The occurrence of potentially hazardous trace elements in five Highveld coals, South Africa

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Abstract

Permian coals of the southern hemisphere are generally considered to contain lower concentrations of sulfides, halogens, and trace elements when compared to northern hemisphere Carboniferous coals. Few studies have considered the trace element content in South African coals, and little or no work has been published for Highveld coals. Of the nineteen coal fields in South Africa, the Highveld coal field is one of the nine currently producing, and is second largest in terms of production. Five run of mine samples and a high ash middlings product from the Number 4 Lower seam were analyzed, totaling six sample sets. Fourteen trace elements (As, Cd, Co, Cr, Cu, Hg, Mn, Mo, Ni, Pb, Sb, Se, V, and Zn) were selected for this study based on the global perception that these elements may be hazardous to human health and/or the environment when they are released during coal utilization. Several sample preparation techniques were tested using certified reference materials (SARMs 18, 19 and 20) to determine the most repeatable technique for these coals. The samples were analyzed by ICP-AES and CVAA (Hg only). Microwave digestion proved to be generally unreliable despite the utilization of several different methods. A slurry direct injection method into the ICP-AES provided good correlations with the reference material, but requires further development to enhance the confidence level in this relatively unexplored technique. Samples prepared based on three ASTM standards for the determination of trace elements in coal provided repeatable results in most instances, and were the preparation methods utilized for the Highveld coals.

The trace element values determined for the Highveld coals are generally in good agreement with values available in literature for South African coals, with the exception of Hg, Mn and Cr. Hg values reported here are lower, Cr and Mn higher. Results generally agree well with analyses on the same samples conducted by the United States Geological Survey. When considering the global ranges for trace elements, the Highveld range values are within Swaine's range boundaries with the exception of Cr. Compared to the cited global average values for the fourteen trace elements determined, the values obtained for the Highveld coals generally fall below or well below these average values, with the exception of Cr and Mn. Concentrations of Cd and Cu are lower compared to global average values, and As, Mo, Pb, Se, Sb, and Zn can be considered low to very low. Arsenic is ten times lower compared to typical USA values. Concentrations of Co and Ni are similar to global averages, with V and Hg being very slightly higher. The middlings samples reported higher concentrations of most elements, related to the higher ash content of these samples. Of interest, the chalcophile elements determined are all depleted in the Highveld coals compared to global averages, and the siderophile elements are enriched or comparable to global averages.

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Risk-based health studies in the USA on coals with similar or higher Hg and significantly higher As contents have not reported negative health effects, and therefore it could be assumed that the mobilization of these trace elements from the five Highveld coals are unlikely to cause human health problems. Work is ongoing to determine the modes of occurrence of these HAPs and to address the partitioning behaviors and speciation states of these elements during coal utilization.

1. Introduction

South Africa is the worlds' 6th largest producer of coal, mining around 220 Mt of coal per annum, over a third of which is exported (DME, 2004). Relatively poor quality coal is used for combustion and gasification processes in South Africa. The organic and inorganic constituents have been well studied over the years, but the trace element concentrations (<1000 part per million (ppm) by weight on a dry basis) are less well known. Trace elements occur at ppm (or ppb levels) in coals, and the large tonnages of coal utilized produce significant quantities of potentially toxic trace elements to accumulate and become a concern in the environment and to human health.

Several lists of potentially toxic elements have been compiled. The USA Clean Air Act Amendment of 1990 (Title III) lists 189 potentially hazardous air pollution substances (HAPs), 15 of which are inorganic elements potentially originating from coal utilization (Huggins, 2002), and may in time become regulated; mercury has already been regulated to some extent globally. Title III Hazardous Air pollutants include antimony (Sb), arsenic (As), beryllium (Be), cadmium (Cd), chlorine (Cl), chromium (Cr), cobalt (Co), fluorine (F), lead (Pb), manganese (Mn), mercury (Hg), nickel (Ni), selenium (Se), thallium (Th), and uranium (U) (Finkelman, 1994; Huggins, 2002). Booth et al. (1999) list As, B, Cd, Hg, Mo, Pb, and Se as elements of greatest environmental concern; Cr and Ni moderate concern; and Li and Sb of minor concern. The US National Committee for Geochemistry lists As, B, Cd, Hg, Pb, Mo, and Se as those trace elements of major environmental concern, and Cr, Cu, F, Ni, V, and Zn of moderate concern (Bushell and Williamson, 1995). The Canadian Environmental Protection Act lists As, Cd, Hg, Ni, and Pb as toxic elements of concern. Goodarzi (2002) lists As, Cd, Cr, Cu, Hg, Mo, Pb, Se, V, and Zn as elements of

prime environmental concern. Based on the above, the following fourteen elements were selected for the current study: As, Cd, Co, Cr, Cu, Hg, Mn, Mo, Ni, Pb, Sb, Se, V, and Zn.

A few studies have considered the trace element contents in South African coals. Table 1 shows published trace element values for coals from this region compared to USA, Australia, and global values (Zhang et al., 2004 after Beaton et al., 1991; Ketris, in press). Willis (1983) obtained samples from the Klip River (Newcastle area), Sasolburg, Witbank, and Eastern Transvaal coal fields and concluded that, in general, the trace element content of the South African coals analyzed was lower than that reported for coals from the USA, Germany, Belgium, and Australia. Watling and Watling (1982) concluded, from a study on South African coals, that a vertical variation in trace metal content was more notable than a horizontal variation, indicative of different depositional environments vertically and possibly of localized metamorphism. Although Watling and Watling (1982) did not include Highveld coals in this study, Highveld coals from the same seam are likely to exhibit similar trace element composition to Witbank Coals. Cairncross et al. (1990) also considered the geochemical and sedimentological relationship between coals from the Witbank Coal field, specifically the Number 2 seam. The values reported by Cairncross et al. (1990) are generally in agreement with those of Watling and Watling (1982), despite different analytical techniques. A report by ACARP (1996) compares the trace element content of six South African thermal export coals to Australian thermal export coals. The Australian samples have lower trace element contents than the South Africa coals, but the two southern hemisphere sample sets are more comparable with each other than comparable to USA coals. Swaine (1990) included selected South African coals (data obtained from published literature) in the

Table 1
Comparison of trace elements in South African and global coals (ppm, unless specified)

Trace element	Witbank No 2 seam (Cairncross et al., 1990)	South African coals (Watling and Watling, 1982)	South African Coals (Willis, 1983)	USA/USGS (Orem and Finkelman, 2004)[a]	West Virginia Coals (WVGES, 2002)	Australian thermal export coals mg kg^{-1} (ACARP, 1996)[b]	Global range (Swaine, 1990)	Average global values (Zhang et al., 2004)[c]	Average global values (Ketris, in press)[d]
Antimony	0.47			1.2	1.02	0.47	0.05–10	3.0	1.0 ± 0.09
Arsenic	4.6		0.9–8.2	24.0	17.13	1.26	0.5–80	5.0	9.0 ± 0.7
Cadmium		0.39		0.47	0.1	0.067	0.1–3	0.6	0.2 ± 0.03
Chromium	28	25	12–63	15.0	17.85	15.9	0.5–60	10	17.0 ± 1
Cobalt	7.9	7.8	3.3–14	6.1	7.41	4.48	0.5–30	5	6.0 ± 0.2
Copper	9.7	10.9	4.2–16	16.0	20.4	9.8	0.5–50	15	17.0 ± 1
Lead	10	10.1	1.9–25	11.0	8.19	6.8	2–80	25	9.0 ± 0.7
Manganese		30		0.11	21.29	51.4	5–300	50	76.0 ± 6
Mercury		0.327		0.17	0.19	0.042	0.02–1	0.12	0.1 ± 0.01
Molybdenum			<1–2.7	3.3	2.37	1.71	0.1–10	5	2.1 ± 0.1
Nickel	17	15.5	6.9–32	14.0	13.99	11.5	0.5–50	15	17.0 ± 1
Selenium	0.9		<0.4–0.9	2.8	4.2	0.5	0.2–10	3	1.6 ± 0.1
Vanadium	27		17–43	22.0	24.36	20.6	2–100	25	28.0 ± 1
Zinc	10	18.1	3.2–16	53.0	14.97	12.0	5–300	50	28.0 ± 2

[a] Arithmetic mean.
[b] Average value of 10 coals.
[c] Extracted from Zhang et al. (2004), compiled from Valkovic (1983), after Beaton et al. (1991).
[d] In press. Translated by Dr Y. Yudovich (personal communication); hard coals.

determination of a global range for each trace element present in coal; South African values tend to fall towards the lower boundary of these global range values. Zhang et al. (2004) (after Beaton et al., 1991) and Ketris (in press) recently reported average global values for trace elements in coals. Generally the values reported for South African coals in Table 1 are lower than (Sb, Cd, Cu, Pb, Mn, Mo, Se, Zn), or comparable to (As, Co, Ni, V) Zhang et al. (2004) global values, with the exception of Cr and the possible exception of Hg. Arsenic is four to five times lower than typical USA values (Orem and Finkelman, 2004). The new data presented in this paper will enhance the database of the occurrence of potentially hazardous trace elements in South Africa, specifically in the Highveld coal field.

A major consideration in the determination of trace elements in coal and other materials is the sample preparation technique. A wide variety of sample preparation and analytical techniques are available (Ebdon and Wilkinson, 1987; Finkelman, 1994; Atkin and Clift, 1995; Bushell and Williamson, 1995; Querol et al., 1995, 1996; Briggs, 1997; Meier, 1997; Palmer and Klizaz, 1997; Booth et al., 1999; Richaud et al., 2000; Khan et al., 2002; Huggins, 2002). Several sample preparation techniques are discussed in this paper, including preparation by sequential leaching, microwave digestion, ASTM standards, and a slurry direct injection ICP technique.

2. Geological setting and typical coal properties

South Africa is a country rich in mineral resources (Fig. 1), and has approximately 75% of the coal resources of Africa. Of the nineteen coal fields in South Africa (Fig. 2), the Highveld coal field (number 12 in Fig. 2) is one of the nine currently producing, and is second largest in terms of production. The Highveld coal field is located in the province of Mpumalunga, approximately 200 km south-east of Pretoria, due south of the Witbank Coal field, and covers approximately 7000 km^2 (Jordaan, 1986). The Vryheid Formation of the mid-Permian Ecca Group of the Karoo Supergroup hosts the sedimentary succession in which the coal deposits of the Highveld coal field occur (Fig. 3) (Falcon, 1986b). Coals in this sequence were de-

posited in the Karoo Basin in a cool to warm deltaic environment with run-off water originating from the retreating glaciated highlands to the north. The mineralogy of the coal seams in the Witbank Coal field strongly reflects that of the northerly source region by having mineral and elemental compositions similar to the granitic highlands (Cairncross et al., 1990). Changing palaeoenvironments, progressing from glacial to deep marine, to deltaic, fluvial, and ending with aeolian during the Permian (Falcon, 1986a) affected the composition of the coals. Post-Karoo erosion removed substantial volumes of coal, specifically along the northern margin, and giving rise to the coal seams varying from 300 m to very thin in the north (Jordaan, 1986). The coals from the Highveld coal field are typically low rank bituminous (mean %RoV around 0.58 to 0.65) with a moderate to high ash content (20–30%).

Permian coals of the southern hemisphere generally contain lower sulfides, chlorine, and trace elements, and have higher ash and inert organic matter than Carboniferous coals of the northern hemisphere (Falcon, 1986a). The fluctuating water levels and salinity levels, varying temperatures, humidity, rainfall, and differing plant communities affected the geochemical environment during coalification, influencing the organic and inorganic affinities of trace elements in coal (Cairncross et al., 1990). Ion exchange between mineral matter and macerals following coalification gives added complexity to establishing the distribution of trace elements in coals (Bushell and Williamson, 1996). Penetration of the South African coal-bearing sequences by large-scale igneous intrusions after coalification may have also influenced the geochemistry of the coals; in addition the sills and dykes had a destructive effect on the coals in most areas of the coal field (Jordaan, 1986).

The Highveld coal seams have a similar nomenclature to those of the Witbank Coal field, the seams being numbered from the base upwards in chronological order from seam 1 to 5 (seam 6 rarely occurs) (Fig. 4). The number 4 lower seam (No 4L) is the main pay zone, and is reasonably well developed throughout the Highveld area, ranging in thickness from 1 to 11 m, 4 m on average (Jordaan, 1986). High ash content typifies the upper sections of the seam. Generally, the in-situ coal qualities of the High-

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Fig. 1. Location of mineral deposits in South Africa. ©—coal (source: http://minerals.usgs.gov/minerals/pubs/country/maps/92359.gif Downloaded 04/01/2005).
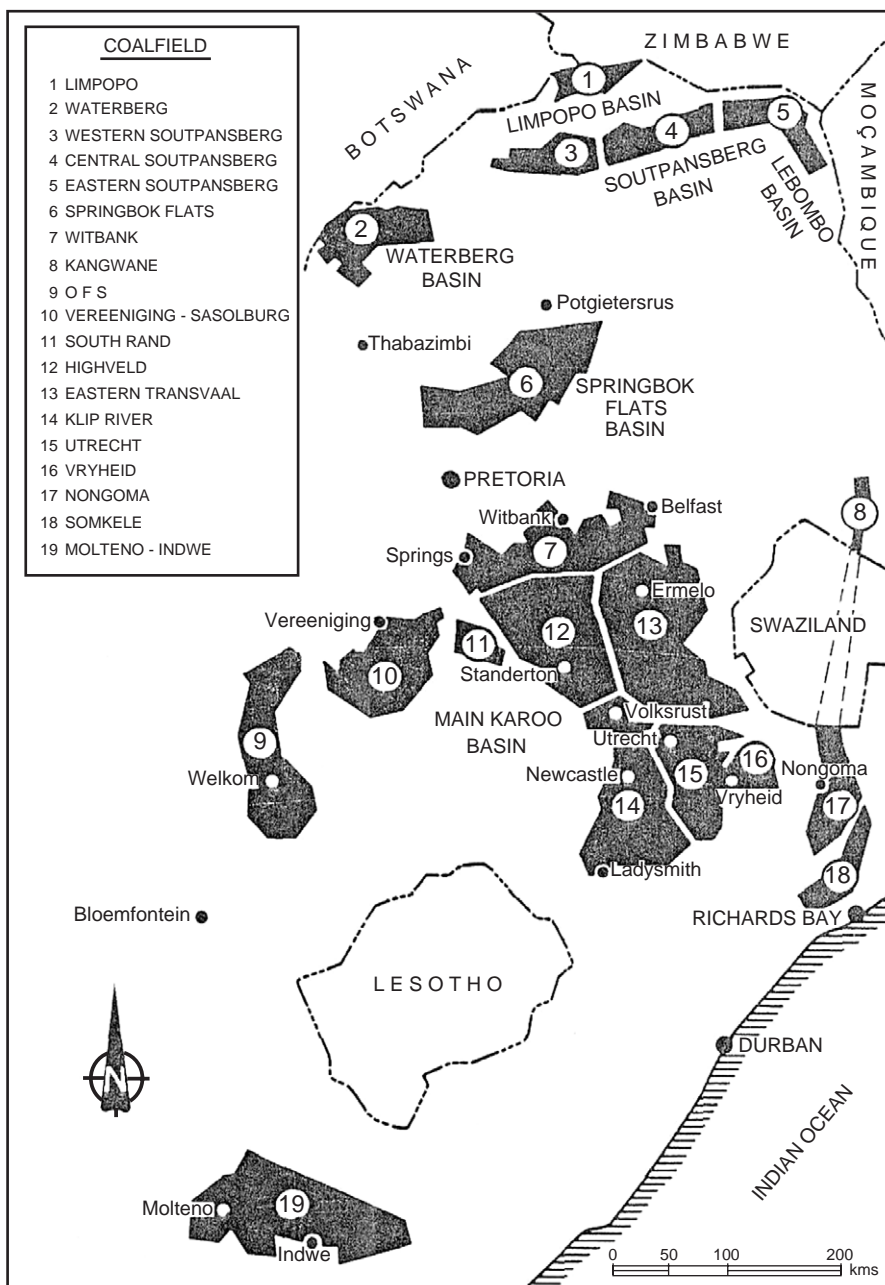
Fig. 2. Coalfields of South Africa (Pinheiro, 2000).

veld coals are lower than those of the Witbank Coals, and export coals are not typically generated in this basin (although two mines are currently exporting a washed product). Dolerite intrusions (sills and dykes) have disturbed the region and have caused localized

devolatilization of the coal, resulting in mine planning and development problems. The No 4L Seam is characterized by ubiquitous laminae and thin mudstone beds which are mined (Pinheiro, 2000). Kaolinite dominates the mineral matter composition of the No

Fig. 3. Sedimentary succession Witbank–Highveld coal field (source: Falcon, 1986b).

4L seam (43.7%), followed by quartz (24.7%), pyrite (8.5%), calcite (7.82%) and dolomite (7.1%) (Buhmann, 1991).

3. Samples and analytical methods

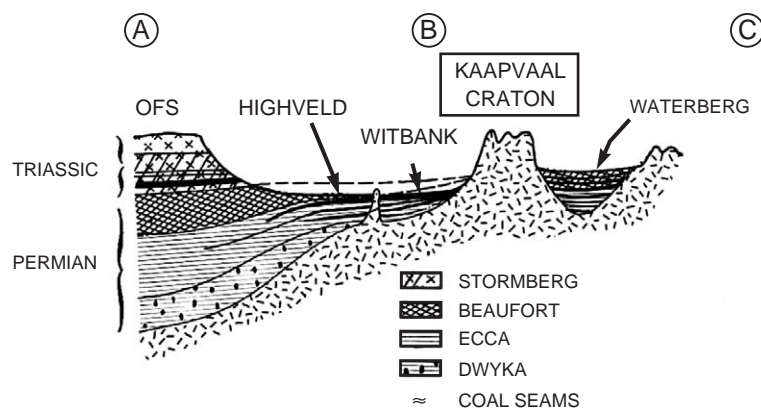The coals used in this investigation are run-of mine from the No 4L seam. Samples were obtained from five different mines in relative close proximity at various times during 2002 and 2003. Six sample sets were analyzed, including a screened middlings product from one of the mines, totaling 32 samples. Two samples from each set were split, and submitted to the USGS laboratory as well as the local laboratory; the results obtained are compared. This was conducted as a bench-marking exercise as laboratories in South Africa are relatively new to popular trace element analytical methods. Typical proximate, ultimate, and petrographic values obtained for the six Highveld coal samples under discussion are found in Table 2.

A wide variety of sample preparation and analytical techniques are available for the determination of trace elements. Palmer and Klizaz (1997) and a team at the USGS reported a detailed investigation using seventeen different procedures involving eleven different techniques to determine the concentrations of 67 different elements. Most literature reviewed report several combinations of instrumental techniques for trace elemental determination, a common selection being the combination of XRF, XRD, and ICP techniques (Huggins, 2002; Querol et al., 1995, 1996). A single technique is unlikely to determine all the trace elements in coal due to instrumental limitations. Inductively coupled plasma atomic emission spectroscopy (ICP-AES) or inductively coupled plasma mass spectroscopy (ICP-MS) are regarded as the preferred analytical techniques for the determination of trace elements in solution. Cold-vapor atomic-absorption spectrometry (CVAAS) is the most common technique used for mercury determinations. A Perkin Elmer 4300 DV ICP spectrometer with axial-torch configuration and a CCD detector (ICP-AES), and a Perkin Elmer MAS-50-A Coleman Hg analyzer (CVAA) were used during this study.

As ICP and CVAA typically require solutions for analysis, the trace elements in solid samples require extraction via destructive digestion or dissolution techniques. A major concern in trace element assessments is these sample preparation techniques. Typically coals can be ashed to remove the organic fraction, and the remaining inorganic fraction dissolved in an acid solution to extract the elements of interest for analysis. However, due to their volatility, some elements are lost as volatile gases; Hg for example is likely to be released by 100 to 150 °C. Hence preparation should be conducted in a closed vessel to retain all gases, and an ashed sample cannot be considered truly representative for all elements in coal samples. Sample preparation by leaching or microwave digestion (closed vessel) techniques reduces or even eliminates the loss of the more volatile elements (Atkin and Clift, 1995; Querol et al., 1996; Briggs, 1997; Richaud et al., 2000). Microwave digestion appears currently to be the most popular prep-
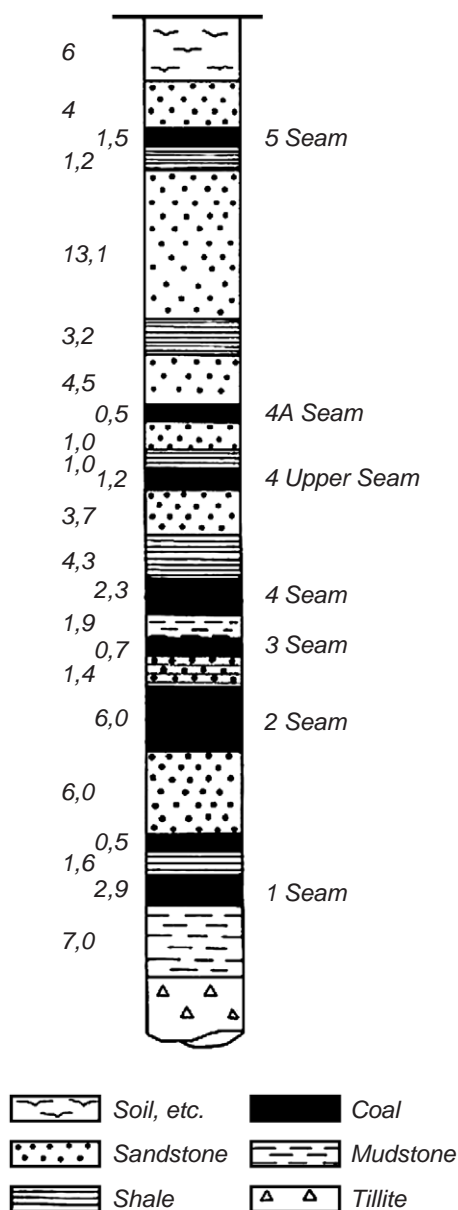
Fig. 4. Stratigraphic column of the Witbank–Highveld coal field (source: Lurie, 1989).

aration technique, possibly due to the comparatively rapid sample preparation and the reduction of contamination. In principle, preparation by microwave digestion should offer complete digestion and good repeatability of results in a short time period, and in addition is less harmful to laboratory personal when compared to conventional methods.

Several sample preparation methods were tested during this study in order to determine the most appropriate preparation technique for our laboratory and South African coals (Hlatshwayo, 2002). Sequential leaching, ASTM methods, microwave digestion, and a slurry direct injection method by ICP-AES were investigated. Certified reference materials (SARM 18, 19 and 20) were used as controls for each investigation, and all samples were analyzed by ICP or CVAA at our laboratory. For the Highveld coals, standard dry coal crushing, milling and screening was employed to obtain particle size of less than 250 μm. A splitter was used to obtain a representative sample. The analyses on the Highveld coals were run in batches, with each batch including a standard reference sample.

Due to the trace amounts requiring detection, it is essential to eliminate all possible sources of contamination. All plastic ware, glassware, and apparatus were acid washed with 10% nitric acid and thoroughly rinsed with distilled water prior to use. Analytical grade reagents from Merck and Sigma Aldrich were used for all experiments.

3.1. Sequential leaching (slurry and column methods)

The procedure described by Khan et al. (2002) was applied. 5 g of coal was sequentially leached at 50 °C with ammonium acetate, 3 M HCl, 2 M HNO_3, and a mixture of H_2O: HNO_3: HCl (10:5:1). The sample was slurried in 50 cm^3 of extraction solution in a beaker with a coated magnetic stirring bar. The contents were stirred in a 50 °C water bath for 2 h, then filtered using Whatman filter paper. The residual coal was washed with large amount of boiling distilled water, and the filtrates and washings from each extraction were combined and evaporated to a lower volume. The filter paper was dried at 40 °C in a nitrogen atmosphere; the remaining particles were then wiped into the beaker and the leaching repeated 3 times. A draw-back of this method is that complete extraction of trace elements is not achieved, with some elements remaining encapsulated in clays or undigested coal particles. There are also organically bound elements and elements in silicates which may not be dissolved effectively.

A second trial was conducted using a 37-cm glass column at room temperature to obtain leachate solutions. 30 ml of each filtrate sample was used in this

Table 2
Typical proximate, ultimate and petrographic values for the selected Highveld coals (DME, 2004)

Sample no	Calorific value MJ/kg	Proximate analyses (% air-dried)					Ultimate analyses (% air-dried)				Petrographic data (vol. %)			Rank (mean random percent)
		H_2O	Ash	Volatile matter	Fixed carbon	Total sulphur	Carbon	Hydrogen	Nitrogen	Oxygen	Vitrinite	Liptinite	Inertinite	
1	22.64	4.3	22.9	22.7	50.1	1.12	58.23	3.04	1.44	8.97	22	4	74	0.60
2	21.03	4.2	26.9	21.5	47.4	0.92	52.22	2.60	1.30	9.05	33	5	62	0.61
3	20.34	3.9	29.7	22.2	44.2	1.23	54.81	2.74	1.34	9.09	17	3	80	0.64
4	22.27	6.2	20.5	26.9	46.4	0.74	58.19	3.05	1.44	9.88	30	4	66	0.58
5[a]		4.6	24.8	23.7	46.8	0.99	56.11	3.13	0.56	9.81	24	3	73	0.61
6[a]		4.4	31.2	21.9	42.2	1.11	49.7	2.83	0.56	10.2	20	4	76	0.61

[a] In-house data.

extraction. Cotton wool was used as a filter in the mouth of the column. The same sequence was followed as in the above method (ammonium acetate, 3 M HCl, 2 M HNO_3, and a mixture of H_2O: HNO_3: HCl (10:5:1)). Residence time of the first solution was about 2 h, followed by 30 min each for the other solutions.

3.2. ASTM methods

Two ASTM methods were followed for the preparation of the samples for Hg, As, and Se analysis namely: ASTM D6414-99 (1999) for Hg determination and ASTM D4606-95 (2000) for Se and As determination. The Hg preparation method is an incomplete dissolution in an acid mixture; the As and Se techniques include controlled ashing. The only notable difference to the standard methods utilized is that ICP-AES was used for the detection of As and Se instead of CVAA.

A slightly modified ASTM D6357 was followed for the other elements. 5-g sample is ashed by heating at 300 °C for 1 h in a muffle furnace, then at 500 °C for a minimum of 3 h until ashing is complete. The ash is dissolved in a mixture of perchloric and hydrofluoric acids in a Teflon beaker at low heat; $HClO_4$ and HF give complete dissolution of the ash. The liquid is made up to 100 ml with distilled H_2O for ICP analysis.

3.3. Microwave complete digestion

The microwave digestion is a relatively new technique, substituting for digestion using beakers on a hot plate in a fume hood. In both techniques, the coal particles are broken down by acids with the addition of heat to ensure that all the elements requiring detection are in solution. The advantage of the microwave digestion is that it reduces sample preparation time by more than 90% while improving precision and repeatability. Very little sample is required for this technique, the maximum being 0.5 g for organic samples, less for inorganic samples. Microwave digestion retains semi-volatile elements, eliminates cross-contamination, reduces acid trace impurities for lower detection limits, and eliminates worker exposure to toxic and hazardous fumes. Due to the high volatility of Hg and possible high volatility of As and Se, these elements were not prepared using this technique. The microwave used in this study is a CEM MARS 5, which can take up to 12 Teflon digestion vessels, including the control, and allows temperature and pressure variations.

Two digestion methods are reported here, one using only nitric acid (70%) (method 1) and method 2 using a mixture of nitric acid (70%), hydrochloric acid (40%) and hydrofluoric acid (55%) with a ratio of 1:3:2 respectively. Both techniques are slightly modified versions of available techniques. In both methods 0.3 g of sample (−250 μm) is placed in the vessel with 10 ml of nitric acid solution and typically two steps are followed. In method 1, the samples were heated to 210 °C at 10.9 atm for 25 min, followed by a cooling and second digestion using a further 10 ml nitric acid to ensure maximum digestion. In method 2, samples were heated to 210 °C at 24.5 atm for 15 min, followed by a cooling and the addition of the other solutions for step 2 (5 ml HF and 1 ml hydrochloric acid). Boric acid is required to volatilize F in HF prior to ICP analysis. Blank samples were also prepared.

The vessels were carefully opened after digestion to minimise any loss of analyte, the contents transferred to a 25-ml polyethylene volumetric flask. Distilled water was used to wash the vessels and make-up the solution to the required mark. In method 1, the digested solution was filtered to remove any undigested material.

3.4. Whole-coal analysis via slurry direct injection method

ICP is typically regarded as the best analytical technique for the determination of a number of trace elements in solution. However, a few researchers (Ebdon and Wilkinson, 1987; O'Hanlon, 1997; Marjanovic-Bakovic, 2003) have reported successful results using slurry atomization to introduce aqueous suspensions of coal, carbon black, cement, gypsum or fly ash via a high-solids nebuliser directly into an ICP, thus eliminating the ashing and dissolution steps. Ebdon and Wilkinson (1987) report a 95% recovery for Mn, and encouraging results for Cu and V. O'Hanlon (1997) reported that the observed values for the certified reference materials were all within range of the certified values. Marjanovic–Bakovic assisted with initial in-house trials at our laboratory, the results of which appeared to be acceptable, promoting further tests.

SARM 19 was used as a control sample. The CRM was crushed extremely fine to a top size of 10 μm. 0.1- and 0.15-g coal were weighed into a volumetric flask. A solution containing 1% glycerol and 1%HCl was added to the mark of the volumetric flask. The flask was placed in an ultrasonic bath for 20 min to ensure thorough mixing and all particles are evenly distributed through the solution. The prepared sample was immediately introduced directly into the ICP chamber and analyzed as per routine samples. Different wavelength and sample weights were tested to determine optimal operating conditions.

4. Results and discussion

Results on the certified reference materials, excluding the sequential leaching data, are presented in Table 3. Results for the Highveld coals are presented in Tables 4 and 5, and Fig. 5a and b.

4.1. Certified reference material (SARMs 18, 19 and 20)

The sequential leaching technique via the slurry and column methods proved to be an unreliable preparation technique; preparation is time consuming, the risk of contamination high, and the ICP results highly variable. Of the two methods, the column method exhibited a slightly better extraction. Typically sequential leaching techniques are used in the determinations of modes of occurrence of trace elements in coal for selected elements (Finkelman personal communication, 2004; Querol et al., 1996; Feng and Hong, 1999; Wang et al., 2003). Leaching techniques are omitted from further consideration in the current study.

Reliable results could not be obtained using the microwave digestion technique, despite applying and adapting manufacturer and various literature-recommended digestion programs. Incomplete digestion occurred when using nitric acid only, with possibly the silicates remaining. Digestion was very poor for SARM 18, but better for SARM 20, indicating the success of sample preparation is dependent on the nature of the sample and the mode of occurrence of the trace elements (Lachas et al., 1999). Complete dissolution was obtained with the three acid solutions. Good repeatability and reproducibility were obtained with SARM 20, but the certified values could not be obtained for all elements. Certain analytes may be lost during the opening of the digestion vessels, although vessels opened at ambient temperature or cooled to 4 °C did not appear to differ in terms of the trace element values obtained. Zinc and barium contamination was picked up in the blank sample, highlighting the essential need for careful washing of all apparatus and the use of very pure reagents when conducting trace element work. The dilution factor was also considered as a possible reason for the unreliable results from the microwave digested samples, and ICP-MS may be a better tool to use rather than ICP-AES.

The whole-coal analysis via slurry direct injection method proved to be reliable for approximately half of the elements analyzed based on the certified results for SARM 19. Preparation is easy and reduces the risk of contamination once the sample has been successfully crushed to −10 μm. The initial results appeared very promising, but as this

Table 3
Results from various preparation techniques using certified reference materials (ppm)

	SARM 18					SARM 19						SARM 20					
	Certified	Uncertified	Range	Preparation method		Certified	Uncertified	Range	Preparation method			Certified	Uncertified	Range	Preparation method		
				ASTM 3	Micro. Digest Acid mix[a]				ASTM	Direct slurry inject.					ASTM	Microwave digestion	
									2, 3	0.1 g	0.15 g				1, 2, 3	HNO3	Acid mix[a]
Hg							0.2		0.24	0.37	0.28	0.25		0.18–0.27	0.25		
As						7		6–8	7.5	5.4	6.4	4.7		4.6–6	5.3		
Se							1		1.2	1.02	0.79	0.8		0.7–1.0	0.91		
Pb		5			<9.5	20		17–23	20	19.4	19	26		20–29	25	17	21
Cd		0.032[b]	~0.002		<0.56				0.23				0.1[b]	~0.010		<0.10	0.81
Ba	78		71–82	86	82	304		295–318	300	266.4	273.4	372		363–384	356	323	250
Mo		1		2.8	<2.4		2		3				1.37[b]	~0.13		1.5	6.5	3.7
Ni	10.8		10.1–11.5	11.6	7.1	16		13–20	15	12.8	13.3	25		23–26	22	18	13
Mn	22		21–23	24	19	157		143–168	152	155.6	159.98	80		77–82	73	64	55
Cr	16		14–18	15	14	50		47–58	37	47.9	45.8		67		52	54	51
V	23		21–25	24	21	35		33–37	37	34.2	29.7	47		45–50	45	32	40
Zn	5.5		5.2–6.8	7.1	3.1	12		12–16	14	21	18.4	17		14–18	16		12
Cu	5.9		5.2–6.4	5.8	6	13		11–14	12	13.6	13.4	18		15–19	16		19
Co	6.7		5.5–7.2	7.3	6.5	5.6		5.0–6.6	8.6			8.3		7.6–9	12	7.4	9.1

ASTM 1—D6414-99; ASTM 2—D4606-95; ASTM 3—D6357-00a.

~—Plus/Minus.

[a] Acid mix = $HNO_3/HCL/HF$.

[b] Fadda et al. (1995).

Table 4
Trace element values for selected Highveld coals sampled during 2002–2003 (ppm)

	As	Cd	Co	Cr	Cu	Hg	Mn	Mo	Ni	Pb	Se	Sb	V	Zn	S (%)	Ash (%)
1	4.2	0.26	7.3	23	14	0.20	105	1.4	19	11	0.75	<0.094	37	9.9	0.96	24.1
1	2.1	0.28	8.0	57	13	0.14	102	2.2	20	7.0	0.88	<0.094	33	9.0	1.10	26.3
1	2.6	0.06	7	45	11	0.23	99	<5	15	4.3	1.2	0.2	33	8	–	–
1[a]	5.6	0.49	6.4	64	14	0.31	106	1.36	25	7.7	0.96	0.4	36	11.8	–	–
1[a]	4.2	0.39	6.9	80	13	0.24	119	1.16	21	7.2	1.1	0.3	36	11.7	–	–
mean	3.74	0.29	7.12	53.8	13.0	0.22	106.2	–	20.0	7.44	0.98	–	35.0	10.1	–	–
Std. dev.	*1.403*	*0.16*	*0.589*	*21.370*	*1.224*	*0.06*	*7.660*	–	*3.60*	*2.390*	*0.177*	–	*1.871*	*1.666*	–	–
2	1.9	0.16	6.0	47	15	0.17	105	<1.2	16	7.3	1.1	<0.094	33	10	0.93	22.7
2	3.9	<0.12	6.2	37	15	0.11	97	2.9	16	7.3	<0.50	<0.094	31	17	1.02	24.0
2	1.2	0.15	12	41	12	0.18	92	<5	12	4.2	1.2	0.2	31	9	–	–
2[a]	2.5	0.52	6.0	61	16	0.19	126	0.84	16	6.9	1	0.3	37	16.9	–	–
2[a]	2.3	0.21	5.7	59	12	0.24	113	1.1	20	3.9	1	0.3	33	24.5	–	–
mean	2.36	–	7.2	46.5	14.3	0.178	106.6	–	16.0	5.92	–	–	33.0	15.5	–	–
Std. dev.	*0.994*	–	*2.415*	*10.504*	*1.862*	*0.046*	*13.465*	–	*2.828*	*1.712*	–	–	*2.449*	*6.279*	–	–
3	2.7	0.26	6.8	26	14	0.12	86	2.7	16	3.7	0.67	<0.094	34	9.1	0.65	25.6
3	2.0	0.25	5.6	46	14	0.20	94	1.9	15	10	1.0	<0.094	31	11	0.85	25.7
3	2.9	0.05	5	43	11	0.27	92	<5	12	4.9	1.3	0.3	34	8	–	–
3	–	0.51	6.7	42	12	0.19	84	0.4	13	6.1	–	–	28	11	1.25	23.5
3[a]	1.9	0.39	5.6	62	13		92	1.25	18	6.2	1.5	0.3	34	14.7	–	–
3[a]	4.3	–	5.4	60	12	0.26	110	1.14	15	7.4	2.2	0.4	33	11	–	–
mean	2.76	0.29	5.85	46.5	12.7	0.21	93.0	–	14.83	6.38	*1.33*	–	32.5	10.8	–	–
Std. dev.	*0.963*	*0.172*	*0.731*	*13.232*	*1.211*	*0.060*	*9.187*	–	*2.137*	*2.174*	*0.577*	–	*2.588*	*2.282*	–	–
4	4.4	0.44	6.6	57	13	0.040	117	<1.2	19	11	1.5	<0.094	25	19	0.40	27.2
4	4.7	<0.12	6.0	29	12	0.14	100	2.2	16	10	0.88	<0.094	23	17	0.61	24.5
4	1	0.05	5	39	9	0.07	103	<5	12	6.4	0.9	0.2	25	15	–	–
4[a]	1.9	0.34	6.5	68	11	0.10	132	0.78	18	11.0	0.49	0.3	27	23.9	–	–
4[a]	2.0	0.39	6.5	53	12.8	0.18	134	1.2	19	11.4	1	0.3	28	28.5	–	–
mean	2.8	–	6.12	49.2	11.6	0.10	117.2	–	16.8	9.96	0.94	–	25.6	18.7	–	–
Std. dev.	*1.647*	–	*0.668*	*15.336*	*1.633*	*0.055*	*15.802*	–	*2.949*	*2.056*	*0.361*	–	*1.949*	*3.817*	–	–
5	2.1	0.39	7.2	42	12	0.14	105	1.5	23	5.0	<0.50	<0.094	32	9.8	0.87	23.1
5	3.1	0.64	7.8	69	14	0.14	109	1.4	23	11	0.77	<0.094	35	14	0.76	25.3
5	2.5	0.06	6	57	11	0.14	93	<5	17	4.7	0.8	0.2	35	10	–	–
5	3.1	0.49	8.2	35	12	0.19	102	<0.24	19	5.6	0.9		31	10	1.27	19.3
5[a]	3.4	0.56	7.2	96	12	0.16	126	1.27	24	8.3	0.61	0.3	36	18.5	–	–
5[a]	3.3	0.71	7.2	102	16	0.18	138	1.69	35	5.1	0.61	0.3	35	17.7	–	–
mean	2.84	0.47	7.3	59.8	12.8	0.16	112.1	–	23.5	6.61	–	–	34	13.3	–	–
Std. dev.	*0.471*	*0.232*	*0.745*	*24.159*	*1.835*	*0.022*	*16.678*	–	*6.253*	*2.516*	–	–	*2.0*	*4.023*	–	–
6	2.5	0.31	8.0	30	17	0.28	140	4.3	22	20	1.2	<0.094	41	50	1.29	30.7
6	2.6	0.19	8.0	73	20	0.20	126	<1.2	20	17	0.79	<0.094	44	10	0.97	32.8
6	2.1	0.06	17	65	17	0.22	118	<5	16	6.9	1.4	0.2	50	10	–	–
6[a]	3.2	0.17	5.9	74	13.1	0.26	125	1.19	17	14.2	1.0	0.5	30	31	–	–
6[a]	2.9	0.16	6.4	81	15	0.22	118	1.03	30	18.6	1.2	0.3	40	9	–	–
mean	2.66	0.178	9.06	64.6	16.4	0.23	125.4	–	21.0	15.34	1.12	–	41.0	22.0	–	–
Std. dev.	*0.416*	*0.089*	*4.437*	*20.157*	*2.575*	*0.033*	*8.989*	–	*5.567*	*5.19*	*0.231*	–	*7.280*	*18.179*	–	–

[a] Analyses conducted by USGS JH Bullock, Jr/RB Finkelman.

technique is new to us and not standardized, further trials are required to increase confidence levels and to determine ideal sample weights and wavelengths.

The three ASTM preparation techniques produced repeatable and reliable results for almost all of the elements requiring detection. Richaud et al. (2000) report good agreement at 20%. As these techniques are proven, the Highveld coals under consideration were prepared in this manner, with a SARM included in each batch.

Table 5
Mean values for Highveld coal samples (ppm)

Trace element	Highveld coals (excl. et 6 and USGS data)		USGS data means (excl set 6)	SARM 19 and 20				Average global values (Zhang et al., 2004)	Average global values (Ketris, in press)[b]
	mean values	Range		LOQ[a]	Obtained	Actual	Range		
Sb	<0.136 ± 0.06	<0.094–0.3	0.32		<0.094	(0.4)	Uncertified	3.0	1.0 ± 0.11
As	2.7 ± 1.0	1.0–4.7	3.14	0.0013	6.9	4.7	4.6–65.0	5.0	9.0 ± 0.8
Cd	0.24 ± 0.17	0.05–0.51	0.44	0.056			Uncertified	0.6	0.2 ± 0.05
Cr	43.2 ± 12.0	23–69	70.5	0.15	45	50	47–58	10	17.0 ± 1
Co	6.9 ± 1.6	5–12	6.3	0.062	8	5.6	5.0–6.6	5	6.0 ± 0.2
Cu	12.6 ± 1.6	9–16	13.2	0.024	13	13	11–14	15	17.0 ± 1
Pb	7.0 ± 2.6	4.2–11	7.51	0.94	292	304	295–318	25	9.0 ± 0.9
Mn	99.1 ± 8.4	84–117	19.6	0.0076	138	157	143–168	50	70.0 ± 6
Hg	0.15 ± 0.05	0.04–0.27	0.20	0.003	0.19	0.25	0.18–0.27	0.12	0.1 ± 0.01
Mo	2.09 ± 1.06	0.4–<5	1.18	0.24	2	(2)	Uncertified	5	2.0 ± 0.1
Ni	16.6 ± 3.4	12–23	21.1	0.18	16	16	13–20	15	16.0 ± 1
Se	0.99 ± 0.24	<0.5–1.5	1.05	0.0015	0.58	0.8	0.7–1	3	1.4 ± 0.1
V	31.2 ± 3.9	23–37	33.5	0.068	34	35	33–37	25	29.0 ± 1
Zn	11.6 ± 3.4	8–19	17.9	0.066	16	12	12–16	50	29.0 ± 2

[a] LOQ=3.333 limit of detection.
[b] In prep. Translated by Dr Yudovich (personal communication); hard coals.

4.2. Highveld coals

All samples reported in Table 4 are from the same coal seam (No 4L) and coal field within in a 50-km radius. Mean values and ranges are reported in Table 5, actual values in Table 4. The trace element values are generally comparable between the six sample sets, although some variation is noted. Concentrations of As are greater at locality 1, the concentrations of Hg are lower at locality 4, concentrations of Ni are highest at locality 5, Cr values are very high in sample sets 5 and 6, and Se concentrations are highest in sample set 3. Sample set 6 is the middlings product, and contains the highest ash content, as well as higher V, Cr, Cu, Co, and Zn contents, and a significantly higher mean Pb content (15.34 ppm) compared to the other five sets. Set 6 is omitted from the calculations in Table 5. The results within a sample set are generally comparable, although the samples were taken at different times during the year, indicating some degree of horizontal uniformity of these elements within the No 4L seam in this Highveld study area. This is in agreement with findings by Watling and Watling (1982).

Certain samples were split and analyzed at the South African and USGS Labs for benchmarking. Results from the USGS generally compare well with the South African generated-dataset, with the excep-

tions of Cr, Mn and Mo (Fig. 5a and b), and the possible exception of Hg and Sb. Reasons for these discrepancies are being addressed further.

Most results obtained during this study are comparable to those determined previously by Cairncross et al. (1990), Willis (1983), and Watling and Watling (1982) on South African coals, with the exceptions of Hg, Mn, and Cr. Findings for Hg are lower and can be considered more realistic in the current study due to more appropriate preparation and analytical techniques. Cr and Mn are enriched in the Highveld coals.

An interesting observation, when comparing the Highveld trace element values obtained to cited global average, is highlighted in Table 6. The siderophile elements are enriched or comparable to global averages, and contrastingly all the chalcophile elements are depleted (siderophile and chalcophile element classification after Vassilev et al., 2005). Chalcophile elements have an affinity for sulfides, and are soft acids; siderophile elements have an affinity for iron (soluble in molten iron), and are hard acids. The total sulphur content in South African coals is generally lower than northern hemisphere coals, with typical values for the samples analyzed here ranging from 0.92 to 1.23%. Over 90% of the sulphur in South African coals is likely to be associated with pyrite, the remaining being
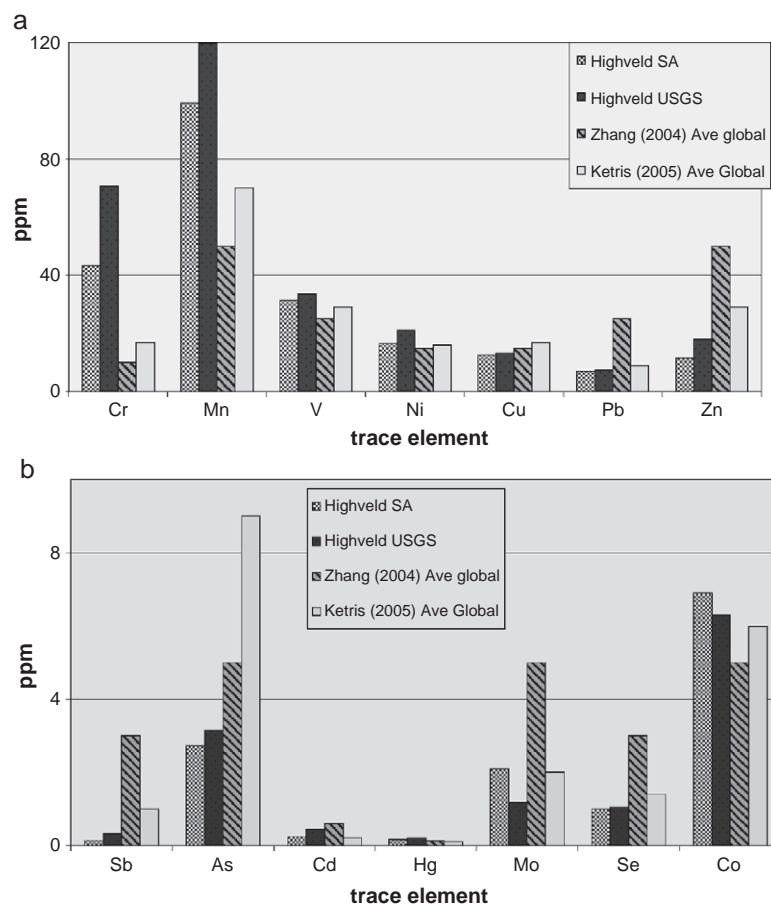
Fig. 5. (a) Comparison of Highveld data and global values. (b) Comparison of Highveld data and global values.

organically bound (personal communication, Chris van Alphen). Ash oxide Fe_2O_3 values for the Highveld coals are in the order of 3.9–5.7%, and SO_3 2.3–5.0% (Pinheiro, 2000). Arsenic, Cd, Cu, Pb, Sb, and Zn are all known to have primary affinities for pyrite and/or accessory sulfide minerals (Orem and Finkelman, 2004; Finkelman, 1994), as discussed further below. Manganese has a strong affinity for carbonate minerals (Orem and Finkelman, 2004), specifically siderite ($FeCO_3$) which is known to occur in South African coals. Chromium has an affinity for clays (aluminosilicates) (Orem and Finkelman, 2004), although organic and fine-grained Cr-bearing ($FeCr_2O_4$) mineral associations cannot be excluded (Finkelman, 1994). Ash oxide CaO values for these Highveld coals are in the order of 3.59–9.57%, and SiO_2 44.4–57.0% and Al_2O_3 23.3–

30.7% (Pinheiro, 2000). The only lithophile element determined here was Mo, which is comparable with global average values.

Certain trace elements are discussed in further detail.

Table 6
The enrichment of siderophile[a] and chalcophile[a] elements in Highveld coals compared to global average values

Siderophile elements		Chalcophile elements	
Mn	Highly enriched	As	Very depleted
Cr	Highly enriched	Cd	Depleted
Co	Comparable	Cu	Depleted
Ni	Comparable	Pb	Very depleted
V	Comparable	Sb	Very depleted
		Se	Very depleted
		Zn	Very depleted

[a] Categorised as per Vassilev et al. (2005).

4.2.1. Antimony

Antimony was determined in low to very low concentrations in the Highveld coals when compared to global values (Fig. 5b) and typical USA data (Table 1). The SA-generated data generally reports Sb as less than 0.094 ppm, or below the detection limit of the equipment, but the USGS data constantly reports actual figures. The differences in results can be attributed to different analytical techniques, and should be addressed further. The occurrence of Sb in coals appears to be difficult to determine, although Finkelman (1994) and Karayigit et al. (2000) report that it may be present in solid solution in pyrite and as minute accessory sulfides dispersed through the organic matrix. Due to the low Sb occurrence in these Highveld coals, Sb is unlikely to be of health or environmental concern.

4.2.2. Arsenic

Although locality 1 reports a slightly higher mean As value than the other sample sets, As levels in these Highveld coals are very low compared to USA values, and fall well below global coal average values (Table 1, Fig. 5b). Arsenic is generally thought to be associated with sulfide minerals, specifically pyrite (Ding et al., 2001; Diehl et al., 2004; Mardon and Hower, 2004), although a small proportion may also be organically associated (Goodarzi, 2002; Finkelman, 1994). Arsenic is a volatile trace element and will exist in a vapor phase at 400 °C. USA risk-based health studies have not reported negative health effects from As emissions in coals with significantly higher As values compared to these Highveld As values. Therefore, mobilization of this trace element from the Highveld coals in this study is unlikely to cause human health problems.

4.2.3. Chromium

All Cr values reported for these Highveld samples (including the USGS generated data) and other South African data previously reported (Table 1) are much higher than global coal averages documented by Zhang et al. (2004) and Ketris (in press) (Fig. 5a). Willis (1983) reports a Cr range of 12–63 ppm for South African coals; a range of 23 to 102 ppm (the latter value determined by the USGS) was determined in this investigation. Sample set 6 (middling samples, thus slightly higher ash than other sample sets), on average, report the highest mean Cr value (64.6 ppm), higher than the global range as documented by Swaine (1990). The Highveld coals thus appear to be enriched in Cr. However, Finkelman (1994) refers to coals of over 500 ppm as having high Cr concentrations; these coals were found to contain chromite ($FeCrO_4$). Brownfield et al. (1995) discusses Tertiary coals enriched in Cr with an average concentration of 120 ppm where Cr-bearing spinels were weathered from nearby ophiolite bodies and accumulated as detrital minerals in the coals forming peat. Ruppert et al. (1996) concludes that the occurrence of high chromium values in Serbian lignites (up to 176 ppm) may be due to the deposition of detrital Cr-bearing minerals transported into the palaeoswamp by rivers draining two Paleocene laterites. Therefore, although South African and in particular these Highveld coals Cr values can be considered high, higher values have been documented since Swaine's (1990) publication. Considering the palaeoenvironment of the Karoo Basin, it is possible that the Cr enrichment originates from chromite originally found in the Witwatersrand Basin. Although these minerals have not been determined to date in the Highveld coals using XRF techniques, it is possible they were subsequently dissolved and redistributed as elements or other minerals.

Chromium occurs in most bituminous coals as Cr^{3+} in organic associations and Cr^{3+} in illite, but Cr occurrences in chlorite, chromite/magnetite spinel, and crocoite have also been reported (Huggins and Huffman, 2004). Goodarzi (2002) indicates that Cr is mostly associated with clay minerals in the organic fractions, and possibly with pyrite and carbonates in high sulphur coals. Chromium occurring as Cr^{3+} (or in the form of chromate or dichromate oxo-anions) is non-toxic and is therefore not of concern for human health. However, Cr is listed as a Title III HAP by the 1990 US Clean Air Act Amendment due to the hexavalent chromium state (CR(VI)). Cr(VI) compounds can be highly soluble in aqueous media. Sheps et al. (1997a,b) and Huggins et al. (1999) report concentrated Cr(VI) determined in fly ash samples from an Israeli combustion plant utilizing South African coals. Separate samples from the combustion of a South African coal indicated $19 \pm 5\%$ Cr(VI) of the total Cr content in the coal. A coal ash from sub-bituminous Wyodak coal,

USA, reported $52 \pm 5\%$ Cr(VI). In evaluating potential environmental and health risks posed by the release of Cr during coal utilization and waste disposal, it is very important that the oxidation state be determined and quantified. Work is ongoing to identify the oxidation state of chromium in these Highveld coals and associated ashes.

4.2.4. Lead

Sample set 6 has a much higher mean Pb content (mean 15.34 ppm) compared to the other five sample sets. Lead is generally associated with mineral matter in coal, primarily with sulfides such as galena (PbS), clausthalite (PbSe) (Hower and Robertson, 2003) and pyrite (Diehl et al., 2004), as well as aluminosolicates and carbonates (Goodarzi, 2002; Finkelman, 1994; WVGES, 2002; Wang et al., 2003). The removal of lead is dependent on its mode of occurrence (cleats or micron-sized crystals for example). Although the middlings Pb values are the highest values reported for these Highveld coals, they are well below the global average of 25 ppm (Zhang et al., 2004) (Fig. 5b), but comparable to Ketris (in press). Excluding the middling samples, the other Pb values determined in this study are comparable to previous findings for South African coals and are similar to typical USA values (Table 1). Lead concentrations reported here are unlikely to be of concern to human health and the environment.

4.2.5. Manganese

Manganese values for these Highveld coals are high when compared to average world coals (Fig. 5a), but moderate compared to the ranges proposed by Swaine (1990) (Table 1). Previous Mn data for South African coals indicated much lower Mn concentrations than obtained during this study. Manganese is typically associated with carbonates (siderite, dolomite and calcite), but has also been determined to be organically associated in some low-rank coals. The Highveld coals in this study are both low rank and contain carbonate minerals, generally expressed as CaO in the order of 5–11% in ash. Generally Mn is generally considered to be a non-volatile element, but is classified as a hazardous air pollutant due to its potential negative impact on plant growth. No health or environmental problems due to Mn in coal mining and utilization have been reported (Swaine, 1990).

4.2.6. Mercury

Locality 4 reports slightly lower Hg values compared to the other sample sets. There may be some relationship between this and the lower sulphur content reported for this sample set, as Hg is known to have an inorganic affinity for pyrite (Diehl et al., 2004; Goodarzi, 2002; Swaine, 1990). Mercury has also been determined in sphalerite and cinnabar and in organic matter in coals (WVGES, 2002). Feng and Hong (1999) determined a negative correlation between Hg and organic matter.

Mercury is a trace element of major environmental concern globally due to its potential toxicity and global movement; it is highly volatile and readily emitted during coal utilization even at 100 °C. Formal regulation is imminent in the USA for the reduction of Hg emissions from coal utilization. The mean Hg content for the Highveld coals is comparable with that published for USA coals (Orem and Finkelman, 2004) and world coals (Zhang et al., 2004; Swaine, 1990). In the USA, the mean Hg value for ROM is 0.17 ppm, and 0.1 ppm for beneficiated combustion coal (Quick et al., 2003).

Although sample set 4 is constantly lower in Hg, there is essentially little variation between all the Highveld coal samples; a mean value of 0.15 ± 0.05 ppm was determined (Table 5, excludes USGS data and set 6). Risk-based health studies in the USA on coals with similar or higher Hg contents have not reported negative health effects, and therefore it could be assumed that mobilization of these trace elements from these Highveld coals should not cause human health problems.

4.2.7. Molybdenum

Mean Mo content in these samples is comparable with typical USA data and Ketris (in press), but occurs in very low concentrations when compared to Zhang et al. (2004) global values (Fig. 5b). Some degree of variability was noted between the different sample sets. Molybdenum is believed to be dominantly associated with sulfide minerals and organic matter in coal. It is not classified as a hazardous air pollutant, but several papers cite Mo as being of environmental concern (Booth et al., 1999; Bushell and Williamson, 1995). Molybdenum in these Highveld coals is highly unlikely to be of local environmental concern due to the low levels determined.

4.2.8. Selenium

Se is believed to be of environmental concern, particularly in arid regions, as it can become concentrated in soil and accumulate to potentially toxic levels in plants (WVGES, 2002). Se is highly volatile and readily released in the vapor phase, and Se compounds may be five times as toxic as As. In coals, Se is most commonly associated with pyrite (WVGES, 2002), but can have many other associations including clausthalite (PbSe) (Hower and Robertson, 2003) and organic associations (Goodarzi, 2002; Finkelman, 1994). Selenium concentrations determined in this study are low to very low compared to world coal ranges and average values (Table 1). Selenium is generally constant between the Highveld sample sets, with sample sets 3 and 6 reporting the highest average values. Due to the very low concentrations determined for these Highveld samples, it is unlikely that Se is of local environmental concern.

4.2.9. Zinc

Zinc was determined in low concentrations in the Highveld coals when compared to global values (Fig. 5a). The mean Zn value is comparable to typical USA data. Zinc is typically associated with sphalerite minerals (Finkelman, 1994; WVGES, 2002), and is also believed to be associated with pyrite (Goodarzi, 2002). One sample from sample set 6 has a very high Zn value. This particular sample also has a higher than average S content, but not in the same order of magnitude as compared to the Zn content. It is possible that this particular sample contained sphalerite. Zinc is not listed as a Hazardous Air pollutant, but the US National Committee for Geochemistry lists Zn as an element of moderate environmental concern (Bushell and Williamson, 1995).

5. Conclusions

- For the determination of potentially hazardous trace elements in six Highveld coal samples analyzed, three sample preparation techniques were applied, namely: ASTM standard for Hg, ASTM standard for As and Se, ASTM standard for other elements in ash. Solutions prepared by microwave digestion did not appear to be easily repeatable. In-house trials on SARM 19 for the whole-coal analysis via slurry direct injection method indicated good recoveries, showing promise as an alternative technique for trace element determination where sample dissolution is eliminated; further in-house work is required to enhance confidence levels.

- The values for the six Highveld sample sets as determined here are generally in good agreement to those values previously reported on other South African coals; the slight variations could be due to different preparation and analytical techniques, and different coal fields and seams. The values obtained can generally be considered to be low or comparable to the global ranges. Concentrations of As, Cd, Cu are lower compared to global average values, and Mo, Pb, Se, Zn and Sb can be considered low to very low. Arsenic is ten times lower compared to typical USA values. Concentrations of Co and Ni are similar to global averages, with V and Hg being very slightly higher. However, Cr and Mn values were found to be much higher in the Highveld coals compared to typical USA values and cited average global values.

- The elements were selected due to their known or possible health and environmental effects due to coal utilization. Risk-based health studies in the USA on coals with similar or higher Hg and significantly higher As contents have not reported negative health effects, and therefore it could be assumed that the values reported for these five Highveld coals should not be of concern to human health.

- Although the values reported can generally be considered low, due to the high tonnages of coal utilized in the Witbank–Highveld area, there exists the potential that high levels of toxic elements are being emitted into the atmosphere. On utilization, certain elements will vaporize rapidly (Hg, Se, As) and other elements (including As, Cd, Pb, Mn) are likely to become bound to fly ash and could be emitted via stacks. To effectively reduce, mitigate, and/or prevent negative environmental and human health impacts from coal utilization, it is crucial to understand the geological origin of coal, its mineralogical and elemental content, as well as the mode of occurrence of these elements. Research is ongoing to determine the modes of occurrence of the

elements in the Highveld coals discussed in this paper.

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