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

By Allan Kolker, Constance L. Senior, and Chris van Alphen

Open-File Report 2014–1153

Version 2.0, May 2016

U.S. Department of the Interior
SALLY JEWELL, Secretary

U.S. Geological Survey
Suzette M. Kimball, Director

U.S. Geological Survey, Reston, Virginia
First release: 2014
Revised: May 2016 (ver. 2.0)

Cover photograph by Gunnar Futsaeter, UNEP

Preface

This is a report sponsored by the Mercury Control from Coal Combustion Partnership Area of the United Nations Environment Programme (UNEP) Global Mercury Partnership, and can be found on the UNEP Chemicals Branch Web site at: http://www.unep.org/chemicalsandwaste/Mercury/InterimActivities/ Partnerships/Coalcombustion/tabid/3530/language/en-US/Default.aspx. Based on the agreement between the UNEP, Division of Technology, Industry and Economics, Chemicals Branch, and the U.S. Geological Survey (USGS), the USGS has undertaken the project entitled: "Collaborative studies for mercury characterization in coal and coal combustion products, Republic of South Africa." This project report was prepared by the USGS, Eastern Energy Resources Science Center, Reston, Virginia, U.S.A. The work was funded by the European Union, and USGS participation in the study was supported by the USGS Energy Resources Program.

This publication may be produced in whole or in part and in any form for educational or nonprofit purposes without special permission from the USGS or UNEP, provided acknowledgment of the source is made. Material in this report can be freely quoted or reprinted. UNEP and the USGS would appreciate receiving a copy of any publication that uses this report as a source.

No use of this publication may be made for resale or for any other commercial purpose whatsoever without prior permission in writing from the United Nations Environment Programme.

Preface to Revised Version, 2016

Reanalysis of the suite of 42 samples of feed coal and 8 density separates discussed in the revised version of this report revealed significant changes to values for trace element determinations by inductively coupled plasma-mass spectrometry (ICP-MS) reported in table 6 of the original (2014) version of this report. Duplicate ICP-MS redeterminations by a commercial laboratory (Activation Laboratories, Ltd. [Actlabs], Ancaster, Ontario, Canada) and by USGS laboratories in Denver are in good agreement. Table 6 of this revised version has been updated to include these new results. In most cases, especially for transition metals, values reported here are lower than those originally reported, and in some cases, the corrected results are less than 50 percent of their original values. The extent to which trace element determinations differ from values originally reported varies by element, and for a given element, there is also considerable variation in the extent of the correction versus results originally reported. For consistency, Actlabs results compose the bulk of table 6, with the exception of USGS reanalysis determinations for chromium, arsenic, and antimony, which are prone to loss in the Activation Laboratories Ultratrace-4 sample digestion procedure used in these determinations. Actlabs and USGS reanalysis results are compared in appendix 1.

Note that results for mercury (Hg) contained in the original report are unaffected by revisions to ICP-MS data included here, because Hg was determined by atomic absorption spectrophotometry and not by ICP-MS. For ease of comparison with other results, Hg data are now reported on a whole-coal dry basis. Data for halogens (chlorine, fluorine) determined by ion-specific electrode were originally reported on a dry basis and are unchanged in the revision. This revised version also includes the following updates: (1) data for selenium, which were not available for inclusion in the original publication, are now provided in table 6; (2) results for ICP-MS trace element data reported here are expressed on a whole-coal dry basis because this facilitates comparison with published results for coals elsewhere; and (3) the text has been updated to take into account the U.S. Supreme Court decision of June 29, 2015, which puts on hold implementation of U.S. Environmental Protection Agency (EPA) Mercury and Air Toxics Standards (MATS) in the United States.

Acknowledgments

Contents

Figures

Tables

Abbreviations, Chemical Terms, and Definitions

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
destoned coal	washed coal from which the highest density fraction has been removed
EPA	U.S. Environmental Protection Agency
ESP	electrostatic precipitator
F	fluorine
feed coal	pulverized coal feeding a power station
FF	fabric filter
FGD	flue gas desulfurization
Hg	mercury
ICP–MS	inductively coupled plasma-mass spectrometry
ICR	Information Collection Request (EPA)
IPP	independent power producer
MATS	Mercury and Air Toxics Standards (EPA)
MFC	mill feed coal
middlings	washed coal from which the highest and lowest density fractions have been removed
mill feed coal	raw coal feeding a pulverization mill
Mn	manganese
Mo	molybdenum
MJ	megajoule
MW	megawatt
Ni	nickel
NIST	U.S. National Institute of Standards and Technology
O_2	dioxygen
PAC	powdered activated carbon
PCD	particulate control device
Pb	lead
PFC	pulverized feed coal
ppb	parts per billion
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	World Coal Quality Inventory (USGS)
Zn	zinc

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

By Allan Kolker,[1] Constance L. Senior,[2] and Chris van Alphen[3]

Executive Summary

Mercury (Hg) 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 the late 2000s. 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 is effective in reducing Hg levels to the range of the other Eskom power stations. This finding is promising for 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 Hg self-capture by particulate control devices (PCDs) is rather limited.

Eight density separates of a South African Highveld (#4) coal were also provided by Eskom for analysis. These samples show a strong mineralogical association of Hg (and arsenic) with pyrite. For this coal, reduction of pyrite by coal washing is very likely to result in reduced Hg contents, as well as lowering sulfur emissions. The density separates were used to predict Hg contents of coal products used in South Africa or exported. These contents range from less than 100 parts per billion (ppb; 0.10 parts per million [ppm]) for washed export coals having ash contents less than 16 percent, to more than 400 ppb (0.40 [ppm] for ash-rich (stone) material that is often discarded. Intermediate Hg contents are calculated from the density separates for predicted coal products used for power generation in South Africa, such as destoned coal (240 ppb; 0.24 ppm), middlings (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 a previous (2010) United Nations Environment Programme-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, Hg 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 Hg than those equipped with electrostatic precipitators. In each station, Hg capture is affected by differences in operating conditions of the boiler and air pollution control devices (APCDs). This variation should be considered in determining emission factors used to

estimate Hg emissions. Paired sampling of feed coal and fly ash could be used by Eskom to track the performance of its APCDs 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 PCD, as has been done in previous estimates. Apart from tracking APCD performance individually, changes resulting in improved mercury capture of the Eskom fleet are discussed. These include Hg reduction through coal selection and washing, as well as through optimization of equipment and operational parameters. 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. A series of plant operational changes leading to increased mercury capture is also presented. 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 sulfuric acid 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 desulfurization (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 sulfur dioxide emissions, and FGDs are installed to meet these standards, further reduction in Hg emissions will be a co-benefit of this installation.

1. Introduction

1.1 Project Scope and Objectives

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. In addition, samples of pulverization mill feed coal (MFC) and fly ash from Eskom's Kendal and Duvha power stations, collected in 2010 in sampling by the U.S. Environmental Protection Agency (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) 24 samples of raw pulverization MFC and 24 samples of 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 (IPPs). Combined power generation by Sasol and the IPPs 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 and others, 2008; Leaner and others, 2009; Masekoameng and others, 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 Standards (MATS) (EPA, 2011). Additional information providing context for the study is given in the remainder of this section. The sections that follow include results for Eskom feed coals (Section 2); density separates of a Highveld (#4) coal (Section 3); supplemental results for the Kendal and Duvha power stations (Section 4); discussion (Section 5); and conclusions (Section 6).

1.2   Background

Mercury 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). To address this issue, 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. The purpose of the 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. 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 percent 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.

Figure 1. Map showing Eskom power stations in South Africa. Coal-fired stations (green triangles) are concentrated in west-central Mpumalanga 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 desulfurization (FGD) technology. All boilers have pollution 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 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 (sulfuric acid vapor [SO_3] or sulfuric acid [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 where there is a significant amount of pyrite in the coal and that pyrite contains Hg.

Table 1. Description of Eskom coal-fired power plants.

[MW, megawatts; PCD, particulate control device; FF, fabric filter; FGC, flue gas conditioning; SO_3, sulfuric acid vapor; SO_2, sulfur dioxide; ESP, electrostatic precipitator; --, not available; FGD, flue gas desulfurization]

Station	Plant capacity (MW)	No. boilers	Commission date	Status	Coal washing	Type of PCD	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 x 3	None	None
Komati	940	9	1961	Returned to service	None	ESP	Yes	None
Medupi	4,788	6	Future	Construction	--	FF	None	FGD (technology not final)
Kusile	4,800	6	Future	Construction	--	FF	None	FGD (technology not final)

1.4   Feed Coals and Coal Consumption

A suite of 42 samples of pulverized feed coals provided by Eskom includes from 2 to 4 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 destoned product where only the discard fraction is removed (section 3).

5

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	No. of samples	A	B	C	D
1	Arnot	2	June 2009	June 2012		
2	Camden	4	Feb. 2009	April 2010	Jan. 2011	**2012**
3	Duvha	3	Dec. 2010	**2012**	July 2012	
4	Grootvlei	4	Dec. 2009	Jan. 2011	**2012**	June 2012
5	Hendrina	3	**2010**	**2011**	**2012**	
6	Kendal	4	April 2009	Aug. 2010	Jan. 2011	Jan. 2012
7	Kriel	3	March 2009	Feb. 2009	April 2011	
8	Komati	3	April 2009	May 2009	June 2009	
9	Lethabo	3	Jan. 2009	Jan. 2011	**2012**	
10	Majuba	4	Jan. 2009	Nov. 2010	March 2011	**2012**
11	Matimba	3	April 2010	Nov. 2010	Feb. 2011	
12	Matla	3	Nov. 2010	May 2011	**2012**	
13	Tutuka	3	Jan. 2009	Dec. 2010	May 2011	

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 and others, 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 percent 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 and others, 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. 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	Kendal	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, one of two new power stations being added by Eskom. 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 them (Jeffrey, 2005; Wagner and Tlotleng, 2012). The 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, and the 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 mercury (Hg) speciation measurements were obtained by EPA Method 30B using carbon sorbent traps (EPA, 2008). Reporting for this study emphasized these emissions measurements (Scott, 2011). Pulverization mill feed coal (MFC) 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 laboratories, 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 are available in Eskom internal reporting (Gericke and others, 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 and others, 2002), was obtained by the USGS in the early 2000s for the World Coal Quality Inventory (WoCQI; Tewalt and others, 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 parts per million (ppm; <30 to 830 parts per billion [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 and others (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 the 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-percent range are typical. Sulfur and pyritic S contents

are relatively low. Moisture contents are less than 5 percent in all but one sample (5.1 percent in sample 9, from a 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 (on an as-determined basis).[1]

[%, percent; wt. %, weight percent; BTU/lb, British thermal units per pound]

Station number	Station (No. of 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	9,233–9,396
2	Camden (4)	3.1–3.7	27.6–32.4	0.79–1.18	0.34–0.63	8,516–9,067
3	Duvha (3)	2.1–2.3	29.4–30.5	0.84–0.98	0.40–0.48	9,074–9,402
4	Grootvlei (4)	3.5–3.9	29.4–31.1	1.06–1.23	0.40–0.55	8,284–8,675
5	Hendrina (3)	3.0–3.2	27.1–27.7	1.21–1.27	0.73–0.81	9,312–9,448
6	Kendal (4)	3.0–3.5	31.9–33.8	0.76–0.80	0.36–0.45	7,982–8,402
7	Kriel (3)	3.8–4.2	21.7–24.8	0.66–0.73	0.22–0.27	9,119–9,637
8	Komati (3)	3.9–4.1	29.2–32.3	0.80–1.01	0.46–0.53	8,161–8,653
9	Lethabo (3)	2.9–5.1	39.3 –40.9[3]	0.68–0.84	0.36–0.48	6,579–9,591
10	Majuba (4)	3.3–3.6	27.7–28.5	0.81–1.01	0.38–0.56	8,925–9,039
11	Matimba (3)	2.0–2.4	33.9–34.4	1.21–1.25	0.59–0.66	8,414–8,606
12	Matla (3)	2.2–4.4	25.3–33.3	0.84–1.36	0.43–0.75	8,561–9,113
13	Tutuka (3)	3.6–3.9	28.6–30.2	0.72–1.14	0.53–0.76	8,864–8,905

[1]Values obtained by USGS contract laboratory. See appendix 1 for comparison with Eskom data.

[2]To convert to megajoule per kilogram, 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 reanalysis in USGS Denver laboratories in appendix 1. Mercury results by power station are shown in figure 2. Results for Hg in the 42 feed coals give a mean of 241±75.1 ppb expressed on a dry basis.[4] The range in Hg values (from 125 to 487 ppb, dry basis) is similar to that of power station feed coal averages given previously by Gericke and others (2007; from 0.17 to 0.45 ppm [170 to 450 ppb], basis unspecified). 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 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.

---

[4]Mercury results are expressed in ppb where possible due to greater precision. To compare results given in ppm: 1 ppm=1,000 ppb.

Table 5. Mercury in 42 Eskom feed coal samples (this study) and previous results for feed coals in Eskom power stations (in parts per million, on a dry basis).

Station number	Station	This study[1] (samples A, B, C, D)	Composite year(s)	Gericke and others (2007)[2]
1	Arnot	0.17, 0.12		0.17
2	Camden	0.21, 0.26, 0.22, **0.20**	2012	N.A.
3	Duvha[3]	0.22, **0.18**, 0.19	2012	0.23
4	Grootvlei	0.39, 0.29, **0.35**, 0.33	2012	N.A.
5	Hendrina	**0.29, 0.24, 0.22**	2010–2012	0.21
6	Kendal[3]	0.22, 0.21, 0.19, 0.22		0.44
7	Kriel	0.13, 0.13, 0.15		0.29, 0.38
8	Komati	0.24, 0.21, 0.25		N.A.
9	Lethabo	0.42, 0.49, **0.16**	2012	0.36
10	Majuba	0.30, 0.24, 0.29, **0.22**	2012	0.29
11	Matimba	0.23, 0.26, 0.20		0.45
12	Matla	0.29, 0.24, **0.21**	2012	0.29
13	Tutuka	0.19, 0.32, 0.22		0.29

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

[2]Multiyear average Hg content as reported by Scott (2011); basis unspecified.

[3]Excludes results for 2010 samples from Duvha and Kendal stations presented in section 4.
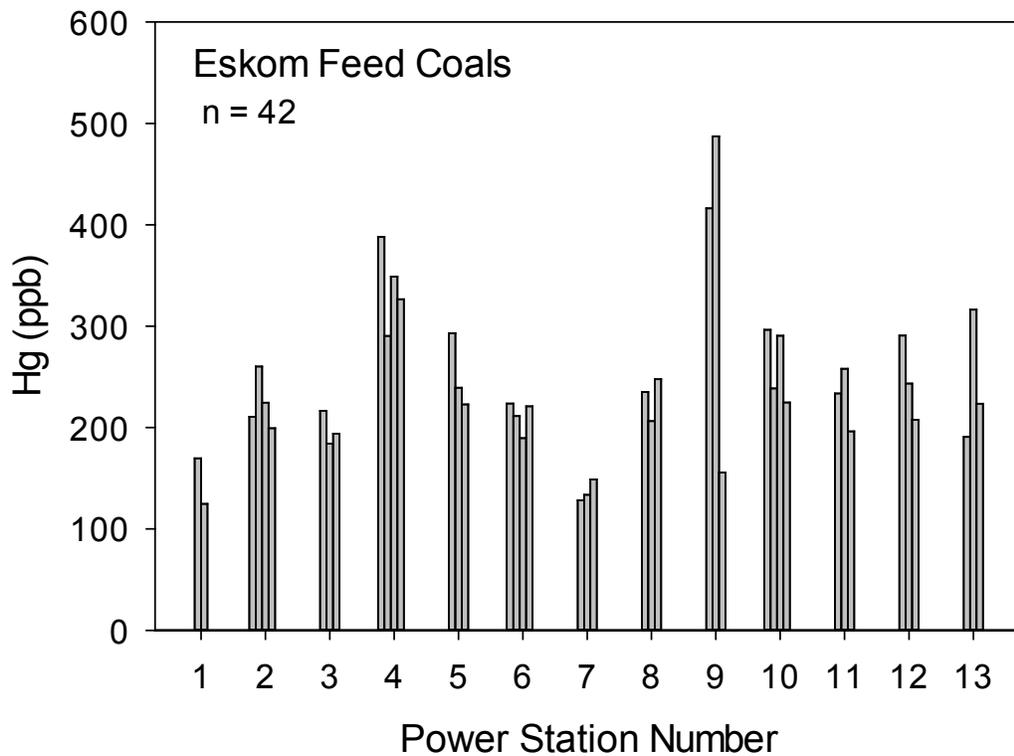
Figure 2. Variation in mercury (Hg) content of feed coals (in parts per billion [ppb] on a dry basis) by power station number. Samples and power stations are as listed in table 2. n, number of samples.

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, 2015). These Hg–Cl complexes or compounds can be captured by APCDs 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, dry basis), 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 percent of Cl contents (Vosteen and others, 2010; Kolker and Quick, 2015), a more sensitive method for Br determination is needed.
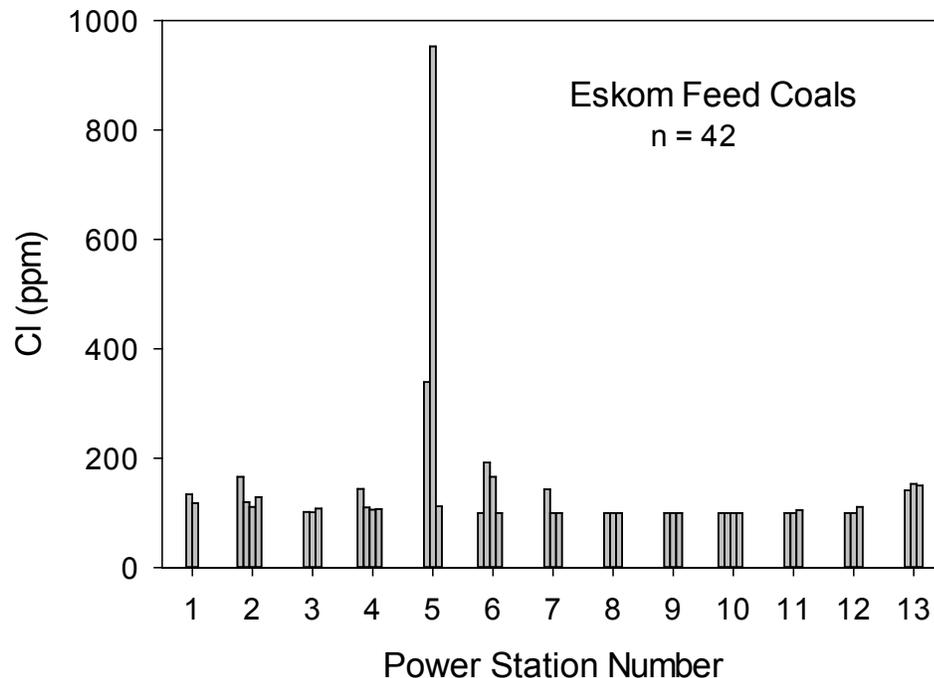
Figure 3.   Variation in American Society for Testing and Materials chlorine (Cl) content in feed coals by power station number, reported on a dry basis. Power stations are as listed in table 2. Samples having values below the detection limit (100 parts per million [ppm]) are plotted at the detection limit (n, number of samples).

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 beryllium (Be), chromium (Cr), manganese (Mn), cobalt (Co), nickel (Ni), As, molybdenum (Mo), cadmium (Cd), antimony (Sb), thallium (Tl), and lead (Pb), are relatively uniform (table 6; fig. 4). Relative to global averages, South African coals are higher in Cr and Mn, and lower or much lower in As, Cd, and Sb (Bergh and others, 2011; Wagner and Tlotleng, 2012). Wagner and Hlatshwayo (2005) also found that Pb, and zinc (Zn) were 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 values for the feed coals in the present study are at or below the global average, agreeing well with results for five Highveld samples given by Wagner and Hlatshwayo (2005).
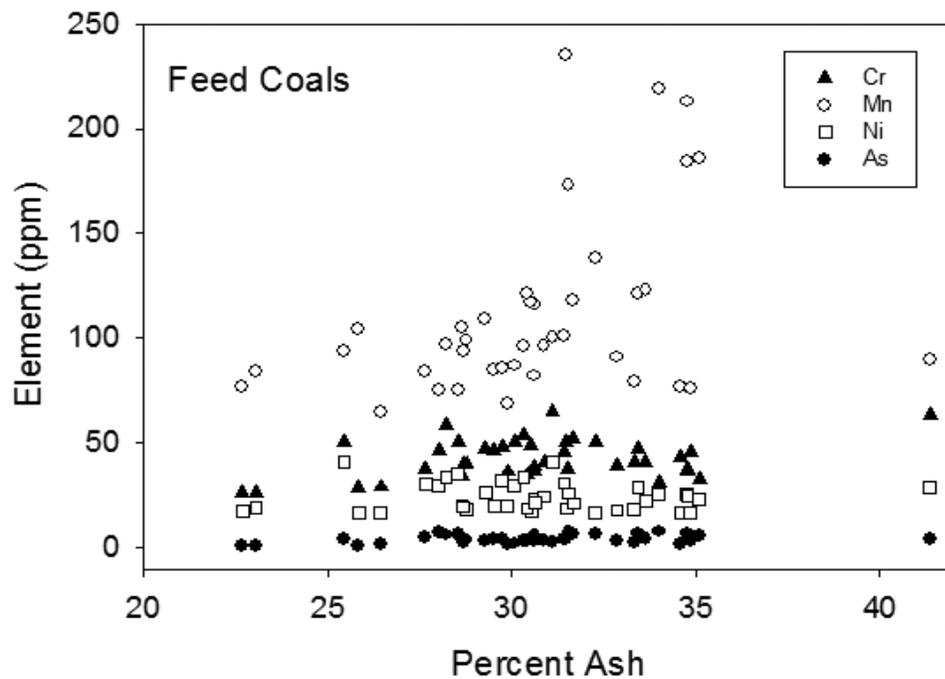
Figure 4.   Plot showing ranges for chromium (Cr), manganese (Mn), nickel (Ni), and arsenic (As) in feed coals (in parts per million [ppm] on a dry basis).

Table 6. Trace element data (in parts per million, on a whole-coal dry basis).[1]

[Be, beryllium; F, fluorine; Cl, chlorine; Cr, chromium; Mn, manganese; Co, cobalt; Ni, nickel; Zn, zinc; As, arsenic; Se, selenium; Mo, molybdenum; Cd, cadmium; Sb, antimony; Hg, mercury; Tl, thallium; Pb, lead. Cl and F are proposed to be regulated as acid gases HCl, HF; Zn, Mo, and Tl are not proposed to be regulated under EPA Mercury and Air Toxics Standards. Elements are listed in order of atomic number from 4 (Be) to 82 (Pb)]

Sample	Be[2] 4	F[3] 9	Cl 17	Cr[4] 24	Mn 25	Co 27	Ni 28	Zn 30	As 33	Se 34	Mo 42	Cd 48	Sb 51	Hg 80	Tl 81	Pb 82
1A	1.9	84	134	50	94	12	41	22	2.8	1.1	1.7	0.1	0.2	0.17	0.43	17
1B	2.6	113	118	38	84	10	31	23	3.2	1.1	1.4	0.1	0.2	0.12	0.45	23
2A	3.5	137	166	47	121	8.5	29	28	5.3	1.6	2.1	0.1	0.4	0.21	0.63	27
2B	2.8	127	120	38	173	9.3	26	25	5.4	1.5	2.6	0.1	0.3	0.26	0.71	27
2C	2.7	130	111	39	116	6.6	24	20	4.4	1.2	1.9	< 0.1	0.2	0.22	0.53	21
2D	2.5	118	129	34	105	7.3	20	28	3.6	1.2	1.9	0.1	0.4	0.20	0.33	18
3A	2.4	215	102	65	100	8.6	41	26	3.8	1.0	2.2	0.1	0.3	0.22	0.47	21
3B	2.4	208	101	50	87	7.1	30	23	3.2	1.0	1.9	0.1	0.3	0.18	0.37	20
3C	2.5	239	108	54	96	8.0	34	25	3.4	1.0	2.1	0.1	0.3	0.19	0.42	23
4A	3.2	158	144	51	138	4.4	17	14	6.1	1.4	2.0	<0.1	0.3	0.39	0.34	26
4B	2.7	149	110	49	117	4.8	18	12	3.8	1.4	1.8	<0.1	0.3	0.29	0.20	22
4C	3.0	153	106	50	235	4.7	19	15	4.3	1.6	0.89	<0.1	0.3	0.35	0.18	23
4D	3.3	189	107	52	118	7.6	21	17	6.2	1.5	2.1	<0.1	0.3	0.33	0.26	27
5A	2.5	37	339	46	75	8.9	29	18	5.9	1.0	1.8	0.1	0.2	0.29	0.71	18
5B	3.6	75	953	51	75	9.9	36	26	5.4	1.0	2.3	< 0.1	0.2	0.24	0.77	18
5C	2.6	117	112	58	97	9.9	34	24	5.3	1.0	1.7	< 0.1	0.2	0.22	0.63	18
6A	3.4	175	<100	41	79	4.9	19	12	2.4	1.6	1.7	<0.1	0.3	0.22	0.23	19
6B	3.2	168	192	39	91	5.5	18	20	3.6	1.2	1.8	<0.1	2.3	0.21	0.34	19
6C	2.7	166	166	43	77	4.2	17	14	2.5	1.1	1.4	<0.1	0.3	0.19	0.22	17
6D	2.8	47	<100	45	76	4.5	17	11	2.8	1.3	1.6	0.1	0.4	0.22	0.23	16
7A	1.7	164	143	27	84	3.4	19	3.5	1.3	1.0	1.2	<0.1	0.2	0.13	0.08	12
7B	1.6	97	<100	26	77	3.0	17	3.3	1.0	0.8	0.99	<0.1	0.2	0.13	0.07	9.2
7C	1.7	158	<100	29	104	3.3	17	6.0	1.3	0.9	1.1	<0.1	0.3	0.15	0.12	8.5
8A	2.1	95	<100	41	96	6.7	24	30	2.9	1.1	1.0	< 0.1	0.2	0.20	0.33	18
8B	1.9	98	<100	35	121	6.1	19	20	2.2	1.2	1.3	< 0.1	0.2	0.21	0.28	18

Table 6. Trace element data (in parts per million, on a whole-coal dry basis).[1]—Continued

[Be, beryllium; F, fluorine; Cl, chlorine; Cr, chromium; Mn, manganese; Co, cobalt; Ni, nickel; Zn, zinc; As, arsenic; Se, selenium; Mo, molybdenum; Cd, cadmium; Sb, antimony; Hg, mercury; Tl, thallium; Pb, lead. Cl and F are proposed to be regulated as acid gases HCl, HF; Zn, Mo, and Tl are not proposed to be regulated under EPA Mercury and Air Toxics Standards. Elements are listed in order of atomic number from 4 (Be) to 82 (Pb)]

Sample	Be[2] 4	F[3] 9	Cl 17	Cr[4] 24	Mn 25	Co 27	Ni 28	Zn 30	As 33	Se 34	Mo 42	Cd 48	Sb 51	Hg 80	Tl 81	Pb 82
8C	2.0	98	<100	41	123	7.6	22	20	3.1	1.2	1.7	<0.1	0.2	0.25	0.42	17
9A	2.6	124	<100	67	107	5.6	25	21	4.0	1.6	1.6	<0.1	0.3	0.42	0.31	24
9B[5]	2.6	119	<100	64	90	4.9	29	15	3.7	1.4	1.7	<0.1	0.3	0.49	0.27	21
9C	2.3	189	<100	53	80	4.4	15	14	4.8	1.0	1.4	< 0.1	0.3	0.16	0.22	20
10A	2.2	157	<100	47	85	4.0	20	10	3.3	1.3	2.2	<0.1	0.2	0.30	0.22	16
10B	2.7	145	<100	40	99	4.9	18	19	3.5	1.2	1.5	<0.1	0.3	0.24	0.27	17
10C	2.5	173	<100	40	94	4.1	20	13	2.9	1.2	1.9	< 0.1	0.2	0.29	0.24	20
10D	2.7	186	<100	47	109	4.6	26	14	3.0	1.3	2.1	< 0.1	0.2	0.22	0.28	20
11A	3.0	217	<100	37	184	11	25	55	5.4	1.2	2.8	0.2	0.6	0.23	0.57	26
11B	2.8	89	<100	33	186	10	24	52	4.9	1.3	2.6	0.2	0.5	0.26	0.57	26
11C	3.1	205	105	37	213	11	25	58	5.4	1.5	2.9	0.2	0.5	0.20	0.61	28
12A[5]	1.5	152	<100	36	69	4.7	20	9.8	2.1	1.1	1.7	<0.1	0.3	0.29	0.23	18
12B[5]	1.6	154	<100	29	65	4.8	17	9.3	1.8	0.8	1.6	<0.1	0.3	0.24	0.21	15
12C	2.9	189	111	31	219	12	25	70	5.3	1.2	2.9	0.2	0.5	0.21	0.61	24
13A	3	86	141	37	82	6.8	22	15	2.5	1.2	1.4	< 0.1	0.2	0.19	0.30	20
13B	3.3	106	153	48	86	10	32	20	3.3	1.2	1.5	< 0.1	0.2	0.32	0.44	18
13C	3.9	93	150	45	101	9.7	31	25	3.3	1.2	1.5	< 0.1	0.2	0.22	0.51	19
14A[6]	0.8	311	540	31	29	9.3	15	3.0	0.5	0.5	1.7	< 0.1	0.5	0.06	< 0.05	2.6
14B	1.4	239	1084	39	43	5.2	16	4.7	0.9	1.0	1.5	< 0.1	0.6	0.06	0.06	7.1
14C	1.6	171	1037	34	62	2.8	15	4.3	1.0	1.0	1.6	< 0.1	0.6	0.10	0.07	6.8
14D	1.7	140	770	33	74	2.0	14	4.4	1.2	1.0	2.1	< 0.1	0.4	0.25	0.11	7.5
14E	2.6	154	807	59	67	2.5	18	4.9	1.7	1.2	3.2	< 0.1	0.3	0.32	0.22	10
14F	1.8	129	573	50	59	2.7	21	8.3	2.9	1.5	4.1	< 0.1	0.4	0.62	0.25	10
14G[7]	2.9	120	536	65	55	2.4	24	15	3.2	1.5	2.9	< 0.1	0.4	0.45	0.28	12
14H[7]	1.8	140	428	70	51	8.7	41	21	4.4	1.3	3.5	< 0.1	0.5	0.47	0.51	11

(see footnotes on next page)

Table 6. Trace element data (in parts per million, on a whole-coal dry basis).[1]—Continued

[1]Emissions proposed for regulation under U.S. EPA Mercury and Air Toxics Standards (EPA, 2011) are shown in boldface.

[2]The following elements were determined using ICP-MS by Actlabs, Ancaster, Ontario, Canada: Be, Mn, Co, Ni, Zn, Se, Mo, Cd, Tl, Pb

[3]The following elements were determined using ion-selective electrode by Geochemical Testing, Inc., Somerset, Pa., U.S.A.: F, Cl.

[4]The following elements were determined using ICP-MS by USGS in reanalysis of values originally reported in OF-2014-1153: Cr, As, Sb.

[5]Mercury values for samples 9B, 12A, and 12B are averages of multiple analyses (appendix 1).

[6]Fourteen-series samples are Highveld #4 density separates (section 3). Mercury values for these samples are averages of multiple analyses (appendix 1).

[7]USGS value was used for Mo in 14H; USGS and Actlabs values were averaged for Zn in 14G.
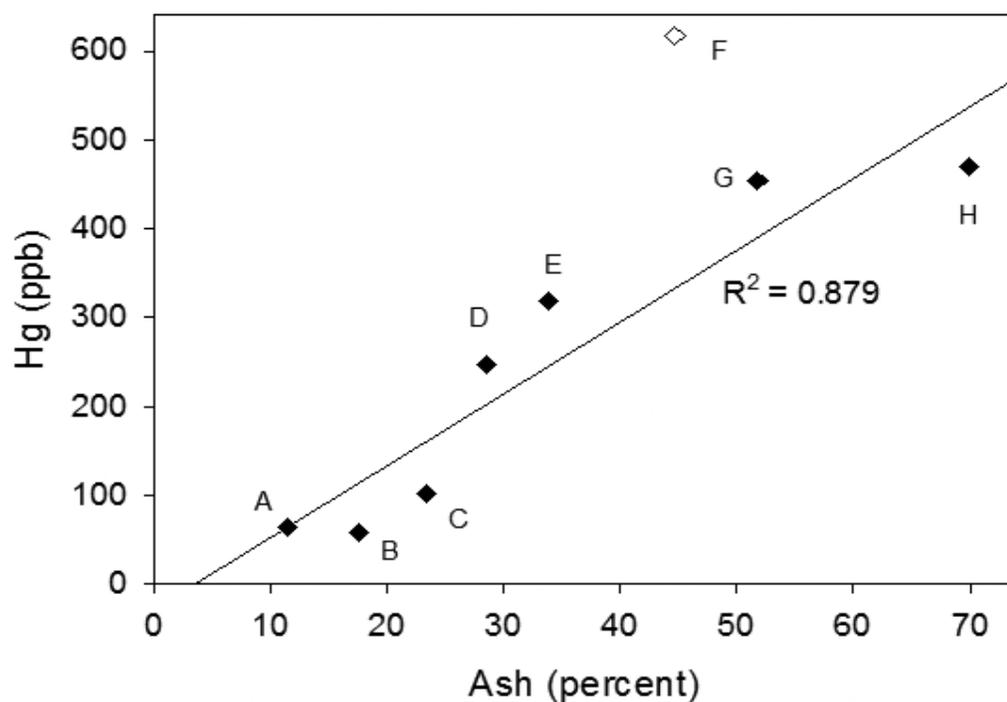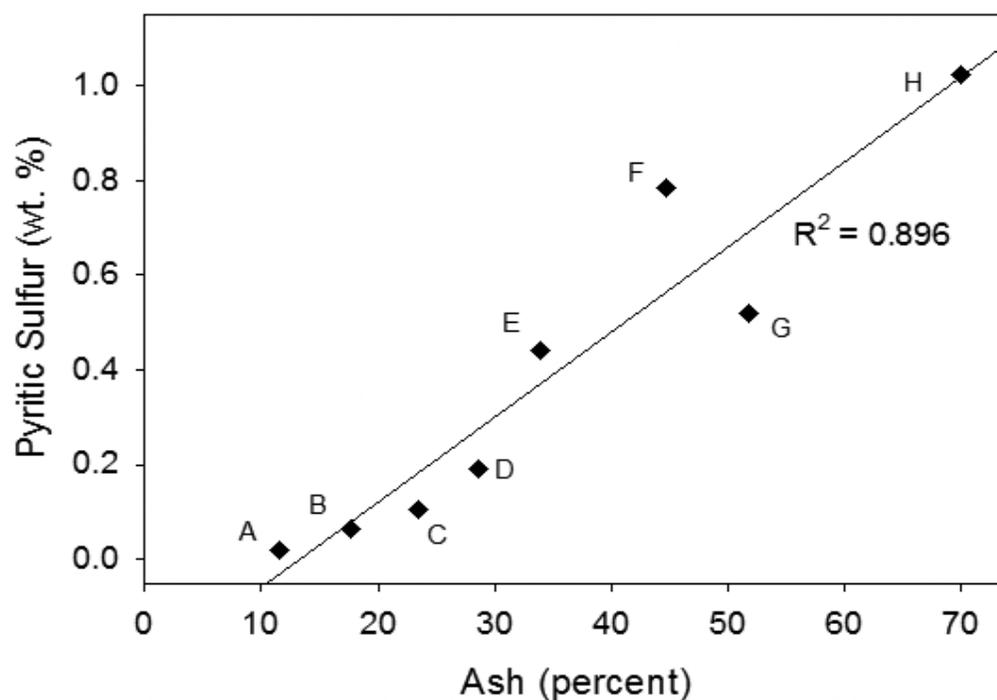
3.   Density Separates of Highveld (#4) Coal

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 grams per cubic centimeter (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 destoned 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, and 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 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 redistributed, which would explain the uniform Cr enrichment.

Figure 5. Plots of ash yield versus pyritic sulfur (upper plot; in weight percent [wt. %]) and mercury (lower plot) for Highveld (#4) density separates, showing concentration of pyrite and mercury (Hg) in the high-density cuts (in parts per billion [ppb], on a dry basis; R^2, correlation). Corresponding densities are noted in text. Sample 14F (open symbol) is omitted from linear regression in bottom plot.

17
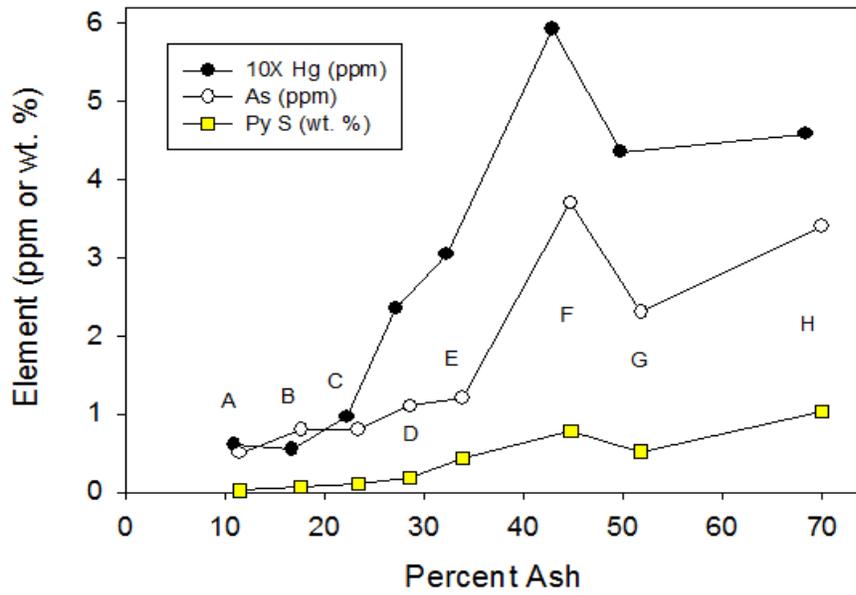
Figure 6. Plot showing increase in mercury (Hg) and arsenic (As) in separates prepared at increasing separation densities, and corresponding increase in pyrite content (as pyritic sulfur [Py S]; in parts per million [ppm] or weight percent [wt. %]) on a dry basis.
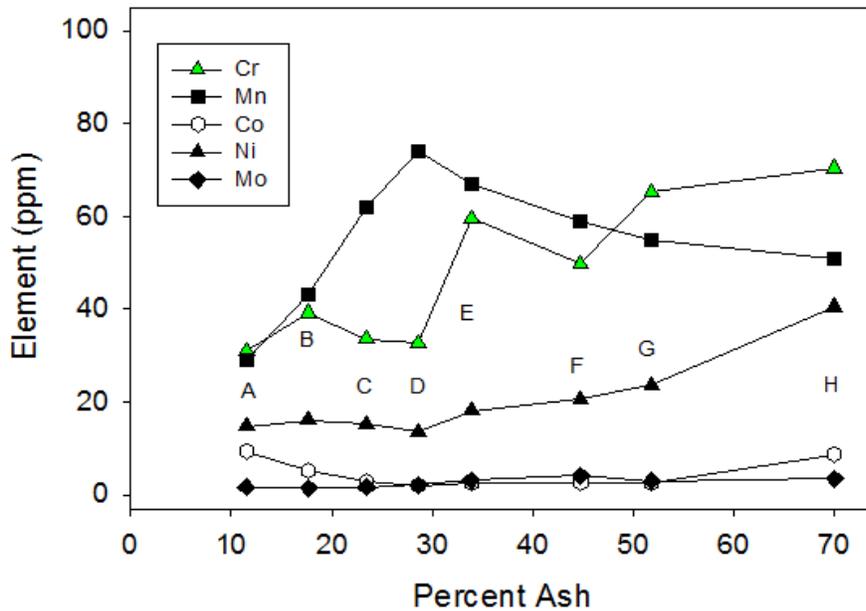
Figure 7. Partitioning of elements chromium (Cr), manganese (Mn), cobalt (Co), nickel (Ni), and molybdenum (Mo), indicating a mixed association for these elements (in parts per million [ppm] on a dry basis).

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 zinc chloride 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.
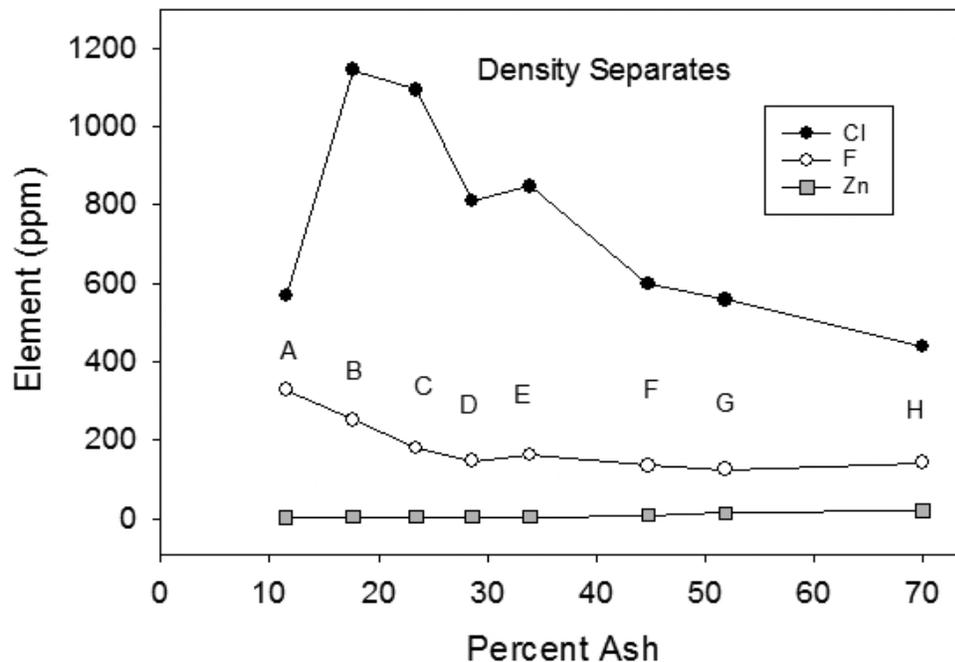
Figure 8. Partitioning of chlorine (Cl) and fluorine (F) among Highveld #4 density separates showing that halogens are preferentially concentrated in the low-density fractions indicating an organic affinity (in parts per million [ppm] on a dry basis; Zn, zinc).

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) destoned; (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 percent 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 and others, 2010).

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

[wt. %, weight percent; ppb, parts per billion]

Product	Samples (averaged)	Ash (wt. %)	Hg (ppb)	Approximate cut point
Export	14A	11.5	64	Cut at 1.4
Destoned	14A–F	26.6	235	Cut at 1.9
Middling	14B–F	29.7	269	1.4 to 1.9
Run-of-mine	14A–H	35.2	291	No washing
Middling+discard	14B–H	38.6	324	>1.4
Stone (discard)	14G, H	60.9	461	>2.1

3.2.2 Microanalysis

Polished mounts of each density separate were prepared for characterization by microanalysis methods. Pyrite grains for laser ablation inductively coupled plasma-mass spectrometry (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 micrometers (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 give 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 and others, 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).
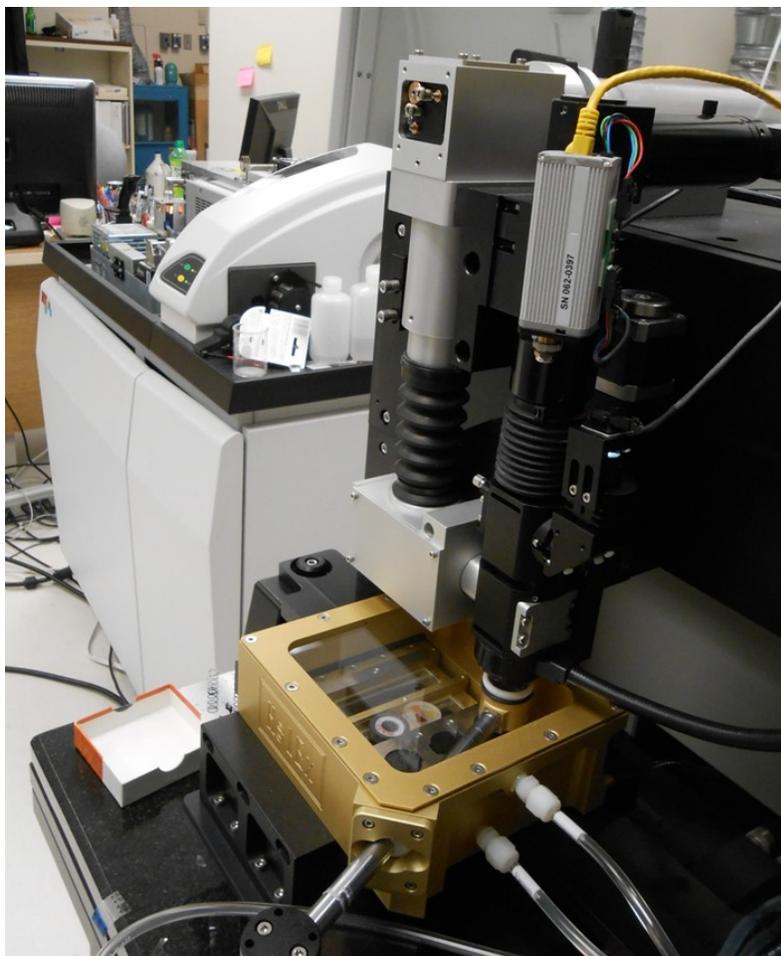
Figure 9. U.S. Geological Survey laser ablation (foreground) inductively coupled plasma-mass spectrometer (background) instrument.

In addition to Hg, minor or trace elements detected in pyrite by laser ablation include Mn, Co, Ni, Cu (copper), Zn, As, Se, Mo, Tl, Pb, and Bi (bismuth) (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 50 percent of the analyses resulted in detection of an element, by substituting 55 percent of the detection limit for nondetects (Sanford and others, 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 (dry basis). Including data for both the 25- and 20-micron-spot sizes, pyrite is enriched by factors of 20.3 to 33.2 (As), 13.5 to 17.4 (Mo), 3.9 to 8.4 (Hg), 29.5 to 36.4 (Tl), and 2.1 to 4.4 (Pb) relative to the respective calculated whole-coal values. Results for each element are consistent with variation seen in the bulk samples with progressive increases corresponding to an increase in the proportion of pyrite contained. For Hg, the higher mean value for the 20-micron data (2.43 ppm) versus the 25-micron results (1.14 ppm) reflects heterogeneity of the sample populations and the fact that several (six) 10+-ppm Hg points are included in the 20-micron mean.
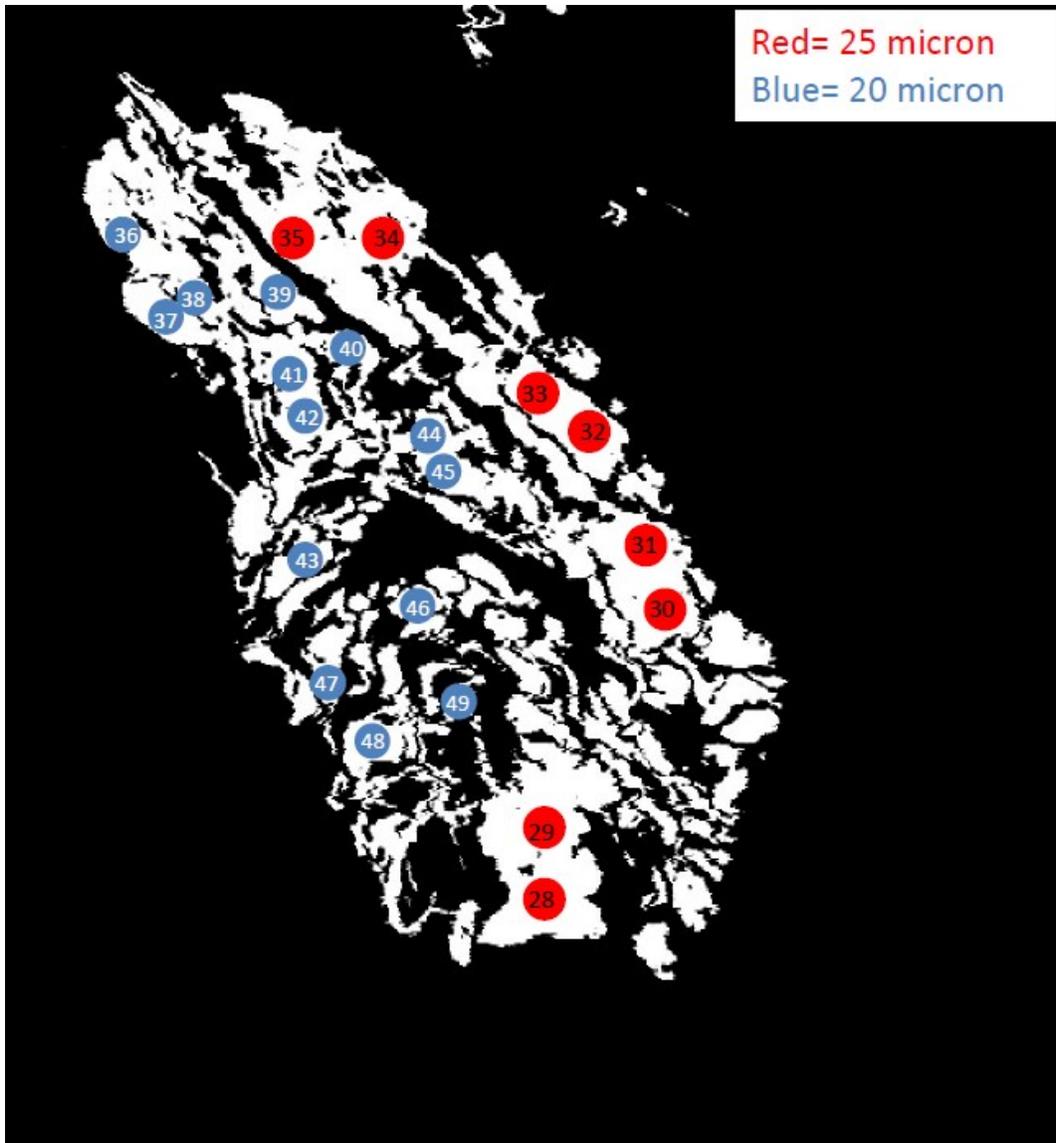
Figure 10.   Backscattered electron image of composite pyrite in density separate sample 14F (1.9 float) from Highveld (#4) coal showing laser ablation spot analysis points using 25-micrometer (red; micron) or 20-micrometer (blue) laser diameter. Width of field of view is 600 micrometers.
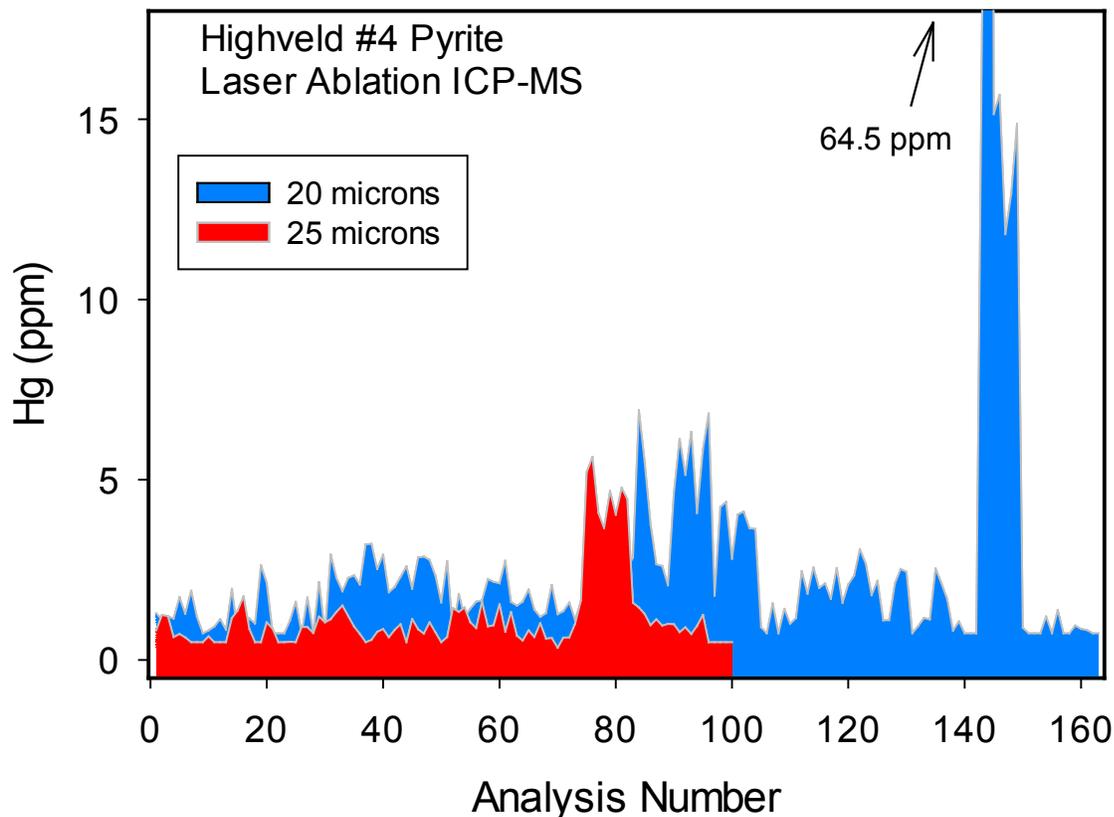
Figure 11. Laser ablation inductively coupled plasma-mass spectrometry (ICP–MS) spot analyses for mercury (Hg) in pyrite from Highveld (#4) coal density separates. Most analyses range from the detection limits to about 3 parts per million (ppm), but several points exceed 5 ppm and one analysis exceeds 50 ppm. Nondetects 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 inductively coupled plasma–mass spectrometer analysis data showing detection limits; calculated mean values for arsenic (As), molybdenum (Mo), mercury (Hg), thallium (Tl), and lead (Pb) (>50 percent [%] detected); and element enrichment factors in pyrite relative to calculated whole coal.

[Mn, manganese; Co, cobalt; Ni, nickel; Se, selenium; ppm, parts per million; n, number of analyses; ---, not determined]

	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)	---	---	---	66.4[1]	---	45.3	2.43[1]	6.92	36.9[1]
Calculated whole coal[2]				2.0		2.6	0.29	0.19[3]	8.4
Enrichment factor				33.2		17.4	8.4	36.3	4.4

23

Table 8. Laser ablation inductively coupled plasma–mass spectrometer analysis data showing detection limits; calculated mean values for arsenic (As), molybdenum (Mo), mercury (Hg), thallium (Tl), and lead (Pb) (>50 percent [%] detected); and element enrichment factors in pyrite relative to calculated whole coal.—Continued

	Mn	Co	Ni	As	Se	Mo	Hg	Tl	Pb
				25-micrometer spot (n = 100)					
Detection limit (ppm)	16.4	8.8	37.1	15.3	163[4]	11.2	0.49	0.78	1.93
Percent detects	47%	28%	23%	72%	9%	75%	80%	68%	73%
Mean (ppm)	---	---	---	40.5	---	35.1	1.14	5.60	17.8
Calculated whole coal[2]				2.0		2.6	0.29	0.19[3]	8.4
Enrichment factor				20.3		13.5	3.9	29.5	2.1

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

[2]Whole-coal value estimated by averaging eight density separates as in table 7; values in ppm on a dry basis.

[3]Whole-coal value estimated for Tl includes one non-detect counted as 70 percent of the detection limit

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

Other elements detected: copper, zinc, and bismuth.

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 PCD. The EPA sampling methodology is described in detail by Forte and others (2012).

4.2 Solid Samples

Two raw pulverization 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 MFC samples was originally analyzed for Hg by the EPA (appendix 1). Splits of the 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 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 MFC coal Hg content of the Kendal samples was 249±81 ppb (on a dry basis) and the average of the Duvha samples was 207±55 ppb (on a dry basis). These Hg values are consistent with those of pulverized boiler feed coal samples received from Eskom for the

respective plants, which ranged from 190 to 224 ppb for Kendal and 184 to 216 ppb for Duvha (dry basis). 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 (349 to 362 ppb, dry basis) 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 samples collected in 2010 are shown in figure 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 (parts per billion [ppb]), on a dry basis for coal and an as-determined basis for fly ash) analyzed in USGS Reston laboratories. Coal samples are adjusted to a dry basis using moisture determinations from USGS contract laboratory.

Power Station	Unit	Sample	Material	Hg concentration [ppb]	Sample	Material	Hg concentration [ppb]
Kendal	1	KFC-1A	Coal	189	KFA-1A	Fly ash	89.3
Kendal	1	KFC-1B	Coal	168	KFA-1B	Fly ash	88.3
Kendal	2	KFC-2A	Coal	197	KFA-2A	Fly ash	80.5
Kendal	2	KFC-2B	Coal	251	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	173	KFA-4B	Fly ash	157
Kendal	5	KFC-5A	Coal	350	KFA-5A	Fly ash	84.9
Kendal	5	KFC-5B	Coal	362	KFA-5B	Fly ash	77.3
Kendal	6	KFC-6A	Coal	360	KFA-6A	Fly ash	30.1
Kendal	6	KFC-6B	Coal	349	KFA-6B	Fly ash	35.2
Duvha	1	DFC-1A	Coal	151	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	176	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	204	DFA-5A	Fly ash	208
Duvha	5	DFC-5B	Coal	219	DFA-5B	Fly ash	215
Duvha	6	DFC-6A	Coal	279	DFA-6A	Fly ash	180
Duvha	6	DFC-6B	Coal	247	DFA-6B	Fly ash	200
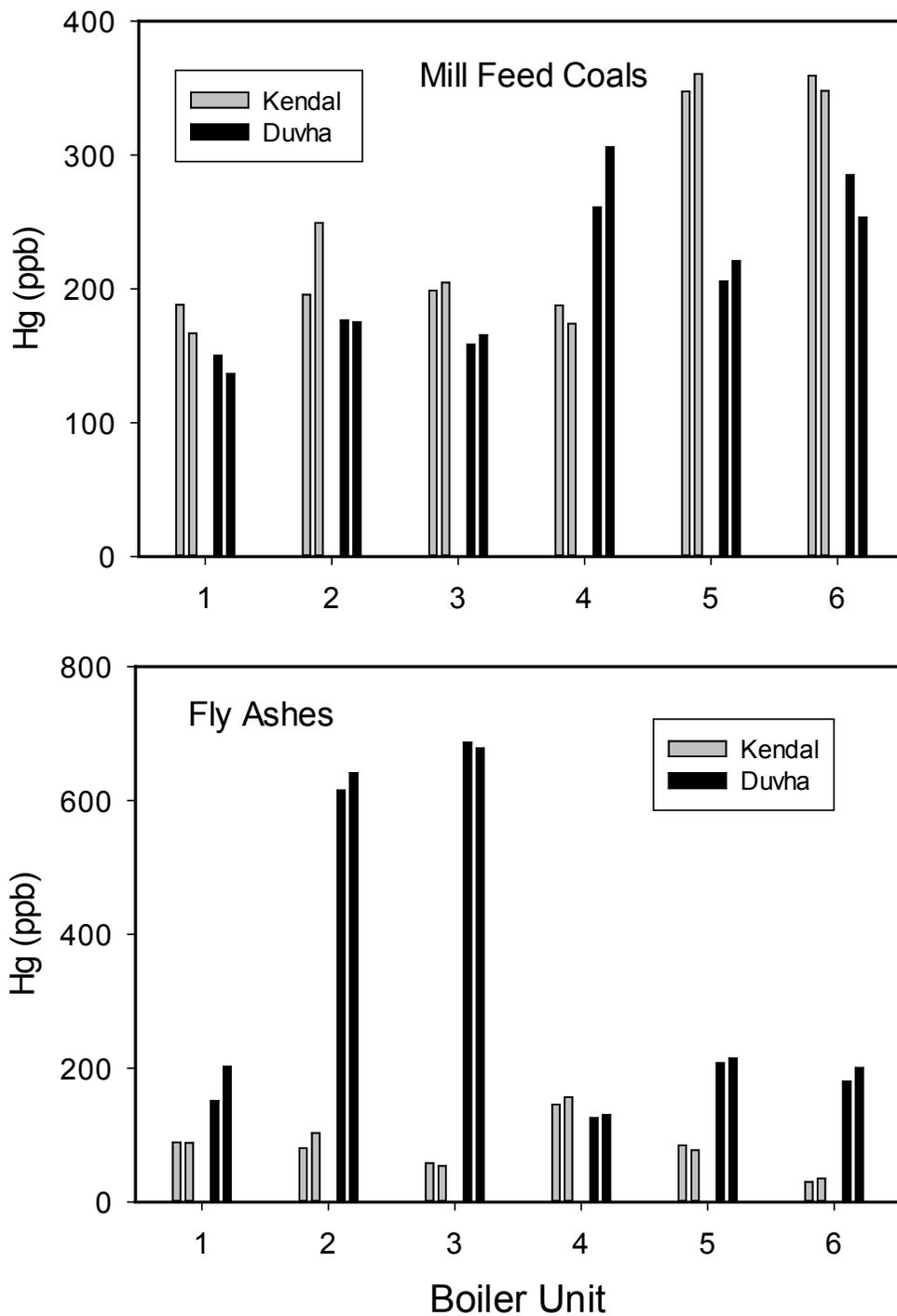
Figure 12. Mercury data (in parts per billion [ppb on a dry basis]) for duplicate mill feed coal (upper plot) and fly ash (lower plot; ppb on an as-determined basis) samples collected from Duvha and Kendal power stations in previous United Nations Environment Programme-sponsored sampling. Duvha units 1–3 are equipped with fabric filters; all other units have electrostatic precipitators. Samples are courtesy of the U.S. Environmental Protection Agency.
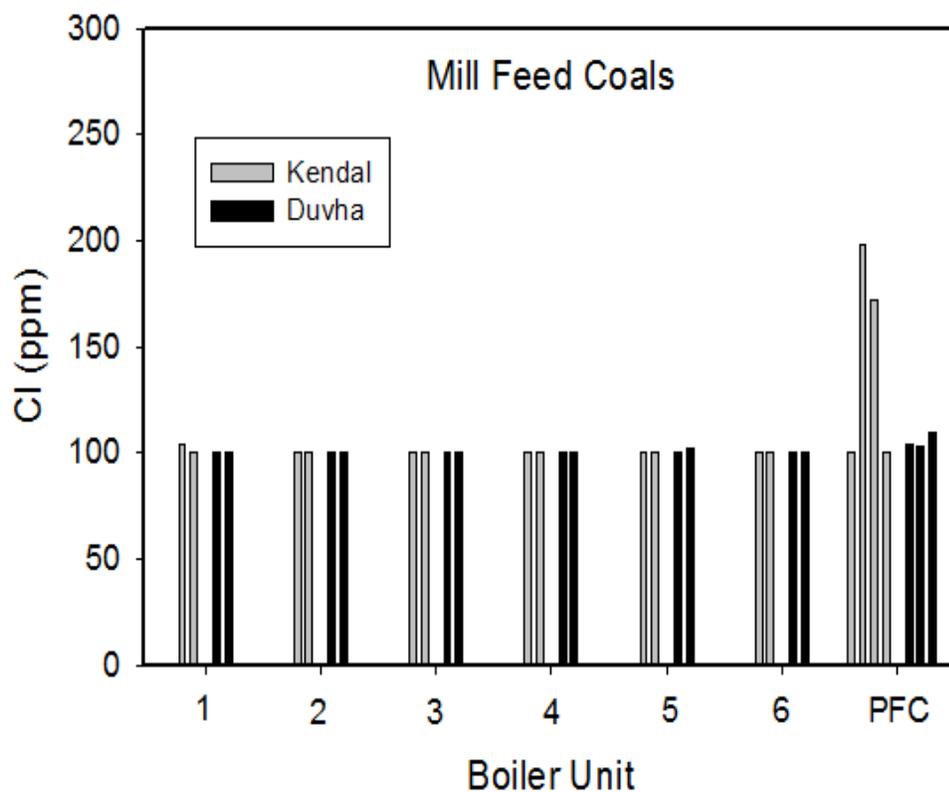
Figure 13. Chlorine (Cl) data by boiler for raw mill feed coal samples from Duvha and Kendal power stations collected in 2010 U.S. Environmental Protection Agency-South African Department of Environmental Affairs sampling (boilers 1–6) and Cl data for samples 6A–D (Kendal) and 3A–C (Duvha) from the group of 42 pulverized feed coal (PFC) samples provided by Eskom in the present study. Cl is expressed on a whole-coal dry basis. Results show that for most samples, Cl content is at or below the detection limit of 100 parts per million (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 air pollution control devices.

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 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 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.[1]

[Hg, mercury; $\mu g/m^3$, micrograms per cubic meter; %, percent; O_2, dioxygen]

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%

[1]Source: Scott, 2011.

4.4   Mass Balance Calculations

The fractions of Hg removed in the PCDs 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 Eskom PFC samples; and (3) the carryover of fly ash from the boiler is 80 percent, a typical proportion. Figures 14 and 15 show the estimated Hg collection efficiency of the PCDs at Duvha and Kendal, respectively. The Hg collection efficiency for the ESPs at Kendal ranged from 2 to 22 percent (10 percent average). The average Hg collection efficiency for the boilers with ESPs at Duvha was 17 percent, while the average Hg collection efficiency for the boilers with FFs was 72 percent.
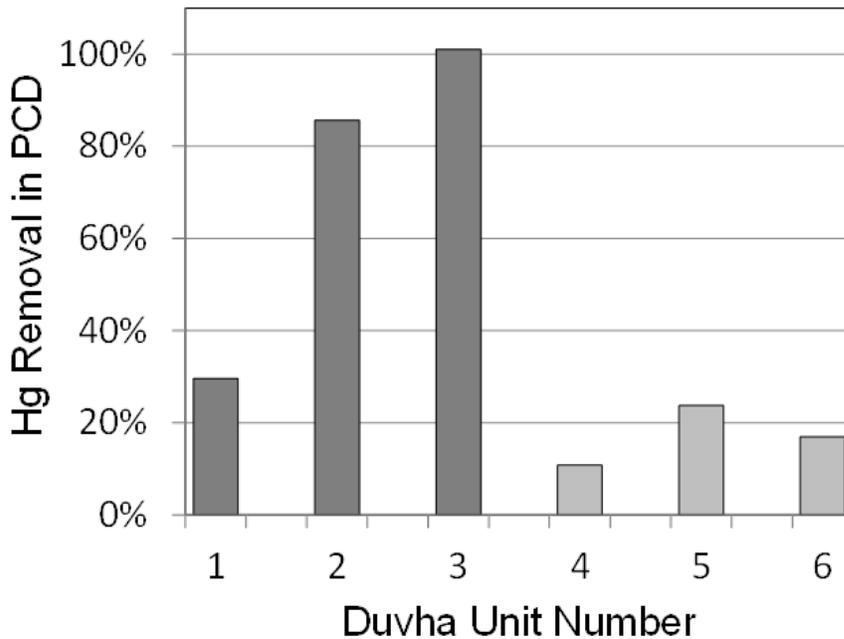
Figure 14.   Estimated mercury (Hg) removal across particulate control devices (PCDs) at Duvha power station. Duvha units 1–3 are equipped with fabric filters; all other units have electrostatic precipitators.
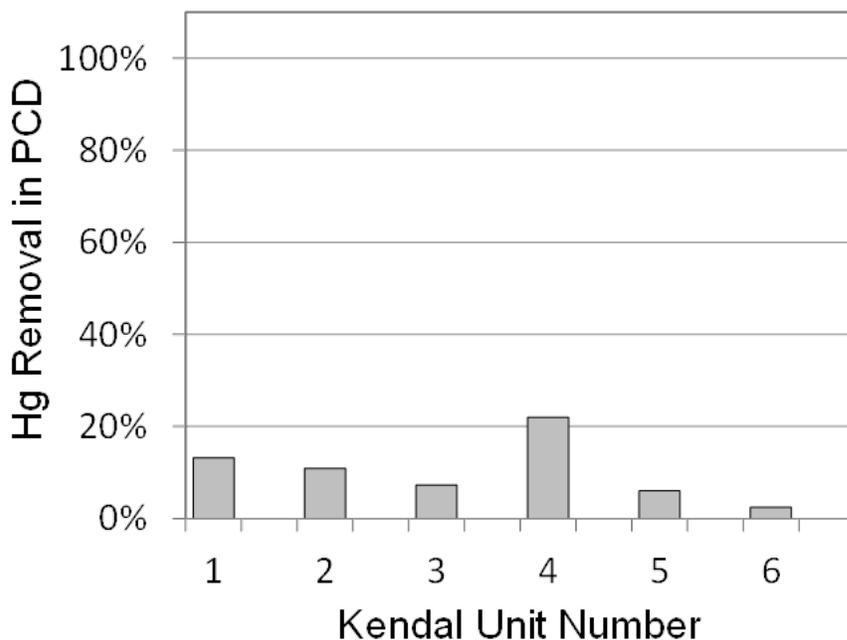
Figure 15. Estimated mercury (Hg) removal across particulate control devices (PCDs) at Kendal power station. All units have electrostatic precipitators.

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 PCDs, 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 APCD (Kilgroe and others, 2002). Using these data, one can calculate the fraction of oxidized Hg at the outlet and the removal efficiency of Hg for PCDs.

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 PCD 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-percent Hg^{2+}, which is consistent with ICR data; the exception is one data point (70-percent Hg^{2+}) from the Kendal power station, which is higher than most of the other ESP data.

Mercury removal (fig. 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

30

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 PCD to remove Hg include: (1) type of PCD, (2) chlorine content of coal, (3) concentration of unburned carbon in fly ash, (4) temperature of PCD, and (5) concentration of sulfuric acid (as SO_3) in the flue gas.
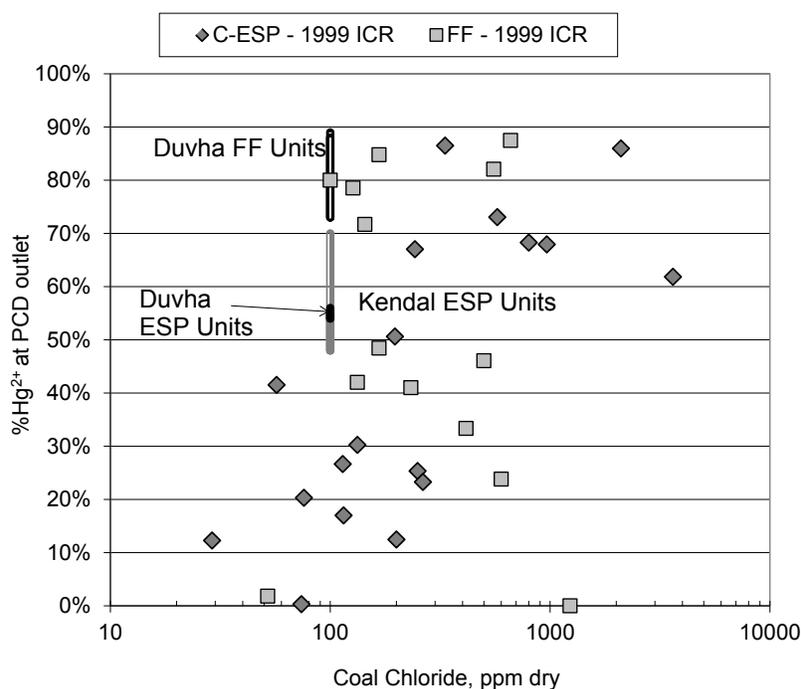
Figure 16. Fraction of oxidized mercury (Hg^{2+}) at the particulate control device (PCD) outlet as a function of coal chlorine content (in parts per million [ppm]): comparison of data from Duvha (fabric filter [FF] and cold-site electrostatic precipitator [C-ESP] units) and Kendal power stations with 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.

31

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 FFs (La Marca, and others, 2006). The temperature of the flue gas at the PCD also affects capture of Hg by fly ash particles and the subsequent removal in the PCD.
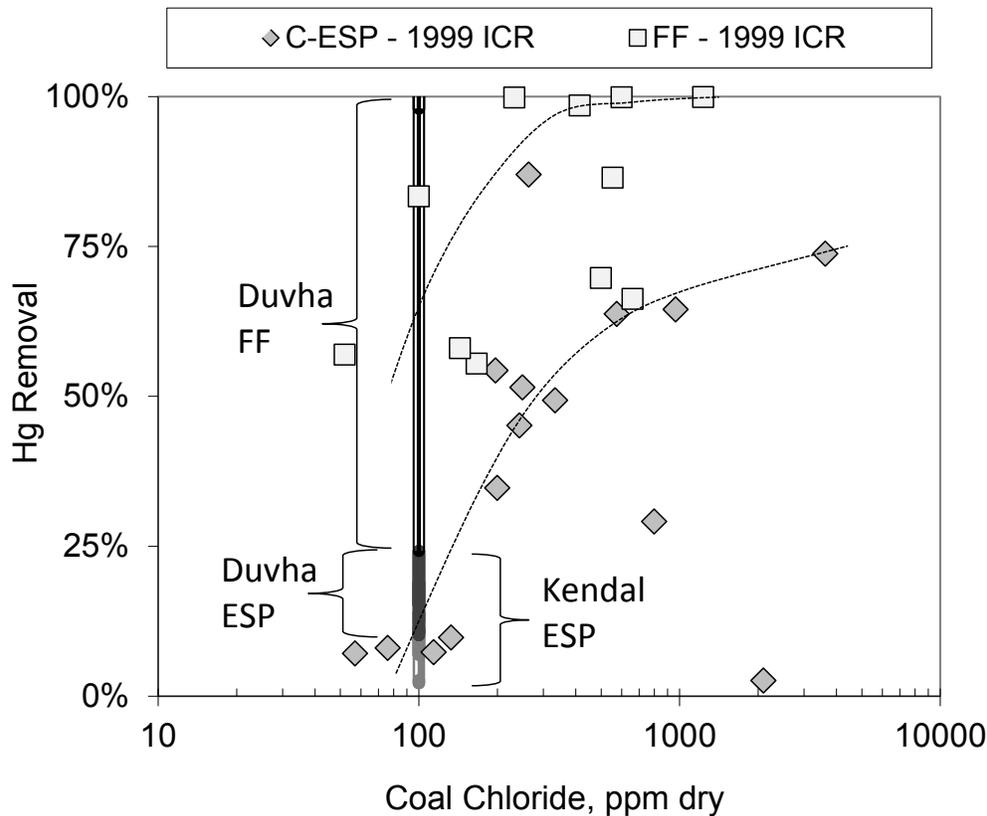
Figure 17. Removal of mercury (Hg) across the particulate control device outlet as a function of coal chlorine content (in parts per million [ppm]): comparison of data from Duvha (fabric filter [FF] and cold side electrostatic precipitator [C-ESP] units) and Kendal power stations with EPA 1999 Information 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 PCD would have the effect of reducing the adsorption of Hg by unburned carbon in ash.
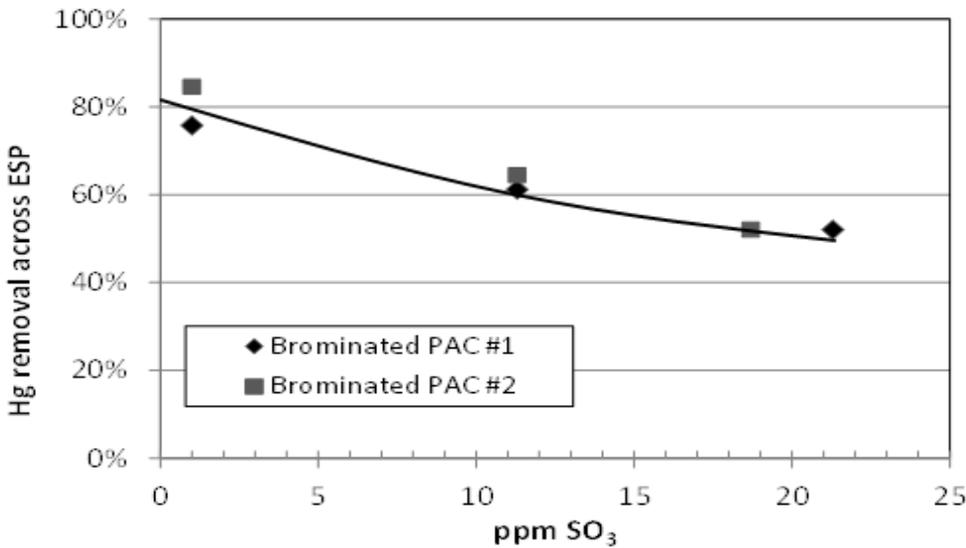
Figure 18. Effect of sulfuric acid vapor (SO$_3$; in parts per million [ppm]) addition on performance of brominated activated carbon (PAC) for mercury (Hg) removal across electrostatic precipitator (ESP). Figure shows results from injection of 160 mg/m^3 PAC upstream of the air preheater (APH) at the 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 on the removal of Hg in certain APCDs (as previously illustrated in figs. 16 and 17). The longer contact time between ash particles and Hg-containing flue gas in a FF, as compared to an ESP, means that the removal of Hg by FFs 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 PCD, 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 units 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 APCDs (Senior, 2015).

Hg removal across ESPs at the different units at Duvha or Kendal also shows considerable variation, from about 2 percent removal to about 22 percent 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.

33

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 #4 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 iron 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 South African Highveld (#4) coal indicate that Hg input to the boiler can be reduced by discarding the stone fraction as is practiced by Eskom. To the extent possible, 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.

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 PCD or by absorption of Hg in a FGD scrubber. To increase Hg removal in the Eskom fleet, several approaches are available.

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

Use of sorbents. The addition of reagents and (or) sorbents can improve Hg capture in existing APCDs. 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 (for example, activated carbon) can be injected into the flue gas upstream of the PCD 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 FF instead of an ESP. Alternatively, a dedicated FF can be installed downstream of an existing ESP. A Hg control sorbent can be injected into the FF in this arrangement, known as a TOXECON FF (Granite and others, 2015; and references therein). Because the fly ash is almost entirely collected in the ESP, the TOXECON FF can be much smaller (less capital cost) than a FF that is designed to remove fly ash and sorbent.

Addition of FGD. Eskom's current fleet of coal-fired boilers has PCDs, but does not have FGD scrubbers. If FGD scrubbers were installed, they should be able to remove gaseous-oxidized Hg with an efficiency of 90 percent or higher. At Duvha and Kendal, gaseous-oxidized Hg amounted to about 50 percent at the exit of the ESPs and 70 to 90 percent 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 FF 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.   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 the Camden, Grootvlei, and Komati stations returned to service since the previous sampling show that input Hg for these 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. Chlorine contents of South African coals are generally low. As such, the extent of Hg self-capture by PCDs is relatively limited.

Results for density separates of a Highveld (#4) coal are useful in predicting Hg variation in coal products used in or exported from South Africa. 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 S 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.

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 PCD and the coal composition (Cl and S contents, in particular). However, variation in operating conditions in the boiler and APCDs affect the Hg emission factors. Greater accuracy in estimation of emission factors can be achieved if differences in these operating conditions are considered. Tracking 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 PCD, as has been done in previous estimates. As shown in Section 4, collection of paired coal and fly ash samples provides a simple and inexpensive way to track the relative performance of APCDs in removing Hg.

References Cited

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., Falcon, R.M.S., and Falcon, L.M., 2011, Trace element concentration reduction by beneficiation of Witbank Coalfield no. 4 Seam: Fuel Processing Technology, v. 92, p. 812–816.

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, v. II: Geological Society of Southern Africa, p. 1899–1921 [not seen; cited in Wagner and Hlatshwayo, 2005].

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 (not seen; results given in Scott, 2011).

Granite, E.J., Pennline, H.W., and Senior, C., eds., 2015, Mercury control; For coal-derived gas streams: Weinhem, Germany, Wiley-VCH, 448 p.

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, N.C., 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., 2015, Mercury and halogens in coal, *in* Granite, E.J., Pennline, H.W., and Senior, C., eds., Mercury control; For coal-derived gas streams: Weinhem, Germany, Wiley-VCH, p. 13–44.

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, June 2006: Pisa, Italy, 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, *in* Air Quality VII—Proceedings, October 2009: Arlington, Va., 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., 2015, Mercury behavior in coal combustion systems, *in* Granite, E.J., Pennline, H.W., and Senior, C., eds., Mercury control; For coal-derived gas streams: Weinhem, Germany, Wiley-VCH, p. 109–132.

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 of the 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 Statistics 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 U.S. Environmental Protection Agency (EPA) Method 7473, in which samples are heated and the evolved Hg is selectively captured as an amalgam and measured by atomic absorption spectrophotometry (EPA, 2007). The Reston MA-3000 has a detection limit of 0.002 nanograms (ng) of 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 milligrams was found to insure complete thermal decomposition. The MA-3000 is calibrated using solutions prepared from high-purity mercuric chloride 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 percent 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.

The 42 feed coal samples and 8 density separates run on the Reston instrument were rerun in Denver as part of the USGS multi-element package. These results are compared in figure A1. There is no systematic difference between the two laboratories, and in most cases, the results agree within 20 percent or better. For the feed coals, three samples (9B, 12A, and 12B) give values that deviate by more than 25 percent between the two laboratories (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 six samples were reanalyzed by both laboratories and in each case, the reruns 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 laboratory. The 48 samples of coal and fly ash from the 2010 sampling at Kendal and Duvha power stations were analyzed for Hg only in the Reston laboratory, and interlaboratory comparison with the Denver instrument is unavailable. However, some coal samples from this group were determined in 2010 at EPA laboratories in Research Triangle Park, North Carolina, by using a Lumex Zeeman instrument; as a check, some of the same powders were analyzed in 2011 using the USGS Reston Hg instrument. The results show good interlaboratory 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 laboratories. 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 (Hg) analysis, USGS Reston laboratory.

Sample	Material	Sample weight [grams]	Hg measurements [nanograms]	Hg concentrations [parts per billion]	Date	Mean [parts per billion]
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. U.S. National Institute of Standards and Technology (NIST) standard mercury (Hg) analysis, USGS Reston laboratory.

NIST	Sample weight [grams]	Hg measurements [nanograms]	Hg concentrations [parts per billion]	Date	Mean [parts per billion]	Certified value [parts per billion]
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
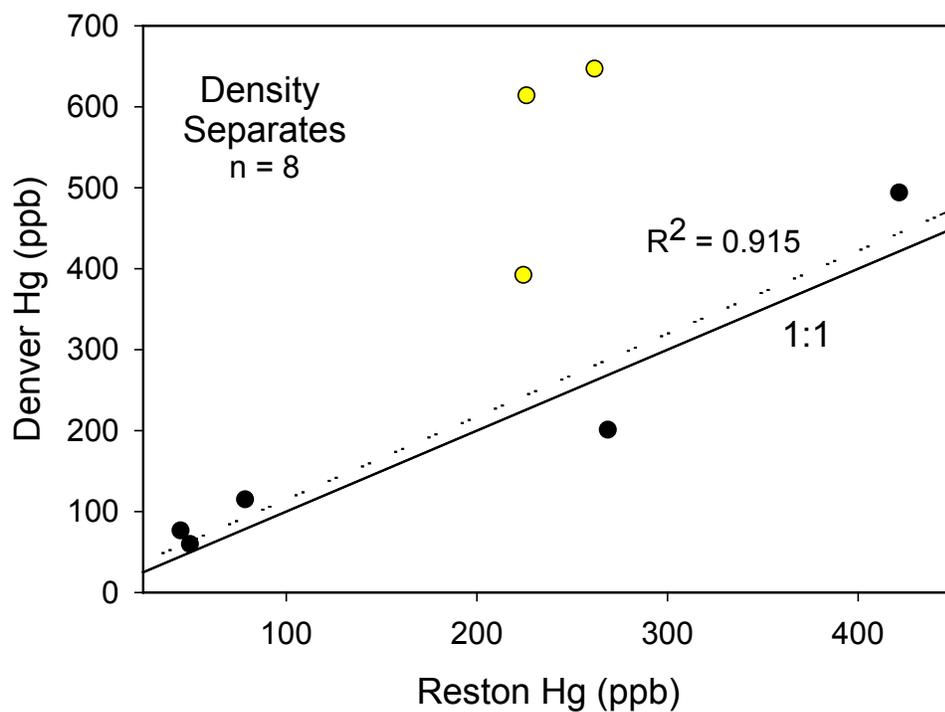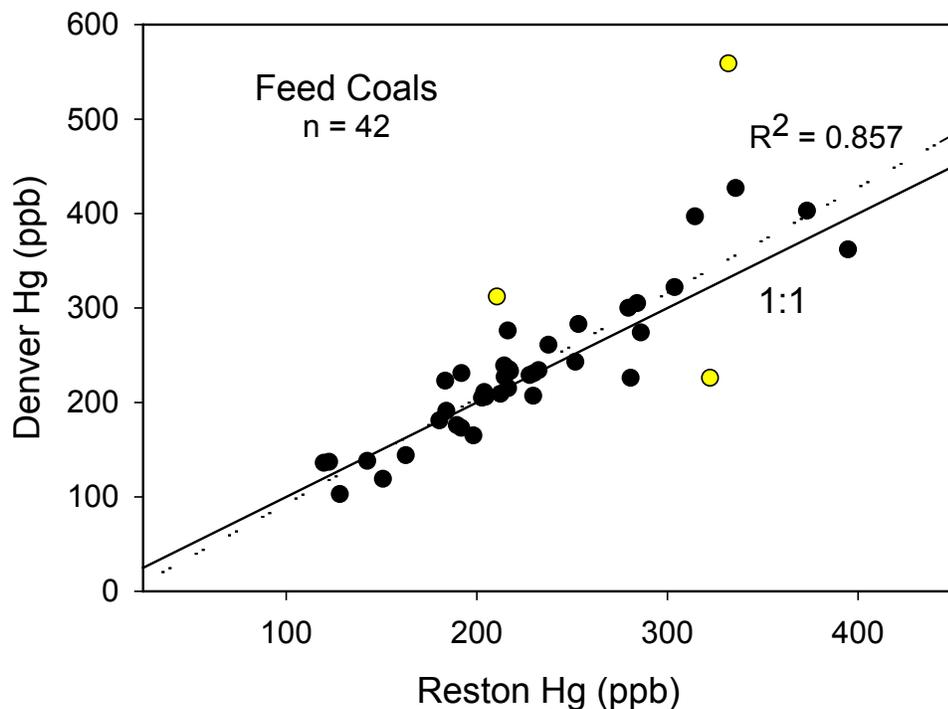
Figure A1. Plots showing correspondence between mercury (Hg) values (ppb, parts per billion) as determined in USGS Reston and Denver Hg analyzers. Solid lines indicate perfect (1:1) correspondence (n, number of samples; R^2, correlation). Dashed lines show linear regression, excluding three samples in each group shown in yellow that were reanalyzed by both laboratories (table A3).

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

Feed coals	Reston original	Denver original	Denver rerun 1	Denver rerun 2	Reston rerun	Mean
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 Inductively Coupled Plasma-Mass Spectrometry

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 (nitric, hydrochloric, and hydrofluoric) 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, by use of preprogrammed 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 2 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 mercury data for 2010 mill feed coal samples; Kendal and Duvha power stations versus previously unpublished determinations on the same splits.

[In parts per billion, on an as-determined basis; --, not determined).

| 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, S, moisture, and calorific value), S forms (consisting of organic, pyritic, and sulfate), and halogens (consisting of total Cl, fluorine, and Br)—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; and Bromine (no ASTM method available).

Results for ash yield and moisture obtained from Geochemical Testing, Inc., 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 laboratories. 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 laboratories. 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.
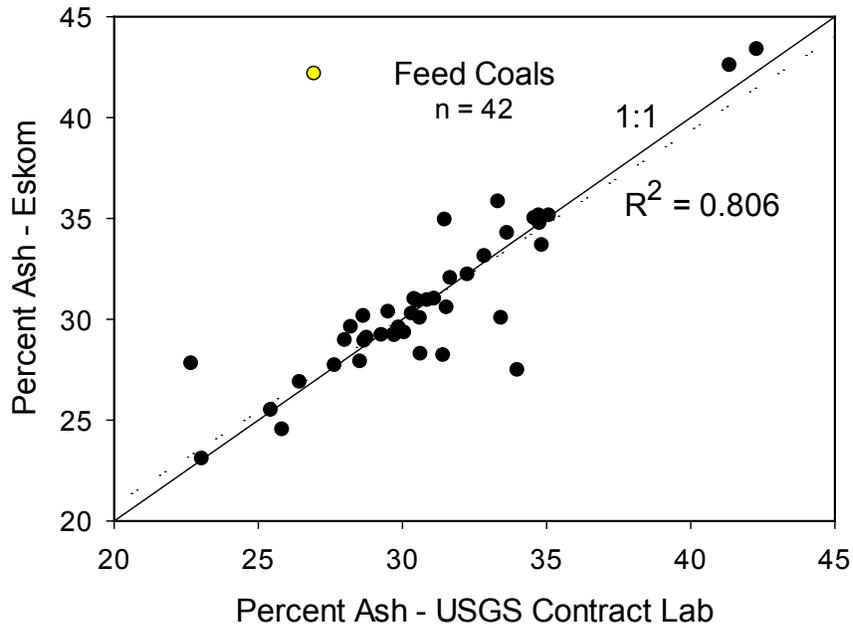
Figure A2. Plot of ash yield determinations (on a dry basis; n, number of samples; and R^2, correlation) for USGS contract laboratory and results provided by Eskom. One sample shown in yellow (9C) is omitted from the linear regression. Eskom ash value for this sample is used in table 4.
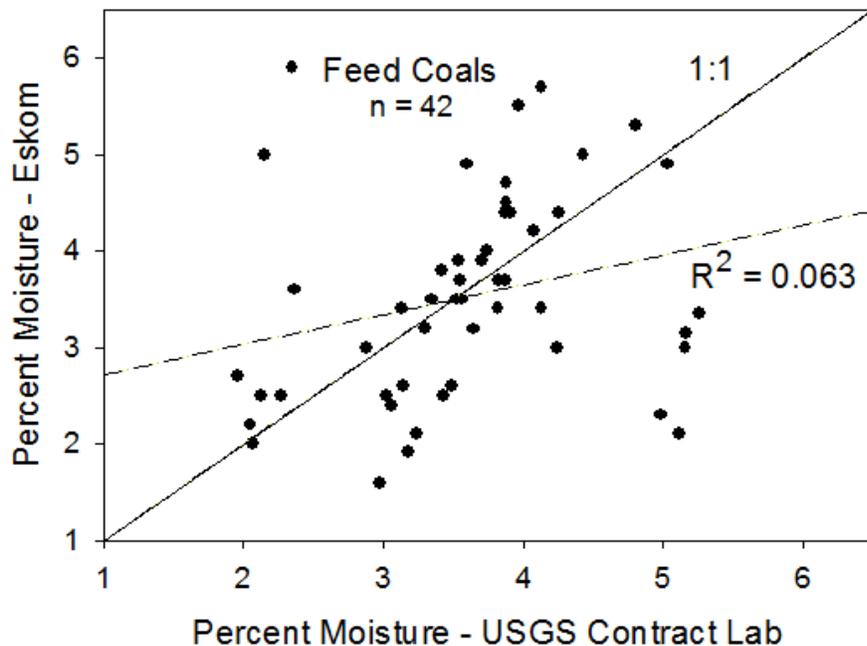
Figure A3. Plot of moisture determinations (n, number of samples; R^2, correlation).

Revisions to Trace Element Results

All 50 samples in this study were redetermined by Actlabs (Ancaster, Ontario, Canada) using their Ultratrace-4 sample digestion procedure. This procedure, along with the suite of elements obtained, most closely replicates the USGS approach originally used in this study. Prior to analysis, coal samples were first ashed by Actlabs at 525 °C for 36 hours, replicating the procedure used in the USGS laboratories. The prepared coal ash was then digested using Actlabs' 4-acid (nitric, hydrochloric, hydrofluoric, perchloric) Ultratrace-4 procedure. In this digestion procedure, loss of Cr, As, and Sb may occur by volatilization during sample dry-down; for this reason, results for these three elements determined by Actlabs are considered unreliable.

To further insure the validity of trace element data contained in the revised version of this report, all samples were redetermined at USGS laboratories in Denver using appropriate ICP-MS protocols. In these re-analyses, coal samples prepared by ashing at 525 °C for 36 hours were digested using the USGS 3-acid (nitric, hydrochloric, hydrofluoric) procedure. Trace element results (by ICP-MS) given in table 6 reflect values obtained from Actlabs except for Cr, As, and Sb, for which USGS determinations were substituted in table 6 due to the potential for loss of these elements in the Actlabs digestion procedure. Together, these redetermined results replace the original determinations by ICP-MS included in table 6 of the previous version of this report. In both the Actlabs and USGS redeterminations, conversion of results to a whole-coal dry basis was calculated using moisture values obtained from Geochemical Testing, Inc., a USGS contract laboratory (table 4; appendix 1). Note that results for mercury given in table 6 are unchanged from those given in the previous version of this report, except for minimal adjustments to express

46

the results on a whole-coal dry basis. Results for halogens, determined by Geochemical Testing, Inc., using ion-selective electrodes, were already expressed on a dry basis in the previous version of this report and are unchanged here.

Comparison of ICP-MS results obtained in redeterminations by Actlabs and by the USGS is given in table A5, showing correlation by element expressed as R^2 values for the combined suite of feed coals and density separates. Overall, agreement between the two sets of redeterminations is very good. Correlations tend to be less robust for elements having sub-ppm concentrations (for example, Tl, Sb), which is expected as method detection limits are approached. Differences found for Cr (seven samples) and Sb (two samples) are consistent with loss of these elements in the Actlabs determinations, and USGS results for these elements are substituted in table 6 of the revised version of this report. USGS results for As are also reported in table 6 because of the potential for As loss in the Actlabs digestion procedure. For As, however, results for the two laboratories agree well ($R^2 = 0.83$) and no systematic differences were found.

Table A5. Linear regression results (R^2) comparing values obtained by USGS contract laboratory Actlabs and USGS Denver laboratories in 2015 ICP-MS reruns of Eskom feed coals and density separates described in this report.

Element	Regresssion (R^2) Actlabs vs. USGS	Number of Samples	Source of Data used in Table 6
Be	0.869	50	Actlabs
Cr	0.478	50	USGS
Mn	0.957	50	Actlabs
Co	0.959	50	Actlabs
Ni	0.912	50	Actlabs
Zn	0.888	50	Actlabs
As	0.829	50	USGS
Mo	0.699	49[1]	Actlabs
Pb	0.812	50	Actlabs

[1]Sample 14H is excluded from linear regression for Mo.