh coal bed and operates with electrostatic precipitators (ESPs), with flue gas temperatures of about 163 °C in the ESPs. At this plant, As, Pb, Hg, and Se have the greatest median concentrations in FA samples, compared to BA and EFA. A mass balance (not including the FGD process) suggests that the following percentages of trace elements are captured in FA: As (48%), Cr (58%), Pb (54%), Se (20%), and Hg (2%). The relatively high temperatures of the flue gas in the ESPs and low amounts of unburned C in FA (0.5% loss-on-ignition for FA) may have led to the low amount of Hg captured in FA.

The Colorado Plateau plant burns a blend of three low-S (about 0.74 wt.%) bituminous coals from the Upper Cretaceous Fruitland Formation and operates with fabric filters (FFs). Flue gas temperatures in the baghouses are about 104 °C. The elements As, Cr, Pb, Hg, and Se have the greatest median concentrations in the fine-grained fly ash product (FAP) produced by cyclone separators, compared to the other CCPs at this plant. The median concentration of Hg in FA (0.0983 ppm) at the Colorado Plateau plant is significantly higher than that for the Appalachian plant (0.0315 ppm); this higher concentration is related to the efficiency of FFs in Hg capture, the relatively low temperatures of flue gas in the baghouses (particularly in downstream compartments), and the amount of unburned C in FA (0.29% loss-on-ignition for FA).

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## 1. Introduction

Characterizing the distribution of potentially toxic trace elements in feed coals and coal combustion products (CCPs) of coal-fired power plants is important for evaluating the possible impact of CCPs on the environment and human health. Bottom ash (BA), economizer fly ash (EFA), and fly ash (FA) are produced during coal combustion, and the partitioning of trace elements during the combustion process redistributes trace elements into these CCPs and flue gas (Clarke and Sloss, 1992; Goodarzi et al., 2008; Li et al., 2005; Meij, 1994; Meij and te Winkel, 2009; Pires and Querol, 2004; Querol et al., 1995; Stergarsek et al., 2008; Yudovich and Ketris, 2005).

Coal and oil-fired electric generating units at power plants are currently the dominant emitters of Hg, acid gases, and many toxic metals in the USA, according to the U.S. Environmental Protection Agency (U.S. EPA, 2012). The United States Congress identified As, Be, Cd, Co, Cr, Hg, Mn, Ni, Pb, Sb, Se, and radionuclides as hazardous air pollutants in the 1990 Clean Air Act Amendments. In December

2011, the U.S. EPA finalized the first national Clean Air Act standards to reduce Hg and other toxic air pollution from coal- and oil-fired power plants. The Mercury and Air Toxics Standards (MATS) will reduce emissions of Hg; other toxic metals such as As, Cr, and Ni; and acid gases, including HCl and HF (U.S. EPA, 2012). These air pollutants are known or suspected of causing cancer and other serious health problems in humans. In a study of low-rank, high-mineral matter Bulgarian coals, Silva et al. (2012a) suggest that nano-scale minerals can contain hazardous elements and, along with metal-bearing multiwalled nanotubes, be a path for the entry of hazardous particles into the lungs and other organs.

The primary use for FA is as an ingredient in concrete, but other uses include structural fills, cement, waste stabilization, mine reclamation, soil stabilization, road base and embankments, and soil amendments (EPRI, 1998). FA that is not beneficially used is placed in landfills and impoundments. FA is also used for recovery of rare and base metals, such as Al, Ga, and rare earth elements (Dai et al., 2012a,b; Seredin, 2012).

Although there are many studies of the distribution of trace elements in CCPs and factors related to the partitioning of trace elements in power plants in the literature (e.g., Bhangare et al., 2011; Córdoba

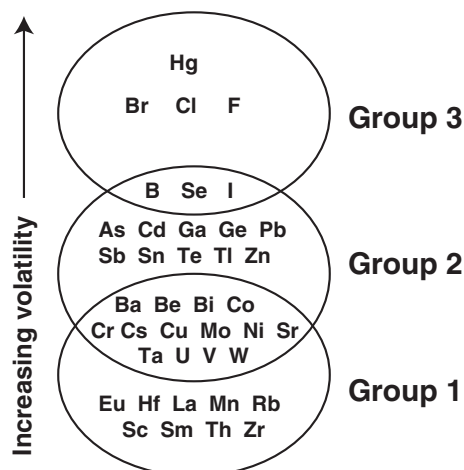
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et al., 2011, 2012; Dai et al., 2010; Goodarzi and Hower, 2008; Hower et al., 2009; Kolker et al., 2006; Levandowski and Kalkreuth, 2009; Mardon et al., 2008; Querol et al., 1995; Ribeiro et al., 2011; Silva et al., 2012a,b; Singh et al., 2011; Wilcox et al., 2012), fewer studies compare the distribution of trace elements in CCPs from plants operating with different types of particulate capturing devices and using different feed coals (e.g., Aunela-Tapola et al., 1998; Sjöström et al., 2002; Wang et al., 2008; Yudovich and Ketris, 2005; Zhang et al., 2008). In this paper, we examine the partitioning of As, Cr, Hg, Pb, and Se in CCPs from (1) a Central Appalachian basin power plant that burns a high volatile A bituminous, high-sulfur feed coal (Pittsburgh coal, mean sulfur content about 3.9 wt.%) and operates with ESPs, and (2) a Colorado Plateau power plant that burns a high volatile C bituminous, low-sulfur feed coal (blend of three coals from the Fruitland Formation, mean sulfur content about 0.74 wt.%) and operates with baghouses, also called fabric filters (FFs). We evaluate the partitioning of trace elements in relation to the design of the power plants, temperature of the flue gas, carbon content and particle sizes of FA, and composition of the feed coals.

### 1.1. Partitioning of trace elements in CCPs

The partitioning behavior of trace elements in relation to their volatility has been described in numerous studies (Clarke and Sloss, 1992; Meij, 1994; Meij and te Winkel, 2009; Ratafia-Brown et al., 2002). Group 1 elements (Fig. 1) are the least volatile and are concentrated in the coarse residues, such as BA, although they may be equally distributed between BA and FA (Clarke and Sloss, 1992; Xu et al., 2003). Group 2 elements are concentrated more in the particulates (such as FA), compared with coarse slag (such as BA). These elements volatilize during combustion and then condense onto particle surfaces in the flue gas stream during cooling (Clarke and Sloss, 1992; Meij, 1994). Group 3 elements (including Cl, Hg, and Se) are the most volatile, and show little to no tendency to condense from the vapor phase (Meij, 1994; Ratafia-Brown et al., 2002). These elements are thought to be almost entirely emitted from the stack.

Greater concentrations of Hg in FA have been found to be associated with lower temperatures of particulate capturing devices (Gibb et al., 2000; Goodarzi et al., 2008; Hower et al., 2009, 2010; Lee et al., 2006; Senior and Johnson, 2005). In a survey of all coal-fired power plants in Kentucky, Hower et al. (2009) found that volatile trace elements in FA increase in concentration from the first to the last row of



**Fig. 1.** Classification of trace elements by their behavior during combustion and gasification (Clarke and Sloss, 1992). Group 1=elements that are concentrated in coarse residues (such as bottom ash) or are partitioned equally between coarse residues and particulates. Group 2=elements that are concentrated more in particulates than in coarse slag or ash. Group 3=elements that volatilize most readily and are depleted in solid phases.

pollution control systems due to decreasing flue gas temperature and decreasing particle size. The elements As, Pb, and Se generally increase in concentration with decreasing temperature at the collection point of FA in both ESP and FF systems, and coarser FA tends to preferentially collect in the first row of an ESP or FF (Hower et al., 2008). In a study of a plant burning a high volatile A bituminous coal in Kentucky, Mardon and Hower (2004) demonstrated that the third (last) row of the ESPs captured significantly more Hg than the first row of the ESPs.

Increased trace element concentrations in FA have been found to be associated with finer particles, due to the greater surface-to-volume ratio of these particles (Clarke and Sloss, 1992; Hower et al., 1999; Linak and Wendt, 1994; Mardon et al., 2008; Querol et al., 1995; Wilcox et al., 2012). For Hg, the amount and type of C present in FA is a dominant factor affecting capture in pollution control devices (Abad-Valle et al., 2011; Goodarzi and Hower, 2008; Hower et al., 2000, 2009, 2010; Kostova et al., 2011; López-Antón et al., 2009; Sakulpitakphon et al., 2000; Senior and Johnson, 2005). Hg capture in FA increases with greater concentrations of C in FA, and with greater surface area of C, which is related to the form of the C and rank of the feed coal (Hower et al., 2010). Goodarzi and Hower (2008) described vitrinitic char as primarily responsible for the capture of most Hg in FA, in a study of FA produced from Canadian power plants using pulverized coal and fluidized bed combustors. Hg condenses mainly on the unburned C, bonding onto active centers rather than the full sorbent surface (Yudovich and Ketris, 2005). Carbon derived from combustion of low-rank coals has a greater surface area than C from bituminous and anthracite rank coals (Hower et al., 2010). Kostova et al. (2011) demonstrated that when Hg is expressed proportionately to C content, subbituminous coal-derived FA C (that does not exceed 1.6%) is more efficient in capturing Hg than ashes having much higher levels of C from bituminous feed coals. High temperatures are known to decrease FA C surface area, due to sintering (Hurt and Gibbons, 1995; Wilcox et al., 2012), whereas low-temperature combustion increases the surface area of the unburned C (Gao et al., 2002), enhancing its uptake of Hg (Mardon and Hower, 2004; Sakulpitakphon et al., 2000; Serre and Silcox, 2000).

The composition of power plant feed coal may have a significant effect on the composition of CCPs. In a study of power plants burning low- and high-sulfur feed coals in Indiana, USA, Mastalerz et al. (2004) found that the properties of FA reflected the chemical properties of the feed coal, particularly for S and spinel content; As, Pb, and Zn in FA were also found to be closely related to concentrations of these elements in the feed coal. The elements As, Hg, and Pb were found to attain their highest concentrations in ashes from 1–2%-S feed coals, in a study of power plants in Kentucky, USA (Hower et al., 2009). Hower et al. (2010) indicated that although the amount of Hg in FA is related to temperature of the flue gas and the amount of C, it is also a function of the amount of Hg in the feed coal.

Although ESPs and FFs are both highly efficient particulate removal devices, FFs are known to be much more effective at removing Hg than ESPs (Wang et al., 2008; Yudovich and Ketris, 2005). Cold-side ESPs and hot-side ESPs, capture, on average, 27% and 4% of Hg, respectively, whereas FFs are more effective, with approximately 58% Hg removal (Wang et al., 2010; Wilcox et al., 2012). Selective catalytic reduction (SCR), used at power plants to satisfy NO<sub>x</sub> emission regulations, is effective for oxidizing Hg to Hg<sup>2+</sup>, which allows for easier removal of Hg in downstream flue gas desulfurization (FGD) units (Kolker et al., 2006; Wilcox et al., 2012). The effectiveness of SCR catalysts on Hg oxidation is highly dependent upon coal composition, including C content, and concentration of HCl, S, and inorganic metal oxides such as CaO or MgO (Cao et al., 2007; Wilcox et al., 2012). In a pilot scale study, a high-S bituminous coal was found to have a significant increase in Hg<sup>2+</sup> at the exit of the SCR unit, whereas a low-S, low-Cl, subbituminous coal did not (Gutberlet et al., 2000; Wilcox et al., 2012).

## 1.2. Operation of the Appalachian and Colorado plateau plants

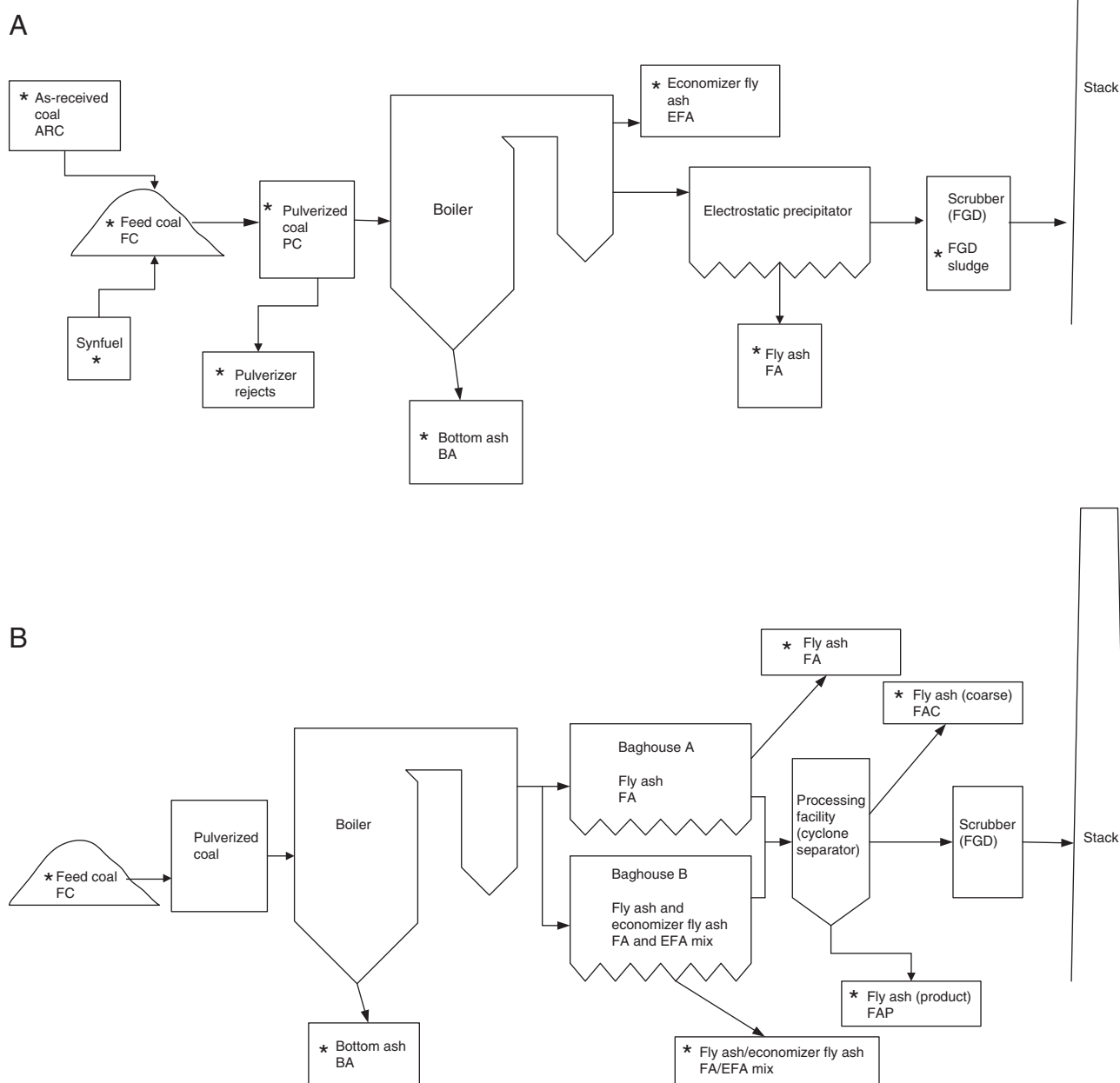
### 1.2.1. Operation of the Appalachian plant

The Appalachian power plant in this study operates with SCRs, ESPs, and a Mg-lime wet FGD system (Fig. 2A). The systems operate in the following order: boiler, SCRs, ESPs, FGD unit, and stack. The feed coal is beneficiated at the mine and pulverized at the power plant. Synfuels (latex binder) were sometimes used at the plant for binding coal refuse to potentially create briquettes for burning. During this study, synfuels were added to feed coal alone during the last six days of the sampling period (see Methods section). Quicklime

was injected between the air heaters and ESPs for  $\text{SO}_3$  mitigation. Trona ( $\text{Na}_2\text{CO}_3 \cdot \text{NaHCO}_3 \cdot 2\text{H}_2\text{O}$ ), a high-reactivity sorbent, was used for  $\text{SO}_3$  emission control at the plant, and it was injected in the air heater outlet duct, prior to SCR. The FGD system produces calcium sulfite, as opposed to gypsum (calcium sulfate), sludge. The FGD sludge is mixed with lime and FA for stabilization and disposed in an onsite landfill.

### 1.2.2. Operation of the Colorado Plateau Plant

The Colorado Plateau power plant operates with FFs, a processing facility for FA (cyclone separator), and an inhibited oxidizing scrubber



**Fig. 2.** Flow diagram indicating the power plant operation and sample collection points for the (A) Appalachian power plant; and (B) Colorado Plateau power plant. \* = sample collection point, FGD = flue gas desulfurization.

for flue gas (Fig. 2B). After FA exits the baghouses, it is transferred to silos and pushed at the rate of about 80 short t/h into a cyclone separator. The fine FA resulting from the separation process is fly ash product (FAP), which is powdery, typically light-colored, and sold as a product primarily for use in cement and concrete.

## 2. Methodology

### 2.1. Sample collection

At the Appalachian plant, a total of 106 coal and CCP samples were collected by power plant operators during twice weekly sampling events over an 8-week period from August 14 to October 6, 2006. The feed coal was from the Upper Pennsylvanian Pittsburgh coal from the Monongahela Group of the Central Appalachian Basin. Samples collected included (1) as-received coal from the mine (ARC); (2) feed coal (as-received, beneficiated coal) (FC); (3) pulverized feed coal (PC); (4) pyrite rejects from pulverization; (5) EFA; (6) FA; and (7) BA (Fig. 2A). BA samples did not contain pyrite rejects. FA and EFA samples were each collected as composite samples from several outlets at the plant. Synfuels were added to feed coals from September 19 to October 3, 2006. One sample of FGD sludge was collected on August 29, 2006.

At the Colorado Plateau plant, a total of 102 coal and CCP samples were collected by power plant operators during daily sampling events over an 18-day period from July 22 to August 8, 2007. The feed coal consisted of a blend of several coal beds from the Upper Cretaceous Fruitland Formation. Samples collected consisted of (1) FC, (2) BA, (3) a mixture of EFA/FA, (4) FA, (5) coarse FA from the cyclone separator (FAC), and (6) FAP from the cyclone separator (Fig. 2B). Pulverized coal samples were not collected at this plant.

### 2.2. Analytical methods

Coal and CCP samples from the Appalachian and Colorado Plateau plants were analyzed for major, minor, and trace elements by U.S. Geological Survey (USGS) laboratories (Central Energy Resources Science Center, Denver, Colorado, USA). All analytical data for the Appalachian and Colorado Plateau power plants are in Affolter et al. (2011). In this section, we describe analytical methods for the potentially toxic trace elements (As, Cr, Hg, Pb, and Se) discussed in this study. Cadmium and Ni duplicated poorly in quality control analyses and are not included in the study. USGS methods for determination of Cl and S are also discussed below. Standard operating procedures are available at the following website: <http://energy.usgs.gov/GeochemistryGeophysics/GeochemistryLaboratories/GeochemistryLaboratoriesMethods.aspx>.

For trace elements As, Cr, and Pb, samples were ashed at 525 °C and analyzed using inductively coupled plasma-mass spectrometry (ICP-MS). ICP-MS analyses are reported on an ash basis. In the digestion process for trace elements, 0.2 g ash (LOI 500 °C) was placed in the digestion vessel, followed by the addition of 4 mL HNO<sub>3</sub> (concentrated trace grade) and 10 mL 70/30 HCl/HF (concentrated trace grade). The mixture was digested in a temperature-controlled graphite hot block designed for 50 mL vessels. The hot block was set at 90 °C for 2.5 hours, and then cooled for 15 minutes. The hot block temperature was raised to 110 °C, and the mixture was heated to dryness for a few

hours. The sides of tubes were rinsed with deionized (DI) water and taken to dryness, and then cooled for 5 to 10 minutes. One mL of concentrated HNO<sub>3</sub> (trace grade) and 19 mL of DI water were added. The mixture was heated at 90 °C for an additional hour.

Concentrations of As, Cr, and Pb were determined in coal and CCP samples by ICP-MS using a PerkinElmer Elan 6100. Calibration was performed with a series of multi-element solution standards. All calibration standards were prepared in 2% HNO<sub>3</sub> starting with 10,000 mg/L or 1000 mg/L single element solutions. The final volume was 40 mL for all calibration standard solutions. The performance of the method was checked using digested control materials as well as water control materials from USGS: T141, T167, and T177 (all analyses were within 15% of certified values). Standard reference materials used for the analysis were CLB-1, 1632c, 1633b, GSS-5, GSD-3, CWE-1, T-141, T167, and T177. In case of greater deviation from the certified values, the samples were re-analyzed by ICP-MS. If the deviation remained, the samples were re-prepared, re-digested, and re-analyzed. The correction for the Ar/Cl interference was used for As determinations as described in ASTM method D6357.

Mercury and Se were analyzed in the raw coal and CCP samples using direct mercury analysis and hydride-generation atomic absorption methods, respectively. Coal analyses are reported on a whole-coal basis. Proximate and ultimate analyses for coal samples were provided by a contract laboratory using ASTM methods. General characteristics of as-received, feed, and pulverized coals for the Appalachian and feed coal for the Colorado Plateau plants are summarized in Table 1.

Chlorine was determined using a TOX 100 instrument. Reference standards 1632-C, ES-6, and ES-2 were used for coal samples and the reference standard SY-3 was used for ash samples. Sulfur for coal and CCP samples used in mass balance for the Appalachian plant were determined using a LECO SC 632. Chlorine and S analyses are reported on a whole coal basis for coal samples.

Scanning electron microscopy was used to examine the mode of occurrence of trace elements in feed coals and CCPs from each of the plants. Samples of FA, EFA, and BA were mounted in epoxy, polished, carbon-coated, and examined in the back-scattered mode. Inorganic constituents were identified with an attached energy-dispersive x-ray unit. Typical examples of BA from the Appalachian plant and FA from the Colorado Plateau plant are shown in Fig. 3.

### 2.3. Statistical approach

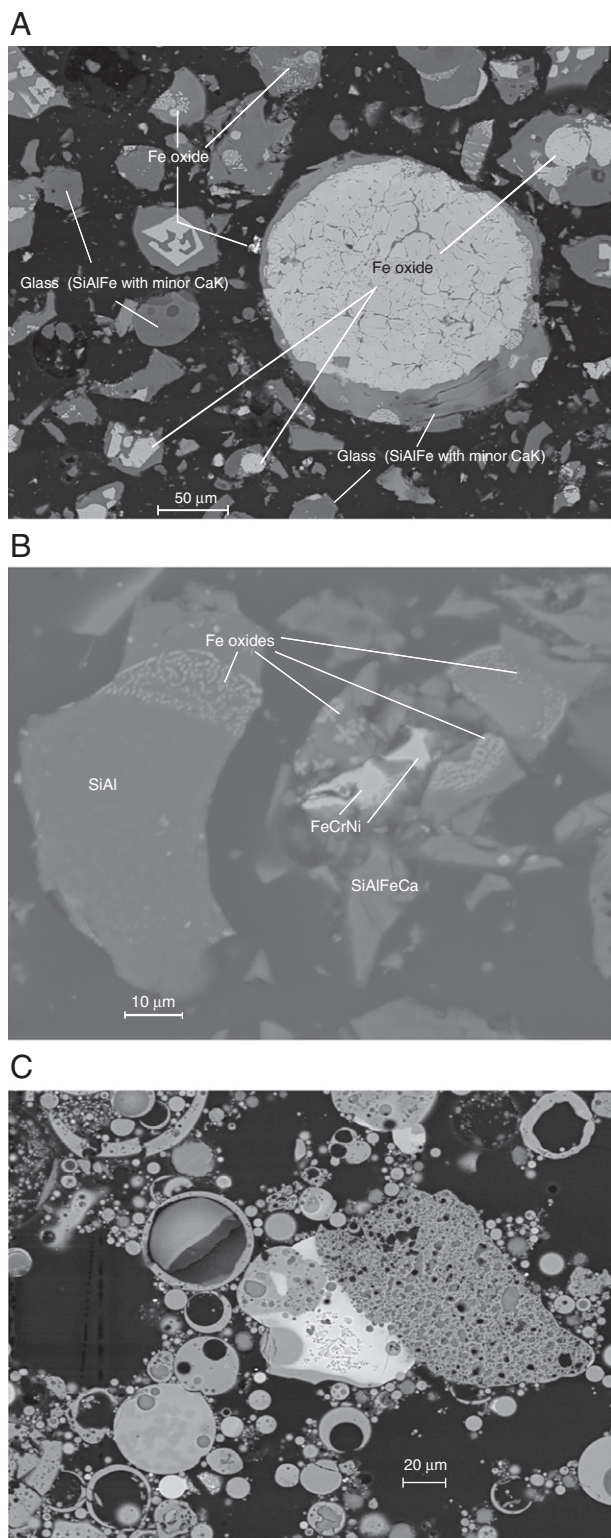
To assess variations in concentrations of the trace elements between CCPs, we calculated summary statistics for each element and CCP, and compared median values (Table 2). Both power plants had samples with concentrations of Hg and Se reported as being below the method detection limit (mdl), these data are known as censored data. To properly account for the presence of censored data, robust regression on order statistics (ROS) were used to calculate the means, medians and standard deviations for Hg and Se in the CCPs. ROS is an imputation method that fills in non-detect data on the basis of a probability distribution of samples that exceed the mdl (Helsel, 2005). Data for As, Cr, and Pb contained no censored data in the CCPs, and the medians for these elements were calculated using standard methods.

**Table 1**

Average values for proximate and ultimate data for as-received, feed, and pulverized coals for the Appalachian and Colorado Plateau power plants. ARC = as-received coal; FC = feed coal; PC = pulverized coal; equil. = equilibrium; res. = residual; and nd = no data. Six of the pulverized coal samples for the Appalachian contained synfuels. All analyses are from a contract laboratory and are on an as-received basis.

Power plants	Sample type	N	ASTM ash (%)	Calorific value (Btu/lb)	Moisture (%)	Air dried loss (%)	Equil. mois. (%)	Volatile matter (%)	Res. moisture (%)	Total sulfur (%)	Chlorine (ppm)
Appalachian Basin	ARC	15	9.5	12507	5.2	4.4	0.9	39.0	0.9	3.93	470
	FC	16	9.5	12513	5.1	4.0	1.1	38.9	1.1	3.82	530
	PC	14	9.8	13164	1.5	nd	nd	40.6	nd	3.94	507
Colorado Plateau	FC	17	22.9	8839	12.0	9.4	nd	31.2	2.8	0.74	110





**Fig. 3.** Back-scattered scanning electron microscopy photomicrographs of (A) the Appalachian power plant bottom ash, (B) stainless steel in bottom ash of the Appalachian plant, and (C) the Colorado Plateau power plant fine fly ash. The Appalachian plant bottom ash is dominated by SiAl-rich glass containing various amounts of Fe, Ca, and K. Iron oxides are common as coatings and discrete grains. The Colorado Plateau fine fly ash is composed primarily of SiAlCa-rich glass that often contain minor amounts of Ti and Fe. Iron oxides, as coatings and discrete grains, are common. Accessory phases (not pictured) include zircon, barium silicate, TiFe oxide, and CeLa phosphate.

**Table 2**

Median concentrations of selected trace elements (ppm; As, Cr, and Pb on ash basis; Se and Hg on whole coal basis) and average loss-on-ignition (LOI, %) values for pulverized coal and coal combustion products from the Appalachian and Colorado Plateau plants. *N* = number of samples; FC = feed coal, PC = pulverized coal, BA = bottom ash, EFA = economizer fly ash, FA = fly ash, FAC = fly ash coarse, FAP = fly ash product, FGD = flue gas desulfurization, Avg. = average, and nd = no data. All data are from USGS analytical laboratories on an as-determined basis.

Power plants	Sample type	<i>N</i>	Avg. LOI	As	Cr	Pb	Se	Hg
Appalachian Basin	PC	15	nd	91.8	195	53	1.650	0.109
	BA	15	0.15	5.3	374	15.0	0.074	<0.005
	EFA	15	0.12	41.6	264	20.4	0.134	<0.005
	FA	12	0.49	59.7	131	41.8	4.000	0.0315
Colorado Plateau	FC	17	nd	10.4	28.5	46.8	1.680	0.0913
	BA	18	1.69	2.18	20.7	19.2	0.186	<0.01
	EFA/FA Mix	17	0.22	10.6	30.1	41.1	3.940	0.0311
	FA	17	0.29	9.64	25.4	43.1	3.910	0.0983
	FAC	16	0.47	6.74	26.3	23.9	4.260	0.0902
	FAP	16	0.39	19.1	36.1	62.6	8.670	0.119

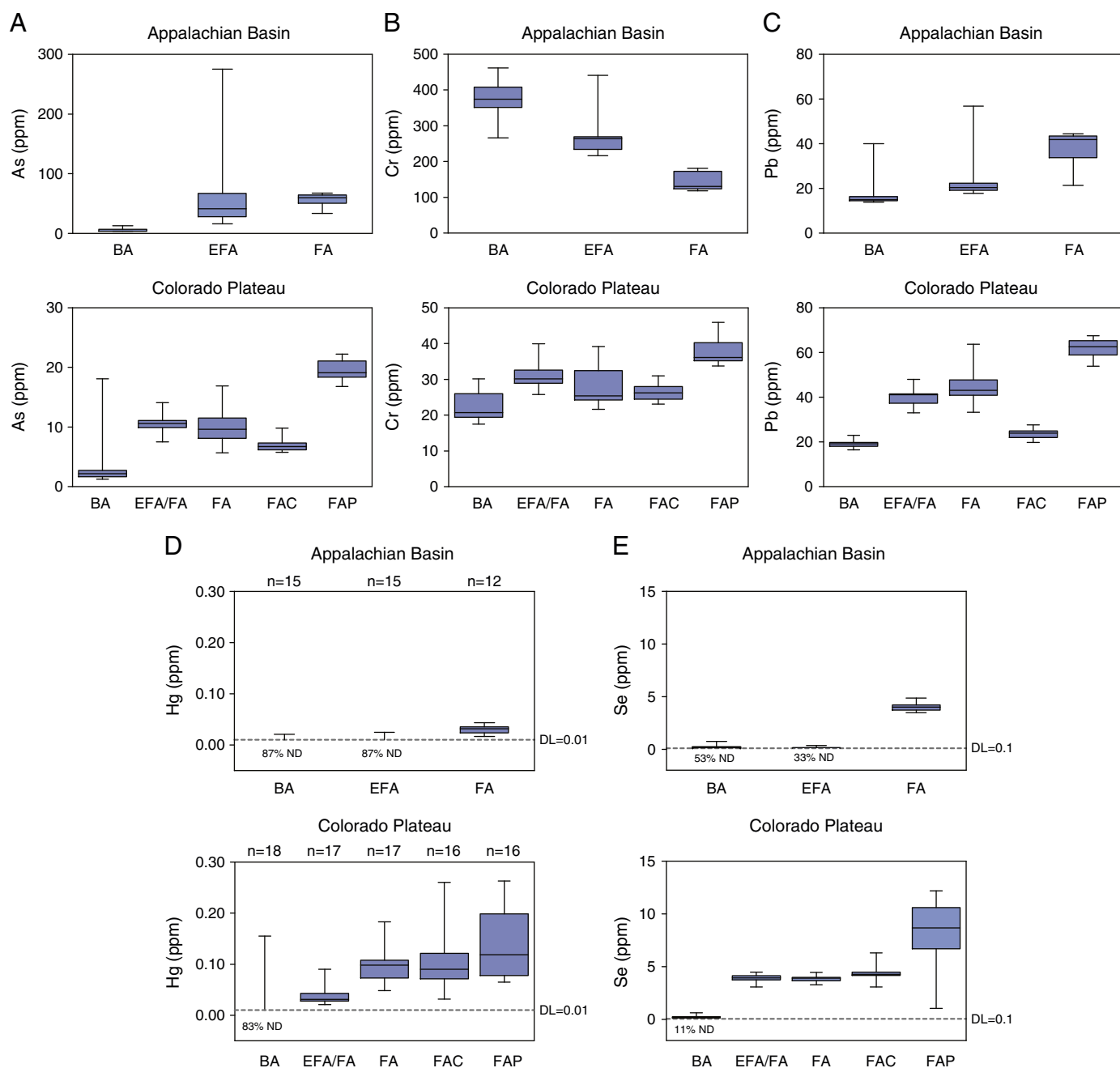
To examine for statistical differences in trace element median concentrations among the CCPs in cases where there was overlap in the interquartile range of the groups, Kruskal–Wallis tests were conducted for each element using a cutoff of  $p < 0.05$ . This test is valid for this type of dataset, where there is a single detection limit for each element, and no concentrations were reported below the detection limit for any sample (Helsel, 2005). In cases where differences between medians were indicated by Kruskal–Wallis analysis, multiple comparison tests were completed to show which CCPs exhibited differing median values. To visually compare trace element concentrations for As, Cr, Hg, Pb, and Se, boxplots were generated to show the partitioning of trace elements in the CCPs for the Appalachian Basin and Colorado Plateau power plants (Fig. 4). Because LOI values were very low for the CCPs (0.1–1.7%), as-determined values for trace elements were used in the statistical analysis.

For the Appalachian plant, statistics were based on the trace element characteristics of CCPs derived from a total of 16 pulverized coal samples: 10 samples without synfuels, and six samples containing synfuels. Comparison of median concentrations between synfuel-mixed samples and coal-only samples for feed coal, pulverized coal, and CCPs for the As, Cr, Hg, Pb, and Se show no statistically significant differences based on Mann–Whitney *U* tests ( $p < 0.05$ ), with one exception (As in EFA). With the  $p$ -value cutoff of 0.05, one would expect one significant difference due to random chance for every 20 tests and we conducted 25 in this study. For this reason, there is little evidence to suggest there are differences in the distribution and behavior of As, Cr, Hg, Pb, and Se in the coal and CCP samples between synfuel-mixed and coal-only samples.

#### 2.4. Mass balance: Appalachian plant

A mass balance was calculated for samples from the Appalachian plant to indicate the percentages of the selected trace elements (As, Cr, Hg, Pb, and Se) and S captured in BA, EFA, and FA, compared to the pulverized feed coal ash. A similar mass balance could not be calculated for the Colorado Plateau plant, because pure samples of EFA were not collected by the plant (EFA samples were mixed with FA samples in the baghouse).

The mass balance for the Appalachian plant is based on estimates provided by plant personnel indicating the percentages of feed coal ash captured in BA (~20%), EFA (2–3%), and FA (~80%). It is important to note that results of the mass balance indicate the percentage of each element left in flue gas *before* the FGD process; S and trace elements were also removed from flue gas during the FGD process.



**Fig. 4.** Boxplots showing distribution of concentrations for (A) As, (B) Cr, (C) Pb, (D) Hg, and (E) Se in CCPs. BA = bottom ash, EFA = economizer fly ash, FA = fly ash, EFA/FA = economizer fly ash and fly ash mixture, FAC = fly ash coarse, and FAP = fly ash product. Horizontal dashed line indicates method detection limit.

The formula used to calculate percentages of trace elements captured in CCPs is listed below (after Goodarzi and Hower, 2008):

$$A = \frac{\text{Trace element in CCP}}{\text{Trace element in pulverized coal}} \times (\text{percentage of ash in coal} \times B)$$

Where, *A* is the estimated percentage of trace element captured by CCP; CCP is bottom ash, economizer fly ash, or fly ash; and *B* is 0.2 for bottom ash, 0.025 for economizer fly ash, 0.775 for fly ash (based on power plant estimate). For calculation, elements determined on an ash basis (As, Cr, and Pb) were converted to a whole-coal basis prior to use in the equation.

Sample sets used in the mass balance calculation were composed of PC, BA, EFA, and FA. In each sample set, BA, EFA, and FA were grouped with the appropriate PC, based on the timing of the power plant operation. A total of 10 sample sets were used in the calculation. PC samples (coal only, no synfuels) were collected from August 15, 2006 to September 14, 2006. Samples containing synfuels in the feed coal were not used in the mass balance calculation. Results of the mass balance are in Table 3.

We estimate the uncertainty for these mass balance calculations at roughly 20%, based on results for Ti, a non-volatile element. The total of the CCPs for titanium (as TiO<sub>2</sub>) ranges from 98% to 133%, with a median value of 114%, based on nine sample sets. The uncertainty in the mass balance calculation may result from analytical error, sampling

**Table 3**

Results of the mass balance calculation, indicating average percentages of selected elements that were captured in CCPs (%). Percentages of elements in flue gas were determined by subtracting total CCP percentages from 100%. The potential error in the mass balance is about 20%. *N* = number of samples; BA = bottom ash, EFA = economizer fly ash, FA = fly ash, FGD = flue gas desulfurization, and DL = below detection limit.

Sample type	As	Cr	Pb	Hg	Se	Sulfur
BA	1	39	6	DL	DL	DL
EFA	3	4	1	DL	DL	DL
FA	48	58	54	2	20	1
Flue gas before FGD	49	DL	39	98	79	98
<i>N</i>	9	9	9	8	7	7

artifacts, degree of homogenization, and errors in estimating distribution of mass among the CCPs.

### 3. Results and discussion

The median concentrations of As, Cr, Hg, Pb, and Se in CCPs from the Appalachian and Colorado Plateau plants were compared to determine the partitioning of trace elements within each plant, and to compare differences in partitioning between the two plants (Table 2).

#### 3.1. Appalachian plant

The partitioning of trace elements observed in this study generally corresponds to the levels of volatility described in numerous previous studies (Clarke and Sloss, 1992; Meij, 1994; Meij and te Winkel, 2009). The following discussion is focused on a comparison of the median concentrations of As, Cr, Hg, Pb, and Se in the CCPs and the results of the mass balance.

##### 3.1.1. Comparison of median concentrations of trace elements in CCPs

At the Appalachian plant, As, Hg, Pb, and Se have the largest median concentrations in FA, compared to BA and EFA (Fig. 4, Table 2). These differences are statistically significant (using a cutoff of  $p < 0.05$ ) in all cases, except for the comparison of FA to EFA for As. The elements As, Pb, and Se would be expected to condense on the surfaces of FA particles as flue gas temperatures cooled in the ESPs. Mercury is likely to have condensed predominantly on the unburned C, rather than on the full sorbent surface of FA. Although it is expected that condensation of volatile trace elements occurred to the greatest degree in the cooler rows of the ESP array, this effect could not be observed because the FA samples were composite samples collected from several ESP outlets. The low median concentrations for As, Hg, Pb, and Se in BA and those for Hg and Se in EFA are consistent with the high volatility of these elements and the high temperatures associated with the boiler and economizer.

The partitioning of Cr contrasts with that of As, Hg, Pb, and Se. The largest median concentration of Cr is in BA (374 ppm) and the smallest median concentration is in FA (131 ppm) (Fig. 4). These differences are statistically significant and may be due, in part, to the lower volatility of Cr (Groups 1 and 2, Fig. 1) compared to the other trace elements studied. However, stainless steel (FeCrNi phase) contamination is fairly common in the BA, and probably contributes to the high levels of Cr in the BA (Fig. 3B). The presence of Cr oxides or spinel in the feed coal may also contribute to high concentrations of Cr in BA. Chromium oxides show stability at very high temperatures and are believed to remain unaltered during combustion (Stam et al., 2011).

##### 3.1.2. Mass balance calculation: trace element partitioning

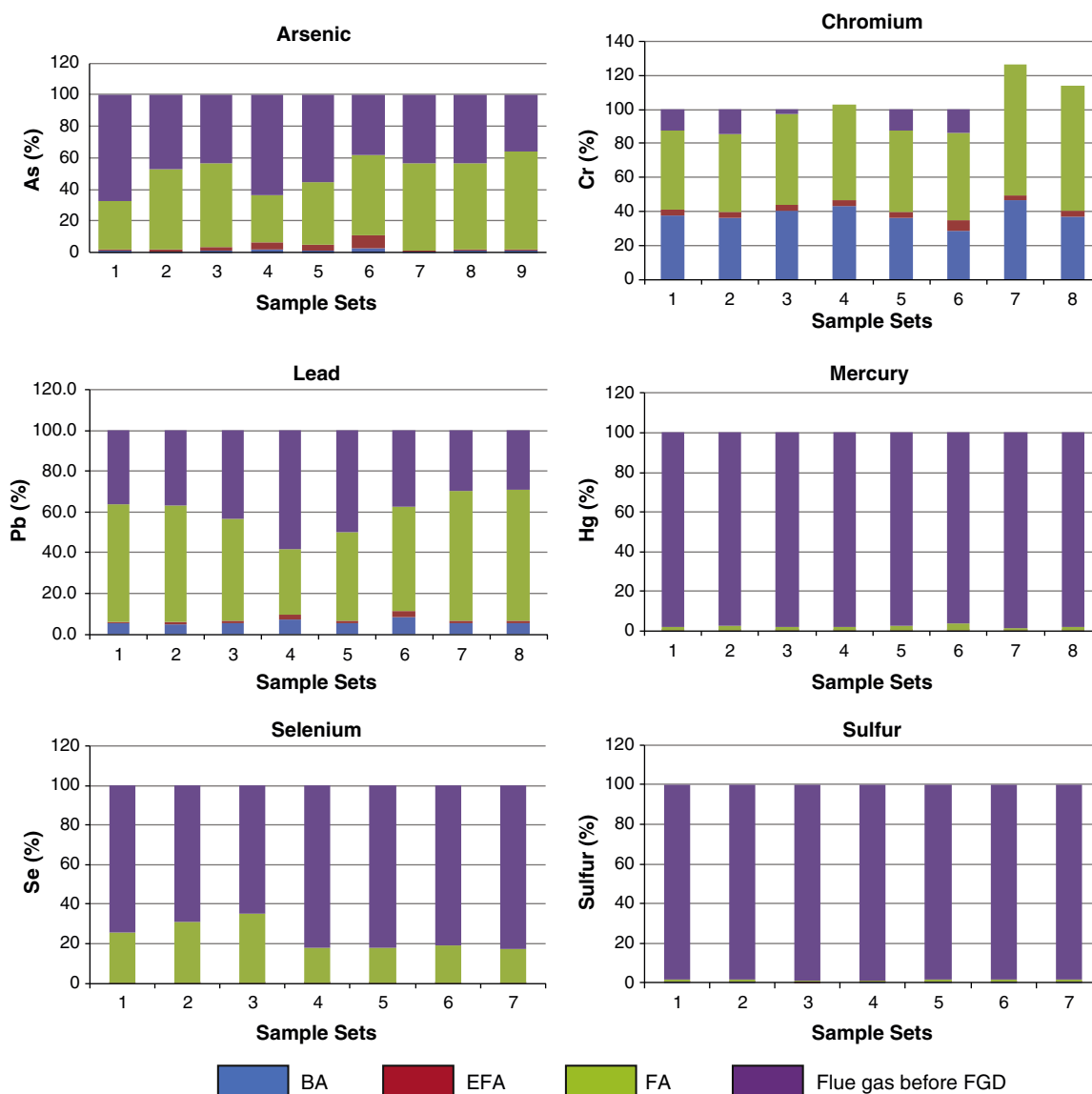
The mass balance calculation provides an estimate of the percentages of elements captured in each of the CCPs, compared to the pulverized coal burned in the boiler (Fig. 5, Table 3). Although the

estimate of uncertainty for the mass balance is about 20%, results are useful for showing a general trend in partitioning during the combustion process. All percentages in the following discussion are averages, based on seven to nine sample sets for each element. Each of the sample sets are composed of PC, BA, EFA, and FA. Results suggest that nearly half of the As and Pb from the pulverized coal is captured in FA (48% and 54%, respectively, Table 3), and that a small amount of these elements is captured in BA (1% and 6%, respectively) or EFA samples (3% or 1%, respectively). This distribution is in agreement with the comparison of the median concentrations for the CCPs, where FA samples were found to be enriched in As and Pb, compared to the BA and EFA samples. A notable amount of As and Pb (49% and 39%, respectively) apparently remains in the flue gas before the FGD process. The mass balance also suggests that about 20% of the Se in the pulverized coal is captured in FA by the ESPs, and that an average of 79% remains in the flue gas before the FGD process. This result is not surprising due to the extremely high volatility of Se and the chemical similarity of Se to S. However, the partitioning behavior of Se can be variable, as shown in a study of Kentucky power plants, where Se was found to have no consistent pattern of concentration related to ESP rows (Hower et al., 2009).

The mass balance also suggests that a large fraction of Cr is captured in both BA and FA (39% and 58%, respectively), and that very little Cr remains in flue gas after the ESP process (Fig. 5; Table 3). These results agree with previous work indicating that Group 1 elements may partition in both BA and FA (Clarke and Sloss, 1992). However, the distribution of Cr differs from the distribution suggested by the comparison of the median concentrations of CCPs, where the highest median concentrations of Cr were found in BA samples and the lowest median concentrations were found in FA samples. These differences are explained by the mass balance calculation itself, where a greater weight (about 78%) was assigned to FA in the calculation, based on estimates from the plant.

The levels of As and Se (48% and 20%, respectively) retained in FA at the Appalachian plant contrast with those of previous studies. In a study of a power plant burning a blend of bituminous and sub-bituminous feed coals, Córdoba et al. (2012) noted that relatively high levels of As and Se were captured in FA from ESPs (95% and 53%, respectively); lower As contents of the Appalachian plant FA may be due to temperature differences in the ESP or other differences in operating conditions. In stoker-fired combustion tests using bituminous coals, only 10–16% of the recovered As was found to be partitioned in FA, whereas 84–90% of the recovered As failed to leave the firebox (Li et al., 2005). The authors attributed this partitioning to the association of As with clay minerals in the feed coal, since a large proportion of the As would have been trapped in iron oxide glass after the clay was broken down during combustion. Because As in the feed coal for the Appalachian plant is thought to be primarily associated with pyrite (Finkelman, 1980; Ruppert et al., 1992), the higher levels of As captured in FA (48%), compared to the FA of the stoker-fired combustion tests (10–16%), would be expected. In a study of an eastern Kentucky plant burning a high volatile A bituminous coal, 99% of the Se was estimated to be captured by the ESP FA in the first-row ESP ash (Hower et al., 2009; Mardon and Hower, 2004). Because FA samples collected at the Appalachian plant were composite samples, a comparison of hot-side ESP FA samples with cold-side ESP FA samples was not possible.

Finally, the mass balance calculation suggests that very small amounts of Hg in the pulverized coal of the Appalachian plant are captured in FA (average of 2%; Fig. 5, Table 3) and that Hg is not captured to any real extent in any other CCP collected. The capture of Hg by cold-side ESPs at this plant may have been masked, because the FA samples were composite samples. The partitioning behavior of Hg is similar to that for S, which is also highly volatile. Results (Table 3; Fig. 5) show that essentially no S is captured in BA or EFA, whereas a small amount is captured in FA (1%). An average of 98% of S remains in the flue gas before the FGD process (Table 3).



**Fig. 5.** Results of mass balance for selected trace elements (As, Cr, Pb, Hg, and Se) and S for the Appalachian power plant. BA = bottom ash, EFA = economizer fly ash, FA = fly ash, and FGD = flue gas desulfurization.

The low level of Hg captured in FA at the Appalachian plant is probably related to the relatively high temperatures (163 °C) of the flue gas in the ESPs, which may have caused sintering of the FA C and a decrease in the FA C surface area. The low levels of C in the FA (mean LOI of 0.5%) may also have limited Hg capture. Although the Appalachian plant operates with SCRs, which are effective for oxidizing Hg to Hg<sup>2+</sup> and thereby increasing the potential for capture by ESPs (Wilcox et al., 2012), the relatively high temperature of the flue gas may have limited capture of Hg in FA. The rank of the feed coal (high volatile A bituminous) may also be a factor, since C derived from the combustion of bituminous coals is known to have a decreased surface area compared to that of lower rank coals (Hower et al., 2010; Kostova et al., 2011).

The fraction of Hg (2%) removed by ESPs at the Appalachian plant is significantly lower than fractions reported in a statistical survey of Dutch coal-fired power stations, where an average of about 50% of the Hg was removed by ESPs (Meij and te Winkel, 2006). The greater Hg removal by ESPs of these plants may be related to the lower flue gas temperatures (~120 °C) of the ESPs in the Netherlands (Meij and te Winkel, 2006). In a study of six power plants burning bituminous

coals in China, the average Hg removal efficiencies of ESPs was found to be 11.5%; these low efficiencies were thought to be related to the low Cl content of the coal (Zhang et al., 2008). One plant in the study by Zhang et al. (2008) had a very high Hg removal efficiency, with almost all of the Hg captured by the FA from ESPs; this efficient Hg capture was suggested to be related to high Cl content in the feed coal (875 ppm) and a high unburned C content in the FA (10.8%). In contrast, the fairly high concentrations of Cl in the pulverized coal of the Appalachian plant (average of 507 ppm) did not appear to enhance the capture of Hg in FA.

The FGD system of the Appalachian plant removed Hg from the flue gas stream, as indicated by a Hg concentration of 0.366 ppm (as-determined basis) in one sample of FGD sludge. Since our mass balance calculation did not include the FGD process, we were not able to estimate the effectiveness of the FGD process for removal of Hg. However, a mass balance study published by the Appalachian power plant indicates that 85% of the Hg in the feed coal is partitioned to FGD slurry, 12% is released through the stack, and 3% is captured in FA and BA. The results of the plant are consistent with our study, where we found about 2% of the Hg to be captured in FA. The results



for Hg captured in FA are also somewhat similar to those of stoker-fired combustion tests (Li et al., 2005), where more than 90% of the Hg was found to be partitioned into the flue gas.

Chlorine was found to be highly enriched in the FGD sludge at the Appalachian plant (2,740 ppm, as-determined basis). The enrichment of Cl in FGD sludge is consistent with studies of SCR-equipped units (Withum, 2006), where scrubber liquid chloride concentrations are found to be statistically significant factors related to Hg removal. The elements As, Cr, Pb, and Se were not enriched in the FGD sludge sample (35.8, 61.3, 19.6, and 3.3 ppm, respectively), compared to the rest of the CCPs studied.

### 3.2. Comparison of median concentrations of trace elements in CCPs: Colorado Plateau Plant

The distribution of trace elements in FA samples at the Colorado Plateau plant is variable. Median concentrations for Pb are statistically greater in FA (Fig. 4), compared to BA and FAC ( $p < 0.05$ ); these results are consistent with the high volatility of Pb (Fig. 1). Pb would be expected to condense on the surfaces of FA particles during the cooling of flue gas (Clarke and Sloss, 1992), resulting in enrichment in FA. Although the median concentration for Pb in FA samples is greater than that for EFA/FA samples, this difference is not statistically significant.

The distribution of As is somewhat similar to that of Pb. Median As concentrations are greater in FA samples than in BA samples, and the multiple comparison tests indicate that these differences are statistically significant. The partitioning of As in FA is consistent with its high volatility (Fig. 1). Although the median concentration for As in FA samples (9.6 ppm) is lower than that for the EFA/FA samples (10.6 ppm), this difference was not found to be statistically significant. A high median As concentration in EFA/FA samples compared to FA samples would not be expected, since the economizer of the power plant operates at significantly higher temperatures (about 427–454 °C) than the baghouses (104 °C). Finally, although the median As concentration in FA (9.64 ppm) is slightly greater than the median concentration in FAC samples (6.74 ppm), the multiple comparison tests show that this difference is not statistically significant. These results are somewhat surprising, since the FAC samples have larger particle sizes (with a decreased surface area per unit volume), and enrichment of As in FA samples would be expected. The partitioning of Cr is somewhat similar to that of As. The median concentration of Cr in FA samples (25.4 ppm) is lower than that for EFA/FA samples (30.1 ppm); however, these median values are not statistically significantly different at  $p < 0.05$ .

The median concentration for Hg in FA samples at the Colorado Plateau plant is greater than that for BA; these results are statistically significant at  $p < 0.05$ . This distribution is consistent with the extremely high volatility of Hg. FFs are effective at capturing finer particles, compared to other systems, such as ESPs (Clarke and Sloss, 1992), which may possibly affect the capture of Hg. Although the median concentration of Hg in FA (0.0983 ppm) is greater than its median concentrations in EFA/FA (0.0311 ppm) and FAC samples (0.0902 ppm), these differences are not statistically significant at  $p < 0.05$ .

The lowest median concentrations for As, Cr, Hg, Pb, and Se at the Colorado Plateau plant, relative to the other CCPs, are in BA (2.18 ppm, 20.7 ppm, <0.01 ppm, 19.2 ppm, and 0.186 ppm, respectively). However, the multiple comparison tests show that the medians for As and Pb in BA (2.18 ppm and 19.2 ppm, respectively) compared to the medians for these elements in FAC samples (6.74 and 23.9 ppm) are not statistically significantly different. Also, the median concentration of Cr in BA samples (20.7 ppm) is not statistically significantly different than that for FA (25.4 ppm) or FAC (26.3 ppm) samples. The low concentrations of Se and Hg in BA samples are consistent with the high volatility of these elements (Fig. 1). The distribution of Cr in BA, FA, and FAC is

consistent with its lower volatility than As, Hg, Pb, and Se. Chromium is known to partition into both BA and FA (Clarke and Sloss, 1992; Xu et al., 2003).

Arsenic, Cr, Hg, Pb, and Se have the greatest median concentrations in the FAP samples, relative to the other CCPs. All FA and EFA/FA samples were composite samples collected from several outlets in the baghouses. At this plant, FA and EFA/FA samples from the baghouses were processed in cyclone separators to make a fine particle size product (FAP). Enrichment of volatile trace elements (As, Cr, Pb, and Se) in FAP is probably a function of flue gas temperatures in the baghouses and of FA particle size. According to the plant, the baghouse process pushes a large volume of ash to the compartments farthest downstream, and in these areas, the FA particles are smaller and the temperature of the flue gas is slightly (about 3 °C) cooler than in the upstream compartments. The cooler temperatures probably led to increased condensation of volatile trace elements (including As, Cr, Pb, and Se) on the surfaces of the FA particles, and the fine FA particles would be enriched in these elements due to the larger surface-to-volume ratio of fine particles compared to coarse particles. The capture of Hg in FA is primarily related to the amount of C in the FA (average LOI for FA is 0.29%), since Hg is known to condense mainly on unburned C. The cooler downstream compartments probably favored increased condensation of Hg on C, leading to enrichment of Hg in the FA. The enrichment of As, Cr, Hg, Pb, and Se would be even greater in the fine FA produced by cyclone separators (FAP). The partitioning of these trace elements generally agrees with previous studies, in which volatile trace elements (including As, Cr, Hg, and Pb) were found to be largely (>99%) captured by FFs and mechanical cyclone separators (Goodarzi et al., 2008).

### 3.3. Partitioning of trace elements: comparison between power plants

The median concentration of As in FA from the Appalachian power plant (59.7 ppm) is about six times the median concentration of As in FA from the Colorado Plateau (9.6 ppm) (Table 2). The composition of the feed coals appears to be the controlling factor related to this difference in As, as indicated by the greater concentration of As in pulverized feed coals of the Appalachian plant (91.8 ppm) than in feed coals of the Colorado Plateau plant (10.4 ppm). Although the flue gas in the ESPs of the Appalachian plant is significantly hotter than that in the FFs of the Colorado Plateau plant, the composition of the feed coal appears to be the controlling factor.

The distribution of Cr in CCPs at each of the plants is significantly different. At the Appalachian plant, the highest median concentration for Cr (374 ppm) is in BA, whereas at the Colorado Plateau plant, the highest median concentration for Cr (36 ppm) is in FAP (Table 2). The higher level of Cr in BA at the Appalachian plant may be related to a higher level of Cr in the pulverized feed coal (195 ppm), compared to the feed coal of the Colorado Plateau plant (28 ppm). Contamination of the BA at the Appalachian plant by stainless steel is also a possibility.

The median concentration of Hg in FA samples from the Appalachian plant (0.0315 ppm) is significantly lower than the median concentration of Hg in FA and FAP samples from the Colorado Plateau plant (0.0983 and 0.119 ppm, respectively). The difference in the amount of Hg captured in FA at each plant is related to differences in the operating systems (ESPs versus FFs) and temperature of the flue gas. FFs are known to be much more effective at removing Hg than ESPs (Yudovich and Ketris, 2005; Zhang et al., 2008). The higher temperature conditions of the Appalachian plant may decrease the FA C surface area, as the particles are more likely to sinter. Although the Cl content of the feed coal for the Appalachian plant (average of 530 ppm) is higher than that for the Colorado Plateau plant (average of 110 ppm), these higher levels do not seem to increase Hg removal in FA at the Appalachian plant. The high sulfur content of the pulverized coal (3.9 weight percent) may limit the capture of Hg in FA of the Appalachian plant, since previous studies show that sulfur (SO<sub>2</sub>, SO<sub>3</sub>) may reduce the homogeneous oxidation of HgO in flue gas and inhibit the sorption and oxidation of HgO by

carbon surfaces (Kolker et al., 2006; Olson et al., 2003; Qiu et al., 2003). However, further work is needed to determine if high temperatures or other factors are preventing the capture of Hg in FA.

#### 4. Conclusions

For the Appalachian power plant, As, Hg, Pb, and Se have the greatest median concentrations in FA samples, compared to BA and EFA. Mass balance calculations indicate that the following percentages of trace elements are captured in FA: As, 48%; Hg, 2%; Cr, 58%; Pb, 54%; and Se, 20%. The low level of Hg captured in FA may be related to the relatively high temperatures of the flue gas in the ESPs, which may have caused sintering of the FA C (0.5% loss-on-ignition for FA) and a decrease in the fly ash C surface area. Cr is essentially completely captured in the CCPs, with a negligible amount left in flue gas after the ESPs. The FGD system of the Appalachian plant removes Hg from the flue gas stream, as indicated by a Hg concentration of 0.366 ppm (as-determined basis) in one sample of FGD sludge.

For the Colorado Plateau plant, As, Cr, Hg, Pb, and Se have the greatest median concentrations in the fine-grained FAP samples, compared to the other CCPs. The enrichment of these elements in FAP is probably related to the conditions in the downstream compartments of the baghouses, where temperatures of the flue gas are about 3 °C cooler than in upstream compartments. Although FA particles are smaller in the downstream compartments, particle size is not the dominant factor affecting Hg capture, because Hg is known to condense mainly on unburned carbon (average loss-on-ignition is 0.29% for FA, 0.39% for FAP). However, the increased surface-to-volume ratio of FA in downstream compartments would have led to enrichment of As, Cr, Pb, and Se in FA, since these elements would have condensed over the entire FA particle.

The median concentration of Hg captured in FA (0.0983 ppm) at the Colorado Plateau plant is three times the median Hg level for the Appalachian plant (0.0315 ppm). These differences reflect the operating systems at each plant (FFs vs ESPs), temperature of flue gas, and the amount of unburned C in FA. A higher concentration of Cl (average of 530 ppm) in the feed coal for the Appalachian plant, compared to that of the Colorado Plateau plant (average of 110 ppm), does not appear to improve Hg removal in FA. The composition of the feed coal is also an important factor that affects partitioning. Median As concentrations in FA of the Appalachian plant (60 ppm) are greater than those of the Colorado Plateau FA (10 ppm); these differences are apparently not temperature related and may reflect the median concentration of As in the pulverized feed coal for the Appalachian plant (92 ppm) versus that for feed coal for the Colorado Plateau plant (10 ppm).

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