Collaborative studies for mercury characterization in coal and coal combustion products, Republic of South Africa

Project report prepared by:
U.S. Geological Survey (USGS),
Eastern Energy Resources Science Center
Reston, Virginia 20192 USA

(September 2014)

Citation: UNEP, 2014. Collaborative studies for mercury characterization in coal and coal combustion products, Republic of South Africa. UNEP Chemicals Branch, Geneva, Switzerland, 49 p.

This is a report from the Mercury Control from Coal Combustion Partnership Area of the UNEP Global Mercury Partnership

Disclaimer

The material in this publication does not imply the expression of any opinion on the part of the United Nations Environment Programme (UNEP) or the US Geological Survey (USGS) concerning the legal status of any country, territory, city or area or of its authorities, or concerning delimitation of its frontiers or boundaries. Moreover, the views expressed do not necessarily represent the decision or policy of UNEP or the USGS, nor does use of trade names or commercial processes constitute endorsement.

Reproduction

Funding

The work was funded by the European Union. USGS participation in the study was supported by the USGS Energy Resources Program.

Production

Based on the agreement between the United Nations Environment Programme (UNEP), Division of Technology, Industry and Economics (DTIE), Chemicals Branch, and the US Geological Survey, USGS has undertaken the project entitled: “Collaborative studies for mercury characterization in coal and coal combustion products, Republic of South Africa”.

The report can be found on UNEP Chemicals Branch website:
http://www.unep.org/chemicalsandwaste/Mercury/InterimActivities/Partnerships/Coalcombustion/tabid/3530/language/en-US/Default.aspx

The report was prepared by:
Allan Kolker, U.S. Geological Survey, Reston, VA, 20192 USA, akolker@usgs.gov
Constance Senior, ADA Environmental Solutions, Inc., Highlands Ranch, CO, 80129 USA
Chris van Alphen, Eskom Holdings, Ltd., Johannesburg, South Africa

Acknowledgements

This work was performed under an agreement between UNEP, DTIE Chemicals Branch, Geneva, Switzerland, and the U.S. Geological Survey in Reston, Virginia, USA. The project partners acknowledge the contributions of the following individuals:

USGS analytical results were contributed by Nick Geboy (Reston), and Alan Koenig and Jamie McCord (Denver). Peter Kariher (Arcadis, USA) and Jeff Ryan (U.S. EPA) provided samples collected previously. We also thank Kristy Langerman of Eskom for her interest and cooperation.

Project Manager in UNEP was Gunnar Futsaeter.
Cover Photo: Gunnar Futsaeter.

Acronyms, Abbreviations and other Terms

APCD	Air Pollution Control Device
As	Arsenic
ASTM	American Society for Testing and Materials
Be	Beryllium
Br	Bromine
BTU	British Thermal Unit
Cd	Cadmium
Cl	Chlorine
Co	Cobalt
Cr	Chromium
DEA	South African Department of Environmental Affairs
Density Separates	Fractions of whole coal separated by density using heavy media
De-stoned Coal	Washed coal from which the highest density fraction has been removed
EPA	United States Environmental Protection Agency
ESP	Electrostatic Precipitator
F	Fluorine
Feed Coal	Pulverized Coal Feeding a Power Station
FF	Fabric Filter
FGD	Flue Gas Desulphurization
Hg	Mercury
ICP-MS	Inductively Coupled Plasma Mass Spectrometer
ICR	Information Collection Request (U.S. EPA)
IPP	Independent Power Producer
MATS	EPA Mercury and Air Toxics Standards
Middlings	Washed coal from which both the highest and lowest density fractions have been removed
MFC	Mill Feed Coal

Mill Feed Coal	Raw Coal Feeding a Pulverization Mill
Mn	Manganese
Mo	Molybdenum
MJ	Mega Joule
MW	Mega Watt
Ni	Nickel
NIST	U.S. National Institute of Standards and Technology
PAC	Powdered Activated Carbon
PCD	Particulate Control Device
Pb	Lead
PPB	Parts per billion
PFC	Pulverized Feed Coal
PPM	Parts per million
Run-of-Mine	Coal as produced by a mine
S	Sulfur
Sb	Antimony
Se	Selenium
Tl	Thallium
UNEP	United Nations Environment Programme
USGS	U.S. Geological Survey
WoCQI	U.S. Geological Survey World Coal Quality Inventory
Zn	Zinc

Executive Summary

The objective of this project is to provide technical information on the concentration of mercury and associated constituents such as trace elements and halogens in feed coals used in South African utilities. In addition, we provide data to assess mercury removal by coal washing procedures used or being developed in South Africa. These results show how coal selection and operational changes can be used to optimize mercury capture in the South African electric utility sector, thereby reducing emissions.

Mercury analyses were obtained in USGS laboratories for 42 new samples of feed coal provided by Eskom, representing all 13 coal-fired power stations operated by Eskom in South Africa. This sampling includes results for three older power stations, Camden, Grootvlei, and Komati, returned to service starting in late 2000's. Mercury concentrations determined in the present study are similar to- or slightly lower than those previously reported, and input Hg for the three stations returned to service is comparable to that for the other 10 power stations. Results for the Matimba power station burning Waterberg coals show that coal washing currently in use for this station is effective in reducing mercury levels to the range of other Eskom power stations burning coal that does not require washing. This finding is promising for supplying the future Medupi power station that will also use Waterberg coals and require a similar coal washing approach. Determination of halogen contents of the 42 feed coals by a contract laboratory confirms that chlorine contents are generally low, and as such, the extent of mercury self-capture by particulate control devices is rather limited.

Eight separates of a South African Highveld (#4) coal prepared in dense media were also provided by Eskom for analysis. These samples show a strong mineralogical association of mercury (and arsenic) with pyrite. For this coal, reduction of pyrite by coal washing is very likely to result in reduced mercury contents, as well as lowering sulfur emissions. The density separates were used to predict mercury contents of coal products used in South Africa or exported. These contents range from less than 100 parts per billion (ppb; 0.10 ppm) for washed export coals having ash contents less than 16%, to more than 400 ppb (0.40 ppm) for ash-rich (stone) material that is often discarded. Intermediate mercury contents are calculated from the density separates for predicted coal products used for power generation in South Africa, such as de-stoned coal, from which a high-ash fraction has been removed (240 ppb; 0.24 ppm), middlings, from which high-ash and low-ash fractions have been removed (270 ppb; 0.27 ppm), and run-of-mine coal (300 ppb; 0.30 ppm).

A suite of 48 paired samples of pulverization mill feed coal and fly ash collected in previous (2010) UNEP-sponsored study of emissions from the Duvha and Kendal power stations was

obtained for further investigation in the present study. These samples show that in each station, mercury capture varies somewhat by boiler unit. These results also confirm that units equipped with fabric filters for air pollution control are much more effective in capturing mercury that those equipped with electrostatic precipitators as usually found elsewhere . In each station, mercury capture is affected by differences in operating conditions of the boiler and air pollution control devices. This variation should be considered in determining emission factors used to estimate mercury emissions. Paired sampling of feed coal and fly ash could be used by Eskom to track the performance of its air pollution control devices in removing mercury. Analysis of these samples to assess Hg capture on a unit-by-unit basis would provide a much better estimate of the Hg emission rate from the plant than simply assigning a fixed emission factor based on the type of particulate control device, as has been done in previous estimates.

Apart from tracking the performance of air pollution control devices individually, changes resulting in improved mercury capture of the Eskom fleet are presented. These include Hg reduction through coal selection and washing, as well as through optimization of equipment and operational parameters:

Coal washing: Density separates for a Highveld #4 coal indicate that coal washing is effective in reducing the concentrations of pyrite-associated elements such as Hg. Mercury reduction to the boiler can be achieved by discarding the stone fraction, as is already practiced by Eskom, and by retaining as much of the low-ash export fraction as is practical.

Operational improvements: A series of plant operational changes leading to increased mercury capture is also presented including low-cost options. For a given mercury input to the boiler, increasing mercury adsorption on unburned carbon is perhaps the simplest operational way to improve mercury capture. This can be accomplished by lowering the air preheater exit temperature, increasing the amount of unburned carbon in the ash, and minimizing the concentration of SO_3/H_2SO_4 vapor in the flue gas. The first two changes have competing influences on boiler efficiency, which may offset one another while increasing Hg capture. Equipment options for improving Hg capture include addition of fabric filters, use of halogenated sorbents, and addition of flue gas desulphurization (FGD) scrubbers, listed in order of increasing cost. The capital cost of adding FGD scrubbers to existing plants is probably too high to be justified on the grounds of Hg removal alone. However, if future regulations require reductions in SO_2, and FGDs are installed to meet these standards, further reduction in Hg emissions will be a co-benefit of this installation.

Table of Contents

List of Tables

List of Figures

Collaborative Studies for Mercury Characterization in Coal and Coal Combustion Products, Republic of South Africa

1. Introduction

1.1 Background

Mercury (Hg) is a known neurotoxin with demonstrated adverse human health impacts. Coal combustion is the largest industrial contributor to global Hg emissions (Pacyna and Pacyna, 2001 AMAP/UNEP, 2013). Information on the quality of coal and the distribution and mode of occurrence of harmful constituents such as mercury, especially in commercial coals, is needed to help governments, utilities, and decision makers make informed decisions on emission levels, ultimately affecting exposure of citizens to mercury. Towards this goal, the United Nations Environment Programme (UNEP) funded the U.S. Geological Survey (USGS) under a UNEP Small Scale Funding Agreement to partner with Eskom, the national electric utility of South Africa to study mercury in the South African electric utility sector. South Africa is of particular interest because of its status as one of the world's largest coal producers and its reliance on coal (in 2012) for more than 90% of its electric power generation (World Coal Association, 2014). Past sampling of South African coals for Hg analysis is relatively limited, and much of the available results reflect run-of-mine samples or coal prepared for export. In the present study, funds from UNEP are used by the USGS to perform analytical work on samples provided by Eskom, including power station feed coals and coal separates prepared in dense media. The USGS work quantifies current levels of mercury in South African commercial coals, its behavior in selected combustion systems, and the potential for mercury reduction by coal beneficiation, thereby allowing technical recommendations for reducing mercury emissions.

1.2 Objectives, purpose, and scope

The purpose of the UNEP-USGS agreement is to characterize the distribution of Hg in coals used for electric power generation in South Africa, and to provide technical information needed for Hg emissions reduction in the South African utility sector using available APCDs and (or) coal washing methods, as Hg-specific controls are not contemplated.

Using samples of boiler feed coal and coal preparation fractions provided by Eskom, this study considers mercury (Hg) input to the boiler for Eskom's fleet of 13 utility coal-fired generating stations, and the potential for Hg emissions reduction by optimizing Hg capture using conventional air pollution control devices (APCDs), or by coal washing. To show how mercury is partitioned during power plant operation, samples of pulverization mill feed coal and fly ash from Eskom's Kendal and Duvha power stations, collected in 2010 in sampling by the EPA, were obtained for further analysis in the present study. A total of 98 samples were investigated. These include: 1) 42 new samples of pulverized feed coal (PFC) from 13 Eskom coal-fired power stations, including 3 retired stations returned to service starting in the late 2000s that were not available for sampling in the most recent previous studies (Fig. 1). The group of 42 feed coal samples also includes yearly composites for 7 stations, the most recent such data available; 2) 8 density separates of Highveld #4 coal, one of the most important coals used for power generation in South Africa; and 3) 48 samples of raw pulverization mill feed coal (MFC) and fly ash, collected in the 2010 study at Kendal and Duvha power stations.

This study does not consider coal-fired power generation for industrial purposes, of which Sasol is the largest contributor, and several small independent power producers (IPP's). Combined power generation by Sasol and the IPP's is a small fraction of Eskom's combined installed capacity, however, large amounts of coal are used by Sasol as feedstock for conversion to liquid fuels. Measurements of stack Hg emissions are beyond the scope and resources of the present study, however, these measurements were obtained in the 2010 study at Kendal and Duvha power stations from which concurrent samples of coal and coal ash were obtained that were investigated here.

More specific information on Hg in South African feed coal is a key factor in improving Hg emissions estimates for the South African utility sector (Dabrowski et al., 2008; Leaner et al., 2009; Masekoameng et al., 2010). The present study provides an overview of Hg input from coal and a starting point for more detailed sampling, such as that by the EPA in support of its Mercury and Air Toxics (MATS) standards (U.S. EPA, 2011).

Figure 1. Map showing Eskom power stations in South Africa. Coal-fired stations (green triangles) are concentrated in west-central Mpumalamga Province. Coal-fired stations returned to service (Camden, Grootvlei, Komati) are shown as gray inverted triangles, and future stations (Medupi, Limpopo Province, and Kusile, Mpumalanga Province) are shown as blue triangles. Source: Eskom, www.eskom.co.za.

1.3 Technical Overview of Eskom Fleet

Eskom currently operates 87 coal-fired boilers at 13 plants (Table 1). Two plants, Medupi and Kusile (a total of 12 boilers) are under construction. None of the operating boilers have flue gas desulphurization (FGD) technology. All boilers have particulate control devices (PCDs), either a fabric filter (FF) or a cold-side electrostatic precipitator (ESP). Some of the plants that have ESPs use flue gas conditioning (FGC) to reduce the resistivity of the fly ash and make it easier to collect. This conditioning of the fly ash is accomplished by injecting sulfuric acid (SO_3 or H_2SO_4) into the flue gas upstream of the ESP. Some of the coal that Eskom fires in the boilers of its power plants is washed (following section). Coal washing removes some of the minerals (ash) in the coal; in addition to reducing the ash content, coal washing has the potential to reduce both the sulfur (S) content and the Hg content, in the case that there is a significant amount of pyrite in the coal and that pyrite contains Hg.

Table 1. Description of Eskom coal-fired power plants

Station	Plant Capacity (MW)	No. Boilers	Commission Date	Status	Coal Washing	Type of Part. Control Device	FGC with SO_3	Type of SO_2 Control
Arnot	2,352	6	1975	Operating	Partial	FF	None	None
Duvha	3,600	6	1980	Operating	Partial	ESP x 3 FF x 3	Yes	None
Hendrina	2,000	10	1970	Operating	Partial	FF	None	None
Kendal	4,116	6	1988	Operating	None	ESP	Yes	None
Kriel	3,000	6	1979	Operating	None	ESP	Yes	None
Lethabo	3,708	6	1985	Operating	Partial	ESP	Yes	None
Majuba	4,110	6	1996	Operating	None	FF	None	None
Matimba	3,990	6	1988-1993	Operating	Yes	ESP	Yes	None
Matla	3,600	6	1983	Operating	None	ESP	Yes	None
Tutuka	3,654	6	1985	Operating	None	ESP	None	None
Camden	1,510	8	1967	Returned to Service	None	FF	None	None
Grootvlei	1,200	6	1969	Returned to Service	None	ESP x 3 FF x3	None	None
Komati	940	9	1961	Returned to Service	None	ESP	Yes	None
Medupi	4,788	6	Future	Construction	--	FF	None	FGD (tech not final)
Kusile	4,800	6	Future	Construction	--	FF	None	FGD (tech not final)

1.4 Feed Coals and Coal Consumption

A suite of 42 samples of pulverized feed coals provided by Eskom includes from 2 to4 samples from each of the 13 coal-fired electric utility power stations operated by Eskom in South Africa (Table 1). This unique sample set would be unobtainable without Eskom's cooperation. The sampling provides an overview of Hg input to the entire Eskom fleet at selected monthly time-points from 2009 to 2012, including nine yearly composites from seven power stations (Table 2).

Feed coals utilized by Eskom include washed, partly washed and unwashed (run-of-mine) coals (Table 3). Low-ash washed fractions of South African coals are primarily produced for export, with the exception of Waterberg coals used in the Matimba power station. Partly washed feed coals utilized by Eskom include all the remaining fractions, the middlings (fractions remaining after export and discard fractions are removed), or a de-stoned product where only the discard fraction is removed (Section 3).

Table 2. Sampling data for 42 Eskom feed coals. Monthly samples are indicated by month of sampling. Yearly composites are shown in boldface for years indicated. Numbering of feed coal samples corresponds to stations in the order listed and samples A, B, C, or D for each station.

Station Number	Station	Number Samples	A	B	C	D
1	**Arnot**	2	June '09	June '12		
2	**Camden**	4	Feb. '09	April '10	Jan. '11	**2012**
3	**Duvha**	3	Dec. '10	**2012**	July '12	
4	**Grootvlei**	4	Dec. '09	Jan. '11	**2012**	June '12
5	**Hendrina**	3	**2010**	**2011**	**2012**	
6	**Kendal**	4	April '09	Aug. '10	Jan. '11	Jan. '12
7	**Kriel**	3	March '09	Feb. '09	April '11	
8	**Komati**	3	April '09	May '09	June '09	
9	**Lethabo**	3	Jan. '09	Jan. '11	**2012**	
10	**Majuba**	4	Jan. '09	Nov. '10	March '11	**2012**
11	**Matimba**	3	April '10	Nov. '10	Feb. '11	
12	**Matla**	3	Nov. '10	May '11	**2012**	
13	**Tutuka**	3	Jan. '09	Dec. '10	May '11	

Coal production in South Africa has traditionally been concentrated in the Highveld region of Mpumalanga Province where the Witbank, Highveld, and Ermelo coals are worked (Pretorius et al., 2002; Peatfield, 2003; Jeffrey, 2005). This production includes mine-mouth supply of Eskom power stations as well as feedstock for Sasol's coal-to-liquids operations. Reserves of the Witbank and Highveld coals, together with those of the Waterberg coals in Limpopo Province, constitute approximately 70% of South Africa's recoverable coal reserves (Jeffrey, 2005). The Witbank and Highveld coals are laterally contiguous; the same coal beds are present in each coal, but their characteristics may differ. Historically, the Witbank #2 coal has been an important source of low ash, washed export coal. The Witbank and Highveld #4 coals are generally of lower quality but are economically important for domestic power generation, and increasingly, as feedstock for washed export product (Bergh et al., 2011). The Witbank #3 coal is of good quality but relatively thin, and therefore not as economically important as the #4 coal, whereas the Highveld #3 is thin, discontinuous, and of poor quality (Jeffrey, 2005). The #5 coal is relatively thin, but can be of good quality and has been used as a source of metallurgical coal (Jeffrey, 2005).

Table 3. Coal washing and coal consumption data for Eskom power stations. Numbering of feed coal samples corresponds to power stations in the order listed.

Station Number	**Station**	**Consumption** (million tons/yr)	**Coal Preparation**
1	**Arnot**	6.8	A partly washed product is fired
2	**Camden**	4.7	No washing; some sources could be washed[1]
3	**Duvha**	11.7	A partly washed product is fired
4	**Grootvlei**	1.6	No washing; some sources could be washed[1]
5	**Hendrina**	6.9	A partly washed product is fired
6	**Kendall**	13.9	No washing- run-of-mine coal is fired
7	**Kriel**	8.5	No washing- run-of-mine coal is fired
8	**Komati**	0.7	No washing- some sources could be washed[1]
9	**Lethabo**	18.2	A partly washed product is fired
10	**Majuba**	12.3	No washing- some sources could be washed[1]
11	**Matimba**	14.6	Fully washed- cleanest fractions are fired
12	**Matla**	12.4	No washing- run-of-mine coal is fired
13	**Tutuka**	10.6	No washing- some sources could be washed[1]

[1] Run-of-mine is primarily used, but washed coal is available from various market sources

Reserves of Witbank coals are declining, providing motivation to investigate use of other coals for power generation and to better understand element partitioning during coal washing. Density separation of a Highveld #4 coal was tested by Eskom to predict coal quality variation during coal washing, and in the present study, the impact of coal washing on trace element distribution (Section 3).

For Waterberg coals, interest has increased in recent years due to the large reserves, and construction underway in Limpopo Province of the 4,764 megawatt (MW) Medupi power station. When completed, the Medupi power station will burn Waterberg coal, as is currently burned by the Matimba power station nearby. Coal washing is needed for Waterberg coals because of finely laminated mudstone present within these coals (Jeffrey, 2005; Wagner and Tlotleng, 2012). Addition of a second new coal fired power station, the 4,800 MW Kusile station, under construction in Mpumalanga Province, will presumably utilize Witbank/Highveld coals. Each of the two new Eskom coal-fired power stations will be among the largest in the world, exceeding the generating capacity of any of the existing power stations (Table 1).

1.5 Previous Work

The present activity follows from a 2010 investigation conducted under a UNEP-sponsored consortium including Eskom, the South African Department of Environmental Affairs (DEA) and the U.S. Environmental Protection Agency (EPA). In the 2010 study, two of Eskom's coal-fired generating stations, Kendal and Duvha, were sampled in detail (Scott, 2011). In this previous study, stack Hg speciation measurements were obtained by EPA Method 30B using carbon sorbent traps (U.S. EPA, 2008). Reporting for this study emphasized these emissions measurements (Scott, 2011). Pulverization mill feed coal and fly ash were also collected in the 2010 study. A portion of these solid samples were analyzed for Hg using a Lumex instrument upon their return to EPA labs, but these results were never published. This archival sample material was obtained from EPA collaborators for further investigation in the present study.

Average Hg data for previous (2001) sampling of feed coals from South African power stations is available in Eskom internal reporting (Gericke et al., 2007), providing context for comparing the present results. Subsequent coal sampling (in 2004-2005) was used by Roos (2011) to calculate Hg emissions for each of the Eskom power stations, assuming published emission factors; unfortunately, however, Hg data for input coal were not provided with this study. Uncertainties in the values used for the efficiency of the power plants and the heating value of the feed coal made it impossible for us to accurately determine input Hg by back-calculating from emissions projections given by Roos (2011).

Additional data on Hg in South African coal are available for run-of-mine coal samples or specific coal products. A suite of 40 South African coal samples representing coal products including raw, sized, and washed coals (Pretorius et al., 2002) was obtained by the USGS in the early 2000s for the World Coal Quality Inventory (WoCQI; Tewalt et al., 2010). The WoCQI samples include some washed export coals with very low Hg contents. As might be expected, the WoCQI sample set shows a much wider distribution of Hg values (< 0.03 to 0.83 ppm (<30 to 830 ppb)), than power station feed coals determined in the present study. Other recent results for Hg in South African coal have been presented in the context of Hg as one of a number of potentially hazardous elements in coal. Wagner and Hlatshwayo (2005) studied five run-of-mine samples and a middlings split of Highveld #4 (lower) coal, one of the main producing beds. A mean Hg value of 0.15 ± 0.05 ppm (150 ± 50 ppb) is given for the five run-of-mine samples, within error of USGS-determined Hg values for the same sample splits (mean of 0.20 ppm Hg (200 ppb)). For a #4 Witbank coal with 0.3 ppm (300 ppb) Hg, Bergh et al. (2011) compare froth flotation and density separation approaches to trace element reduction, concluding that the density separation approach is more effective for pyrite-associated elements such as Hg.

For Waterberg coals, expanded use expected in the future will require coal washing. Consequently, there has been interest in partitioning of trace elements during washing tests. Wagner and Tlotleng (2012) investigated element partitioning in four run-of-mine samples and corresponding density splits of Waterberg coals. These include three samples (benches 3, 4, and 5) from the Grootegeluk Formation and one sample (bench 11) from the underlying Vryheid Formation. All of the run-of-mine coals have high Hg contents (0.9 to 2.43 ppm (900 to 2,430 ppb)) with the greatest Hg-enrichment in the Vryheid-bench 11 sample. Density splits for the Grootegeluk samples show especially good correlations between Hg (and arsenic [As]) and pyritic sulfur, but this association is less clear for the Vryheid sample. The results indicate that coal washing is promising for Hg reduction of Waterberg coals, particularly those in the Grootegeluk Formation, pending commercial-scale trials.

2. Feed Coals

2.1 Feed Coal Characteristics

Compared to Carboniferous coals of the northern hemisphere, South African coals, and Permian coals in general, have relatively high ash yields and low S and halogen contents (Falcon, 1986; Synman and Botha, 1993; Wagner and Hlatshwayo, 2005). Characteristics of Eskom feed coals are shown in Table 4, with results shown as ranges for each set of power station samples. With the exception of the Lethabo power station, which shows a large range in ash contents and corresponding heating values, each station shows relatively narrow ranges in coal quality parameters. Ash yields in the 30% range are typical. Sulfur and pyritic S contents are relatively low. Moisture contents are less than 5% in all but one sample (5.1% sample 9A Lethabo power station). Results for moisture and ash yield provided by Eskom compared with those obtained in the present study show good or acceptable agreement and no systematic differences (Appendix 1).

Table 4. Characteristics of 42 Eskom feed coal samples (as determined basis)[1].

Station Number	**Station** (# samples)	**Moisture** [wt. %]	**Ash** [wt. %]	**Sulfur** [wt. %]	**Pyritic Sulfur** [wt. %]	**Calorific Value**[2] [BTU/Lb]
1	**Arnot** (2)	3.8 – 3.9	24.5 – 26.6	0.66 – 0.75	0.30 – 0.36	9233 – 9396
2	**Camden** (4)	3.1 – 3.7	27.6 – 32.4	0.79 – 1.18	0.34 – 0.63	8516 – 9067
3	**Duvha** (3)	2.1 – 2.3	29.4 – 30.5	0.84 – 0.98	0.40 – 0.48	9074 – 9402
4	**Grootvlei** (4)	3.5 – 3.9	29.4 – 31.1	1.06 – 1.23	0.40 – 0.55	8284 – 8675
5	**Hendrina** (3)	3.0 – 3.2	27.1 – 27.7	1.21 – 1.27	0.73 – 0.81	9312 – 9448
6	**Kendall** (4)	3.0 – 3.5	31.9 – 33.8	0.76 – 0.80	0.36 – 0.45	7982 – 8402
7	**Kriel** (3)	3.8 – 4.2	21.7 – 24.8	0.66 – 0.73	0.22 – 0.27	9119 – 9637
8	**Komati** (3)	3.9 – 4.1	29.2 – 32.3	0.80 – 1.01	0.46 – 0.53	8161 – 8653
9	**Lethabo** (3)	2.9 – 5.1	39.3 – 40.9	0.68 – 0.84	0.36 – 0.48	6579 – 9591
10	**Majuba** (4)	3.3 – 3.6	27.7 – 28.5	0.81 – 1.01	0.38 – 0.56	8925 – 9039
11	**Matimba** (3)	2.0 – 2.4	33.9 – 34.4	1.21 – 1.25	0.59 – 0.66	8414 – 8606
12	**Matla** (3)	2.2 – 4.4	25.3 – 33.3	0.84 – 1.36	0.43 – 0.75	8561 – 9113
13	**Tutuka** (3)	3.6 – 3.9	28.6 – 30.2	0.72 – 1.14	0.53 – 0.76	8864 – 8905

[1]Values obtained by USGS contract lab. See Appendix 1 for comparison with Eskom data.
[2]To convert to MJ/kg multiply by 0.0023259.
[3]Eskom ash value used for sample 9C (appendix 1)

2.2 Mercury in Eskom Feed Coals

Results for Hg in the 42 samples of Eskom feed coal in the present study are given in Table 5 in comparison to past determinations. Results presented were determined in USGS Reston laboratories and these results are compared with re-analysis in USGS Denver laboratories in Appendix 1. Mercury results by power station are shown in Fig. 2. Results for Hg in the 42 feed coals give a mean of 232 ± 71.3 ppb[1]. The range in Hg values (from 120 to 463 ppb) is similar to that of power station feed coal averages given previously by Gericke et al. (2007; from 0.17 to 0.45 ppm (170 to 450 ppb)). Without knowing more about the source of coal and variations in the coal supply for each power station, and without more detailed sampling, it is difficult to make specific comparisons. From Table 5, it appears that Hg contents determined in the present study are either similar to those obtained previously (for Arnot, Duvha, Hendrina, Lethabo, Majuba, Matla, and Tutuka) or lower (for Kendal, Kriel, and Matimba). Additionally, the sampling provides results for the Camden, Grootvlei, and Komati stations that have been returned to service since previous determinations, showing these three stations are within the

---

[1] Hg results are expressed in ppb where possible due to greater precision. To compare results given in ppm: 1 ppm = 1000 ppb.

range obtained for the other 10 stations. In none of the power stations has there been a pronounced increase in Hg input since the previous determinations. Washed Waterberg coal used to supply the Matimba power station shows that the process is effective in attaining Hg levels comparable to stations supplied by other coals.

Table 5. Mercury in 42 Eskom feed coal samples (this study) and previous results for feed coals in Eskom power stations (in ppm, on an as-determined basis)

Station Number	**Station**	**This Study**[1] (Samples A, B, C, D)	**Composite Year(s)**	**Gericke et al. (2007)**[2]
1	**Arnot**	0.16, 0.12		0.17
2	**Camden**	0.20, 0.25, 0.22, **0.19**	**2012**	N.A.
3	**Duvha**[3]	0.21, **0.18**, 0.19	**2012**	0.23
4	**Grootvlei**	0.37, 0.28, **0.34**, 0.32	**2012**	N.A.
5	**Hendrina**	**0.28**, **0.23**, **0.22**	**2010-2012**	0.21
6	**Kendal**[3]	0.22, 0.21, 0.18, 0.21		0.44
7	**Kriel**	0.12, 0.13, 0.14		0.29, 0.38
8	**Komati**	0.23, 0.20, 0.24		N.A.
9	**Lethabo**	0.40, 0.46, **0.15**	**2012**	0.36
10	**Majuba**	0.29, 0.23, 0.28, **0.22**	**2012**	0.29
11	**Matimba**	0.23, 0.25, 0.19		0.45
12	**Matla**	0.28, 0.23, **0.20**	**2012**	0.29
13	**Tutuka**	0.18, 0.30, 0.22		0.29

[1] Values shown in boldface indicate yearly composites. Other results are monthly samples.

[2] Multi-year average Hg content as reported by Scott (2011).

[3] Excludes results for 2010 samples from Duvha and Kendal stations presented in Section 4.

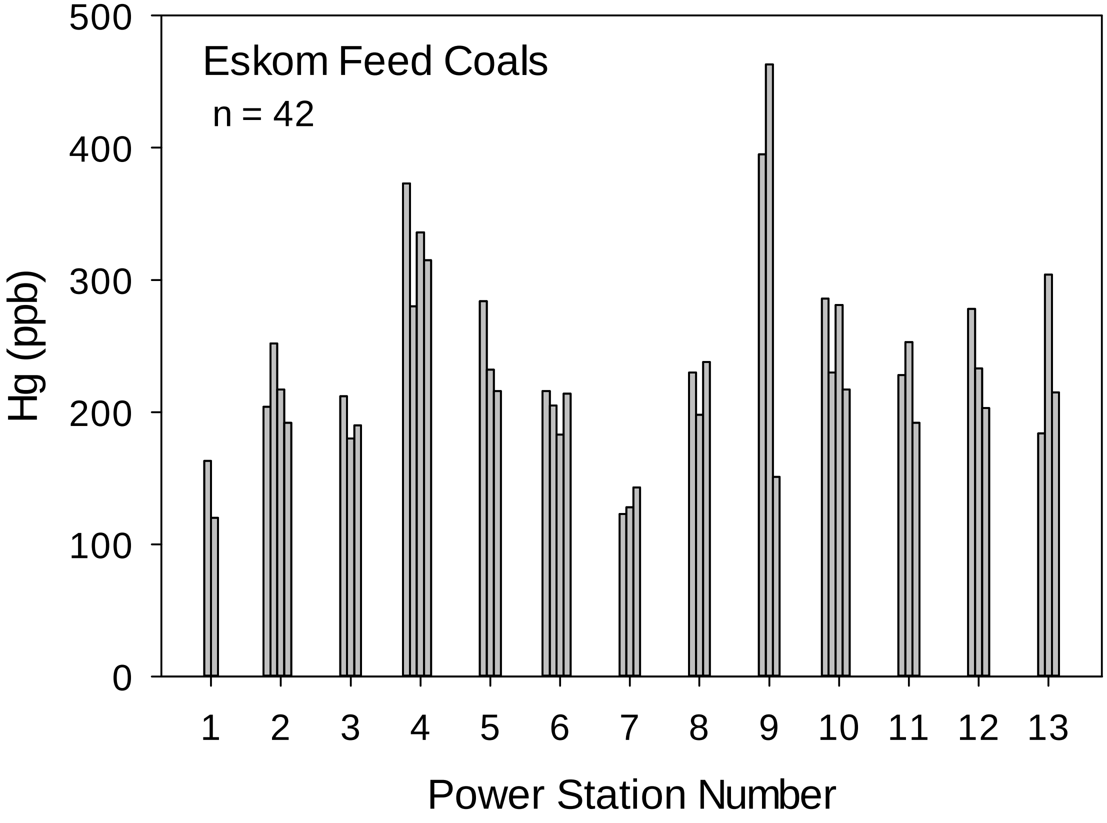

Figure 2. Variation in mercury content of feed coals by power station number. Samples and power stations are as listed in Table 2.

2.3 Halogens in Feed Coals

Chlorine (Cl) is generally the most abundant halogen in coal. At flue gas temperatures, the Cl content of coal strongly influences Hg speciation, converting elemental Hg present at boiler temperatures to oxidized forms that can react to form Hg-Cl complexes or compounds (Senior, 2014). These Hg-Cl complexes or compounds can be captured by air pollution control devices or taken up by halogen-doped sorbents (Section 5). The proportion of oxidized Hg formed in combustion systems increases with increasing Cl, and therefore, the presence of moderate (at least several hundred ppm) Cl contents is advantageous for Hg capture. On a mass equivalent basis, bromine (Br) is considered more effective than Cl in promoting Hg capture.

Halogens in the feed coals were measured using American Society for Testing and Materials (ASTM) methods (ASTM, 2013a,b) by a commercial laboratory. Measured halogen contents in the Eskom feed coals are generally low (Cl ≤ 100 to 200 ppm), with the exception of the Hendrina (#5) power station in which 2010, 2011, and 2012 composite samples show variable Cl contents of uncertain origin (Fig. 3); values in excess of 200 ppm (samples 5A and 5B) are not considered to be representative. Fluorine (F) contents are variable, and in some cases, comparable to those obtained for Cl (Table 6). No ASTM method exists for Br, but by using the same digestion and measurement approach (oxygen bomb combustion and ion selective electrode) Br contents were found to be below the detection limit (20 ppm) in all cases. Given the importance of Br in promoting Hg capture and the fact that Br contents in U.S. coals are typically from 2 to 4% of Cl contents (Vosteen et al., 2010; Kolker and Quick, 2014), a more sensitive method for Br determination is needed.

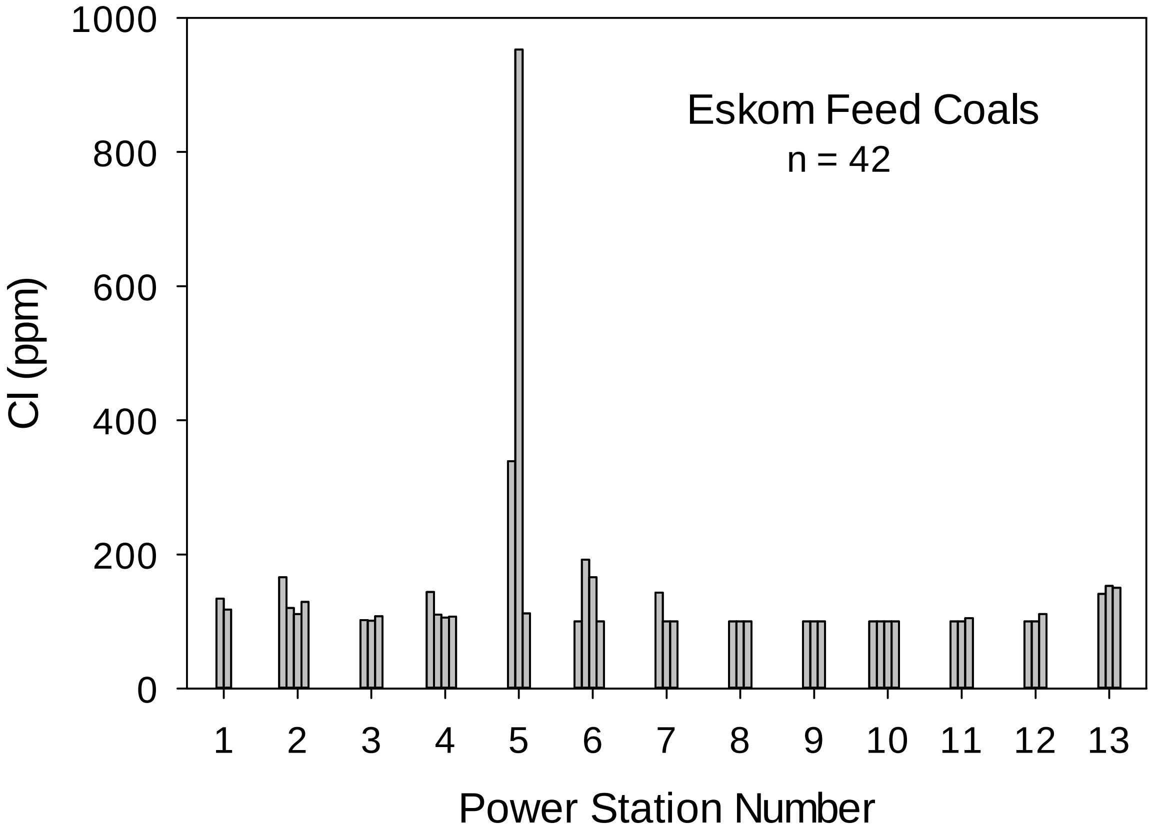

Figure 3. Variation in ASTM chlorine content in feed coals by power station number. Power stations are as listed in Table 2. Samples having values below the detection limit (100 ppm) are plotted at the detection limit.

2.4 Trace Element Data

Trace element results for the 42 feed coals (this Section) and 8 density separates (Section 3) are given in Table 6. For the feed coals, results for a range of elements, including Be, Cr, Mn, Co, Ni, As, Mo, Cd, Sb, Tl, and Pb, are relatively uniform (Table 6; Fig. 4). Relative to global averages, South African coals are much higher in Cr and Mn, and lower or much lower in As, Cd, and Sb (Bergh et al., 2011; Wagner and Tlotleng, 2012). Wagner and Hlatshwayo (2005) also found that Se, Pb, and Zn were very depleted in Highveld coals relative to global averages. For Waterberg coals (samples 11A-C), Mn and Cr are high as in other South African coals; Zn and Pb in these samples are higher than in Witbank and Highveld coals, as also found by Wagner and Tlotleng (2012). Selenium was not determined in the present study.

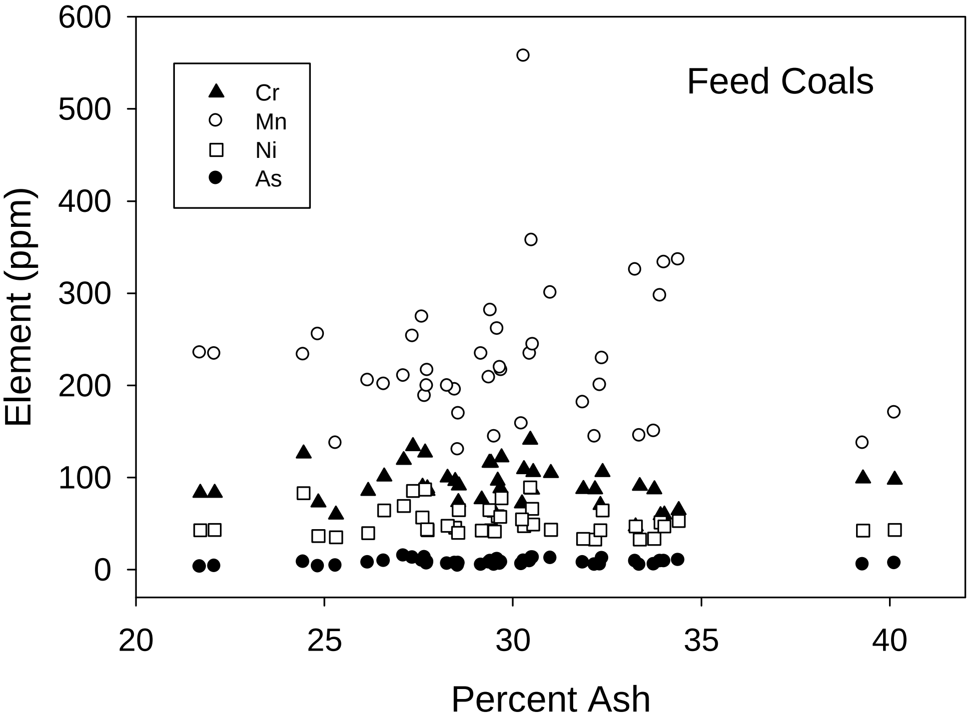

Figure. 4. Plot showing ranges for chromium (Cr), manganese (Mn), nickel (Ni), and arsenic (As) in feed coals (as-determined basis).

Table 6. Trace element data (ppm, as determined basis)[1]

Sample	**Be 4**	**F 9**	**Cl 17**	**Cr 24**	**Mn 25**	**Co 27**	**Ni 28**	Zn 30	**As 33**	Mo 42	**Cd 48**	**Sb 51**	**Hg 80**	Tl 81	**Pb 82**
1A	2.9	84	134	126	233	24	83	64	7.9	3.2	0.16	<0.20	0.16	0.90	28
1B	3.8	113	118	101	201	19	64	70	8.9	3.1	0.15	0.27	0.12	0.48	31
2A	4.1	137	166	106	229	15	64	69	12	2.9	0.15	0.48	0.20	0.44	39
2B	3.6	127	120	87	357	16	66	61	12	3.8	0.12	0.34	0.25	0.47	32
2C	3.9	130	111	97	261	14	58	62	11	3.4	0.12	<0.20	0.22	0.42	30
2D	4.0	118	129	90	274	17	57	76	9.3	3.7	0.12	0.38	0.19	0.29	30
3A	3.2	215	102	141	234	17	89	67	8.7	4.0	0.14	< 0.20	0.21	0.25	29
3B	3.4	208	101	116	208	14	65	65	7.1	3.5	0.16	< 0.20	0.18	0.21	28
3C	3.5	239	108	122	216	15	78	63	7.6	3.7	0.13	0.25	0.19	1.2	32
4A	4.1	158	144	105	300	7.8	43	44	12	3.0	< 0.10	<0.20	0.37	0.28	32
4B	3.8	149	110	116	281	9.7	43	40	8.6	3.1	< 0.10	< 0.20	0.28	< 0.10	31
4C	3.7	153	106	109	557	9.0	47	48	8.9	3.0	< 0.10	< 0.20	0.34	< 0.10	31
4D	4.1	189	107	106	244	13	49	52	13	3.5	< 0.10	< 0.20	0.32	< 0.10	29
5A	4.3	37	339	119	210	20	69	53	15	4.0	0.14	< 0.20	0.28	0.38	28
5B	5.8	75	953	127	188	21	87	67	13	5.6	0.16	< 0.20	0.23	0.64	28
5C	4.1	117	112	134	253	21	85	63	12	6.3	0.17	< 0.20	0.22	0.39	30
6A	4.1	175	< 100	87	144	7.8	33	34	4.8	2.8	< 0.10	< 0.20	0.22	1.1	21
6B	3.6	168	192	88	181	8.8	34	43	7.2	3.0	< 0.10	4.5	0.21	0.25	23
6C	3.3	166	166	91	145	7.7	33	36	4.6	2.3	< 0.10	< 0.20	0.18	< 0.10	24
6D	3.6	47	< 100	87	150	7.4	34	32	5.2	2.5	< 0.10	< 0.20	0.21	< 0.10	24
7A	2.9	164	143	83	234	9.0	43	23	3.4	2.6	< 0.10	< 0.20	0.12	< 0.10	24
7B	3.1	97	< 100	83	235	8.3	43	22	2.7	2.4	< 0.10	< 0.20	0.13	< 0.10	21
7C	2.8	158	< 100	73	255	8.7	37	22	3.2	2.4	< 0.10	< 0.20	0.14	< 0.10	14
8A	3.1	95	< 100	88	219	13	57	69	5.9	2.8	0.10	< 0.20	0.23	< 0.10	29
8B	2.9	98	< 100	76	234	11	43	40	4.7	2.2	0.10	< 0.20	0.20	< 0.10	27
8C	2.7	98	< 100	70	200	11	43	35	5.2	2.2	< 0.10	< 0.20	0.24	< 0.10	25

Sample	**Be 4**	**F 9**	**Cl 17**	**Cr 24**	**Mn 25**	**Co 27**	**Ni 28**	Zn 30	**As 33**	Mo 42	**Cd 48**	**Sb 51**	**Hg 80**	Tl 81	**Pb 82**
9A	3.0	124	< 100	98	170	7.6	43	39	6.6	2.3	< 0.10	< 0.20	0.40	1.2	30
9B[2]	3.2	119	< 100	99	137	6.6	43	33	5.3	2.2	< 0.10	< 0.20	0.46	0.22	24
9C	4.6	189	< 100	86	205	9.3	40	46	7.2	2.9	0.18	< 0.20	0.15	0.10	36
10A	4.3	157	< 100	96	195	7.7	46	33	6.4	4.0	< 0.10	< 0.20	0.29	< 0.10	29
10B	4.3	145	< 100	85	216	9.3	43	40	7.7	3.0	< 0.10	< 0.20	0.23	0.81	29
10C	4.5	173	< 100	88	199	7.5	44	37	6.1	3.6	0.13	< 0.20	0.28	0.23	33
10D	4.3	186	< 100	100	199	7.2	48	33	6.0	3.6	0.11	< 0.20	0.22	0.11	30
11A	4.1	217	< 100	59	297	15	51	79	8.9	4.1	0.30	0.49	0.23	0.24	35
11B	4.1	89	< 100	65	336	16	53	84	9.8	4.4	0.29	0.67	0.25	1.6	37
11C	4.2	205	105	60	333	15	47	81	8.6	3.9	0.24	0.44	0.19	0.52	34
12A[2]	2.7	152	< 100	73	130	8.1	40	26	4.1	3.0	< 0.10	< 0.20	0.28	0.18	28
12B[2]	2.8	154	< 100	60	137	8.6	35	22	3.9	3.2	< 0.10	< 0.20	0.23	< 0.10	25
12C	4.2	189	111	47	325	15	47	85	8.6	4.0	0.27	0.48	0.20	0.20	30
13A	4.9	86	141	62	144	11	41	30	4.8	2.1	0.10	< 0.20	0.18	0.17	31
13B	6.5	106	153	91	169	17	65	34	6.5	2.9	< 0.10	< 0.20	0.30	0.31	32
13C	6.8	93	150	72	158	14	55	41	5.6	2.4	< 0.10	< 0.20	0.22	0.31	31
14A[3]	4.1	311	540	147	152	43	60	24	2.3	13	< 0.10	3.2	0.06	< 0.10	16
14B	4.4	239	1084	118	130	16	42	24	2.5	6.1	< 0.10	2.2	0.05	< 0.10	21
14C	3.8	171	1037	78	164	8.0	33	20	2.2	5.2	< 0.10	1.2	0.10	1.1	17
14D	3.1	140	770	62	144	4.7	25	18	2.4	4.2	< 0.10	0.51	0.24	0.11	12
14E	4.4	154	807	88	103	4.0	32	18	2.8	5.4	< 0.10	< 0.20	0.30	< 0.10	15
14F	2.5	129	573	56	63	3.0	26	18	3.4	5.1	< 0.10	< 0.20	0.59	< 0.10	12
14G	2.8	120	536	54	44	2.1	23	12	2.9	3.4	< 0.10	< 0.20	0.44	< 0.10	11
14H	1.0	140	428	42	31	6.1	32	24	4.8	1.1	< 0.10	< 0.20	0.46	< 0.10	1.7

Notes: [1] Emissions to be regulated under U.S. EPA MATS standards (U.S. EPA, 2011) shown in boldface, excluding Se (not determined). Cl and F to be regulated as acid gasses HCl and HF.

[2] Mercury value for this sample is an average of multiple analyses (Appendix 1).

[3] Fourteen series samples are Highveld #4 density separates (Section 3). Hg values for these samples are averages of multiple analyses (Appendix 1).

3. Density Separates of Highveld (#4) Coal

3.1 Introduction

In addition to power station feed coals, Eskom provided eight sized density separates of Highveld #4 coal from test preparation in heavy media. These samples are especially relevant as they represent one of the most important coals used for domestic power generation and an increasing proportion of the export market from prepared product. The density separates were prepared from a 1 mm size split in heavy media ranging from 1.4 to 2.0 g/cm^3. These include float fractions for densities (g/cm^3) 1.4, 1.5, 1.6, 1.7, 1.8, 1.9, and 2.0, corresponding to samples 14A to G, and the sink fraction for 2.0 (sample 14H). Inclusion of these samples in the present study provides an indication of the partitioning behavior of trace elements during coal washing. Simple calculations using the separates allow prediction of coal quality variations and element partitioning in coal products used in South Africa on a commercial scale. Washed export coals have the lowest ash yields and Hg contents. Feed coals utilized by Eskom (Table 3) may include all the remaining fractions (middling + discard), or the middlings only, from which both the export fraction and a discard fraction have been removed. If the yield of the export fraction is too low, then Eskom may burn an unwashed run-of-mine coal, or commonly, a de-stoned product in which the most ash-rich fraction (discard) has been removed. Eskom emphasizes the importance of removing the stone (discard) fraction. In most cases, coarse pyrite remaining in the raw coal is removed during pulverization, as pyrite rejects.

3.2 Results

3.2.1 Bulk Analysis

For the eight density separates, the separation process is effective in concentrating pyrite in the highest density (2.0 g/cm^3) fractions, either as float or sink. Bulk Hg contents of the separates are well correlated with the amount of pyrite (as pyritic sulfur) present, and with ash yield (Fig. 5). Arsenic enrichment goes along with Hg, but overall As contents in South African coals are relatively low compared to world averages, especially in the separates (Ketris and Yudovich, 2009; Fig 6). Conversely, Cr, Mn, Co, Ni, Mo, and Sb show enrichment in the low density float fractions (Table 6; Fig. 7), despite the fact that some of these elements (Mn, Co, Ni, Mo) are measurable in pyrite (following section). These elements have mixed associations, likely including an organic association in addition to pyrite. Although high Cr contents are characteristic of South African coals, the fact that Cr is enriched in the low-density float fractions suggests that chromite ($FeCr_2O_4$, density 5.09) is not the host, despite the proximity of

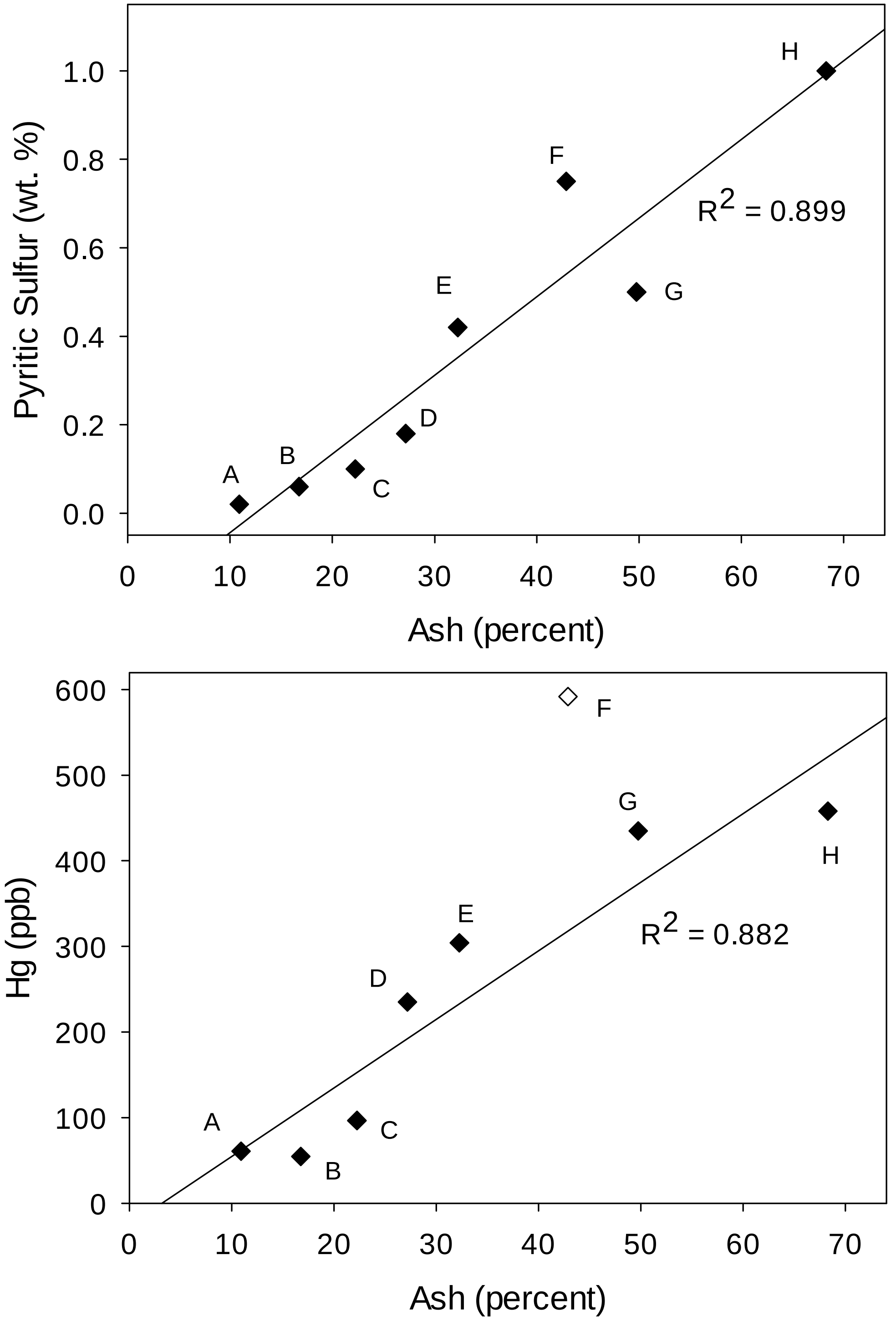

Figure 5. Plots of ash yield vs. pyritic sulfur (upper) and mercury (lower plot) for Highveld (#4) density separates, showing concentration of pyrite and Hg in the high-density cuts (as-received basis). Corresponding densities are noted in text. Sample 14F (open symbol) is omitted from linear regression in bottom plot.

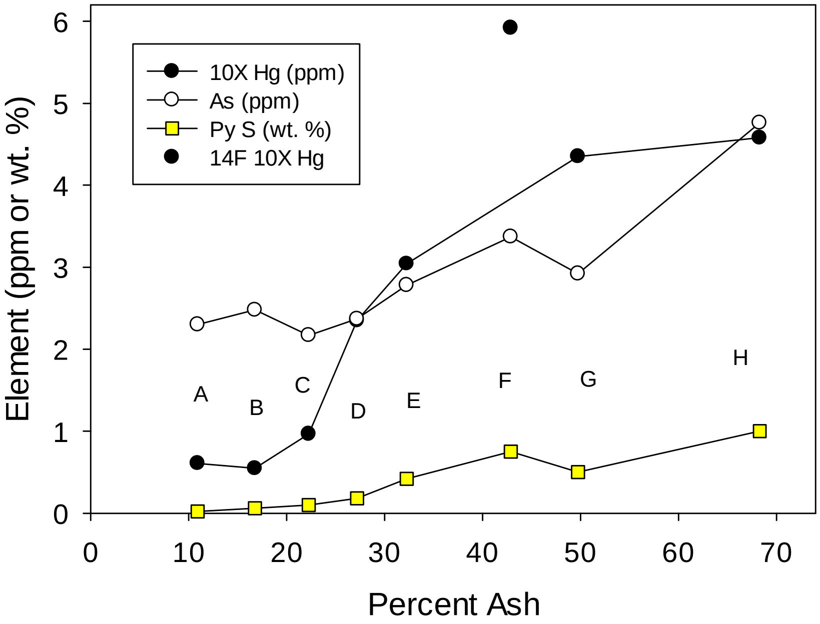

Figure 6. Plot showing increase in mercury and arsenic in separates prepared at increasing separation densities, and corresponding increase in pyrite content (as pyritic sulfur).

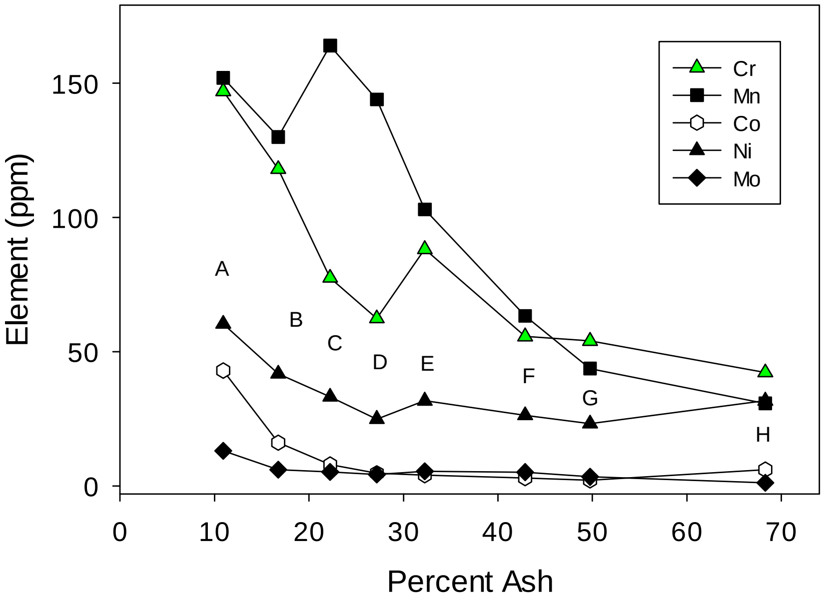

Figure 7. Partitioning of chromium, manganese, cobalt, nickel, and molybdenum in separates, showing relative enrichment in low-density float fractions, indicating an organic or mixed association.

the Witbank coals to the Bushveld Complex, a prominent source of chromite (Cameron, 1977; Hulbert and Von Gruenewaldt, 1985). The Bushveld Complex greatly predates Karoo sediments hosting these coal beds, but it would have to be exposed in Permian time to contribute sediments during coal formation. To explain moderate Cr enrichment in Highveld coals, Wagner and Hlatshwayo (2005) suggest that Cr from primary sources such as chromite was subsequently dissolved and re-distributed, which would explain the uniform Cr enrichment.

Unlike Hg, Cl and F in the Highveld #4 separates are concentrated in the low-ash fractions, consistent with binding of halogens to organic portions of the coal (Huggins and Huffman, 1995) as the dominant mode of occurrence (Fig. 8). Compared to Highveld whole coals, halogen values for the separates are high, possibly a result of $ZnCl_2$ heavy liquids used in their preparation. However, results for Zn do not show enrichment in the separates relative to whole coals, and the observed Cl enrichment decreases with increasing density, opposite of the trend expected as the proportion of heavy liquid in heavy liquid-water mixtures increases.

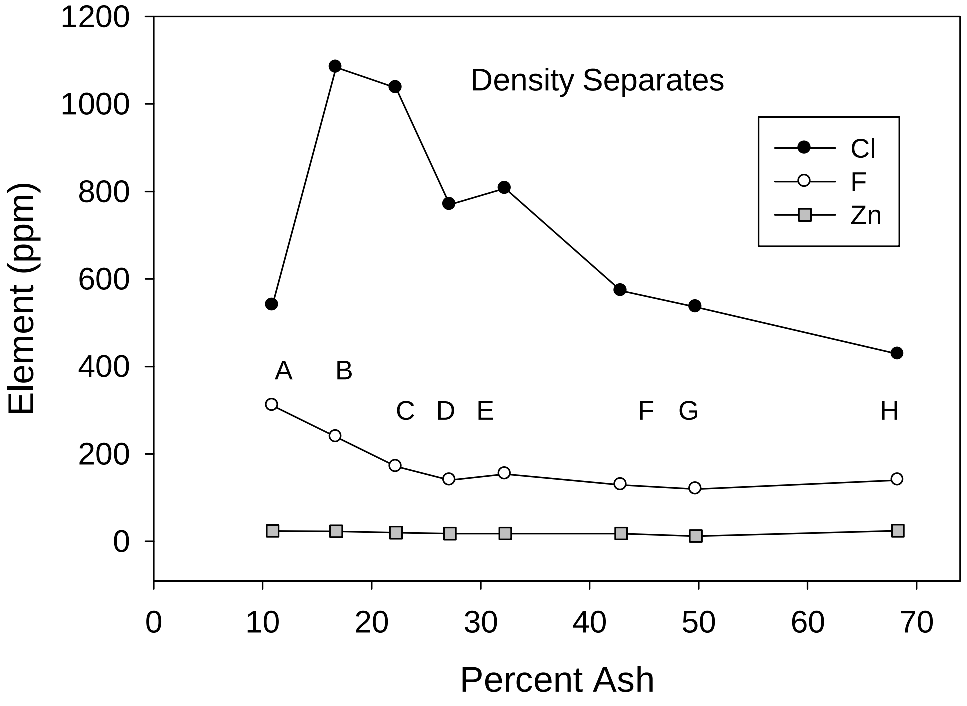

Figure 8. Partitioning of chlorine and fluorine among Highveld #4 density separates showing that halogens are preferentially concentrated in the low-density fractions indicating an organic affinity.

Combinations of the density fractions can be used to predict characteristics of coal products used in South Africa or exported. These include: 1) export; 2) de-stoned; 3) middling; 4) run-of-mine; 5) middling plus discard; and 6) stone (discard), listed in order of increasing ash yield predicted from the density fractions (Table 7). Mercury contents calculated for these products range from approximately 50 ppb for export coal to more than 450 ppb for stone. While these results are limited to a single-size fraction of a single coal, they are illustrative of the difference in quality of coals prepared for export and those used for domestic power generation. In practice, the middlings fraction may have a higher ash yield than run-of-mine coal (Wagner and Hlatshwayo, 2005), but the standard for export coal is to contain no more than 16% ash (Snyman and Botha, 1993), as the density separates predict. Past USGS analysis of export quality Highveld coals confirms Hg contents of 50 ppb or less are attained (Tewalt et al., 2010).

Table 7. Ash yield and mercury contents of coal products predicted from Highveld (#4) density separates, expressed on a dry basis. Hg results used are shown in Appendix 1.

Product	**Samples** (averaged)	**Ash** (wt. percent)	**Hg** (ppb)	**Approximate cut point**
Export	14A	15.5	63	Cut at 1.4
De-stoned	14A-F	29.5	236	Cut at 1.9
Middling	14B-F	32.3	271	1.4 to 1.9
Run-of-mine	14A-H	37.2	295	No washing
Middling + discard	14B-H	40.3	329	> 1.4
Stone (discard)	14G, H	60.5	474	> 2.1

3.2.2 Microanalysis

Polished mounts of each density separate were prepared for characterization by microanalysis methods. Pyrite grains for laser ablation ICP-MS were identified and checked for compositional variation using backscattered electron imaging and wavelength-dispersive elemental mapping, with a JEOL JXA 8900R electron microprobe instrument at the USGS in Reston. This analysis showed no discernable compositional variation. Laser ablation ICP-MS spot analysis was then conducted at the USGS Central Minerals and Environmental Resources laser ablation ICP-MS facility in Denver (Fig. 9). Pyrites were ablated using spot sizes of 25 µm or 20 µm as necessary, giving detection limits for Hg of 0.49 ppm (490 ppb) and 0.74 ppm (740 ppb), respectively. The larger spot sizes gives better detection limits because more material is ablated, but the smaller spot size allows finer intergrowths to be determined (Fig. 10). USGS synthetic sulfide standard MASS-1 (Wilson et al., 2002) was used as the primary calibration standard. MASS-1 is known to be homogeneous to a resolution of 20 µm.

Three distinct pyrite forms were observed. The bulk of the analyses are for complex composite grains that likely have a multistage history (Fig. 10). In addition, framboidal pyrite and cleat pyrite were observed, typically the earliest and latest pyrite generations, respectively, in coal (Kolker, 2012). The number of cleat and framboidal pyrites analyzed was not sufficient to determine if these are compositionally distinct from the large composite grains. A total of 263 points on 21 pyrite grains was determined, including 163 determinations at 20 µm and 100 at 25 µm. Results for Hg show a heterogeneous spatial distribution with typical values ranging from the detection limits to about 3 ppm (3,000 ppb), with a few higher values (Fig. 11).

Figure 9. USGS laser ablation (foreground) ICP-MS (background) instrument.

In addition to Hg, minor or trace elements detected in pyrite by laser ablation include Mn, Co, Ni, Cu, Zn, As, Se, Mo, Tl, Pb, and Bi (Table 8). Detection limits for each spot size vary by element as do the proportion of analyses that exceed the detection limit. Mean concentrations were calculated for conditions where at least about 50% of the analyses resulted in detection of an element, by substituting 55% of the detection limit for non-detects (Sanford et al., 1993). For each spot size, means were calculated for As, Mo, Hg, Tl, and Pb in pyrite (Table 8). Element enrichment factors were determined for pyrite relative to whole coal values obtained by averaging all eight separates. Including data for both the both the 25- and 20 micron spot sizes, pyrite is enriched by factors of 13.1 to22.2 (As), 6.3 to 8.2 (Mo), 3.8 to 8.1 (Hg), and 1.4 to 2.8 (Pb) relative to the respective calculated whole coal values, with insufficient data available for bulk Tl. The results show that that As, Hg, and surprisingly, Mo, which shows a slight decline with increasing ash content (Fig. 7), are most strongly partitioned into pyrite. For Hg, the higher mean value for the 20-micron data (2.42 ppm) versus the 25- micron results (1.13 ppm) reflects heterogeneity of the sample populations and the fact that several (6) 10+ ppm Hg points are included in the mean.

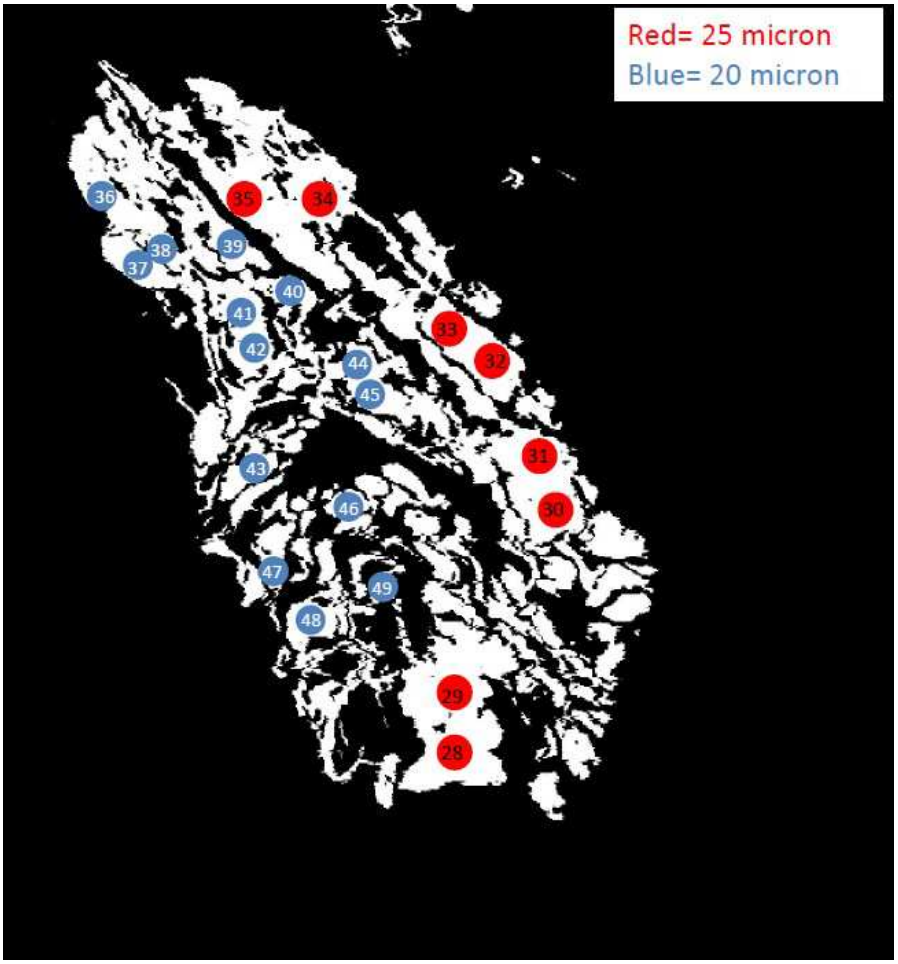

Figure 10. Backscattered electron image of composite pyrite in density separate sample 14F (1.9 float) from Highveld (#4) coal showing laser ablation spot analysis points using 25 micrometer (red) or 20 micrometer (blue) laser diameter. Width of field-of-view is 600 micrometers.

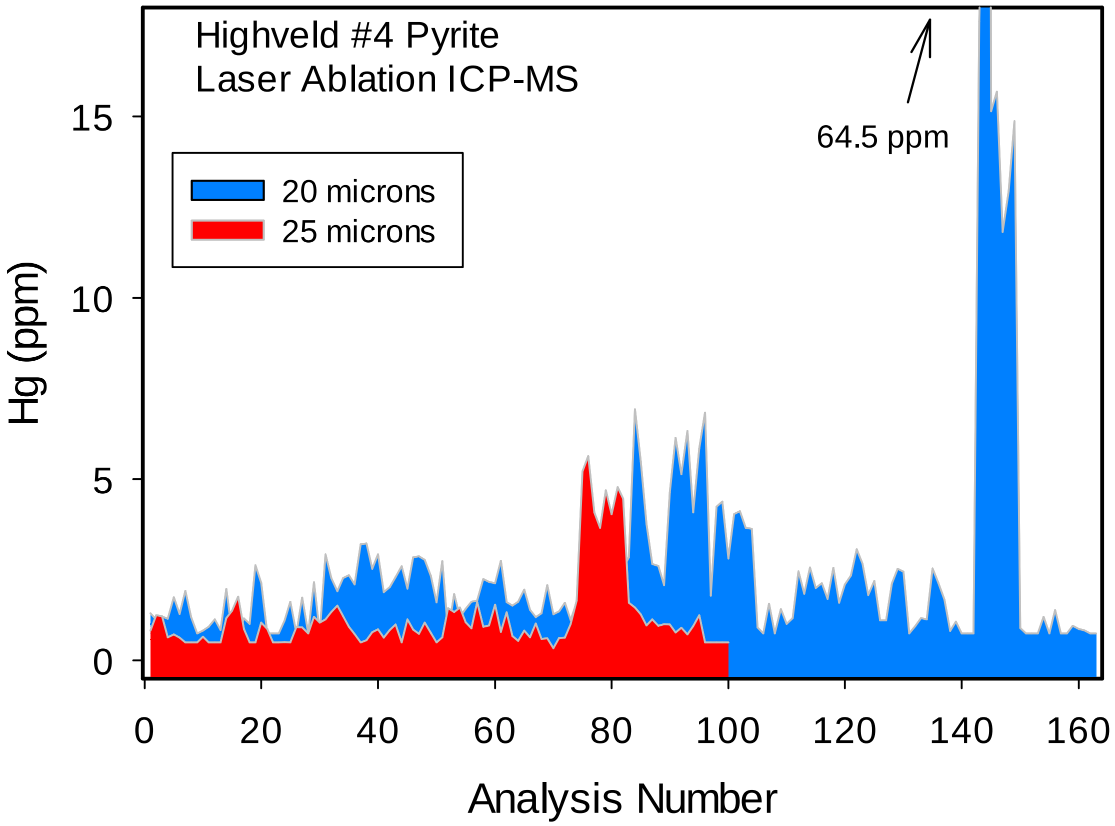

Figure 11. Laser ablation ICP-MS spot analyses for Hg in pyrite from Highveld (#4) coal density separates. Most analyses range from the detection limits to about 3 ppm, but several points exceed 5 ppm and one analysis exceeds 50 ppm. Non detects are plotted at the respective detection limits, 0.49 ppm for 25 micron data and 0.74 ppm for 20 micron data. These values are baselines for each plot.

Table 8. Laser ablation ICP-MS analysis data showing detection limits in ppm, calculated mean values for As, Mo, Hg, Tl, and Pb, (> 50% detected) and element enrichment factors in pyrite relative to calculated whole coal.

	Mn	**Co**	**Ni**	**As**	**Se**	**Mo**	**Hg**	**Tl**	**Pb**
	20 Micrometer Spot (n = 163)								
Detection limit (ppm)	**25.2**	**11.6**	**365**	**40.1**	**20.2**	**15.0**	**0.74**	**1.13**	**2.39**
Percent detects	40%	42%	21%	**56%**	29%	**69%**	**85%**	**72%**	**63%**
Mean (ppm)	**---**	**---**	**---**	**64.5**[1]	**---**	**44.8**	**2.42**[1]	**6.89**	**36.8**[1]
Calculated whole coal[2]				2.9		5.5	0.30	---	13.1
Enrichment factor				**22.2**		**8.2**	**8.1**		**2.8**
	25 Micrometer Spot (n = 100)								
Detection limit (ppm)	**16.4**	**8.8**	**37.1**	**15.3**	**163**[3]	**11.2**	**0.49**	**0.78**	**1.93**
Percent detects	47%	28%	23%	**72%**	9%	**75%**	**80%**	**68%**	**73%**
Mean (ppm)	**---**	**---**	**---**	**40.0**	**---**	**34.8**	**1.13**	**5.57**	**17.8**
Calculated whole coal[2]				2.9		5.5	0.30	---	13.1
Enrichment factor				**13.8**		**6.3**	**3.8**		**1.4**

[1] Excludes one analysis with 983 ppm As, 64.5 ppm Hg, and 6,319 ppm Pb.

[2] Whole coal value estimated by averaging 8 density separates as in Table 7, values in ppm.

[3] Detection limit for Se varies with instrument conditions and was better for 20 micrometer spot.

Other elements detected: Cu, Zn, Bi.

4. Supplemental Results for Duvha and Kendal Power Stations

4.1 Introduction

The EPA measured Hg emissions from the stacks of the boilers at two power stations (Duvha and Kendal) in 2010 (Scott, 2011). The objective of the testing was to collect representative Hg emissions data so that emission factors could be derived from these sources. The Duvha power station was selected because three of the six boilers used fabric filters (FFs) and three used ESPs for particulate control. At the Kendal power station, all six boilers used ESPs for particulate control.

For the stack samples, sorbent trap methods based on EPA Method 30B were used. The sorbent traps contain a carbon that captures and retains the total gaseous Hg in the flue gas. Modifications of the basic Method 30B equipment and procedures can be made to measure gaseous elemental and gas oxidized Hg species separately. Method 30B is not designed to quantify particulate-bound Hg and, therefore, is suitable for measurement downstream of the particulate control device (PCD). The EPA sampling methodology is described in detail by Forte et al. (2012).

4.2 Solid Samples

Two raw pulverization mill coal (MFC) samples and two fly ash samples were collected in one-time sampling from each of the six boiler units at Duvha and Kendal. A portion of these samples was originally analyzed for Hg by the EPA (Appendix 1). Splits of these samples were obtained in the present study. The concentrations of Hg in these samples were determined in the USGS Reston laboratory, while the concentrations of halogens in the coal samples were determined by the same contract USGS contract laboratory, using the same ASTM procedures, as the group of 50 feed coals and density separates provided by Eskom. Table 9 gives the concentrations of Hg in the coal and ash samples. Good agreement was obtained between USGS analyses and the original EPA analysis, as discussed in Appendix 1.

The coal Hg content of the Kendal samples was 248 ± 80 ppb (on an as-determined basis) and the average of the Duvha samples was 208 ± 57 ppb (as-determined). These Hg values are consistent with those of the boiler feed coal samples received from Eskom for the respective plants, which ranged from 180 to 220 ppb for Kendal and 180 to 210 ppb for Duvha. Some difference in Hg contents between Kendal and Duvha stations might be expected due to differences in the coal milling process at each station. At Duvha, pyrite is rejected in the milling process whereas at Kendal it is not. However, this difference is not apparent in the present sampling. Mill input coal for Units 5 and 6 at Kendal has somewhat elevated Hg contents (347 to 361 ppb) but this is not reflected in the ash. Figure 12 displays the MFC coal and fly ash Hg concentrations as a function of unit number for both plants. Duvha, units 4-6 and all the Kendal units have ESPs, while Duvha, units 1-3, have FFs (section 4.4).

Chlorine contents of the 24 Duvha and Kendal MFC coals collected in 2010 are shown in Fig. 13, in comparison with 7 samples from the group of 42 new pulverized feed coal samples provided by Eskom, including 3A to 3C (Duvha) and 6A to 6D (Kendal; Table 6). For both groups of samples, results confirm Cl levels are low, in some cases just above the detection limit of 100 ppm, and in most cases below the detection limit. These contents do little to promote Hg self-capture, as discussed in the following sections.

Table 9. Mercury analysis, 2010 samples, Duvha and Kendal power stations (ppb, as-determined basis) analyzed in USGS Reston laboratories.

Power Station	Unit	Sample	Material	Hg Conc. [ppb]	Sample	Material	Hg Conc. [ppb]
Kendal	1	KFC-1A	Coal	188	KFA-1A	Fly ash	89.3
Kendal	1	KFC-1B	Coal	167	KFA-1B	Fly ash	88.3
Kendal	2	KFC-2A	Coal	196	KFA-2A	Fly ash	80.5
Kendal	2	KFC-2B	Coal	249	KFA-2B	Fly ash	103
Kendal	3	KFC-3A	Coal	199	KFA-3A	Fly ash	57.9
Kendal	3	KFC-3B	Coal	205	KFA-3B	Fly ash	53.9
Kendal	4	KFC-4A	Coal	188	KFA-4A	Fly ash	146
Kendal	4	KFC-4B	Coal	174	KFA-4B	Fly ash	157
Kendal	5	KFC-5A	Coal	347	KFA-5A	Fly ash	84.9
Kendal	5	KFC-5B	Coal	361	KFA-5B	Fly ash	77.3
Kendal	6	KFC-6A	Coal	359	KFA-6A	Fly ash	30.1
Kendal	6	KFC-6B	Coal	348	KFA-6B	Fly ash	35.2
Duvha	1	DFC-1A	Coal	150	DFA-1A	Fly ash	152
Duvha	1	DFC-1B	Coal	137	DFA-1B	Fly ash	203
Duvha	2	DFC-2A	Coal	177	DFA-2A	Fly ash	615
Duvha	2	DFC-2B	Coal	175	DFA-2B	Fly ash	641
Duvha	3	DFC-3A	Coal	158	DFA-3A	Fly ash	687
Duvha	3	DFC-3B	Coal	166	DFA-3B	Fly ash	678
Duvha	4	DFC-4A	Coal	261	DFA-4A	Fly ash	126
Duvha	4	DFC-4B	Coal	306	DFA-4B	Fly ash	130
Duvha	5	DFC-5A	Coal	206	DFA-5A	Fly ash	208
Duvha	5	DFC-5B	Coal	221	DFA-5B	Fly ash	215
Duvha	6	DFC-6A	Coal	285	DFA-6A	Fly ash	180
Duvha	6	DFC-6B	Coal	253	DFA-6B	Fly ash	200

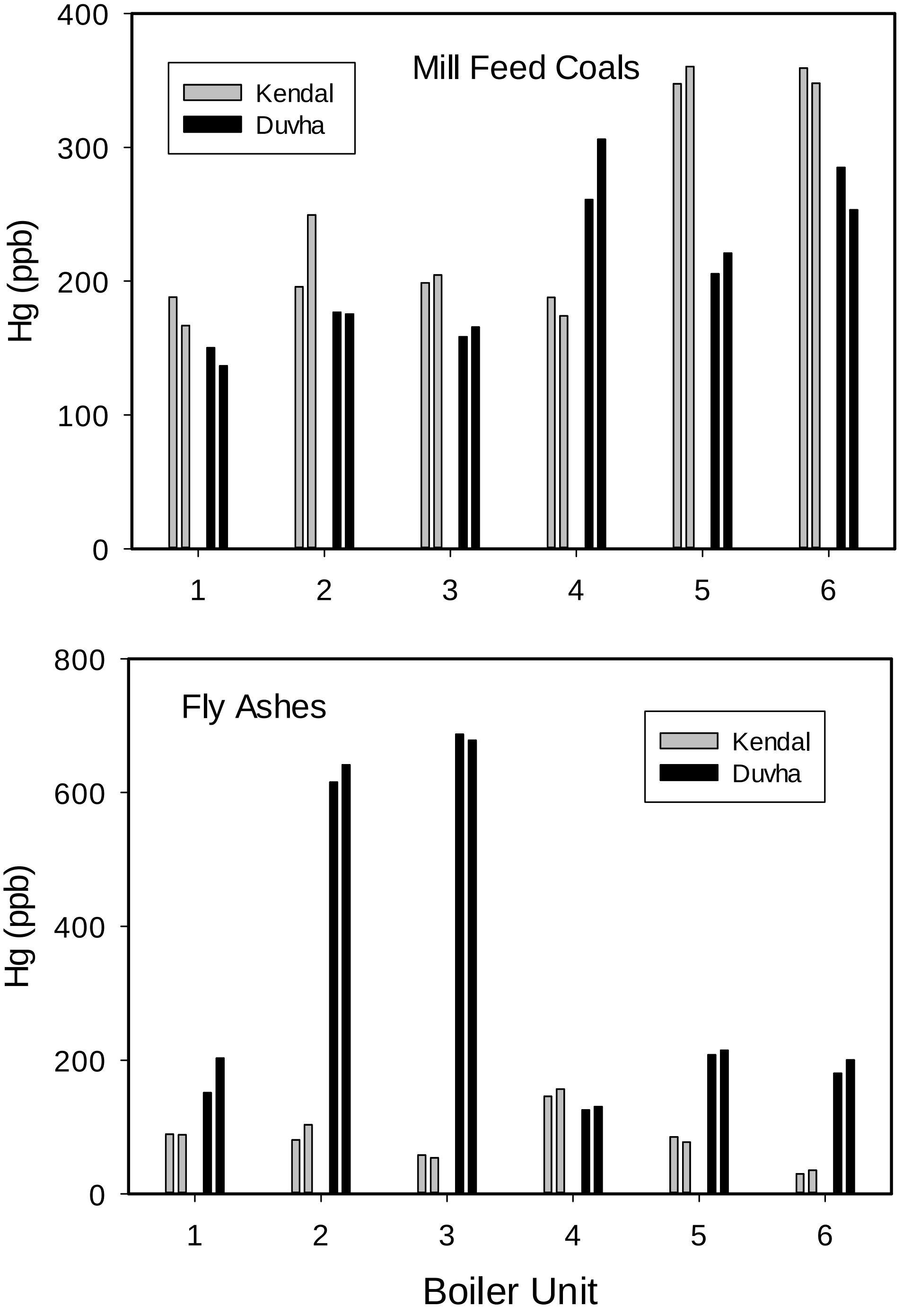

Figure 12. Mercury data for duplicate mill feed coal (upper plot) and fly ash (lower plot) samples collected from Duvha and Kendal power stations in previous UNEP-sponsored sampling. Duvha Units 1-3 are equipped with fabric filters; all other units have ESPs. Samples are courtesy of U.S. EPA.

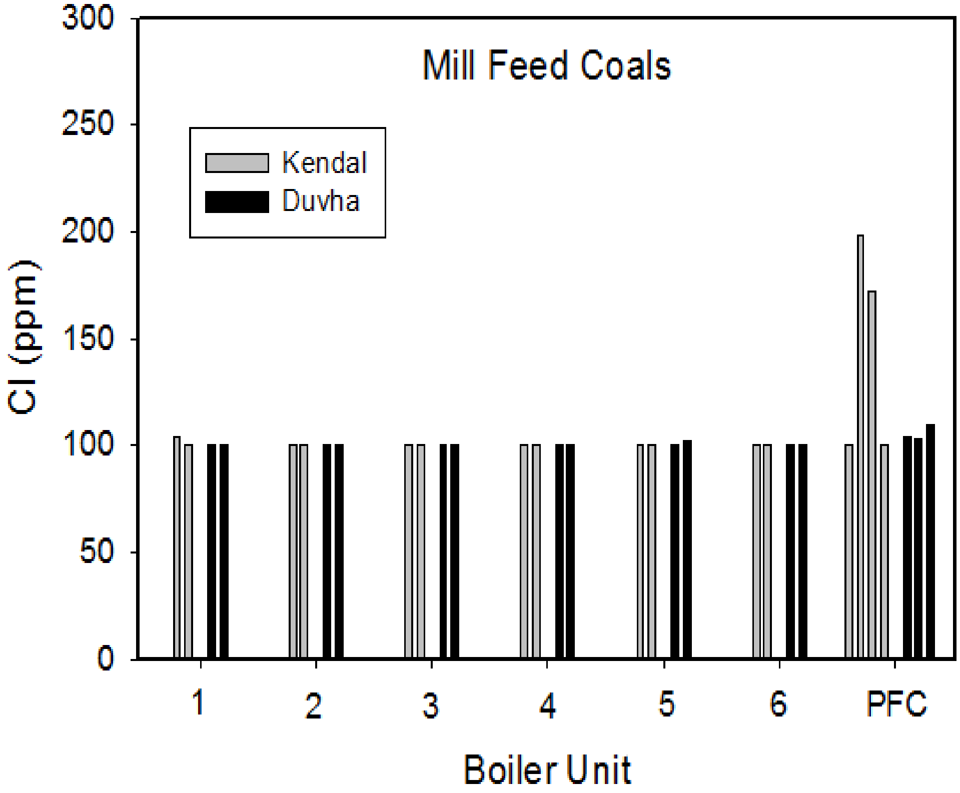

Figure 13. Chlorine data by boiler for raw mill feed coal samples from Duvha and Kendall power stations collected in 2010 EPA-DEA sampling (boilers 1-6) and Cl data for samples 6A-D (Kendal) and 3A-C (Duvha) from the group of 42 pulverized feed coal samples provided by Eskom in the present study (FC). Results show that for most samples Cl content is at or below the detection limit of 100 ppm. Samples having Cl contents below detection are plotted at the detection limit (100 ppm). Results confirm that feed coals used in these power stations have low Cl contents and therefore do little to promote Hg self-capture by APCD's.

4.3 Emission and Speciation Data

Table 10 reproduces the reported data from Duvha and Kendal power stations on the Hg concentrations in the stack gas, as well as the fraction of that Hg that was in the oxidized form. Differences between the Duvha units with FFs and ESPs are apparent. Stack emissions are lower on the units with FFs; a correspondingly high concentration of Hg is present in the fly ash from the FF units (Fig. 12). As discussed below, FFs generally exhibit higher efficiency for Hg capture than ESPs, which is borne out by the Duvha results. There is also more oxidized Hg at the stack in the Duvha units with FFs as compared to the units with ESPs. The results from Kendal, which has ESPs on all six units, are similar to the results from the ESP units at Duvha.

Table 10. Mercury stack concentrations and speciation, Duvha and Kendal power stations (Scott, 2011).

Power Station	Unit Number	Average Hg, $\mu g/m^3$ @ 3% O_2	Fraction of oxidized Hg (% Hg^{2+})
Duvha	1	13.81	89%
	2	4.65	73%
	3	4.09	88%
	4	35.49	56%
	5	29.01	54%
	6	40.37	55%
Kendal	1	39.20	70%
	2	43.45	54%
	3	49.13	52%
	4	46.03	52%
	5	39.47	48%
	6	46.34	54%

4.4 Mass Balance Calculations

The fractions of Hg removed in the particulate control devices at Duvha and Kendal, were estimated from the concentrations of Hg in the coal and fly ash. For these estimates, it was assumed that: 1) Hg in the MFC is representative of the PFC; 2) the ash content of the coal is the average of the PFC Eskom samples; and 3) the carryover of fly ash from the boiler is 80%, a typical proportion. Figures 14 and 15 show the estimated Hg collection efficiency of the particulate control devices at Duvha and Kendal, respectively. The Hg collection efficiency for the ESPs at Kendal ranged from 2% to 22% (10% average). The average Hg collection efficiency for the boilers with ESPs at Duvha was 17%, while the average Hg collection efficiency for the boilers with FFs was 72%.

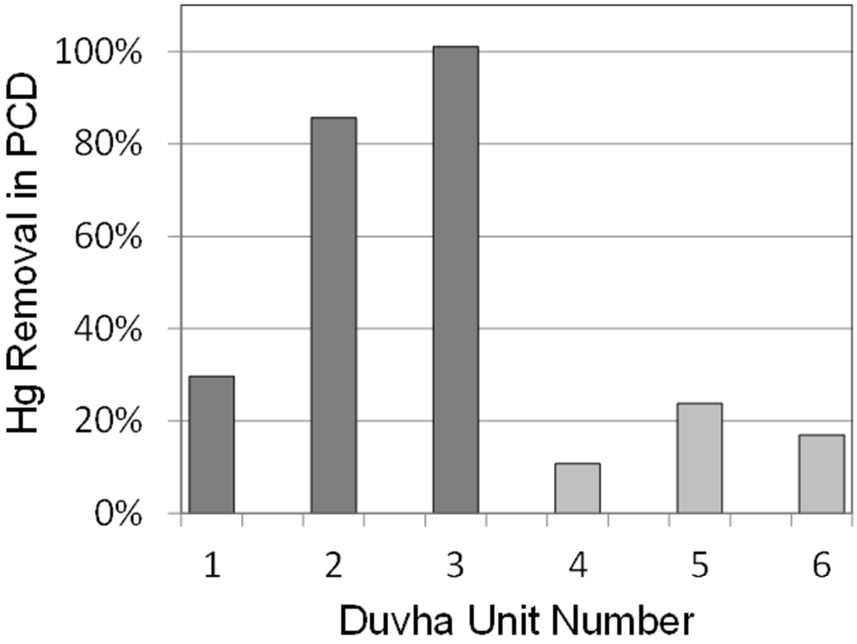

Figure 14. Estimated mercury (Hg) removal across particulate control devices (PCDs) at Duvha power station. Duvha units 1-3 are equipped with fabric filters; all other units have ESPs.

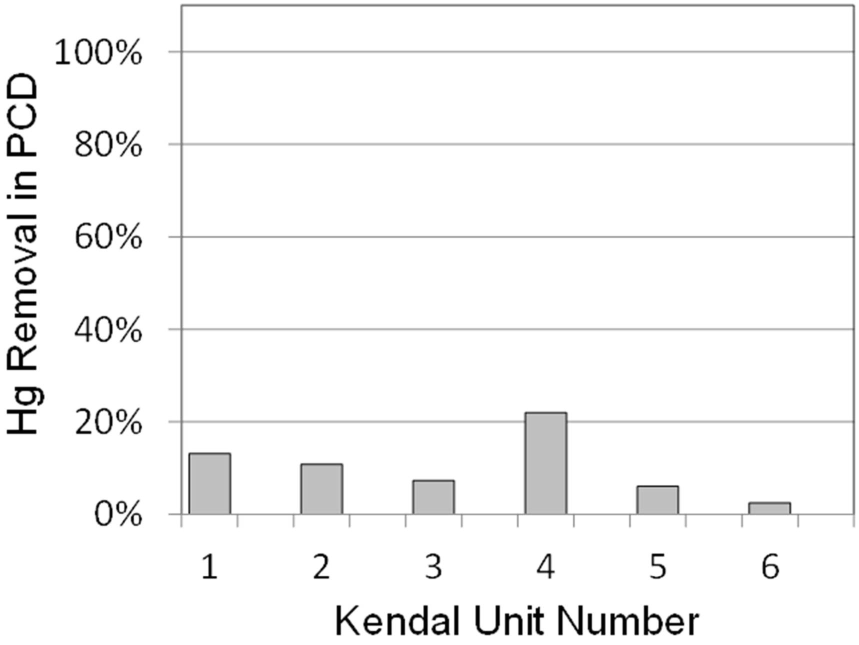

Figure 15. Estimated mercury (Hg) removal across particulate control devices (PCDs) at Kendal power station. All units have ESPs.

4.5 Comparison with Previous Results

There are clear differences between units with FFs and units with ESPs in terms of Hg capture in the particulate control devices, Hg stack emissions, and the speciation of emitted Hg. The factors that affect Hg speciation and emission are discussed in more detail in the next section. A preliminary comparison of the Duvha and Kendal results with other coal-fired boilers will be made here, and subsequently discussed in more detail.

In 1999, the EPA Information Collection Request (ICR) collected data from 83 coal-fired power plants in the United States, consisting of coal samples and speciated Hg measurements at the stack and upstream of the last air pollution control device (Kilgroe et al., 2002). Using these data, one can calculate the fraction of oxidized Hg at the outlet and the removal efficiency of Hg for particulate control devices.

The Cl content of the coal is one of the primary indicators for Hg behavior and fate in coal-fired boilers. The speciation of Hg after the particulate control device is shown as a function of coal Cl content in Figure 16. Individual data points are from the 1999 ICR, while the bars indicate the range of data from Duvha and Kendal. Generally, the fraction of oxidized Hg is higher downstream of FFs than ESPs and is a function of the coal Cl content. The fraction of oxidized Hg at the outlet of the Duvha units with FFs is consistent with the ICR data. Most of the data from the ESP units fall in the range of 40-55% Hg^{2+}, which is consistent with ICR data; the exception is one data point (70% Hg^{2+}) from Kendal power station, which is higher than most of the other ESP data.

Mercury removal (Figure 17) across ESPs is generally low for coals with Cl contents of 100 to 200 ppm, and the Hg removals estimated for the Duvha and Kendal units with ESPs fall in line with the 1999 ICR data. Removal of Hg across FFs is higher than removal across ESPs, as can be seen in the figure. The range of estimated Hg removal across the FFs of the Duhva units is large, but consistent with the 1999 ICR data range.

5. Discussion

5.1 Potential for Mercury Capture in Coal-fired Power Plants with Conventional Controls

There are only two pathways by which Hg can be removed from coal-fired boilers: collection of Hg that has been adsorbed on surfaces (for example, fly ash and sorbents) and absorption of oxidized gaseous Hg species in aqueous media (for example,, FGD, not employed by Eskom).

Additionally, factors that influence the capacity for a particulate control device to remove Hg include: 1) Type of particulate control device; 2) Chlorine content of coal; 3) Concentration of unburned carbon in fly ash; 4) Temperature of particulate control device; and 5) Concentration of SO_3 in the flue gas.

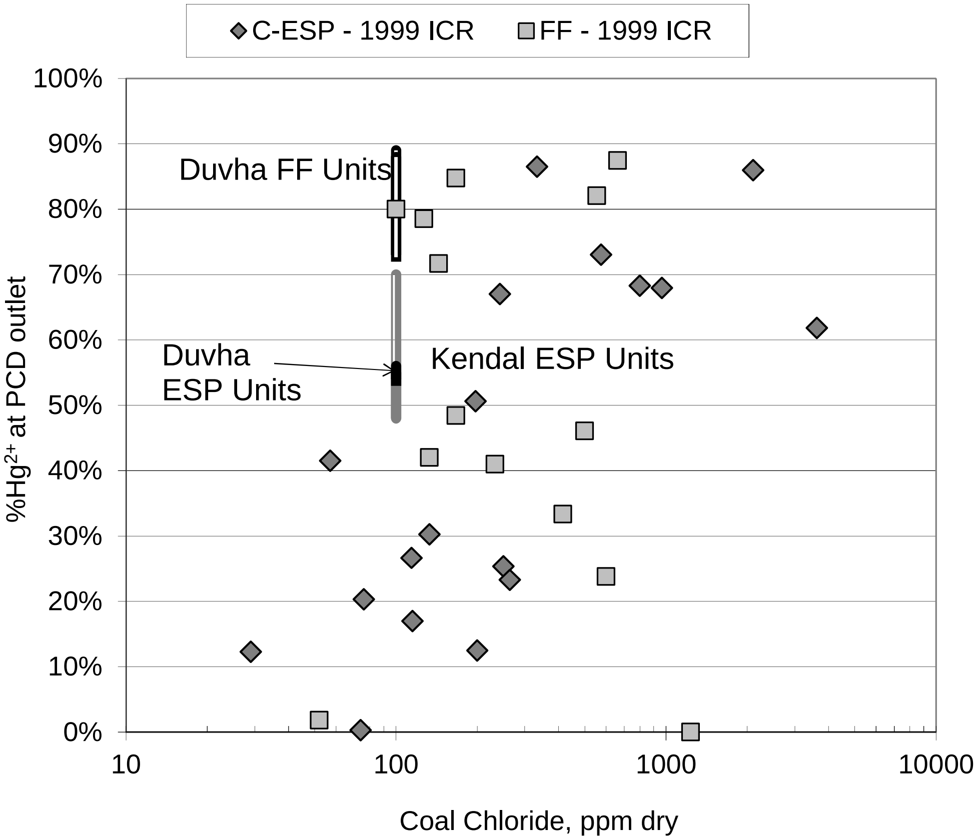

Figure 16. Fraction of oxidized mercury (Hg2+) at the particulate control device (PCD) outlet as a function of coal chlorine content (in parts per million [ppm]): comparison of data from Duvha (fabric filter [FF] and cold-site electrostatic precipitator [C-ESP] units) and Kendal power stations with EPA 1999 Information Collection Request (ICR) data.

Oxidation of the elemental Hg that is present in the flame zone is the key step in the transformation of Hg into forms that can adsorb and/or absorb in downstream air pollution control equipment. Gaseous elemental Hg is oxidized by Cl radicals in the flue gas at temperatures between 300°C and 700°C, which corresponds to the boiler region from the economizer inlet to the air heater inlet. Gas-phase oxidation cannot explain the amount of gaseous oxidized Hg observed in coal-fired boilers. Heterogeneous oxidation (that is, catalyzed by surfaces) is responsible for the formation of most of the gaseous oxidized Hg by Cl species.

Significant oxidation of Hg takes place in the air preheater, and this might be catalyzed by fly ash and/or the heat exchange surface.

Mercury adsorption on carbon surfaces is used in many applications to capture Hg both from gas and liquid media. In a coal-fired power plant, the fly ash often contains unburned carbon from less-than-complete combustion of the coal, and this unburned carbon can adsorb Hg. The unburned carbon content of the fly ash is often correlated with the removal of Hg across ESPs (Senior and Johnson, 2005) and fabric filters (La Marca, et al., 2006). The temperature of the flue gas at the particulate control device also affects capture of Hg by fly ash particles and the subsequent removal in the particulate control device.

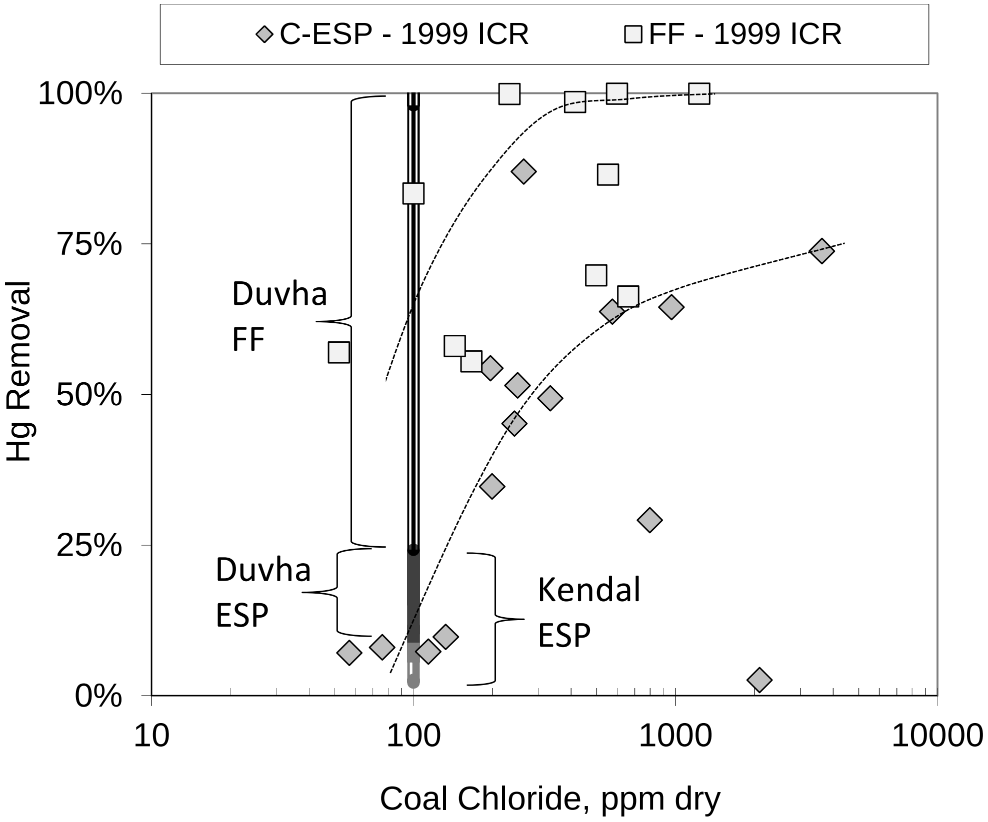

Figure 17. Removal of mercury (Hg) across the particulate control device outlet as a function of coal chlorine content (in parts per million [ppm]): comparison of data from Duvha (fabric filter [FF] and cold side electrostatic precipitator [C-ESP] units) and Kendal power stations with EPA 1999 Information Collection Request (ICR) data .

Certain other constituents in flue gas have negative impacts on the ability of either unburned carbon in fly ash or powdered activated carbon (PAC) to remove Hg (PAC can be added to the flue gas to enhance Hg removal). Sulfuric acid vapor (SO_3 or H_2SO_4) in particular can reduce the effectiveness of carbon surfaces to adsorb Hg. An example of this (pilot-scale testing reported by Pollack, 2009) is shown in Figure 18. The test results shown in the figure are from activated carbon injection, but a similar effect would be expected with unburned carbon in ash. That is, an increase in SO_3 in the flue gas upstream of the particulate control device would have the effect of reducing the adsorption of Hg by unburned carbon in ash.

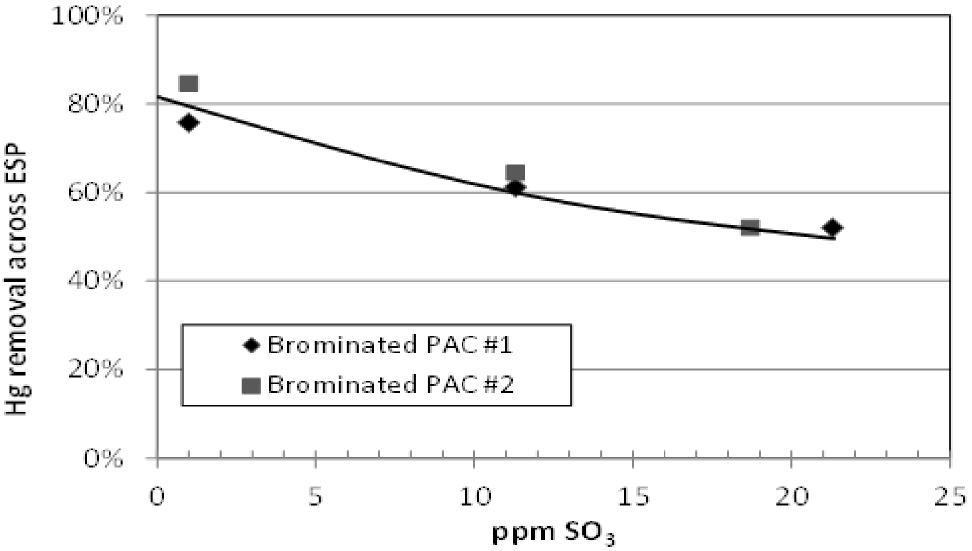

Figure 18. Effect of SO_3 addition on performance of brominated activated carbon for mercury removal. Figure shows results from injection of 160 mg/m^3 PAC upstream of the air preheater (APH) at the pilot combustor. Temperature at the APH inlet is 150 °C. Test assumes a baseline SO_3 concentration of 1 ppm . (Source: Pollack, 2009).

Halogen compounds have long been identified as the most important species for oxidizing Hg in coal combustion systems. Chlorine is the most abundant halogen in coal. Coal Cl content had a strong influence on the oxidation state of Hg in the flue gas as well as the removal of Hg in certain air pollution control devices (as previously illustrated in Figures 16 and 17). The longer contact time between ash particles and Hg-containing flue gas in a fabric filter, as compared to an ESP, means that the removal of Hg by fabric filters is almost always higher than removal by ESPs.

Some of the scatter in the data may be due to the other factors discussed: level of unburned carbon in the ash, temperature at the particulate control device, and concentration of SO_3 in the flue gas. The units at Duvha with FFs, units 1-3, do not have uniformly high levels of Hg removal. Unit 1 has a much lower Hg removal than Unit 2 or Unit 3. This is corroborated by the higher gaseous Hg emission from Unit 1 as compared to Unit 2 and 3. This is mostly likely due to a combination of two factors: the level of unburned carbon in the fly ash and the temperature of the FF. Neither of these parameters was reported in the 2010 sampling. Coal-fired boilers that are nominally “identical” can exhibit differences in combustion efficiency, which can be manifested as different amounts of unburned carbon in the fly ash. Differences in heat transfer between boilers can result in differences in gas temperatures at the air pollution control devices (Senior, 2014).

Hg removal across ESPs at the different units at Duvha or Kendal also shows considerable variation, from about 2% removal to about 22% removal. The factors that are likely responsible are unburned carbon in fly ash, ESP temperature, and the concentration of SO_3, which is added to the flue gas as a conditioning agent to improve the collection of ash in the ESP. None of these parameters are known for the sampling campaigns at Duvha and Kendal.

5.2 Potential for Improving Mercury Capture of Eskom Fleet

5.2.1 Coal Selection and Coal Washing

Combined results from laser ablation ICP-MS of pyrite and bulk analysis of density separates for a Highveld (#4) coal indicate that reduction of Hg and As by coal washing of #4 coal should be straightforward, as both elements reside almost exclusively in pyrite. The extent to which coal washing is effective in reducing pyrite contents should be reflected in the reduction of these elements. Other elements of environmental concern, such as Mn, Cr, Co, Ni, and Pb, while present in pyrite at measurable levels, likely have competing modes of occurrence in the Highveld coal that make it difficult to predict the extent of their reduction upon coal washing without further investigation. The low overall As content in Highveld coals is explained by relatively low concentrations of As in pyrite, approximately 50 ppm on average. Arsenic is the most abundant minor constituent in Fe-disulfides in coal, reaching percent levels in some cases, and in many cases measurable with electron beam instruments having detection limits that are poorer than laser ablation ICP-MS used in the present study (Kolker, 2012). Analysis of density separates of Highveld (#4) coal indicates that Hg input to the boiler can be reduced by discarding the stone fraction, as is practiced by Eskom. , Retention of as much of the low-ash fraction as is practical will also reduce Hg input to the boiler, and would potentially have co-benefits in efficiency of operation. Results for feed coals and coal density separates in the present study, together with other published results, indicate that coal products used for power generation in South Africa are typically enriched by about a factor of four in Hg concentration relative to washed low-ash coals that are exported.

5.2.2 Optimization of Equipment and Operational Parameters

In order to decrease emissions of Hg from a coal-fired boiler (for a given level of Hg input), both equipment and operational changes can be considered. As noted above, Hg is removed by adsorption on solids and the subsequent collection of those solids in a particulate control device or by absorption of Hg in a flue gas desulphurization scrubber. To increase Hg removal in the Eskom fleet several approaches are available, here listed in order of increasing capital and operating cost:

Optimizing operating conditions. Mercury can be adsorbed on the unburned carbon in fly ash. Certain operational changes in the boiler can increase the adsorption of Hg by the fly ash; these include lowering the air preheater exit temperature, minimizing the concentration of SO_3/H_2SO_4 in the flue gas, and increasing the amount of unburned carbon in the ash. As commercial reuse of fly ash in South Africa is extremely limited, increasing its carbon content would not impact ash marketing for beneficial use. Lowering the air preheater exit temperature will also have a slight positive effect on the boiler efficiency, whereas increasing unburned carbon in fly ash will have a slight negative effect on boiler efficiency and these effects may offset one another. The presence of SO_3 in the flue gas is beneficial to the operation of an ESP.

Addition of fabric filters. Changes in air pollution control equipment can improve Hg capture. Fabric filters are generally more efficient at removing Hg than ESPs, as demonstrated under Section 4.. The ESP can be replaced by a fabric filter, either by installing a fabric filter within the existing ESP casing or by bypassing the existing ESP and installing a separate fabric filter unit.

Use of sorbents. The addition of reagents and/or sorbents can improve Hg capture in existing air pollution control devices. For low-Cl coals, such as those from South Africa, the addition of halogens (Cl, and Br, primarily) to the fuel or the boiler will increase the removal of Hg. The equipment for halogen addition is relatively inexpensive, but there will be additional operating costs because of the cost of the halogen compound. Powdered sorbents (e.g., activated carbon) can be injected into the flue gas upstream of the particulate control device to capture additional Hg. The cost of equipment required to inject powdered sorbents is higher than that of a halogen addition system, but it is still relatively low. Operating costs will increase, due to the cost of the sorbent, and the increase in operating costs can be significant, depending on the sorbent requirements. Less sorbent will be required if the unit has a fabric filter instead of an ESP. Alternatively, a dedicated fabric filter can be installed downstream of an existing ESP. A Hg control sorbent can be injected into the fabric filter in this arrangement, known as a TOXECON™ fabric filter. Because the fly ash is almost entirely collected in the ESP, the TOXECON[2] fabric filter can be much smaller (less capital cost) than a fabric filter that is designed to remove fly ash and sorbent.

Addition of FGD. Eskom's current fleet of coal-fired boilers has particulate control devices, but does not have flue gas desulphurization (FGD) scrubbers. If FGD scrubbers were installed, they

---

[2] Use of trade names is for descriptive purposes and does not constitute endorsement by the UNEP or the U.S. Geological Survey.

would remove gaseous oxidized Hg with an efficiency of 90% or higher. At Duvha and Kendal, gaseous oxidized Hg amounted to about 50% at the exit of the ESPs and 70% to 90% at the exit of the FFs. Higher levels of Hg oxidation in the flue gas, particularly on units with ESPs can be achieved through the addition of halogens to the fuel or boiler. The capital cost of adding a FGD scrubber is higher than that of adding a fabric filter or a sorbent injection system and is probably too high to be justified on the grounds of Hg removal alone. However, if future regulations require reductions in the emissions of SO_2 and FGDs are installed to meet these standards, there will be additional reduction in Hg emissions.

6. **Summary and Conclusions**

Results for feed coals provided for this study by Eskom show input Hg concentrations that are similar to or slightly less than those in previous results. Input Hg for three older power stations re-commissioned beginning in the late 2000's after extended shutdowns (Camden, Grootvlei, and Komati stations), is similar to the range obtained for other Eskom power stations. Results for the Matimba power station burning Waterberg coals show that coal washing currently in use is effective in reducing Hg levels to the range of those of other Eskom power stations. This finding is promising for supplying the future Medupi power station that will also use Waterberg coals and require a similar approach. Cl contents of South African coals are generally low. As such, the extent of Hg self-capture by particulate control devices is relatively limited.

Results for density separates of a Highveld (#4) coal are useful in predicting Hg variation in coal products used in South Africa or exported. Results for these separates show a strong mineralogical association of Hg (and As) with pyrite. Reduction of pyrite by coal washing is very likely to result in reduced Hg contents, as well as lowering sulfur emissions. To the extent possible, retention of a greater portion of the low-ash fraction would also reduce Hg input to the boiler and potentially have co-benefits in efficiency of operation. Additional study is needed to predict the coal washing behavior of other South African coals, but comparison of Hg contents in coals used for power generation with those of washed export coals shows that significant percentages of mercury reduction can be achieved by coal washing.

Helping improve estimates of Hg emissions is one of the goals of this study. To estimate Hg emissions, general conclusions about emission factors can be drawn from knowledge of the type of particulate control device and the coal composition (Cl and S contents, in particular). However, variation in operating conditions in the boiler and air pollution control devices affect the Hg emission factors. Greater accuracy in estimation of emission factors can be achieved if differences in these operating conditions are considered.

A relatively simple and inexpensive way to quantify Hg emissions from Eskom plants, which only have a particulate control device for air pollution control, is to collect paired coal and fly ash samples. This approach would allow Eskom to track the relative performance of its air pollution control devices in removing Hg. Analysis of these samples to assess Hg capture on a unit-by-unit basis would provide a much better estimate of the Hg emission rate from the plant than simply assigning a fixed emission factor based on the type of particulate control device, as has been done in previous estimates.

Apart from optimizing coal selection, using more washed coal, and better monitoring of PCD performance, low-cost options for improving Hg capture include simple operational changes such as increasing mercury adsorption on unburned carbon. This can be accomplished by lowering the air preheater exit temperature, to increase the amount of unburned carbon in the ash, as well as minimizing the concentration of SO_3/H_2SO_4 vapor in the flue gas. Equipment options include addition of fabric filters, use of halogenated sorbents, and addition of flue gas desulphurization (FGD) scrubbers, listed in order of increasing cost. The capital cost of adding FGD scrubbers to existing plants is probably too high to be justified only for Hg removal but may be appropriate if future regulations require reduction of SO_2 emissions.

References

AMAP/UNEP, 2013, Technical Background Report for the Global Mercury Assessment 2013: published by Arctic Monitoring and Assessment Programme, Oslo, Norway and UNEP Chemicals Branch, Geneva, Switzerland, 263 p.

ASTM, 2013a, ASTM D3761-13: Standard test method for total fluorine in coal by the oxygen bomb combustion/ion selective electrode method, 4 p., www.astm.org/Standards/D3761.htm , accessed Jan 22, 2014.

ASTM, 2013b, ASTM D4208-13: Standard test method for total chlorine in coal by the oxygen bomb combustion/ion selective electrode method, 4 p., www.astm.org/Standards/D4208.htm , accessed Jan 22, 2014.

Bergh, J.P., 2010, The partitioning of trace elements in the No. 4 seam of the Witbank Coalfield: M.S. thesis, University of the Witwatersrand, 87 p.

Cameron, E.N., 1977, Chromite in the central sector of the Eastern Bushveld Complex, South Africa: American Mineralogist, v. 62, p. 1082-1096.

Dabrowski, J.M., Ashton, P.J., Murray, K., Leaner, J.J., and Mason, R.P., 2008, Anthropogenic mercury emissions in South Africa: Coal combustion in power plants: Atmospheric Environment, v. 42, p. 6620-6626.

Falcon, R.M.S., 1986, Classification of coals in southern Africa: in, Annhaesser, C.R., and Maske, S., eds., Mineral deposits of southern Africa, vol. II, Geological Society of Southern Africa, p. 1899-1921 [not seen].

Forte, Jr., R., Ryan, J.V., Johnson, T.P., and Kariher, P.H., 2012, The United States Environmental Protection Agency's Mercury Measurement Toolkit: An Introduction: Energy & Fuels, v. 26, p. 4643-4646.

Gericke, G., Surender, D., and Delport, W., 2007, Executive summary of mercury research and trace element behavior, Eskom Report C096501, Eskom, Johannesburg (results given in Scott, 2011).

Huggins, F.E., and Huffman, G.P., 1995, Chlorine in coal: An XAFS spectroscopic investigation: Fuel, v. 74, p. 556-569.

Hulbert, L.J., and Von Gruenewaldt, G., 1985, Textural and compositional features of chromite in the Lower and Critical Zones of the Bushveld Complex south of Potgietersrus: Economic Geology, v. 80, p. 872-895.

Jeffrey, L.S., 2005, Characterization of the coal resources of South Africa: The Journal of the South African Institute of Mining and Metallurgy, p. 95-102.

Ketris, M. P., and Yudovich, Y. E., 2009, Estimations of Clarkes for Carbonaceous biolithes: World averages for trace element contents in black shales and coals: International Journal of Coal Geology, v. 78, p. 135-148.

Kilgroe, J.D., Sedman, C.B., Srivastava, R.K., Ryan, J.V., Lee, C.W., and Thorneloe, S.A., 2002, Control of Mercury Emissions From Coal-Fired Electric Utility Boilers: Interim Report Including Errata Dated 3-21-02, U.S. EPA Report EPA-600/R-01-109, Office of Research and Development, National Risk Management Research Laboratory, Research Triangle Park, NC, April 2002.

Kolker, A., 2012, Minor element distribution in iron-disulfides in coal: A geochemical review: International Journal of Coal Geology, v. 94, p. 32-43.

Kolker, A., and Quick, J. C., 2014, Mercury and halogens in coal, in, Granite, E., Pennline, H., and Senior, C., eds., Mercury emissions control for coal-derived gas steams, Wiley-VCH.

La Marca, C., Bianchi, A., Cioni, C., and Malloggi, S., 2006 Impact of Combustion System on Mercury Speciation and Removal in Coal-Fired Units. Italian Section of the Combustion Institute, Proceedings of the 29th Meeting on Combustion, Pisa, Italy, June, 2006, 6 p.

Leaner, J., Dabrowski, J., Mason, R., Resane, T., Richardson, M., Ginster, M., Euripides, R., and Masekoameng, E., 2009, Mercury emissions from point sources in South Africa, in Pirrone, N., and Mason, R., (eds.), Mercury fate and transport in the global atmosphere, Springer Verlag, p. 113-130.

Masekoameng, E., Leaner, J., and Dabrowski, J., 2010, Trends in anthropogenic mercury emissions estimated for South Africa during 2000-2006: Atmospheric Environment, v. 44, p. 3007-3014.

Pacyna, J.M., and Pacyna, E.G., 2001, An assessment of global and regional emissions of trace metals to the atmosphere from anthropogenic sources worldwide: Environmental Reviews, v. 9, p. 269-298.

Peatfield, D., 2003, Coal and coal preparation in South Africa- A 2002 review: Journal of the South African Institute of Mining and Metallurgy, July/August 2003, p. 355-372.

Pollack, N. R., 2009, Novel carbon based sorbents for high SO_3 applications: Proceedings, Air Quality VII, Arlington, VA, October, 2009, 10 p.

Pretorius, C.C., Boshoff, H.P., and Pinheiro, H.J., 2002, Analysis of coal product samples of South African Collieries, 2001-2002: Bulletin 114, Energy Branch, South African Department of Minerals and Energy, Coal and Mineral Technologies (Pty) Ltd, South African Bureau of Standards, Pretoria, 25 p.

Roos, B. L., 2011, Mercury emissions from coal-fired power stations in South Africa: M.S. thesis, University of Johannesburg, 84 p.

Sanford, R.F, Pierson, C.T., and Crovelli, R.A., 1993, An objective replacement method for censored geochemical data: Mathematical Geology, v. 25, no. 1, p. 59-80.

Scott, G., 2011, Reducing mercury emissions from coal combustion in the energy sector in South Africa: Final Project Report, UNEP Global Mercury Partnership, Mercury in Coal Project Area, www.unep.org/ , 18 p., accessed Dec. 17, 2013.

Senior, C. L., and Johnson, S.A., 2005, Impact of carbon-in-ash on mercury removal across particulate control devices in coal-fired power plants: Energy and Fuels, v. 19, p. 859-863.

Senior, C.L., 2014, Mercury behavior in coal combustion systems, in, Granite, E., Pennline, H., and Senior, C., eds., Mercury emissions control for coal-derived gas steams, Wiley-VCH.

Snyman, C.P., and Botha, W. J., 1993, Coal in South Africa: Journal of African Earth Sciences, v. 16, no. 1/2, p. 171-180.

Tewalt , S. J., Belkin, H.E., SanFilipo, J.R., Merrill, M.D., Palmer, C.A., Warwick, P.D., Karlsen, A.W., Finkelman, R.B., and Park, A.J., 2010, Chemical analyses in the world coal quality inventory, version 1: U.S. Geological Survey Open File Report 2010-1196, http://pubs.usgs.gov/of/2010/1196/, 4 p. and data files, accessed Jan. 22, 2014.

U.S. Environmental Protection Agency (EPA),, 2007, Method 7473, Mercury in solids and solutions by thermal decomposition, amalgamation, and atomic absorption spectrophotometry, http://www.epa.gov/wastes/hazard/testmethods/sw846/pdfs/7473.pdf, 17 p., accessed Feb. 25, 2014

U.S. Environmental Protection Agency (EPA), 2008, Method 30B, Determination of mercury from coal-fired combustion sources using carbon sorbent traps, http://www.epa.gov/ttn/emc/methods/method30B.html , 39 p., accessed Feb. 4, 2014.

U.S. Environmental Protection Agency (EPA),, 2011, Mercury and Air Toxics Standards (MATS): http://www.epa.gov/mats/pdfs/20111216MATSfinal.pdf, 1117 p., accessed Feb. 4, 2014

Vosteen, B.W., Winkler, H., and Berry, M.S., 2010, Native halogens in coals from USA, China and elsewhere- Low chlorine coals need bromide addition for enhanced mercury capture: Proceedings, 2010 Power Plant Air Pollutant Control "MEGA" Symposium, Baltimore, MD, Paper 103, 22 p.

Wagner, N.J., and Hlatshwayo, B., 2005, The occurrence of potentially hazardous trace elements in five Highveld coals, South Africa: International Journal of Coal Geology, v. 63, p. 228-246.

Wagner, N. J., and Tlotleng, M.T., 2012, Distribution of selected trace elements in density fractionated Waterberg coals form South Africa: International Journal of Coal Geology, v. 94, p. 225-237.

Wilson, S. A., Ridley, W.I., and Koenig, A.E., 2002, Development of sulfide calibration standards for the laser ablation inductively-coupled plasma mass spectrometry technique: Journal of Analytical Atomic Spectrometry, v. 17, p. 406-409.

World Coal Association, 2014, Coal Facts 2013, http://www.worldcoal.org/resources/coal-statistics/, 3 p., accessed Feb. 4, 2014.

Appendix 1. Analytical Quality Assurance and Inter-laboratory Comparisons

Mercury Analysis

Mercury contents were determined on sample powders at the USGS Eastern Energy Resources Science Center in Reston, Virginia, using a Nippon MA-3000 instrument and at the USGS Central Energy Resources Science Center, in Denver, Colorado, using a Milestone DMA-80 instrument. Both instruments are commercially-available dedicated direct Hg analyzers. Each instrument employs EPA Method 7473, in which samples are heated and the evolved Hg is selectively captured as an amalgam and measured by atomic absorption spectrophotometry (U.S. EPA, 2007). The Reston MA-3000 has a detection limit of 0.002 ng Hg with automatic switching between low (0 to 10 ng) and high (> 10 ng) dynamic measurement ranges. In tests of this instrument for coal samples, a sample size of 50 mg was found to insure complete thermal decomposition. The MA-3000 is calibrated using solutions prepared from high purity $HgCl_2$ at concentrations ranging from 0 to 200 ng Hg. Using these solutions, calibrations of 0.9999 or better are obtained.

Results for replicate analysis of sample unknowns using the Reston instrument are given in Table A1 and analyses of NIST standard 1632d (trace elements in coal) and NIST Standard 1633c (trace elements in fly ash) are given in Table A2. Reproducibility of the analyses is within 10-20% or better and NIST standard values are attained when run as unknowns. These values are typical of what is obtainable with this type of instrumentation. Results are especially good, considering the distribution of pyrite, and of Hg within pyrite, are heterogeneous within the samples determined, especially the density separates. These heterogeneities can contribute to inconsistent results due to a nugget effect for Hg in which overall Hg distribution is strongly controlled by Hg-enriched domains and large variation can result depending on whether these domains are included in the analysis or missed.

The 42 feed coal samples and 8 density separates run on the Reston instrument were re-run in Denver as part of the USGS multi-element package. These results are compared in Fig. A1. There is no systematic difference between the two labs, and in most cases, the results agree within 20% or better. For the feed coals, three samples (9B, 12A, and 12B) give values that deviate by more than 25% between the two labs (Fig. A1). For the density separates, another three samples (14E, 14F, and 14G) show poor agreement between the Denver and Reston determinations (Fig. A1). These 6 samples were reanalyzed by both labs and in each case, the re-runs show better agreement and the average of multiple determinations is between the two original analyses (Table A3).

With the exception of feed coal samples 9B, 12A, and 12B for which averages of 5 available runs are reported, Hg results presented for the group of 42 feed coals samples in this report are from the Reston lab. The 48 samples of feed coal and fly ash from the 2010 sampling at Kendal and Duvha power stations were analyzed for Hg only in the Reston lab, and inter-laboratory comparison with the Denver instrument is unavailable. However, some feed coal samples from this group were determined in 2010 at EPA labs in Research Triangle Park, North Carolina, using a Lumex Zeeman instrument, and as a check, some of the same powders were analyzed in 2011 using the USGS Reston Hg instrument. The results show good inter-laboratory agreement and stability of the samples and the instrumentation over time (Table A4).

The relatively greater Hg heterogeneity shown by the density separates may be attributable to their provision from Eskom as 1-mm size splits rather than as pulverized coal. These splits were ground to a powder (in an agate mortar) prior to the Reston analysis and subjected to further grinding in Denver. In contrast, feed coal samples consist of pulverized coal and in most cases were analyzed as provided, by both the Reston and Denver labs. For the density separates, averages of all available determinations shown in Table A3 are reported in Table 6 and used in plotting.

Table A1. Replicate Mercury Analysis, USGS Reston laboratory

Sample	**Material**	**Sample Weight [g]**	**Hg Meas. [ng]**	**Hg Conc. [ppb]**	**Date**	**Mean**
KFA-3A	Fly ash	0.024	1.390	57.9	Feb. 2014	
KFA-3A-d1	Fly ash	0.023	1.225	53.3	Feb. 2014	
KFA-3A-d2	Fly ash	0.031	1.955	63.1	Feb. 2014	58.1 ± 4.9
DFC-2A	Coal	0.051	8.82	177	Feb. 2014	
DFC-2A-d1	Coal	0.043	6.42	153	Feb. 2014	
DFC-2A-d2	Coal	0.055	8.59	160	Feb. 2014	
DFC-2A-d3	Coal	0.046	7.31	162	Feb. 2014	163 ± 10
ESKO 8A-1	Coal	0.049	9.61	196	May, 2013	
ESKO 8A-2	Coal	0.057	12.40	218	May, 2013	
ESKO 8A-3	Coal	0.049	11.01	225	May, 2013	
ESKO 8A-4	Coal	0.052	13.28	255	May, 2013	
ESKO 8A-5	Coal	0.05	12.83	257	May, 2013	230 ± 26

Table A2. NIST Standard Mercury Analysis, USGS Reston laboratory

NIST	Sample Weight [g]	Hg Meas. [ng]	Hg Conc. [ppb]	Date	Mean [ppb]	Certified Value [ppb]
1632d	0.051	4.75	95.2	Feb. 2014		
1632d	0.050	4.80	98.1	Feb. 2014		
1632d	0.050	4.94	101	Feb. 2014		
1632d	0.046	4.34	96.2	Feb. 2014		
1632d	0.052	4.55	89.3	Feb. 2014		
1632d	0.049	4.27	89.0	Feb. 2014		
1632d	0.043	3.95	93.8	Feb. 2014		
1632d	0.047	4.63	100	Feb. 2014		
1632d	0.052	4.66	91.5	Feb. 2014	94.9 ± 4.2	92.8 ± 3.3
1632d	0.048	4.15	88.3	May, 2013		
1632d	0.050	5.09	104	May, 2013		
1632d	0.050	4.17	85.1	May, 2013		
1632d	0.050	4.74	96.7	May, 2013		
1632d	0.050	4.69	95.9	May, 2013		
1632d	0.052	4.91	96.4	May, 2013		
1632d	0.046	4.21	93.5	May, 2013		
1632d	0.052	4.69	92.1	May, 2013		
1632d	0.050	5.23	107	May, 2013		
1632d	0.048	4.56	97.0	May, 2013		
1632d	0.050	4.66	95.2	May, 2013		
1632d	0.056	5.11	93.1	May, 2013		
1632d	0.053	5.14	98.9	May, 2013		
1632d	0.043	4.32	103	May, 2013		
1632d	0.051	4.47	89.4	May, 2013	95.7 ± 5.9	92.8 ± 3.3
1633c	0.017	18.9	1,112	Feb. 2014		
1633c	0.019	20.2	1,063	Feb. 2014		
1633c	0.017	16.3	961	Feb. 2014		
1633c	0.011	11.9	1,078	Feb. 2014		
1633c	0.016	17.3	1,082	Feb. 2014		
1633c	0.009	8.92	991	Feb. 2014		
1633c	0.011	11.9	1,078	Feb. 2014		
1633c	0.010	9.61	961	Feb. 2014	1,041 ± 56	1,005 ± 22

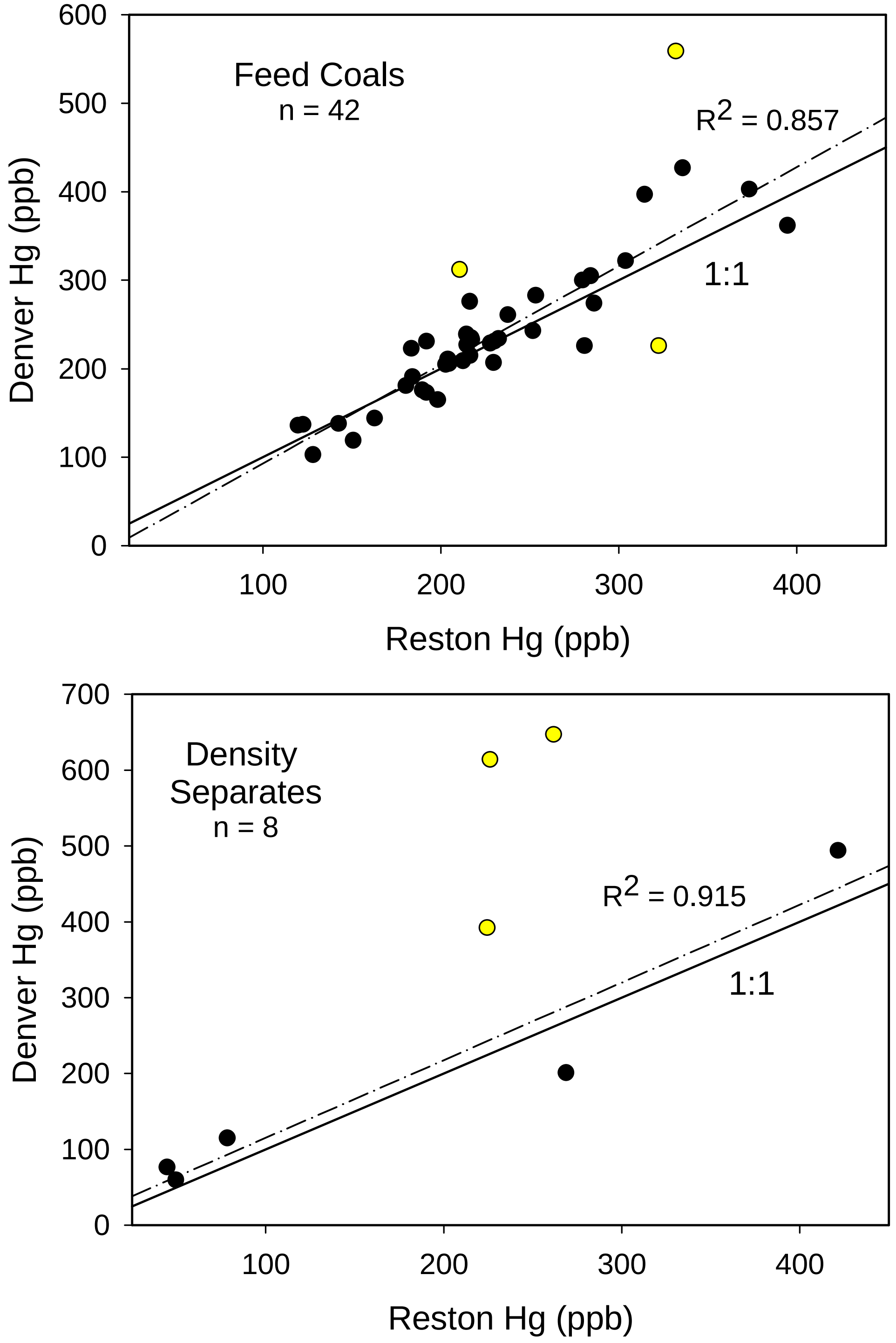

Fig. A1. Plots showing correspondence between Hg values as determined in USGS Reston and Denver Hg analyzers. Solid lines indicate perfect (1:1) correspondence. Dashed lines show linear regression excluding three samples in each group shown in yellow that were re-analyzed by both labs (Table A3).

Table A3. Replicate Hg analyses for density separates, and three feed coal samples showing poor initial correspondence between USGS Reston and Denver laboratories (in ppb on an as received basis). Densities are as indicated with float designated as F and sink as S.

Feed Coals	**Reston Original**	**Denver Original**	**Denver Re-run 1**	**Denver Re-run 2**	**Reston Re-run**	**Mean (n)**
9B	332	559	480	497	449	463 (5)
12A	211	312	310	271	285	278 (5)
12B	322	226	185	195	239	233 (5)
Density Separates						
14A 1.4F	44.6	76.5				60.6 (2)
14B 1.5F	49.5	59.8				54.7 (2)
14C 1.6F	78.4	115				96.7 (2)
14D 1.7F	269	201				235 (2)
14E 1.8F	224	392	285	321	300	304 (5)
14F 1.9F	262	647	697	722	631	592 (5)
14G 2.0F	226	614	544	418	371	435 (5)
14H 2.0S	421	494				458 (2)

Trace element analysis by ICP-MS

With the exception of Hg (and Se), which are determined on whole coal, coal samples for trace element analysis are first prepared by heating 0.2 grams of material at 525°C for 36 hours to obtain laboratory ash. The ash is digested using a method similar to ASTM D 6357-04 in which the prepared sample is digested in a heated 3-acid (HNO_3, HCl, HF) mixture. Calibration standards for ICP-MS analysis are prepared from stock solutions and calibration coefficients of 0.995 or better are obtained for standards before running unknowns. Samples are run at dilutions that fall within the range of the calibration standards. Results are corrected for mass- and polyatomic interferences by selection of alternate isotopes, or if necessary, use of pre-programmed correction factors. A standard or replicate is run for every 10 unknowns to check for instrument drift. Sample moistures are obtained at the time of analysis using a method similar to ASTM D3173-03 in which samples are first weighed, heated to 107°C for two hours, and weighed again in the dried condition. These moistures, and not the values compared in the following section, are used in calculating trace element results determined on an ash basis to a whole coal basis (Table 6).

Table A4. Comparison of Hg Data for 2010 Feed Coal Samples, Kendal and Duvha Power Stations vs. Previous Unpublished Determinations on the Same Splits (in ppb, as-received basis)

Power Station	**Unit**	**Sample**	**Material**	**This Study Feb. 2014**	**USGS Sept. 2011**	**EPA 2010**
Kendal	1	KFC-1A	Coal	188	176	200
Kendal	1	KFC-1B	Coal	167	170	
Kendal	2	KFC-2A	Coal	196		205
Kendal	2	KFC-2B	Coal	249	201	
Kendal	3	KFC-3A	Coal	199		225
Kendal	3	KFC-3B	Coal	205	211	
Kendal	4	KFC-4A	Coal	188		190
Kendal	4	KFC-4B	Coal	174	176	
Kendal	5	KFC-5A	Coal	347		324
Kendal	5	KFC-5B	Coal	361	340	
Kendal	6	KFC-6A	Coal	359		323
Kendal	6	KFC-6B	Coal	348	339	314
Duvha	1	DFC-1A	Coal	150	133	132
Duvha	1	DFC-1B	Coal	137	186	
Duvha	2	DFC-2A	Coal	177		148
Duvha	2	DFC-2B	Coal	175	148	
Duvha	3	DFC-3A	Coal	158		150
Duvha	3	DFC-3B	Coal	166	152	
Duvha	4	DFC-4A	Coal	261		248
Duvha	4	DFC-4B	Coal	306	236	
Duvha	5	DFC-5A	Coal	206		206
Duvha	5	DFC-5B	Coal	221	182	
Duvha	6	DFC-6A	Coal	285		246
Duvha	6	DFC-6B	Coal	253	243	

Coal Quality Determinations

A suite of analyses including short proximate (consisting of ash, sulfur, moisture, calorific value), sulfur forms (consisting of organic, pyritic, and sulfate), and halogens (consisting of total Cl, fluorine and bromine) was performed by Geochemical Testing, Inc., of Somerset, Pennsylvania, a commercial laboratory under contract to the USGS (USGS Contract Lab). The following ASTM methods were used: 1) Moisture, D3302; 2) Ash, D3174; 3) Sulfur, D4239; 4) Calorific Value, D5865; 5) Forms of Sulfur, D2492; 6) Chlorine, D4208; 7) Fluorine, D3761; Bromine- no ASTM method available.

Results for ash yield and moisture obtained from Geochemical Testing are compared with values provided by Eskom in figures A2 and A3, respectively. For ash yield, all but one sample (9C) show an acceptable correspondence and there are no systematic differences in results between the two labs. For moisture, approximately half of the samples plot along a 1:1 line of correspondence and half of the samples do not. This resulted in some divergence between the linear regression and line of 1:1 correspondence (Fig. A3). There are no systematic differences apparent between the two labs. Moisture content is inherently variable as coal samples may lose or adsorb moisture in response to environmental conditions. Overall moisture contents of the samples are low and may reflect some loss of moisture relative to the coals received at each power station.

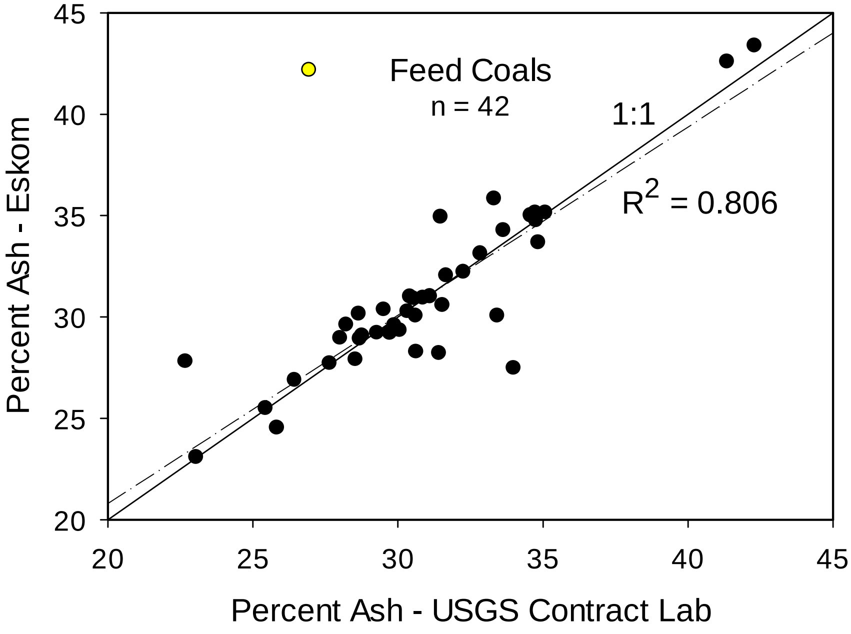

Fig A2. Plot of ash yield determinations (on a dry basis) comparing results for USGS contract lab and results provided by Eskom. One sample shown in yellow (9C) is omitted from the linear regression. Eskom ash value for this sample is used in Table 4.

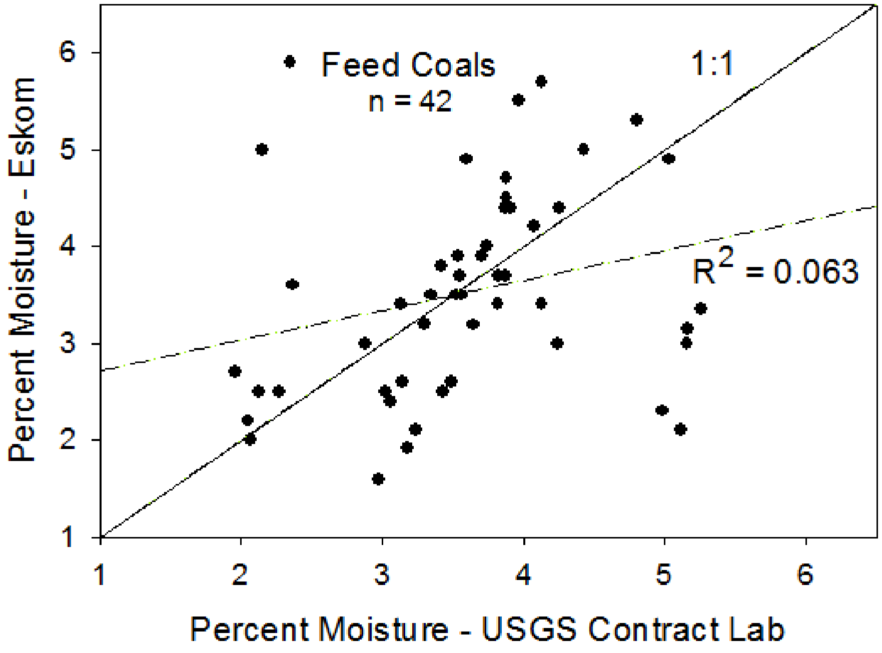

Fig. A3. Plot of moisture determinations.